Black chokeberry (*Aronia melanocarpa*) copigmentation reaction: Thermodynamic and kinetic investigations

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Abstract. Two type of parameters (thermodynamics and kinetics) were used to determine thermal stability of copigmentation process in black chokeberry: chlorogenic acid system. According to thermodynamic investigations copigmentation complex was destroyed at high temperature and restored again at low temperature. Different parameters kinetic rate constant, energy of activation and z-factor were presented and the reaction Based on them the order of the reaction was determined as first order.

1 Introduction

The colorants (pigments) including a group of anthocyanins were basically used in the foods. They have a main role at food processing and storage. The development of copigmentation and encapsulation were recently started [1]. The review of the copigmemtation process was provided from Trouillas et al. [2]. They presented a description in π–π bonds and different interactions in pigment:copigment couples with applications in food chemistry. The presentation of copigmentation process with pigment and different acids was observed [3]. Two acids Ferulic and tannic presented the bathochromic and hyperchromic effect. The ferulic, sinapic and syringic acids in were investigated as copigment with bayberry as pigment [4]. The copigmentation effect was found as significant. Thermodynamic parameters were calculated and all of them were with a negative sign. After the results the copigmentation was determined as spontaneous and exothermic. Hassan et al. [5] investigated effects of copigmentation interactions of pea extracts at different pH.

Influence of sinapic acid into stability of anthocyanin extract obtained after producing of strawberry purees from (Camarosa, Rubygem and Festival) was presented. The process was performed at high-pressure and high temperature stored fruits in refrigerated storage conditions [6]. Anthocyanins color products from sauco (*Sambucus peruviana)* and extract from purple carrots were investigated as pigment:copigment couple. Sauco anthocyanins are more appropriate to provide darker and intense color. Purple carrots present less intense color [7]. Chemical reaction between chlorogenic acid as copigment and strawberry anthocyanins as pigment in chokeberry juices was observed. Chlorogenic acid is used in high concentrations. Application is seen in the change of color intensity of the juices. Interactions

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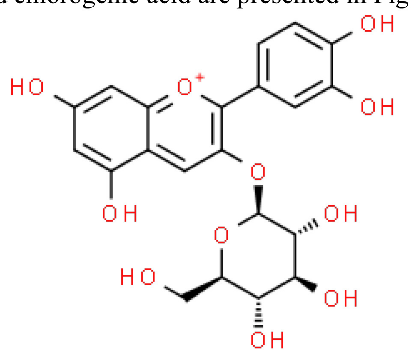
were provide at concentrations 1:1 to 1:50 pigment:copigment couple [8]. Petrova and Gandova [9] presented interactions between pigment and copigment couple in strawberry sistem. This system was investigated for thermodynamic and kinetic stability. Malvidin-3-O-glucoside as pigment takes interaction with sinapic acids as copigment. In these couples is not used influence of pH but is observed at equilibrium at moderately acidic [10]. Copigmentation effect between sinapic acid and anthocyanins in strawberry purees was investigated and was found to not have good copigmentations between them [11]. Copigmentation effect in Cabernet Sauvignon grape extract was investigated [12]. Rose petal polyphenols as copigment were applied by Castaneda-Ovando et al. [13] in fruit juices. The pigment used strawberry anthocyanins. Copigmentation reaction was determined as intermolecular and intramolecular. Eiro et al. [14] investigated interactions in couple strawberry anthocyanin:chlorogenic acid. Copigmentation reaction was determined as intermolecular. Also, pigment:copigment studies were applied intensively the last years from authors [15, 16]. Activation energy was calculated in Black chokeberry fresh fruits using isoconversional analysis [17]. Influence of temperature into black chokeberry juice was presented by measurements of viscosity. All investigation was done in a temperature range of 10 – 60°C. The Arrhenius equation was applied to calculate some kinetic parameters [18].

This work has an aim to use experimental data from spectrophotometer measurements and calculate thermodynamic and kinetic parameters.

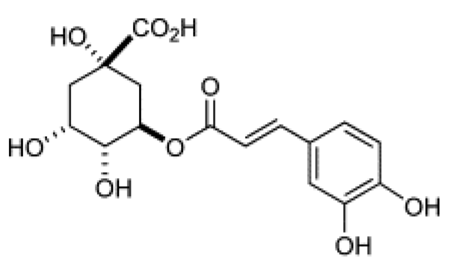
2 Materials and methods

2.1 Experimantal

Chemical the copigment chlorogenic acid was with purification 98 %. The structure formula of cyanidin 3-galactoside and chlorogenic acid are presented in Fig. 1.



a)



b)

Fig. 1. a) Cyanidin 3-galactoside as pigment and b) chlorogenic acid as copigment.

2.2 Extraction and purification

The methodology was presented by Shikov at al. [13].

2.3 Thermodynamic and kinetic calculations

The calculation was made according Skikov at al [13], Petrova et al [16] and Zhu et al [4].

2.4 Statistical analysis

OriginPro 7.0 software was used to presented the work experimet.

3 Results and discussion

Different model solutions were used to investigate the pigment:copigment system. The anthocyanin was with the stoichiometry quantity in the solutions but copigment varies between 1:1 to 1:50 pigment:copigment interaction. Based on the providing experiment the thermodynamic and kinetic parameters were calculated. The calculations were prepared at two temperature ranges at heating and at cooling. First the equilibrium constant was calculated. At heating between 20 to 80°C it presented values between 5754.39 to 478.63, respectively. In high temperatures the constant decreases their values significantly. This indicates thermal instability between pigment:copigment interactions. After cooling it is observed values between 589.04 to 2951.20 for 60°C and 20°C, respectively. These results presented thermal reversibility of pigment:copigment complex. In this case copigmentation reaction presented high importance in food and chemical industries.

After obtaining the equilibrium constants the thermodynamic parameters are determined. The results for them are presented in Table 1.

Gibbs free energy is a temperature dependence parameter. The results presented on the table show that at 20°C at heating the value is -21.45 kJ mol^{-1}. At 20°C at cooling it presented a similar value -21.956 kJ mol^{-1}. These results again confirm reversibility of copigmentation process after heating and following cooling of model solutions. According authors [16] reversibility of their work for the copigmentation process was seen.

Table 1. Thermodynamic parameters obtained in anthocyanins:chlorogenic acid system.

Temperature, °C		Gibbs enegy, kJ mol^{-1}	Enthalpy, kJ mol^{-1}	Entropy, kJ K^{-1} mol^{-1}
Heatig	20	-21.45 ± 0.20	-27.24 ± 0.26	-0.017 ± 0.0
	40	-20.79 ± 0.19	-26.65 ± 0.25	-0.020 ± 0.0
	60	-17.08 ± 0.16	-26.07 ± 0.25	-0.028 ± 0.0
	80	-16.75 ± 0.15	-25.99 ± 0.24	-0.029 ± 0.0
Cooling	60	-17.56 ± 0.15	-26.23 ± 0.24	-0.027 ± 0.0
	40	-21.09 ± 0.19	-26.46 ± 0.24	-0.021 ± 0.0
	20	-21.95 ± 0.20	-29.83 ± 0.27	-0.016 ± 0.0

Zhu et al. [4] obtained small Gibbs energies compared with those obtained in this work (Table 1) between 6.93 and 7.96 kJ.mol^{-1} for complexes for three phenolic acids. Janković et al. [17] investigated degradation of black chokeberry and determined activation energies to 21.831 kJ mol^{-1} and 22.714 kJ mol^{-1}. According to literature data after application of the Arrhenius equation the activation energy was obtained in a range between 22.84 and 40.28 kJ mol^{-1} [18].

After calculations the copigmentation process was presented as spontaneous. Two other parameters enthalpy and entropy were negative at all temperatures and at two types of process at heating and at cooling. Negative enthalpy connected with exothermic processes. The negative entropy is connected with less disorder in the system.

Fig. 2 presented dependences between Gibbs free energy and temperature. On the figure is seen that the system is stable at low temperatures around 20°C. After that at 40°C it is observed thermal instability and at 80°C the system is destroyed. Fig. 3 presented dependences between equilibrium constant and temperature. The figure shows some values of constant heating and cooling. At high temperature the equilibrium constant makes change and presents small values.

Table 2 presented results by obtained kinetic parameters in the system. First the rate constants were calculated. They presented small values at low temperatures and high at high temperatures. These differences are connected with destroying pigment:copigment complex at high temperature. After that linear dependence was observed between anthocyanin concentration and copigmentation time.

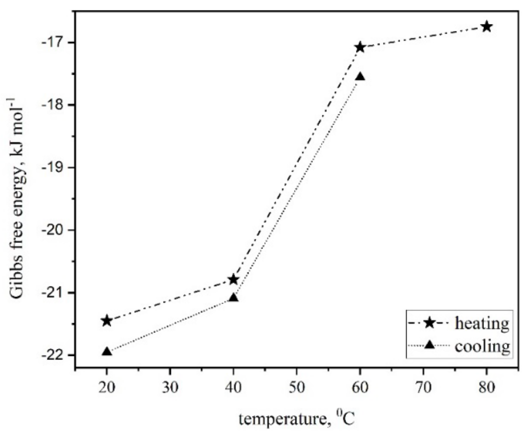


Fig. 2. Temperature dependence of Gibbs free energy.

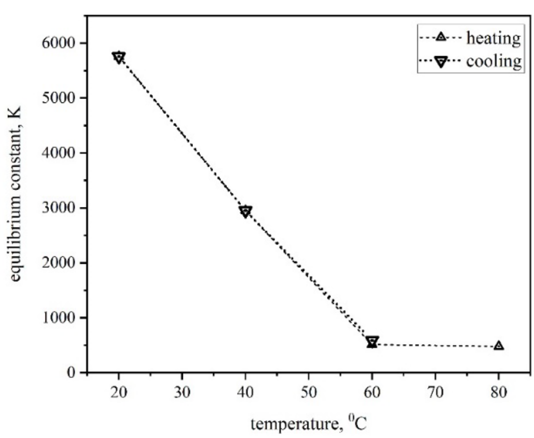


Fig. 3. Temperature dependence of equilibrium constant.

This dependence determined copigmentation reaction as reaction of first order. Linear dependence was presented on Figs. 4 and 5 at heating and cooling. Good correlation coefficients were observed at two temperature ranges. The heating was R^2 = 0.9944 but cooling R^2 = 0.9985.

For calculations the kinetic parameters are obtained. The activation energy is used strong dependencies between natural ln of constants and reciprocal values of temperature. The results are comparable with another found in literature [19].

The half-lives of copigmentation reactions at different temperatures were also calculated. At high temperatures, the rate constants increase and the half-lives decrease which is an indicator of the destruction of the complex in the system. On cooling, half-lives increase as temperature decreases. This is a sign of reversibility of the process and stabilization of the system.

Table 2. Kinetic parameters of the copigmentation interactions between black chokeberry anthocyanins and chlorogenic acid.

System	Temperature, °C	k, s^{-1}	$t_{1/2}$, s	Ea, kJ mol^{-1}	z, °C
black chokeberry: chlorogenic acid	20	0.0504±0.0	297.772±2.80	34.385±0.3	42.493±0.40
	40	0.0721±0.0	258.539±2.40		
	60	0.0928±0.0	224.317±2.11		
	80	0.1147±0.0	196.123±1.80		
	60	0.0975±0.0	212.886±2.08	31.563±0.30	45.967±0.44
	40	0.0798±0.0	245.034±2.15		
	20	0.0541±0.0	272.481±2.40		

The z-factor is a temperature dependent factor. It was determined at heating and at cooling. It is comparable to that reported in the literature. The z-factor was studied in strawberry anthocyanins and quercetin systems under the influence of different temperatures and was determined to be 21.177 [16].

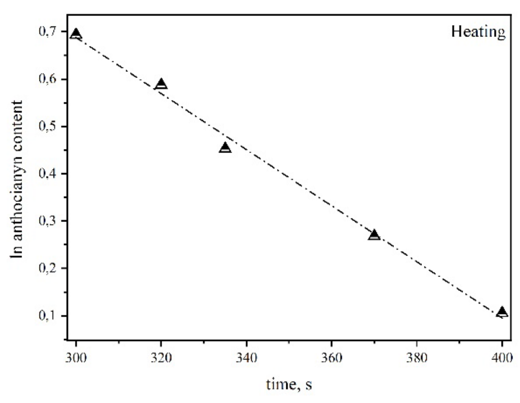


Fig. 4. Reaction order at heating.

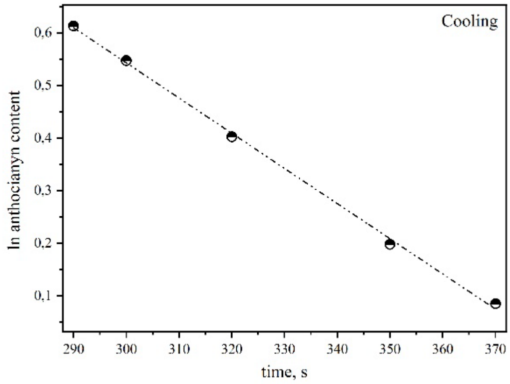


Fig. 5. Reaction order at cooling.

4 Conclusion

Black chokeberry:chlorogenic acid system as pigment:copigment couple was analyzed. The investigations were performed at two temperature ranges. At high temperature 80 ^{0}C destruction of the complex was observed. When the temperature was decreased the restoration of the complex was seen again. After calculations the stable complex was observed based on negative values of all thermodynamic parameters. According to results on the kinetic parameters the reaction was determined as first order. The activation energy at two temperature ranges was calculated and the obtained results again are providing information for reversibility of copigmentation reaction. The use of chlorogenic acid as copigments provides real opportunities for the development of chokeberry functional foods with improved biological properties and increased stability of color and anthocyanin.

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