ŻYWNOŚĆ. NAUKA. TECHNOLOGIA. JAKOŚĆ, 2023, 30, 3 (136), 244 – 264

DOI: 10.15193/zntj/2023/136/465

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EFFECTS OF COMPOSITION OF GLUTEN-FREE BINARY GELS ON THE RETENTION AND RELEASE OF AROMA COMPOUNDS

S u m m a r y

Background. Gluten-free binary gels (BGs) composed of polysaccharides and animal proteins appear to be food products of great practical importance due to the constantly increasing risk of coeliac disease. Moreover, understanding the factors influencing the stability of aroma compounds (ACs) is very important because consumer acceptance of food is mainly dependent on aroma. The objective of this research was to determine the thermodynamic and kinetic behavior of ACs in BGs prepared with starches varying in amylose content depending on the concentration of myofibrillar proteins (MPs). BGs were prepared with 8 % of waxy rice starch (WRS) or tapioca starch (TS) and MPs ranged from 2 to 12 %. BGs were aromatized with: 1-heptanol, nonanal, 2-butanone, ethyl acetate, s-(+)-carvone. The studies included measurements of: rheological properties of BGs, non-covalent interactions between myosin and ACs, retention and release of ACs and enthalpy of ACs vaporization (ΔH_{vap}).

Results and conclusions. The main non-covalent interactions between myosin and ACs were hydrogen bonds and hydrophobic interactions. Retention and release parameters, determined during refrigerated storage (12 days) were statistically significantly ($p \leq 0.05$) dependent on: starch type, MPs concentration and physicochemical properties of ACs. The ACs release rate constants were statistically significantly ($p \leq 0.05$) correlated with those of rheological parameters derived from first order kinetic equation. ΔH_{vap} values found in TS-based BGs were generally lower ($p \leq 0.05$) than in counterparts prepared using WRS. BGs with a relatively high protein content can be intended for direct consumption and as subsystems for other food products to increase ACs stability.

Key words: binary gels, aroma, interactions, retention and release, vaporization enthalpy

Introduction

Gluten-free binary gels (BGs) composed of polysaccharides and animal proteins seem to be very promising food products due to the constantly increasing number of coeliac disease cases [13, 26]. Among the polysaccharides, the most noteworthy is

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starch, which is a biodegradable, inexpensive biopolymer and has been widely used as a functional ingredient of many food products. At the molecular level, starch mainly consists of linear amylose (AM) and highly branched amylopectin (AP) and the AM/AP ratio affects the rheological properties of starch-based gels [27]. Myofibrillar proteins (MPs) are the main component of muscle proteins, accounting for 55 ÷ 65 % of total muscle proteins. Myosin is the most abundant and asymmetric molecule of MPs, with two heavy polypeptide chains and four light polypeptide chains, mainly responsible for gelation in meat proteins [9].

Aroma is considered a key ingredient improving the organoleptic properties of food and increasing its acceptability by consumers [15]. Therefore, scientists take inspiration from manufacturers to increase the stability of aroma compounds (ACs) in food products. Both thermodynamic and kinetic mechanisms influence the retention and release of ACs into the headspace. The thermodynamic parameter is related to the air/matrix partition coefficient, determined under equilibrium conditions, while the kinetic parameter characterizes the rate of ACs release from the matrix [5, 19]. The ACs that can be found in food can be classified as: hydrocarbons, aldehydes, ketones, alcohols, esters, terpenes, sulfur compounds and others [4]. They are at least moderately lipophilic and therefore the lack of lipids in BGs may negatively impact the stability of ACs in food systems. It seems that a certain solution in this regard may be the increased addition of biopolymers that reversibly interact with ACs [7]. ACs form chemical and physical bonds with carbohydrates, but proteins play a key role because strong ACs binding minimizes their release [15]. Therefore, it can be hypothesized that by manipulating the type and concentration of the biopolymer, it would be possible to differentiate the rheological properties of BGs and the range of interactions with ACs belonging to different chemical classes, as well as to model their retention and release from food systems. In the light of this hypothesis, the aim of the study was to determine the thermodynamic and kinetic behavior of ACs in BGs prepared with starches varying in amylose content depending on the increasing concentration of MPs.

Materials and methods

Materials

Beef meat (*M. semimembranosus*) was purchased from a meat purveyor. Pregelatinized starches: tapioca starch, TS (19.2 % amylose) and waxy rice starch, WRS (96.8 % amylopectin) were donated by Ingredion GmbH (Hamburg, Germany). Aroma compounds (purity ≥ 98 %): 1-heptanol, nonanal, 2-butanone, ethyl acetate, s-(+)-carvone) and other chemicals were purchased from Sigma-Aldrich (Poland). The physicochemical properties of ACs are presented in Table 1. Throughout this work, unless otherwise stated, the concentration is expressed in wt %.

Table 1. Physicochemical properties of aroma compounds
Tabela 1. Właściwości fizykochemiczne substancji zapachowych

	MW ($g\ mol^{-1}$)	MV ($cm^3\ mol^{-1}$)	Log P	WSol* ($g\ L^{-1}$)	BP (^oC)	D* ($g\ mL^{-1}$)	OD
HAL	116.2	141.4	2.62	1.25	176	0.821	aromatic / aromatyczny
NAL	142.2	172.4	3.27	0.09	195	0.826	floral / kwiatowy
BAE	72.11	89.62	0.29	136	79.6	0.805	fruit / owocowy
EAE	88.11	97.81	0.73	64.1	77.1	0.902	pineapple / ananasowy
CVE	150.2	156.3	3.07	1.31	231	0.962	spice / przyprawowy

Explanations / Objaśnienia:
(1) Aroma compounds: 1-heptanol (HAL), nonanal (NAL), 2-butanone (BAE), ethyl acetate (EAE), s-(+)-carvone (CVE). (2) Physicochemical and sensory properties of aroma compounds: molecular weight (MW), molar volume (MV), hydrophobicity (Log P), water solubility (WSol), boiling point (BP, 760 mm Hg), density (D), and odor descriptor (OD). (3) Data retrieved from database http://pubchem.ncbi.nlm.nih.gov and http://www.chemicalbook.com
* Values determined at 25 ^oC.
(1) Substancje zapachowe: 1-heptanol (HAL), nonanal (NAL), 2-butanon (BAE), octan etylu (EAE), s-(+)-karwon (CVE). (2) Właściwości fizykochemiczne i sensoryczne substancji zapachowych: masa cząsteczkowa (MW), objętość molowa (MV), hydrofobowość (Log P), rozpuszczalność w wodzie (WSol), temperatura wrzenia (BP, 760 mm Hg), gęstość (D) i deskryptor zapachu (OD). (3) Dane pobrane z bazy danych http://pubchem.ncbi.nlm.nih.gov and http://www.chemicalbook.com
* Wartości wyznaczone w 25 ^oC.

Methods

Fluorescence spectroscopy, determination of Stern-Volmer quenching constants, binding and thermodynamic parameters of ACs-myosin (MYO) interactions

The research was carried out using procedures described by Bortnowska [5], with a slight modification. MYO solution (0.75 mg mL^{-1}) was prepared by dissolving the protein in a phosphate buffer solution (20 mM K_2HPO_4/KH_2PO_4, 0.6 M NaCl, pH 7.0) and stored at 4 ^oC before use. The ACs were added separately to the vials containing MYO solution to obtain final concentrations of $2 \div 12 \times 10^{-5}$ M, and then capped immediately. The control sample contained only MYO solution. All the samples were stored (periodically shaken) at temperatures: 35, 45, 55 and 65 ^oC, and the time of 12 h was sufficient to reach equilibrium for each aroma compound. Fluorescence emission spectra were recorded from 300 to 500 nm after excitation at 280 nm with a LS-55 fluorescence spectrometer (Perkin Elmer, Waltham, USA). The slit widths were 5 nm for both excitation and emission. The fluorescence quenching mechanism induced by

ACs was determined according to Stern-Volmer equation: $F_0/F = 1 + K_{SV}[Q] = 1 + K_q\tau_0[Q]$, where: F_0 and F, are the fluorescence intensity in the absence and presence of quencher; K_{SV}, Stern-Volmer quenching constant; [Q], aroma compound (AC) concentration; $K_q = K_{SV}/\tau_0$, bimolecular quenching rate constant and $\tau_0 = 10^{-8}$ s, average lifetime of the biomolecule without quencher. The binding constant (K_b) and number of binding sites (n_b) associated with the ACs-MYO interactions were calculated from the relationship: $\log [(F_0 - F)/F] = \log K_b + n_b \log [Q]$. Thermodynamic parameters, related to changes: enthalpy (ΔH), entropy (ΔS) and Gibb′s free energy (ΔG) after ACs binding, were determined from the equations: $\ln K_b = -\Delta H/RT + \Delta S/R$ and $\Delta G = \Delta H - T\Delta S$, respectively, where: R, gas constant (J mol^{-1} K^{-1}) and T, temperature (K).

Gluten-free binary gels (BGs) preparation

BGs were manufactured using the procedures of Bortnowska [6], with modification. The MPs were dissolved in 50 mM sodium phosphate buffer including 0.6 M NaCl (pH 6.2) to obtain experimentally required concentrations. Subsequently, WRS or TS were added and the suspensions were mixed together to prepare samples composed of 8 % starch (WRS or TS) and MPs ranging from 2 to 12 %. During the mixing, 0.1 % potassium sorbate was added. Subsequently, the mixtures were pasteurized by heating (5 ^{o}C min^{-1}) in a water bath to 90 ^{o}C, kept at this temperature for 10 min, rapidly cooled to 5 ^{o}C with an ice-water mixture and homogenized for 20 s at 14,000 rpm. Subsequently, the ACs (HAL, NAL, BAE, EAE, CVE) were added separately, each at a concentration of 600 mg L^{-1}. The BGs were stored at 5 ^{o}C for 6 h and then used for further analyses.

Physicochemical properties measurements

The physicochemical properties of the BGs during 12 days of refrigerated (5 ^{o}C) storage (RST) were determined following the general procedures reported previously [6]. For the determination of water holding capacity (WHC), the gel samples (M_1) were centrifuged (2400 g, 15 min) and reweighed (M_2). WHC was calculated from the equation; WHC (%) = $M_2/M_1 \times 100$. The rheological properties of the BGs were determined using a strain/stress controlled AR-G2 rheometer (TA Instruments, New Castle, DE, USA), equipped with a cone–plate geometry (cone angle 2°, diameter 60 mm, gap 62 μm). Flow curves were obtained at shear rates ($\dot{\gamma}$) in the range of 0.01-100 s^{-1} and the data obtained was fitted to the Herschel-Bulkley model: $\tau = \tau_0 + k\dot{\gamma}^n$, where: τ, shear stress (Pa); τ_0, yield stress (Pa); k, consistency index (Pa s^n); and n, flow behavior index (–). Frequency sweep tests were carried out at a frequency of 0.01-100 Hz with 0.1 % fixed strain and: storage modulus (G′, Pa), loss modulus (G″, Pa) were recorded versus frequency (ω). The quality factor was derived from the relation: $Q = 2\pi (K'/K'') \omega^{(n' - n'')}$, where: K′, K″, n′, n″, coefficients derived from the equations: $G' = K'\omega^{n'}$, G″ =

$K''\omega^{n''}$. The values of the determined parameters (P: k, τ_0, Q) were fitted to the first order kinetic equation: $d[P]/dt = \pm k[P]$, and the appropriate rate constants: k_k, $k_{\tau 0}$, k_Q (day^{-1}) were used for further calculations.

Surface hydrophobicity, chemical interactions, total sulfhydryl and free amino groups determination

The surface hydrophobicity (S_o) of MPs was determined using 8-anilino-1-naphthalenesulfonate (ANS), as described by Deng et al. [10], with a slight modification. Fluorescence intensity (FI) was measured using a LS-55 fluorescence spectrometer (Perkin Elmer, Waltham, USA) at 374 nm (excitation) and 485 nm (emission), with excitation and emission slits set at 5 nm. S_o was determined as the slope of the plot of FI against MPs concentration (0.05 ÷ 0.35 mg/mL). The chemical interactions of the MPs were calculated using the method described by Zhou et al. [29]. The soluble protein contents were measured by the Kjeldahl method to quantify: ionic bonds (IB), hydrogen bonds (HB), hydrophobic interactions (HI) and disulfide bonds (DB). Total sulfhydryl (−SH) groups (TSG) content was determined as described by Diao et al. [11] applying 5,5′-dithio-bis (2-nitrobenzoic acid) (DTNB). The absorbance was measured at 412 nm and the TSG content (nm mg^{-1} protein) was calculated using a molar extinction coefficient of 13,600 M^{-1} cm^{-1}. The free amino ($-NH_2$) groups (FAG, nmol mg^{-1} protein) were quantified according to Cao & Xiong [8], with the use of 2,4,6-trinitrobenzenesulfonic acid (TNBS). Absorbance was measured at 420 nm and the FAG content was assessed from the calibration curve produced with L-leucine.

Static headspace gas chromatography-mass spectrometry (SH-GC-MS)

SH-GC analyses were performed on an AutoSystem XL gas chromatograph (Perkin-Elmer, Switzerland), following the previously published procedures by Bortnowska [5], with a slight modification. Headspace vials (22.3 mL) were filled with 5 ± 0.01 mL of BGs, immediately closed and incubated in an ST1/B/60 incubator (Pol-Eko-Aparatura, Poland). A time of 6 h was sufficient to reach equilibrium for each aroma compound, regardless of sample composition. Headspace vials containing BGs were placed into Perkin-Elmer TurboMatrix 16 autosampler, kept at experimentally required temperature and then the headspace sample of 1 mL was automatically withdrawn and injected with splitless mode into a PE-5MS capillary column (30 m × 0.25 mm i.d. × 0.25 μm film thickness) in GC. Helium (purity > 99.99 %) was used as carrier gas at a flow of 1.1 mL min^{-1}. The temperature of the column oven was initially set to 60 °C, subsequently increased to 220 °C with a rate of 15 °C min^{-1}. The quadrupole-type mass spectrometer (MS, TurboMass) operated in the electron impact mode with an electron energy of 70 eV, collecting data at a rate of 1 scan s^{-1}. Blank samples (without ACs) were analyzed to determine whether additional volatiles were formed

during processing and storage. The ACs were identified by comparing the obtained mass spectra and retention indices with those of authentic standards. To quantify the amount of volatiles in the headspace, five ACs calibration curves were plotted using the peak areas obtained from the GC analysis against known concentrations of each volatile.

Retention, release kinetics and half-life of ACs release

The retention and release kinetics of the ACs were tested using the following procedures. Aliquots (400 mL) of each BG were transferred to open 800 mL glass beakers and stored in a refrigerated container at constant temperature (5 ^{o}C, darkness) for 12 days. At fixed time intervals, the retained quantities of the ACs were recorded at equilibrium conditions and retention values (R) were calculated from the equation: $R = M_t/M_{t=0}$, where: $M_{t=0}$ and M_t, initial and determined at the fixed times quantities of the ACs, correspondently. The release kinetics of the ACs from BGs was computed, applying the Avrami′s equation: $R = \exp[-(k_r t)^{nr}]$, where: k_r, release rate constant; n_r, release mechanism. The half-life (HL) of ACs release from the BGs was calculated using the relation: $HL = [(-\ln 0.5)^{1/nr}]/k_r$.

Thermodynamic study of ACs release

Thermodynamic parameters: gas-binary gel (BG) partition coefficient (k_i) and enthalpy of vaporization (ΔH_{vap}) were determined according to Bortnowska [5]. The k_i values were calculated under conditions of thermodynamic equilibrium at temperatures: 5, 10, 15 and 20 °C. The concentration of aroma compound (AC) in BG was determined by subtracting the quantity of AC in the headspace from the amount of AC originally added. ΔH_{vap} (kJ mol^{-1}) was calculated using van′t Hoff equation: $d\ln k_i/dT = \Delta H_{vap}/RT^2$.

Statistical analysis

All the experiments were performed in triplicate. Significant differences between means ($p \leq 0.05$) were confirmed by a one-way analysis of variance (ANOVA) with Tukey′s multiple comparisons. A two-way analysis of variance was used to examine the effects of two variables (factors), both individually and together, on the experimental response. In order to determine the relationship between the studied variables, Pearson correlations were performed. Statistical analyses were carried out using Statistica 8.0 software (StatSoft Inc., USA).

Results and discussion

Surface hydrophobicity and chemical interactions of myofibrillar proteins (MPs)

The values of surface hydrophobicity and chemical interactions of MPs are presented in Table 2. In both sets of samples tested (WRS-based BGs, TS-based BGs) the values of: S_o, IB, HB, HI and DB were positively correlated with the increase in MPs concentration ($r \geq 0.961$; $p \leq 0.01$) and according to ANOVA were mostly dependent on MPs concentration ($F \geq 4.92$, $p \leq 0.01$). Generally, the upward trend in the values of the tested parameters can be considered in terms of the shorter average distance between protein molecules and a possibly larger number of components available for the interactions [16, 25]. Additionally, hydrophobic amino acids were probably exposed during temperature treatment (pasteurization), which contributed to the increase in S_o and HI [21].

Table 2. Surface hydrophobicity and chemical interactions (mg mL^{-1}) of myofibrillar proteins
Tabela 2. Hydrofobowość powierzchniowa i interakcje chemiczne (mg mL^{-1}) białek miofibrylarnych

Waxy rice starch - based binary gels / Żele binarne na bazie skrobi ryżowej woskowej						Tapioca starch - based binary gels / Żele binarne na bazie skrobi tapiokowej					
Myofibrillar proteins concentration (%) / Stężenie białek miofibrylarnych (%)											
2	4	6	8	10	12	2	4	6	8	10	12
Surface hydrophobicity / Hydrofobowość powierzchniowa											
276^{a}	309^{b}	348^{c}	371^{e}	382^{f}	396^{f}	312^{b}	378^{d}	384^{e}	402^{g}	416^{h}	423^{h}
Ionic bonds / Wiązania jonowe											
0.14^{b}	0.16^{c}	0.21^{e}	0.25^{f}	0.27^{g}	0.29^{g}	0.12^{a}	0.13^{a}	0.16^{c}	0.18^{d}	0.19^{d}	0.21^{e}
Hydrogen bonds / Wiązania wodorowe											
0.37^{b}	0.52^{d}	0.58^{e}	0.65^{f}	0.71^{g}	0.74^{g}	0.28^{a}	0.39^{b}	0.48^{c}	0.56^{d}	0.58^{e}	0.62^{f}
Hydrophobic interactions / Oddziaływania hydrofobowe											
2.42^{a}	2.53^{a}	2.84^{b}	3.16^{c}	3.28^{d}	3.45^{e}	3.09^{c}	3.28^{d}	3.45^{e}	3.61^{f}	3.73^{f}	3.91^{g}
Disulfide bonds / Wiązania disiarczkowe											
2.75^{a}	2.81^{b}	2.95^{b}	3.21^{d}	3.49^{e}	3.67^{e}	3.07^{c}	3.26^{d}	3.58^{e}	3.71^{f}	3.95^{f}	4.16^{g}

Explanations / Objaśnienia:
Within the rows, mean values marked with the same letters are not statistically different ($p \leq 0.05$).
W obrębie wierszy wartości średnie oznaczone tymi samymi literami nie różnią się statystycznie ($p \leq$ 0,05).

Water holding capacity (WHC) and rheological properties of binary gels (BGs)

The values of water holding capacity (WHC) and rheological properties of BGs are demonstrated in Table 3. The values of: WHC, τ_0, k and Q parameters were correlated positively with the increase in MPs concentration ($r \geq 0.949$; $p \leq 0.01$), and n negatively ($r \leq -0.949$; $p \leq 0.01$). Moreover, ANOVA revealed a high dependence on

the starch type (ST) and concentration of MPs ($F \geq 4.52$ $p \leq 0.01$). The results showed that all the studied BGs exhibited non-Newtonian shear-thinning behavior, and the n values were much less than 0.5, indicating strong pseudoplasticity [12]. The determined values of τ_0, k and Q were well correlated ($r \geq 0.957$; $p \leq 0.01$) with binding MPs parameters (Table 2), which may suggest the development of a three-dimensional network, and consequently, higher values of the tested rheological parameters [25]. Greater values of the: τ_0, k and Q, found in TS-based BGs, than in the case of WRS-based BGs, may be related to the fact that during the cooling process a large amount of amylose dispersed in hot gelatinized starch may favor the formation of intra- and intermolecular hydrophobic interactions and hydrogen bonds between the starch chains, creating a new crystallized network of hard gel [17].

Table 3. Water holding capacity and rheological properties of binary gels (5 °C)
Tabela 3. Wodochłonność i właściwości reologiczne żeli binarnych (5 °C)

Waxy rice starch - based binary gels / Żele binarne na bazie skrobi ryżowej woskowej						Tapioca starch - based binary gels / Żele binarne na bazie skrobi tapiokowej					
Myofibrillar proteins concentration (%) / Stężenie białek miofibrylarnych (%)											
2	4	6	8	10	12	2	4	6	8	10	12
Water holding capacity, WHC (%) / Wodochłonność, WHC (%)											
84.2^{b}	89.3^{c}	94.7^{d}	98.4^{e}	100^{f}	100^{f}	79.6^{a}	83.5^{b}	89.6^{c}	96.8^{e}	98.7^{e}	100^{f}
Yield stress, τ_0 (Pa) / Granica płynięcia, τ_0 (Pa)											
0.47^{a}	0.72^{b}	1.07^{c}	1.52^{e}	2.49^{g}	3.26^{h}	0.49^{a}	0.87^{b}	1.34^{d}	1.89^{f}	3.51^{i}	4.83^{j}
Consistency index, k (Pa s^n) / Indeks konsystencji, k (Pa s^n)											
2.08^{a}	2.79^{b}	4.02^{d}	5.13^{f}	7.16^{h}	8.93^{i}	2.14^{a}	3.31^{c}	4.65^{e}	6.07^{g}	9.51^{j}	11.6^{k}
Flow behavior index, n (-) / Wskaźnik płynięcia, n (-)											
0.33^{d}	0.31^{d}	0.29^{c}	0.27^{b}	0.25^{b}	0.23^{a}	0.32^{d}	0.29^{c}	0.28^{c}	0.26^{b}	0.22^{a}	0.19^{a}
Quality factor, Q (-) / Współczynnik jakości, Q (-)											
12.7^{a}	15.9^{b}	20.1^{d}	22.6^{d}	26.1^{e}	28.7^{g}	17.4c	21.6^{d}	27.4^{f}	29.6^{g}	33.2^{h}	36.7^{i}

Explanations / Objaśnienia:
Within the rows, mean values marked with the same letters are not statistically different ($p \leq 0.05$).
W obrębie wierszy wartości średnie oznaczone tymi samymi literami nie różnią się statystycznie ($p \leq 0{,}05$).

Stern-Volmer quenching constants, binding and thermodynamic parameters for aroma compounds (ACs) – myosin (MYO) interactions

Fluorescence test results are shown in Table 4. In all the studied BGs, a decrease in fluorescence intensity with increasing ACs concentration was observed (data not shown). The parameters of Stern-Volmer equation (K_{sv}, K_q) were positively correlated ($r \geq 0.794$; $p \leq 0.05$) with the increase in temperature, which may suggest that binding

of the ACs to MYO was an endothermic process and tended to stronger MYO-ACs interactions [3, 18].

Table 4. Stern-Volmer quenching constants, binding and thermodynamic parameters of aroma compounds-myosin interactions

Tabela 4. Stałe wygaszania Sterna-Volmera i parametry termodynamiczne dla interakcji substancji zapachowych z miozyną

	T (K)	Stern-Volmer quenching constants / Stałe wygaszania Sterna-Volmera		Binding parameters / Parametry wiązania		Thermodynamic parameters / Parametry termodynamiczne		
		K_{sv} ($\times 10^{-4}$ L mol^{-1})	K_q ($\times 10^{-12}$ L mol^{-1} s^{-1})	K_b ($\times 10^{-5}$ L mol^{-1})	n_b (−)	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
HAL	308	3.24	3.24	5.57	1.34	−33.9	−39.7	−18.9
	318	6.03	6.03	3.61	1.21	−33.8		
	328	5.57	5.57	2.23	1.16	−33.5		
	338	6.39	6.39	1.42	1.09	−33.2		
NAL	308	2.80	2.80	1.27	1.17	−30.1	36.9	218
	318	4.39	4.39	2.11	1.18	−32.4		
	328	5.98	5.98	3.32	1.19	−34.7		
	338	6.87	6.87	4.47	1.21	−35.6		
BAE	308	2.48	2.48	1.08	1.16	−29.7	34.1	207
	318	4.25	4.25	1.93	1.17	−32.3		
	328	5.91	5.91	2.82	1.18	−34.2		
	338	6.57	6.57	3.46	1.21	−35.8		
EAE	308	2.89	2.89	3.78	1.29	−32.9	−37.1	−13.4
	318	5.13	5.13	2.41	1.18	−32.8		
	328	5.82	5.82	1.59	1.12	−32.6		
	338	5.89	5.89	1.06	1.08	−32.5		
CVE	308	3.04	3.04	2.59	1.24	−31.9	38.7	229
	318	4.72	4.72	4.03	1.25	−34.1		
	328	6.49	6.49	6.64	1.27	−36.5		
	338	7.05	7.05	9.76	1.31	−38.7		

Explanations / Objaśnienia:

(1) Aroma compounds: 1-heptanol (HAL), nonanal (NAL), 2-butanone (BAE), ethyl acetate (EAE), s-(+)-carvone (CVE). (2) Quenching constant (K_{SV}), quenching rate constant (K_q), binding constant (K_b), number of binding sites (n_b), changes: Gibb′s free energy (ΔG), enthalpy (ΔH), entropy (ΔS).

(1) Substancje zapachowe: 1-heptanol (HAL), nonanal (NAL), 2-butanon (BAE), octan etylu (EAE), s-(+)-karwon (CVE). (2) Stała wygaszania (K_{SV}), stała szybkości wygaszania (K_q), stała wiązania (K_b), liczba miejsc wiązania (n_b), zmiany: energii swobodnej Gibbsa (ΔG), entalpii (ΔH), entropii (ΔS).

The K_q values ranged from 2.48 to 7.05 × 10^{12} L mol^{-1} s^{-1} and were larger than the maximum scatter collision quenching constant (2.0 × 10^{10} L mol^{-1} s^{-1}), which indicates that fluorescence quenching had a static mechanism [5]. The K_b and n_b parameters of EAE and HAL were negatively correlated ($r \leq -0.972$; $p \leq 0.05$) with the increase in temperature and those of: NAL, BAE, CVE positively ($r \geq 0.959$; $p \leq 0.05$). The decrease of K_b can be interpreted in terms that EAE and HAL had non-flexible structure, therefore do not fit properly in the protein's cavity and thus, not bind correctly on the protein's surface [15]. Opposite properties most probably exhibited: NAL, BAE and CVE. The values of n_b were higher than 1, suggesting that more than one molecule of the ACs were bound on the MYO surface near the troponin residues [3]. In all the studied samples the ΔG values were negative, pointing out that the ACs-MYO interactions were spontaneous. Moreover, negative ΔG values in relation to EAE and HAL decreased with increasing temperature, while in the case of: NAL, BAE and CVE they increased, and these changes had the same trend as K_b and n_b. This can be interpreted that the ACs-MYO complexes become less and more stable with increasing temperature, respectively [5].

Retention and release of aroma compounds

Aroma compounds (ACs) retention during refrigerated storage (RST, 5 °C, 12 days) in the BGs was determined under equilibrium conditions, which made it possible to assess the impact of all factors on the stability of the ACs in the system. Changes in retention values (RVs) of selected samples are shown in Figure 1 A-D.

The RVs demonstrated a descending trend with increasing RST, clearly dependent on an AC type and the composition of the BGs, particularly, the starch type. The percentage of the ACs retained in the samples after 12 days of RST in relation to: HAL, NAL, BAE, EAE and CVE was as follows: WRS-based BGs, 2 % MPs (49.1, 54.3, 51.2, 44.1 and 59.3 %); WRS-based BGs, 12 % MPs (62.3, 74.1, 68.2, 55.4 and 78.1 %); TS-based BGs, 2 % MPs (58.1, 66.3, 55.1, 47.4 and 63.1 %); TS-based BGs, 12 % MPs (68.2, 83.1, 72.5, 62.1 and 78.4 %). Moreover, comparing the samples containing 12 and 2 % MPs, the RVs were greater by: WRS-based BGs (21.2, 27.1, 25.3, 20.4 and 24.5 %); TS-based BGs (14.7, 20.5, 23.6, 24.2 and 19.3 %). The RVs found after 12 days of refrigerated storage in relation to myofibrillar proteins concentration are presented in Fig. 2A and B. In general, the RVs of ACs were bigger ($p \leq 0.05$) in TS-based BGs than in the corresponding ones prepared with WRS. Moreover, regardless of ST, an increasing concentration of MPs contributed to increased retention ($r \geq 0.908$; $p \leq 0.05$). The effect of biopolymers on the RVs also depended on the type of aroma compound (AC). In the BGs aromatized with HAL and NAL, the RVs were

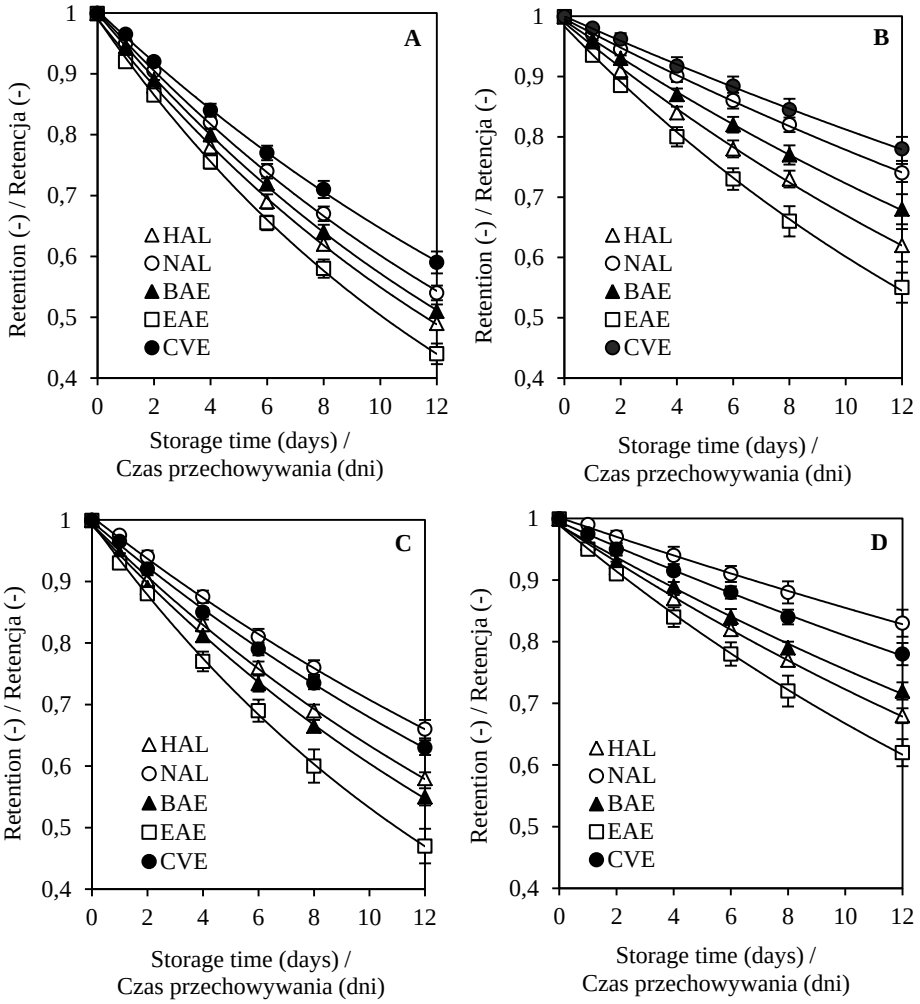

Fig. 1. Retention of aroma compounds in relation to refrigerated storage time (5 °C) in binary gels made with: 8 % waxy rice starch and 2 % myofibrillar proteins (A), 8 % waxy rice starch and 12 % myofibrillar proteins (B), 8 % tapioca starch and 2 % myofibrillar proteins (C), 8 % tapioca starch and 12 % myofibrillar proteins (D).

Rys. 1. Retencja substancji zapachowych w zależności od czasu chłodniczego przechowywania (5°C) w żelach binarnych przygotowanych z użyciem: 8 % skrobi ryżowej woskowej i 2 % białek miofibrylarnych (A), 8 % skrobi ryżowej woskowej i 12 % białek miofibrylarnych (B), 8 % skrobi tapiokowej i 2 % białek miofibrylarnych (C), 8 % skrobi tapiokowej i 12 % białek miofibrylarnych (D).

Explanations / Objaśnienia:

Aroma compounds: 1-heptanol (HAL), nonanal (NAL), 2-butanone (BAE), ethyl acetate (EAE), s-(+)-carvone (CVE).

Substancje zapachowe: 1-heptanol (HAL), nonanal (NAL), 2-butanon (BAE), octan etylu (EAE), s-(+)-karwon (CVE).

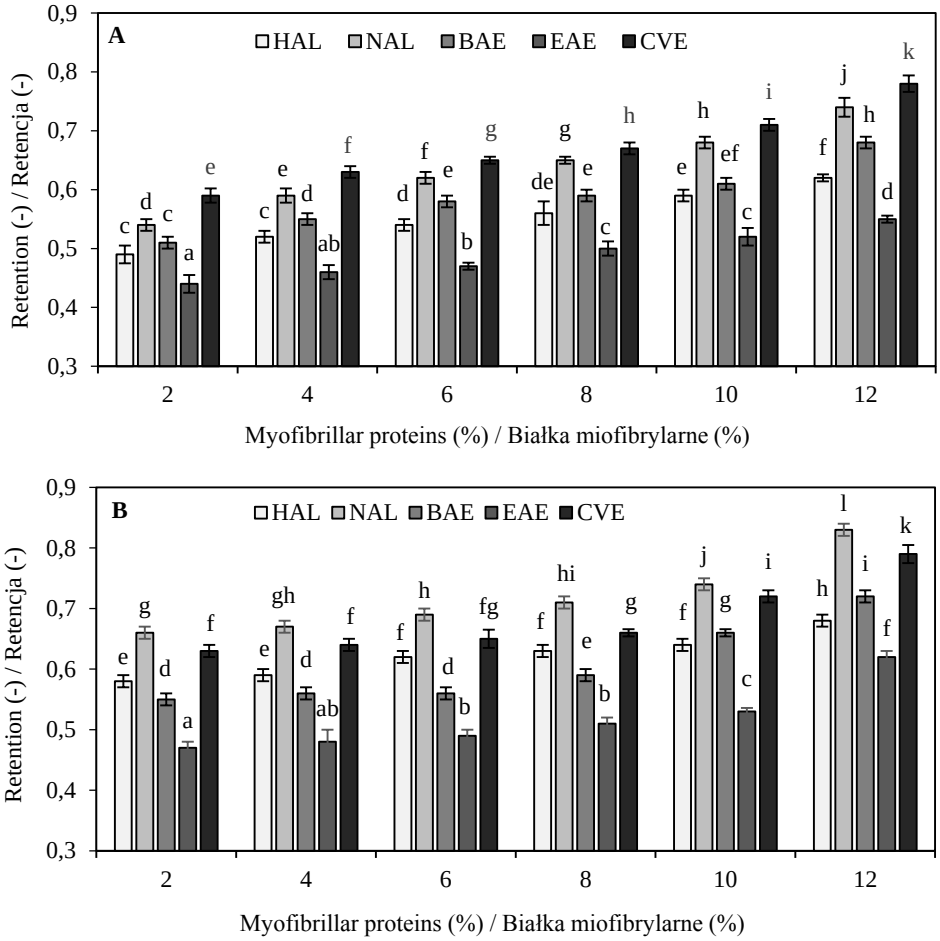

Fig. 2. Retention of aroma compounds after 12 days of refrigerated storage time (5 °C) in waxy rice starch - based binary gels (A) and tapioca starch - based binary gels (B), depending on the concentration of myofibrillar proteins.

Rys. 2. Retencja substancji zapachowych po 12 dniach chłodniczego przechowywania (5 °C) w żelach binarnych na bazie skrobi ryżowej woskowej (A) lub skrobi tapiokowej (B), w zależności od stężenia białek miofibrylarnych.

Explanations / Objaśnienia:

(1) Aroma compounds: 1-heptanol (HAL), nonanal (NAL), 2-butanone (BAE), ethyl acetate (EAE), s-(+)-carvone (CVE). (2) Mean values marked with the same letters are not statistically different ($p \leq 0.05$).

(1) Substancje zapachowe: 1-heptanol (HAL), nonanal (NAL), 2-butanon (BAE), octan etylu (EAE), s-(+)-karwon (CVE). (2) Wartości średnie oznaczone tymi samymi literami nie różnią się statystycznie ($p \leq$ 0,05).

mostly affected by ST ($F \geq 12.3$; $p \leq 0.01$). Whereas in those containing: BAE, EAE, CVE, a greater effect of MPs concentration was observed than ST ($F \geq 4.81$; $p \leq 0.01$).

In complex systems such as BGs, the RVs determined under equilibrium conditions can be related to many factors. The first reason can be attributed to the non-covalent interactions between ACs and proteins. The results, determined by spectrofluorometric assay, are suggesting: hydrophobic interactions (NAL, BAE, CVE) and hydrogen bonding (EAE, HAL). The second reason can be considered in terms of the formation covalent interactions, as detected by changes in the total content of sulfhydryl (–SH) groups (TSG) and free amino ($–NH_2$) groups (FAG), which decreased ($r \leq –0.983$; $p < 0.01$) with increasing RST.

For example, in WRS-based BGs containing 12 % MPs, after 12 days of RST, the TSH values changed from 49.8 nmol mg^{-1} protein (freshly prepared sample) to: 43.2 (EAE), 35.7 (NAL), 38.2 (BAE), 44.4 (HAL) and 37.4 (CVE) nmol mg^{-1} protein. Whereas FAG changed from 78.6 nmol mg^{-1} protein (freshly prepared sample) to: 67.2 (EAE), 52.4 (NAL), 55.7 (BAE), 67.4 (HAL) and 54.6 (CVE) nmol mg^{-1} protein (data not shown). Thus, it is possible to suppose that relatively high RVs found in BGs aromatized with: NAL, BAE and CVE, may be considered the effect of ketones (BAE, CVE) and aldehyde (NAL) covalent binding with amino acids-reactive groups: $–NH_2$ or –SH and the formation of Schiff bases or thioketals and thioacetals [2, 15]. Moreover, the trapping in the complex gel network as a combined effect of starch and MPs should be considered as well [14]. It should be noted here that although covalent interactions increase the retention of ACs in the system, they also reduce their sensory availability. Therefore, a large range of covalent interactions of ACs with the components of the system is rather undesirable.

The release kinetics of the ACs from the BGs was studied during 12 days of refrigerated storage (RST, 5 ^{o}C) in relation to ST (WRS-based BGs, TS-based BGs) and MPs concentration. The data measured during RST were modelled using the Avrami′s equation and thus determined release parameters (release rate constant, k_r; release mechanism, n_r) and half-lives of ACs (HLs) are demonstrated in Table 5. Irrespectively of the ST used (WRS-based BGs, TS-based BGs), k_r and n_r values demonstrated downward trends and were negatively correlated ($r \leq −0.947$; $p \leq 0.01$) with increasing MPs concentration. Moreover, ANOVA revealed that the MPs concentration had the greatest influence on the tested release parameters. The values of HLs were positively correlated with the increase in MPs concentration ($r \geq 0.849$; $p \leq 0.05$) and, according to ANOVA, predominantly affected by MPs content ($F \geq 9.13$; $p \leq 0.001$). In comparison to samples prepared with 2 % MPs, the k_r values in BGs containing 12 % MPs were smaller by: WRS-based BGs (HAL, 67.6 %; NAL, 71.7 %; BAE, 70.5 %; EAE, 55.3 %; CVE, 67.4 %); TS-based BGs (HAL, 71.9 %; NAL, 67.2 %; BAE, 79.7 %; EAE, 67.3 %; CVE, 66.8 %).

Table 5. Parameters of Avrami′s equation and half-lives of aroma compounds in binary gels, depending on starch type and myofibrillar proteins concentration

Tabela 5. Parametry równania Avramiego i okresy półtrwania substancji zapachowych w żelach binarnych, w zależności od rodzaju skrobi i stężenia białek miofibrylarnych

	Waxy rice starch - based binary gels / Żele binarne na bazie skrobi ryżowej woskowej						Tapioca starch - based binary gels / Żele binarne na bazie skrobi tapiokowej					
	Myofibrillar proteins concentration (%) / Stężenie białek miofibrylarnych (%)											
	2	4	6	8	10	12	2	4	6	8	10	12
Release rate constant, $k_r \times 10^3$ (day^{-1}) / stała szybkości uwalniania, $k_r \times 10^3$ ($dzień^{-1}$)												
HAL	42.9^{k}	33.1^{j}	30.2^{i}	22.1^{g}	18.2^{e}	13.9^{c}	30.1^{i}	26.7^{h}	20.4^{f}	15.6^{d}	11.9^{b}	8.46^{a}
NAL	20.5^{h}	15.1^{g}	13.4^{f}	9.92^{e}	7.13^{c}	5.81^{b}	15.6^{g}	10.5^{e}	8.93^{d}	7.24^{c}	5.51b	5.12a
BAE	34.2^{i}	29.2^{h}	24.4^{g}	17.0^{d}	13.3^{c}	10.1^{b}	29.4^{h}	23.9^{f}	21.7^{e}	15.3^{c}	9.51^{a}	5.93^{a}
EAE	56.1^{l}	51.2^{k}	46.3^{j}	39.9^{h}	34.5^{e}	25.1^{b}	46.2^{j}	43.8^{i}	37.2^{g}	32.3^{d}	27.9^{c}	15.1^{a}
CVE	18.2^{i}	13.5^{g}	11.7^{f}	8.42^{d}	7.74^{c}	5.92^{b}	15.7^{h}	14.2^{g}	10.2^{e}	5.71^{b}	5.23^{a}	5.21^{a}
Release mechanism, n_r (−) / Mechanizm uwalniania, n_r (−)												
HAL	0.73^{d}	0.72^{d}	0.69^{c}	0.65^{b}	0.63^{b}	0.61^{a}	0.72^{d}	0.71^{d}	0.67^{c}	0.63^{b}	0.59^{a}	0.58^{a}
NAL	0.64^{d}	0.63^{d}	0.61^{c}	0.59^{c}	0.57^{c}	0.54^{b}	0.63^{d}	0.61^{c}	0.58^{c}	0.55^{b}	0.52^{a}	0.49^{a}
BAE	0.71^{d}	0.71^{d}	0.68^{c}	0.63^{b}	0.61^{a}	0.59^{a}	0.69^{c}	0.67^{c}	0.64^{b}	0.61^{a}	0.58^{a}	0.56^{a}
EAE	0.76^{e}	0.75^{d}	0.73^{d}	0.71^{c}	0.69^{c}	0.65^{b}	0.74^{d}	0.72^{c}	0.69^{c}	0.67^{b}	0.65^{b}	0.62^{a}
CVE	0.66^{c}	0.65^{c}	0.64^{c}	0.61^{b}	0.59^{b}	0.57^{b}	0.65^{c}	0.64^{c}	0.61^{b}	0.54^{a}	0.53^{a}	0.51^{a}
Half-live, HL (days) / Okres półtrwania, HL (dni)												
HAL	14.1^{a}	17.9^{b}	19.6^{c}	25.8^{d}	31.0^{e}	39.4^{f}	20.3^{c}	22.2^{c}	28.3^{d}	35.7^{e}	45.0^{g}	63.5^{h}
NAL	27.5^{a}	37.1^{b}	42.1^{b}	54.4^{c}	74.1^{d}	87.3^{e}	35.8^{b}	52.4^{c}	59.6^{c}	70.9^{d}	90.6^{e}	95.4^{f}
BAE	17.6^{a}	20.4^{b}	23.9^{b}	32.8^{c}	41.4^{d}	53.1^{e}	20.3^{b}	24.2^{b}	26.1^{c}	35.5^{d}	56.2^{e}	87.7^{f}
EAE	11.1^{a}	12.3^{a}	13.2^{a}	14.9^{b}	17.1^{c}	22.7^{d}	13.2^{a}	13.7^{a}	15.8^{b}	17.9^{c}	20.4^{d}	36.8^{e}
CVE	31.6^{a}	42.4^{b}	48.3^{c}	65.6^{d}	69.6^{d}	89.8^{e}	36.3^{b}	39.8^{b}	54.1^{c}	88.7^{e}	96.8^{f}	97.5^{f}

Explanations / Objaśnienia:

(1) Aroma compounds: 1-heptanol (HAL), nonanal (NAL), 2-butanone (BAE), ethyl acetate (EAE), s-(+)-carvone (CVE). (2) Within the rows, mean values marked with the same letters are not statistically different ($p \leq 0.05$).

(1) Substancje zapachowe: 1-heptanol (HAL), nonanal (NAL), 2-butanon (BAE), octan etylu (EAE), s-(+)-karwon (CVE). (2) W obrębie wierszy wartości średnie oznaczone tymi samymi literami nie różnią się statystycznie ($p \leq 0{,}05$).

Generally, ACs release is affected by a number of their parameters like: hydrophobicity, water solubility and volatility, which are usually connected to the volatiles structural properties, concerning: chain length, branching and the presence and position of a functional groups [28]. Moreover, the rheological properties of the BGs had a significant impact on the kinetics of ACs release. For example, it was found that an increase in the MPs concentration corresponded to an increase in the consistency index (Table 3) of the system and a decrease in the k_r values (Table 5), which is essentially

consistent with the relationships presented in the Wilke-Chang equation [5, 22]. The k_r values are expressing changes of RVs during RST and these were well correlated ($r \geq 0.823$; $p \leq 0.05$) with rate constants: k_k, $k_{\tau 0}$, $k_{Q,}$ related to changes during RST of: k, τ_0 and Q, respectively.

Thermodynamic studies

Under strictly defined measurement conditions, the values of partition coefficient (k_i) determined at equilibrium, reflect the impact of the entire system in terms of: composition, intermolecular interactions, physicochemical properties of the system and others on the process of ACs release to the headspace [5]. The k_i values were measured at temperatures ranging from 5 to 20 ^oC, and those found at 20 ^oC are presented in Fig. 3A and B. In both studied sets of samples, an increase in MPs concentration resulted in a decrease in k_i values ($r \leq -0.879$; $p \leq 0.05$). ANOVA revealed with respect to samples aromatized with HAL and NAL that ST predominantly affected k_i ($F \geq 8.16$; $p \leq 0.01$), whereas in the BGs containing: BAE, EAE and CVE, the k_i values were mainly affected by MPs content ($F \geq 15.4$; $p \leq 0.001$). This may suggest that apart from interactions of the ACs with biopolymers that are specified above, HAL and NAL interacted with amylose helices either inside the hydrophobic cavity of the helix or between the free space of the helices [20, 23].

Increasing temperature (5-20 ^oC) contributed to greater values of k_i and their changes in WRS-based BGs and TS-based BGs containing 12 % MPs are presented in Figure 4A and B, respectively.

The studies have shown that the k_i values were positively correlated ($r \geq 0.995$; $p \leq 0.01$) with temperature increasing from 5 to 20 ^oC and those detected at 20 ^oC in comparison to those found at 5 ^oC, for HAL, NAL, BAE, EAE and CVE in WRS-based samples increased by: 30.9, 27.8, 27.3, 37.1 and 26.1 %, respectively. Whereas, regarding TS-based samples the k_i values were greater by: 28.7, 23.6, 25.1, 34.9 and 25.2 %, correspondently. The results are generally in good agreement with the studies of Ammari and Schroen [1] and can be interpreted as the result of the influence of many factors, including varied accelerated diffusion of ACs to the headspace due to the changes in the rheological properties of research matrices and non-covalent interactions between ACs and biopolymers. The van′t Hoff equation was used to evaluate changes of equilibrium constants (k_i) and thus calculated values of enthalpy of vaporization (ΔH_{vap}) are shown in Table 6.

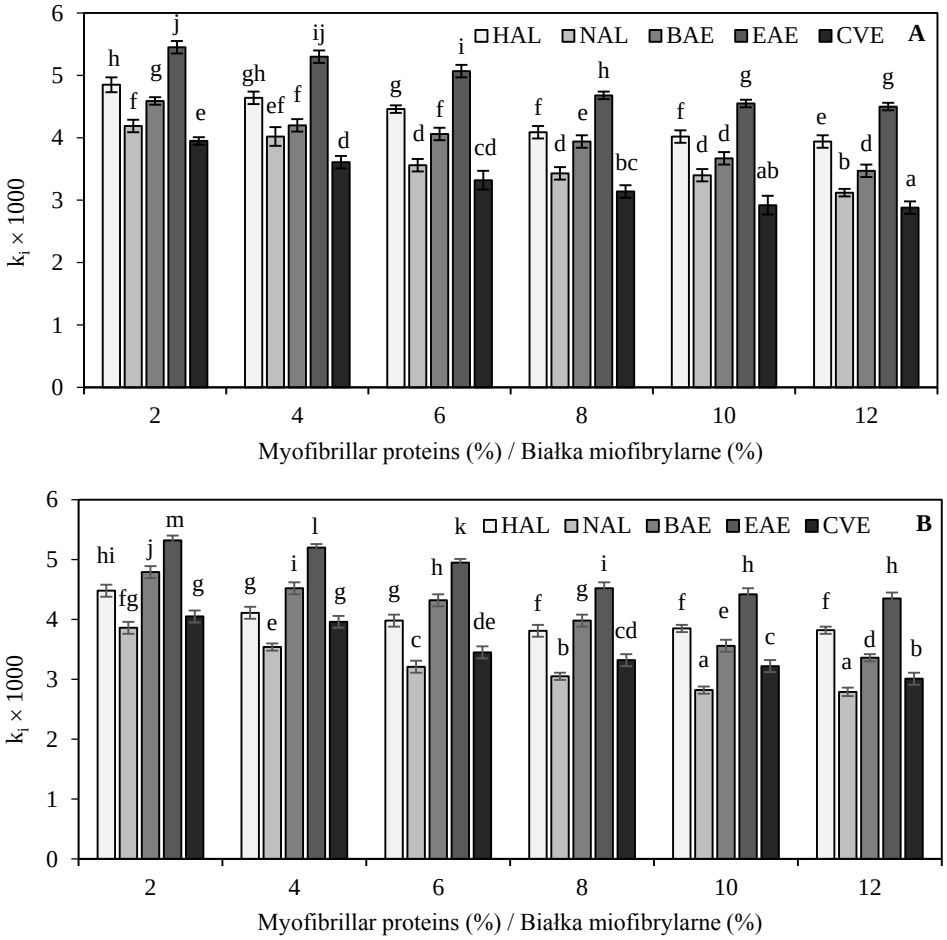

Fig. 3. Partition coefficient of aroma compounds for waxy rice starch - based binary gels (A) and tapioca starch - based binary gels (B), depending on the concentration of myofibrillar proteins.

Rys. 3. Współczynnik podziału dla substancji zapachowych w żelach binarnych na bazie skrobi ryżowej woskowej (A) lub skrobi tapiokowej (B), w zależności od stężenia białek miofibrylarnych.

Explanations / Objaśnienia:

(1) Partition coefficient (k_i, 20 °C). (2) Aroma compounds: 1-heptanol (HAL), nonanal (NAL), 2-butanone (BAE), ethyl acetate (EAE), s-(+)-carvone (CVE). (3) Mean values marked with the same letters are not statistically different ($p \leq 0.05$).

(1) Współczynnik podziału (k_i, 20 °C). (2) Substancje zapachowe: 1-heptanol (HAL), nonanal (NAL), 2-butanon (BAE), octan etylu (EAE), s-(+)-karwon (CVE). (3) Wartości średnie oznaczone tymi samymi literami nie różnią się statystycznie ($p \leq 0{,}05$).

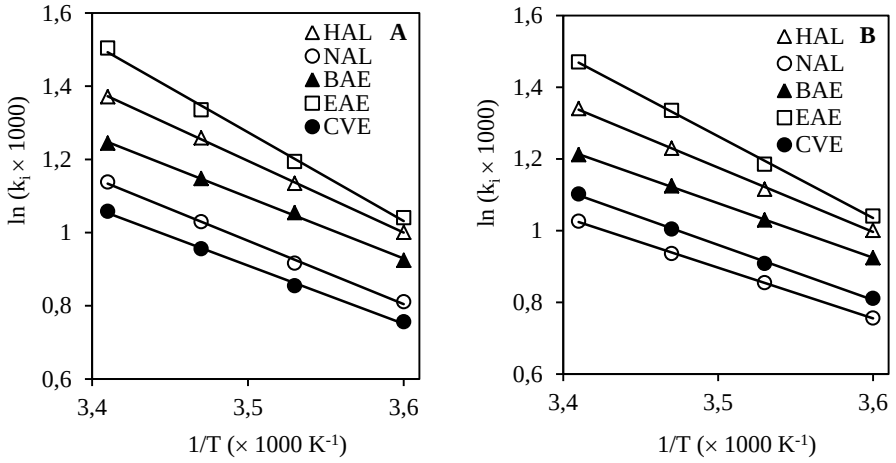

Fig. 4. The ln of the partition coefficient as a function of 1/T (K^{-1}) of aroma compounds for binary gels composed of: 12 % myofibrillar proteins, 8 % waxy rice starch (A) and 12 % myofibrillar proteins, 8 % tapioca starch (B).

Rys. 4. Wartości ln współczynnika podziału w funkcji 1/T (K^{-1}) dla substancji zapachowych w żelach binarnych zawierających: 12 % białek miofibrylarnych, 8 % skrobi ryżowej woskowej (A) lub 12 % białek miofibrylarnych, 8 % skrobi tapiokowej (B).

Explanations / Objaśnienia:

(1) Partition coefficient (k_i). (2) Aroma compounds: 1-heptanol (HAL), nonanal (NAL), 2-butanone (BAE), ethyl acetate (EAE), s-(+)-carvone (CVE).

(1) Współczynnik podziału (k_i). (2) Substancje zapachowe: 1-heptanol (HAL), nonanal (NAL), 2-butanon (BAE), octan etylu (EAE), s-(+)-karwon (CVE).

Table 6. Enthalpy of vaporization of aroma compounds in binary gels, depending on starch type and myofibrillar proteins concentration

Tabela 6. Entalpia parowania substancji zapachowych w żelach binarnych w zależności od rodzaju skrobi i stężenia białek miofibrylarnych

	Waxy rice starch - based binary gels Żele binarne na bazie skrobi ryżowej woskowej						Tapioca starch - based binary gels Żele binarne na bazie skrobi tapiokowej					
	Myofibrillar proteins concentration (%) / Stężenie białek miofibrylarnych (%)											
	2	4	6	8	10	12	2	4	6	8	10	12
HAL	23.3^{e}	23.1^{e}	22.8^{e}	17.2^{b}	16.9^{b}	16.7^{b}	21.2^{d}	18.5^{c}	17.4^{b}	16.5^{b}	15.2^{a}	15.1^{a}
NAL	19.4^{f}	18.8^{f}	17.6^{e}	16.8^{e}	15.9^{d}	14.8^{c}	17.1^{e}	15.8^{d}	13.9^{b}	13.6^{b}	12.2^{a}	12.1^{a}
BAE	21.5^{b}	19.3^{c}	18.4^{d}	18.1^{d}	15.2^{e}	14.3^{f}	22.7^{g}	21.7^{f}	18.6^{d}	15.9^{c}	13.8^{b}	13.1^{a}
EAE	25.7^{e}	24.2^{d}	23.1^{c}	21.5^{b}	21.1^{b}	20.7^{b}	24.6^{d}	23.2^{c}	21.8^{b}	20.3^{a}	19.9^{a}	19.5^{a}
CVE	18.1^{e}	16.8^{d}	15.8^{c}	15.1^{b}	13.9^{a}	13.6^{a}	17.6^{e}	18.2^{e}	16.2^{c}	15.3^{b}	13.5^{a}	13.1^{a}

Explanations / Objaśnienia:

(1) Aroma compounds: 1-heptanol (HAL), nonanal (NAL), 2-butanone (BAE), ethyl acetate (EAE), s-(+)-carvone (CVE).

(2) Enthalpy of vaporization (ΔH_{vap}, kJ mol^{-1}).
(3) Within the rows, mean values marked with the same letters are not statistically different ($p \leq 0.05$).
(1) Substancje zapachowe: 1-heptanol (HAL), nonanal (NAL), 2-butanon (BAE), octan etylu (EAE), s-(+)-karwon (CVE).
(2) Entalpia parowania (ΔH_{vap}, kJ mol^{-1}).
(3) W obrębie wierszy wartości średnie oznaczone tymi samymi literami nie różnią się statystycznie ($p \leq 0{,}05$).

In both studied sets of samples, ΔH_{vap} were negatively correlated with increasing MPs concentration ($r \leq -0.908$; $p \leq 0.05$) and according to ANOVA, in samples aromatized with HAL and NAL, mostly affected by ST ($F \geq 9.48$; $p \leq 0.01$), whereas in those composed of: BAE, EAE, CVE, predominantly by MPs concentration ($F \geq 4.28$; $p \leq 0.01$). The decrease of ΔH_{vap} values was dependent on the AC type and BG composition, and generally was greater ($p \leq 0.05$) in the case of samples containing TS than WRS. During equilibrium vaporization, a certain amount of energy (ΔH_{vap}) must be supplied to facilitate the escaping of ACs from the restraint caused by intermolecular attractive forces [24]. Thus the results obtained give the dependency of the k_i determined at equilibrium with respect to temperature.

Conclusions

1. Gluten-free binary gels (BGs) prepared using myofibrillar proteins (MPs) and starches composed of different amylose/amylopectin ratios enable modelling in a wide range of their rheological properties and the retention and release of aroma compounds (ACs) with different affinities to the oil and water phases.
2. ACs containing carbonyl groups (aldehyde, ketones), due to non-covalent and covalent interactions with myofibrillar proteins (MPs), exhibited higher retention values than other ACs (alcohol, ester).
3. The values of gas/binary gel partition coefficient and enthalpy of vaporization were dependent on the physicochemical properties of AC and BG composition, especially the MPs content in the system.
4. The rheological properties of BGs related to the consistency index and quality factor significantly influenced the kinetics and mechanism of ACs release, to a greater extent in systems containing tapioca starch than in those with waxy rice starch.
5. Gluten-free binary gels containing a relatively large amount (10-12 %) of MPs can be intended for direct consumption and as subsystems for other food products to increase the stability of ACs belonging to various classes of chemical compounds.

This work was financed from statutory funds of the Department of Fish, Plant and Gastronomy Technology, West Pomeranian University of Technology in Szczecin, Poland.

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WPŁYW SKŁADU BEZGLUTENOWYCH ŻELI BINARNYCH NA RETENCJĘ I UWALNIANIE SIĘ SUBSTANCJI ZAPACHOWYCH

S t r e s z c z e n i e

Wprowadzenie. Bezglutenowe żele binarne (BGs) wytwarzane z użyciem polisacharydów i białek zwierzęcych mogą być produktami spożywczymi o dużym znaczeniu praktycznym ze względu na stale postępujące zagrożenie celiakią. Ponadto zrozumienie czynników wpływających na stabilność substancji zapachowych (ACs) jest bardzo ważne, ponieważ akceptacja żywności przez konsumentów zależy głównie od jej aromatu. Celem badań była ocena termodynamicznych i kinetycznych właściwości ACs w BGs

przygotowanych z użyciem skrobi różniących się zawartością amylozy w zależności od stężenia białek miofibrylarnych (MPs). BGs zawierały: 8 % skrobi ryżowej woskowej (WRS) lub skrobi z tapioki (TS) oraz MPs w zakresie 2 ÷ 12 %. Do aromatyzacji BGs zostały użyte: 1-heptanol, nonanal, 2-butanon, octan etylu, oraz s-(+)-karwon. Badania obejmowały pomiary: właściwości reologicznych BGs, niekowalencyjnych oddziaływań pomiędzy miozyną i ACs oraz ich retencji i uwalniania, a także entalpii parowania (ΔH_{vap}).

Wyniki i wnioski. Głównymi niekowalencyjnymi interakcjami pomiędzy miozyną i ACs były wiązania wodorowe i oddziaływania hydrofobowe. Parametry retencji i uwalniania się ACs, wyznaczane w czasie chłodniczego przechowywania BGs (12 dni), były statystycznie istotnie ($p \leq 0{,}05$) zależne od: rodzaju skrobi, stężenia MPs oraz fizykochemicznych właściwości ACs. Stałe szybkości uwalniania się ACs były statystycznie istotnie ($p \leq 0{,}05$) skorelowane z odpowiadającymi im stałymi zmian parametrów reologicznych wyznaczanymi z równania kinetycznego pierwszego rzędu. Wartości ΔH_{vap} w BGs zawierających TS były na ogół mniejsze ($p \leq 0{,}05$) niż w odpowiednikach przygotowanych z dodatkiem WRS. Żele binarne (BGs) o stosunkowo dużej zawartości białka mogą być przeznaczone do bezpośredniego spożycia oraz jako podkłady do innych produktów spożywczych w celu zwiększenia stabilności ACs.

Słowa kluczowe: żele binarne, aromat, interakcje, retencja i uwalnianie, entalpia parowania