

UDC 66.061.34:664.22+664.2.057.2

V.D. Myrhorodska-Terentieva^a, *M.V. Nikolenko*^a, *I.V. Sknar*^a, *Ye.S. Osokin*^b,
O.V. Prylovskiy^a, *O.V. Volnyanska*^a, *M.O. Mironyak*^a

PSEUDOCATALYTIC ACCELERATION OF HYDROTHERMAL LEACHING OF AMYLOSE FROM STARCH IN ACIDIC MEDIA

^a Ukrainian State University of Chemical Technology, Dnipro, Ukraine

^b Primus Inter Pares School, Dnipro, Ukraine

Kinetic studies were conducted at 60–70°C using buffer solutions with pH 3–5 to establish the effect of solution acidity on the efficiency of amylose leaching from starch. It was shown that the kinetic data are well described by the Kruger-Ziegler model. It was established that as the pH of the solutions decreases from 5.0 to 3.0, the activation energy of amylose leaching process decreases from 185 to 22 kJ/mol, and its dependence on hydrogen ion concentration is described by two linear segments within the pH ranges of 3.0–3.3 and 3.6–5.0. The effect of reducing the hydrogen bond energy upon addition of an additional proton to the water molecule was demonstrated through quantum-chemical modeling using the Gaussian 09 software. It was shown that protonation of the water molecule leads to a decrease in the effective charge on the oxygen atom from –0.626 to –0.142 unit of electron charge. At the same time, the linearity of the hydrogen bond along the –O...H–O– atoms is violated, the length of the hydrogen bond increases from 1.856 to 2.370 Å, and the binding energy decreases by 4.6 times. Thus, hydrogen ions can be considered as a kind of pseudo-catalyst for the process of amylose leaching from starch grains, since in their presence the activation energy of the process decreases and its rate increases. It was concluded that the process of hydrothermal leaching of amylose from starch can be intensified by carrying it out in acidic media without additional heating of starch suspensions.

Keywords: amylose, leaching, Kruger-Ziegler equation, activation energy, hydrogen bond.

DOI: 10.32434/0321-4095-2023-150-5-72-81

Introduction

Despite the long history of the starch study, this research does not lose its relevance due to its wide use not only in food technology but also in the pulp and paper industry, the construction industry, the textile industry, and, for example, disposable tableware and packaging materials [1–4]. First of all, starch and its modifications are of interest due to their properties of forming pasty solutions. There are chemical, mechanical and hydrothermal methods of gelatinization of starches. Hydrothermal gelatinization of starch is a process of destruction of starch granules in hot solutions, which is accompanied by the removal (technical term – leaching) of amylose and the formation of a starch hydrogel.

Separation of amylose from amylopectin by the method of hydrothermal leaching is carried out by heating a suspension of starch in an excess of water to a temperature slightly above the temperature of gelatinization, so as not to disturb the integrity of the granules. Amylose after leaching can be separated from amylopectin and the remains of starch granules by centrifugation are separated from the solution by precipitation with the addition of a hydrophobic reagent that forms the inclusion complexes [5].

Our studies of the amylose hydrothermal leaching kinetics from potato starch showed that the time dependence of the amylose extraction degree well obeys the Kruger-Zigler equation [6]. This equation was proposed for modeling heterogeneous chemical processes in «solid–solution» systems.

© V.D. Myrhorodska-Terentieva, M.V. Nikolenko, I.V. Sknar, Ye.S. Osokin, O.V. Prylovskiy, O.V. Volnyanska, M.O. Mironyak, 2023



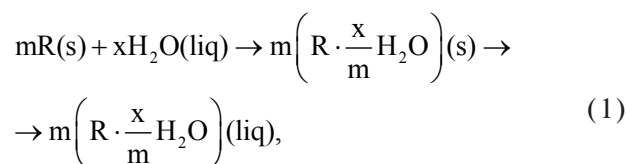
This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

V.D. Myrhorodska-Terentieva, M.V. Nikolenko, I.V. Sknar, Ye.S. Osokin, O.V. Prylovskiy, O.V. Volnyanska, M.O. Mironyak

Calculations showed that the activation energy of the amylose leaching process is 191 kJ/mol at the temperatures of 60–70°C, whereas it decreases to 22 kJ/mol at the temperatures of 80–90°C. The dependence of the activation energy of the gelatinization process on temperature is well known, but the reasons for this regularity are still debatable. For example, it is proposed to describe such an effect in terms of a certain «breaking point» in the kinetics of the process (the so-called critical temperature point of the «solid-liquid» phase transition) which divides the gelatinization process into two following stages: (1) the swelling of the amorphous part; and (2) the destruction of the crystalline part of the starch granules [7,8]. It is assumed that at first the gelatinization takes place in the amorphous areas, and after the «breaking point» it occurs in the crystalline areas. However, for all studied starches, the activation energy is initially higher, and after reaching the «break point» temperature, its value decreases sharply. It is obvious that amorphous formations in starch granules are easier to «destroy» than crystalline ones, i.e. from the point of view of the sequential dissolution of amorphous and crystalline parts of the granule, there should be an inverse relationship: at first, the activation energy has a low value and then it increases. It is obvious that the idea of a «breaking point» in the process kinetics does not allow us to explain the patterns observed. In our opinion, the concept of the critical temperature point of the phase transition is valid only for whole granules. The fact is that when starch is extracted from vegetable raw materials, a part of its granules is destroyed. Obviously, for destroyed granules, the stage of its swelling accelerates significantly. This could explain the observed decrease in the temperature at the start of gelatinization. This feature is well confirmed by the known facts of the possibility of partial gelatinization of starch at temperatures below the «breaking point» [9].

It is believed that the main problem in explaining the effect of the dependence of the activation energy of the gelatinization process on temperature is its high value at low temperatures. If the value of the activation energy at the level of 22 kJ/mol can be attributed to the diffusion process, then the energy values at the level of 200 kJ/mol can be understood only if they characterize chemical interaction. In our opinion, a way out of this paradox is possible using the idea of numerous hydrogen bonds between amylose macromolecules. If breaking one hydrogen bond, for example, in a water dimer requires the energy of 21 kJ/mol, then for ten such bonds between OH groups of amylose macromolecules,

the breaking energy should be of the order of two hundred kilojoules. From this point of view, amylose leaching can be considered a heterogeneous pseudo-chemical process in which amylose (the solid reactant) «reacts» with water as follows:



where R is the amylose macromolecules in starch granules connected by intermolecular bonds;

$\left(R \cdot \frac{x}{m} H_2O\right)$ is hydrated amylose in starch granules with broken intermolecular bonds.

From the point of view of presenting the leaching of amylose by a heterogeneous pseudo-chemical process, it should be concluded that leaching at temperatures of 60–70°C proceeds in a kinetic mode. This conclusion makes it possible to determine the following methods of process intensification: an increase in the process rate due to an increase in temperature and/or the use of a catalyst. The effect of temperature is well known and it was quantitatively described elsewhere [6]. It is of scientific and practical interest to consider the possibility of catalytic acceleration of the amylose leaching process from starch granules.

Acids, which are used industrially in starch hydrolysis processes to obtain glucose and other saccharides, are often indicated as a catalyst for the conversion of starches in the literature. Acids are also used in dextrin production (modified starch with a reduced degree of polymerization of amylose and amylopectin). To accelerate the processes of its thermal destruction, pre-saturation of starch with inorganic acids is used, which intensifies the hydrolysis processes. It is believed that two following processes occur during acid hydrolysis of starch: (1) the destruction of associative bonds between amylose and amylopectin macromolecules, and (2) the breaking of their α -D-(1,4)- and α -D-(1,6)-bonds. Despite the industrial use of acid hydrolysis of starch, there are no published studies on the mechanism and kinetic laws of the influence of acids on the process of amylose leaching from starch. It can be assumed that the weakening and breaking of associative bonds between starch macromolecules will contribute to the process of extracting amylose from

starch granules, but it is not possible to predict at which pH values and to what extent this process will accelerate.

Thus, the aim of the work was to determine the influence of the solution acidity on the efficiency of the amylose leaching process from starch. To quantify this issue, it was of interest to evaluate the effect of acid on the activation energy of the amylose leaching process.

Experimental

Potato starch of the highest grade (Ukrainian state standard DSTU 4286:2004) with 16.8% moisture and 0.30% total ash was used in the experiments. 8.5 cm³ of 0.10 M NaOH solution was used to neutralize 100 g of starch (in terms of dry matter).

To study the kinetics of amylose leaching, 400.0 ml of buffer solution was poured into a round-bottomed flask with a paddle stirrer. A 0.05 M solution of potassium phthalic acid (pH 4.0) and its mixture with hydrochloric acid or sodium hydroxide were used as buffer solutions (to vary the pH in the range of 3–5). The flask was placed in a thermostat and heated to a set temperature in the range of 60–70°C. Then, at constant stirring, a portion of starch weighing 4.00 g was added to the solution. 5 ml of the solution was periodically taken for spectrophotometric analysis of the amylose content during leaching. The measurement method is described in detail elsewhere [6]. The chosen conditions of the experiment made it possible to obtain amylose solutions in concentrations that did not go beyond the linear dependence of light absorption of its complexes with iodine on concentration (0–2.2 mg/ml).

The leaching degree was calculated based on the data of three parallel measurements as the ratio of the current values of light absorption of amylose solutions with iodine to its maximum value for the given conditions of the isothermal experiment, which was determined after 6 hours of leaching.

The rate constants were determined by the Kruger-Ziegler equation:

$$k \cdot \ln t = \left(1 - (1 - X)^{1/3}\right)^2, \quad (2)$$

where X is the degree of amylose extraction; k is the observed rate constant of the process; and t is the isothermal holding time.

The content of reducing substances in starch (i.e. aldehyde groups formed during the hydrolysis of starch) was determined by potentiometric titration in a slightly alkaline environment (pH ~9) using titrated solutions of iodine and sodium thiosulfate [10]. The possibility of hydrolysis of starch was also

checked by determining the change in weight of its samples when they were treated with acidic solutions with a pH of 3–5. It was assumed that during hydrolysis, water-soluble fragments of polymers can be formed, which will lead to a decrease in the mass of starch. Portions of starch (2 g) were weighed on an analytical balance and kept at intensive stirring for one hour in buffer solutions (volume 75 ml) at a temperature of 50°C. Then the sediments were washed three times with distilled water, dried at 100–110°C and weighed.

Results and discussion

A natural increase in the degree of amylose extraction was observed with increasing duration of leaching in all experiments on hydrothermal leaching of starch in solutions with a pH of 3–5. In addition, as in the case of amylose leaching from aqueous solutions [6], X(t) dependences have the form of convex curves that tend to saturation with increasing the leaching time.

To choose a kinetic model, the obtained data were analyzed using known kinetic equations that are used to describe processes in «solid–liquid» systems: one- and two-dimensional diffusion, Yander, «anti-Yander», Kruger-Zigler, Ginstling-Brownstein, Zhuravlev-Lesokhin-Tempelmann, Avrami-Yerofeev, compressible sphere, zero, first and second order, exponential and power. Statistical processing of the kinetic dependences X vs. t in the coordinates of these equations according to the Fisher variance ratio at a significance level of 0.05 showed that the best results ($R^2 > 0.99$) were obtained when the kinetic data were described by the Kruger-Zigler equation. Figures 1–5 show the results of kinetic measurements in the coordinates of this equation. As can be seen from the presented plots, the experimental dependences X vs. t are well linearized in the selected coordinates.

The fundamental difference of this Krueger-Ziegler model from other models of heterogeneous chemical processes is that the diffusion coefficient of transported ions or molecules is not considered a constant, but a variable value that is inversely proportional to time (Appendix A). Since the hydration of the outer layers of starch granules changes the architecture of their intermolecular bonds, the variability of the diffusion coefficient of water molecules as a reagent in this model is quite understandable. The assumption of Krueger and Ziegler that the diffusion coefficient can be inversely proportional to time is well fulfilled in this case: the longer the hydration time, the thicker the layer of hydrated macromolecules and the smaller the diffusion coefficient.

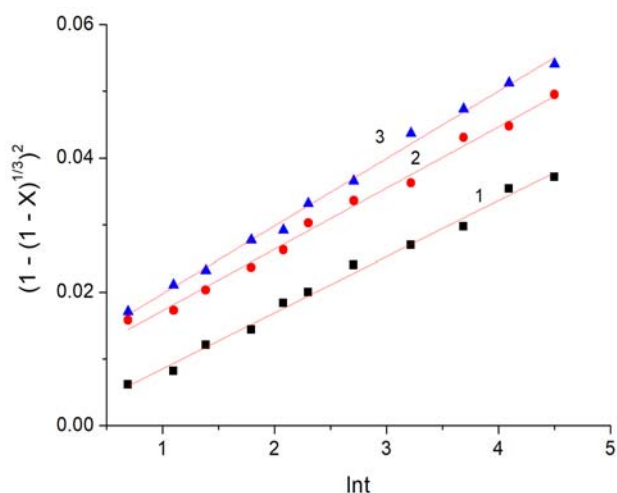


Fig. 1. Dependences of the amylose extraction degree from starch in a buffer solution with pH 3.0 on the time of isothermal holding at temperatures of 62°C (1), 66°C (2) and 69°C (3) in the coordinates of the Kruger-Zigler equation

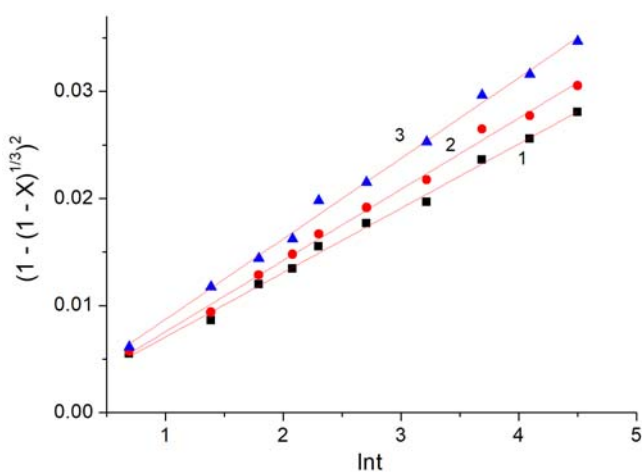


Fig. 2. Dependences of the amylose extraction degree from starch in a buffer solution with pH 3.3 on the time of isothermal holding at temperatures of 62°C (1), 66°C (2) and 70°C (3) in the coordinates of the Kruger-Zigler equation

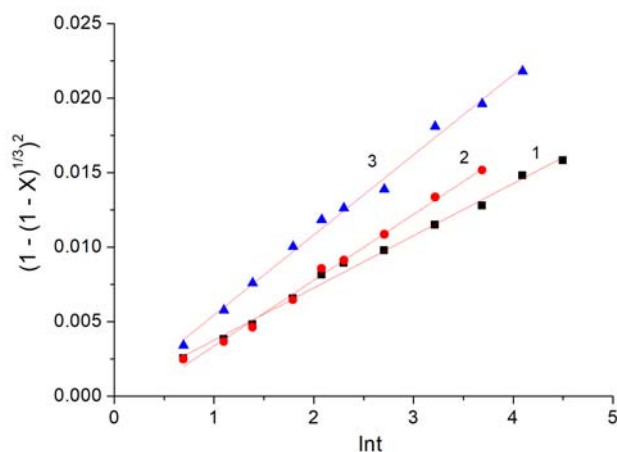


Fig. 3. Dependences of the amylose extraction degree from starch in a buffer solution with pH 3.6 on the time of isothermal holding at temperatures of 62°C (1), 66°C (2) and 70°C (3) in the coordinates of the Kruger-Zigler equation

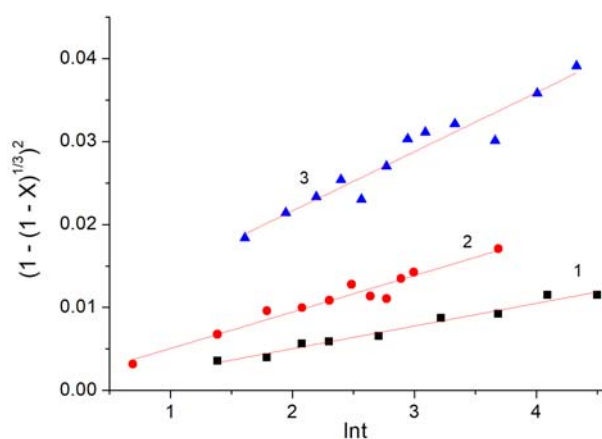


Fig. 4. Dependences of the amylose extraction degree from starch in a buffer solution with pH 4.0 on the time of isothermal holding at temperatures of 62°C (1), 66°C (2) and 70°C (3) in the coordinates of the Kruger-Zigler equation

The rate constants of the amylose leaching process at different temperatures were calculated from the slopes of the straight lines in Figs. 1–5. The treatment of the temperature dependences of the calculated rate constants in the coordinates of the Arrhenius equation (Fig. 6) allows determining the activation energies of the researched processes (Table 1).

From the obtained data, first of all, we note the complex nature of the dependence of the rate constants on the pH of the solutions in which leaching was carried out. If its values naturally decrease with an increase in the pH of the media at temperatures below 66°C, then this sequence is broken at higher

temperatures. It is obvious that this is due to a sharp decrease in the activation energies of the leaching process, the values of which naturally increase with increasing pH.

In the coordinates of the dependence of activation energies on the concentration of hydrogen ions (Fig. 7), the effect of the acidity of the media on E_a can be described by two linear sections on the graph. In the pH range from 5 to 3.6, the activation energy of the amylose leaching process from starch decreases linearly with increasing hydrogen ion concentration. Then, in the area of pH 3.3–3.6, a sharp change in the slope of the E_a vs. C_{H^+} dependence is observed.

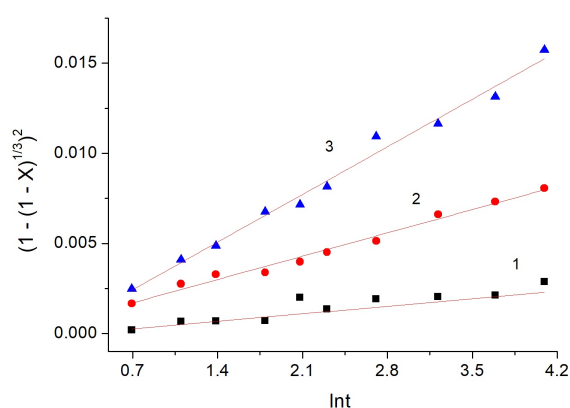


Fig. 5. Dependences of the amylose extraction degree from starch in a buffer solution with pH 5.0 on the time of isothermal holding at temperatures of 62°C (1), 66°C (2) and 70°C (3) in the coordinates of the Kruger-Ziegler equation

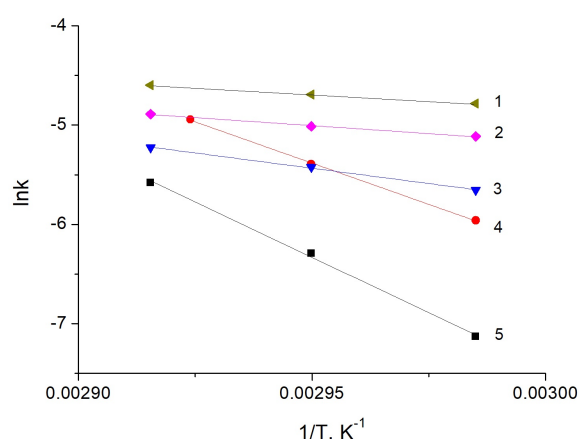


Fig. 6. Comparison of the rate constants of the leaching process of amylose from starch in buffer solutions with pH 3.0 (1), 3.3 (2), 3.6 (3), 4.0 (4), and 5.0 (5) in the temperature range of 62–70°C in the coordinates of the Arrhenius equation

Table 1
The rate constants of the Kruger-Ziegler equation at different pH and temperatures and the activation energy of the amylose extracting process from potato starch in the range of 62–70°C

pH	$t, ^\circ\text{C}$	$-\ln k$	$E_a, \text{kJ/mol}$
3.0	62	4.783	22.2
	66	4.694	
	69	4.597	
3.3	62	5.114	26.8
	66	5.013	
	69	4.890	
3.6	62	5.655	51.1
	66	5.424	
	70	5.227	
4.0	62	5.960	138.1
	66	5.393	
	70	4.943	
5.0	62	7.131	185.2
	66	6.293	
	70	5.581	

In our opinion, this nature of the dependence of the activation energy on the solution acidity can be explained by the influence of hydrogen ions on the strength of intermolecular bonds of amylose, namely on the strength of hydrogen bonds between their OH groups. For example, according to ref. [11], the strength of intermolecular bonds of amylose well correlates with the volume density of hydrogen bonds available for formation. Obviously, as the concentration of hydrogen ions increases, the share of protonated oxygen atoms in the OH groups of starch polymers increases and the strength of hydrogen bonds decreases

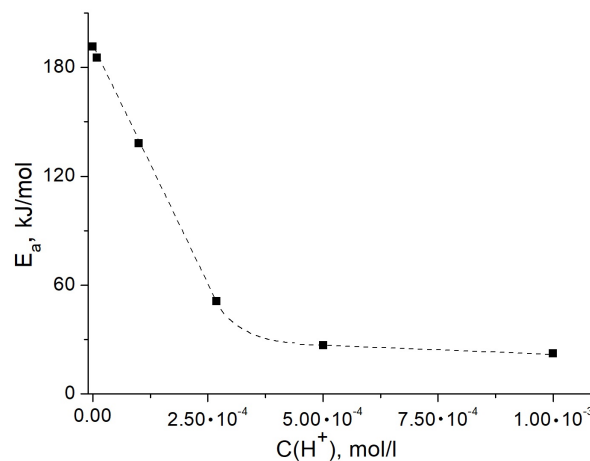


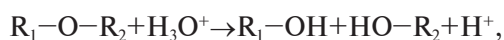
Fig. 7. Dependence of the activation energy of amylose extracting process from potato starch on the concentration of hydrogen ions for the temperature range of 62–70°C

proportionally. After saturation with protons, this effect should decline, which explains the second section in Fig. 7. To confirm the hypothesis about protons' influence on the hydrogen bond's strength, we performed quantum chemical modeling (Appendix B).

As is known, a hydrogen bond can be considered a type of covalent bond, since its formation is accompanied by a redistribution of electron density and can lead to qualitative changes in the structure of the interacting molecules. Currently, it is considered that the description of the hydrogen bond within the framework of the MO method is the most favorable approximation. To simplify the model, we considered

the water dimer before and after the addition of a proton. Calculations showed that the protonation of the water molecule leads to a decrease in the effective charge on the oxygen atom from -0.626 to -0.142 unit of electron charge. At the same time, the linearity of the hydrogen bond along the $-O\cdots H-O-$ atoms is violated, the equilibrium length of the hydrogen bond increases from 1.856 \AA to 2.370 \AA , and the binding energy decreases by 4.6 times. Thus, the performed simulation shows that the regularities of Fig. 7 can be explained by a decrease in the energy of hydrogen bonds with an increase in the concentration of hydrogen ions. Obviously, when starch granules are saturated with protons, a further increase in their concentration no longer affects the strength of hydrogen bonds so effectively and we observe a decrease in the rate of change of the activation energy at $\text{pH} < 3.6$ on the E_a vs. C_{H^+} curve.

It should be noted that the decrease in the activation energy of the amylose extraction process at a reduced pH of the solution can be explained not only by a change in the strength of intermolecular hydrogen bonds but also by the possibility of gradual hydrolysis of amylose and amylopectin, that is, by the disintegration of their macromolecules into smaller fragments as a result of the $-C-O-C-$ bond breaking:



where R_i is the fragments of amylose or amylopectin macromolecules.

Since hydrogen ions are not consumed in such reactions, they are considered a catalyst. Oligosaccharides formed by this reaction are divided into reducing and non-reducing. The thing is that during the hydrolysis of starch, reducing ends are formed at the places where macromolecules are broken (an open form of glucose with a free reactive aldehyde group). Therefore, under industrial conditions, the hydrolysis of starch is characterized by a change in the so-called reducing index. The research was performed on the content of reducing substances in amylose solutions obtained by leaching in buffer solutions. The analysis was carried out by the method of potentiometric titration using titrated solutions of iodine and sodium thiosulfate. It was found that in the amylose solution obtained by leaching from 1.00 g of starch in 100 ml of a buffer solution with a pH of 3.0 at a temperature of 70°C for 60 minutes, the content of reducing substances was $3.8 \cdot 10^{-5}$ mol. In our opinion, a relatively small content of reducing substances in acidic solutions of amylose may indicate not only its partial hydrolysis but also

an increased probability of opening glucose cycles at the ends of amylose macromolecules. Therefore, the possibility of the hydrolysis of starch under the conditions of our experiment was also checked by determining the change in the weight of its samples when they were treated with buffer solutions at a temperature of 50°C , that is, before the start of the gelatinization process. Studies have shown that the changes in the weight of starch in experiments with distilled water and solutions with pH 3.0 and 4.0 are the same and amount to 16.75%. A similar decrease in weight by 16.75% was observed when drying starch at the same temperatures, which indicates a decrease in weight due to its dehydration. Therefore, in the experiments performed at pH 3–4, we did not confirm the formation of water-soluble starch oligomers, which allows us to conclude that there is no hydrolysis under the chosen experimental conditions. Thus, it should be concluded that the obtained features of the decrease in the activation energy with a decrease in the pH of the solution are not related to the partial hydrolysis of starch, but are the result of the influence of hydrogen ions on the strength of the hydrogen bond.

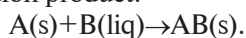
Conclusions

The performed studies showed that an increase in the acidity of the solutions leads to an acceleration of the amylose leaching from potato starch at temperatures of $60-70^\circ\text{C}$. The obtained regularities are well explained by the influence of hydrogen ions on the strength of intermolecular hydrogen bonds of amylose. Based on the data of quantum chemical simulation, it can be assumed that the protonation of the OH groups of starch polymers leads to a decrease in the effective charge on the oxygen atoms, disrupts the linearity of the hydrogen bond along the $-O\cdots H-O-$ atoms, and increases the length of the hydrogen bond. All these factors decrease the binding energy between amylose macromolecules, which lowers the energy barrier in the way of their leaching process.

Despite the absence of a chemical reaction, hydrogen ions can be considered as a kind of pseudo-catalyst in the process of extracting amylose from starch granules, since in its presence the activation energy of the process decreases and its rate increases. The formal use of a mathematical description of the leaching process by using the Kruger-Ziegler equation proved to be justified from the point of view of establishing the regularities of the process and the possibility of a quantitative assessment of its parameters. It was found for the first time that the process of hydrothermal leaching of amylose from starch can be intensified by using acidic media without additional heating of starch suspensions.

Appendix A. Kruger-Ziegler kinetic model

As is known, the Kruger-Ziegler model considers a heterogeneous chemical process between solid reagent A and soluble reagent B with the formation of a solid reaction product:



For a spherical particle of a solid reactant with an effective radius r_0 , a product layer with a thickness of z will form during the time interval t as a result of the reaction:

$$r = r_0 - z,$$

where r_0 is the initial radius; z is the thickness of the reaction product layer; and r is the radius of a solid particle at a certain time t .

The conversion degree of a solid reactant $(1-X)$ can be written in terms of the ratio of its volumes at the moment of time t and before the beginning of the conversion:

$$1 - X = \frac{\frac{4}{3}\pi(r_0 - z)^3}{\frac{4}{3}\pi(r_0)^3}.$$

From this equation, it follows that

$$z = r_0 \left(1 - (1 - X)^{\frac{1}{3}} \right).$$

Kruger and Ziegler proposed to take into account the possibility of changing the diffusion coefficient of reagent B, transferred through the layer of the reaction product AB: $D = k_1/t$. Using the Yander model (with a parabolic law of dependence on the time of the gradual growth of the reaction product layer), they presented the rate of change in the thickness of the reaction product layer in the following form:

$$\frac{dz}{dt} = \frac{DV_m C_0}{z} = \frac{k_1 V_m C_0}{tz},$$

where D is the diffusion coefficient; V_m is the molar volume of the reaction product; and C_0 is the concentration of the soluble reagent on the surface.

After the separation of variables and integration of this equation:

$$\int z dz = \int V_m C_0 k_1 \frac{dt}{t},$$

one can get the following expression:

$$z^2 = 2V_m C_0 k_1 \ln t.$$

Combining this equation with the previous formula for z , one can obtain:

$$r_0^2 = \left(1 - (1 - X)^{\frac{1}{3}} \right)^2 = 2V_m C_0 k_1 \ln t.$$

To simplify the equation, we denote the product of constant quantities by a new constant (k) and obtain the Kruger-Ziegler equation:

$$k \ln t = \left(1 - (1 - X)^{\frac{1}{3}} \right)^2.$$

The validity of using the Kruger-Ziegler model to describe the starch gelatinization process can be demonstrated by the scheme for the starch hydration stage (Eq. (1)). It can be considered that the stage of amylose hydration is characterized by a variable diffusion coefficient of water molecules through the

product layer $\left(R \cdot \frac{x}{m} H_2O \right)(s)$ as a result of a change in the conformational structure of the polymer during the destruction of intermolecular bonds.

Appendix B. Quantum-chemical modeling of proton influence on hydrogen bond energy

Quantum chemical simulation was performed using the Gaussian 09 software using the 6-311++G(2d, 2p) basis set [12]. The DFT calculation method with the B3LYP hybrid functional was used. Solvation effects were taken into account using two models: the polarization continuum PCM [13] and the universal solvation model based on the SMD electron density [14]. Using the AIM2000 and AIMALL programs, a topological analysis of electron density distribution functions was performed using the QTAIM method. The formation of hydrogen bonds was determined by the presence of a critical point of type (3;-1) between water molecules in the dimer. The binding energy of the hydrogen bond was calculated according to the equation given in ref. [15]: $E_b = 0.5 \cdot V(r_{avg})$, where E_b is the binding energy of interatomic interaction, and $V(r_{avg})$ is the potential energy density at the corresponding critical point.

Table 2
Values of binding energies and potential energy density at the critical point (3;-1) for dimers $[H_2O \cdots H_2O]$ and $[H_2O \cdots H_3O^+]$

Dimer	Eb, kJ/mol		V(r_{avg}), Hartree atomic units	
	PCM	SMD	PCM	SMD
$H_2O \cdots H_2O$	-28.16	-30.24	-0.021452	-0.023033
$H_2O \cdots H_3O^+$	-	-6.60	-	-0.005025

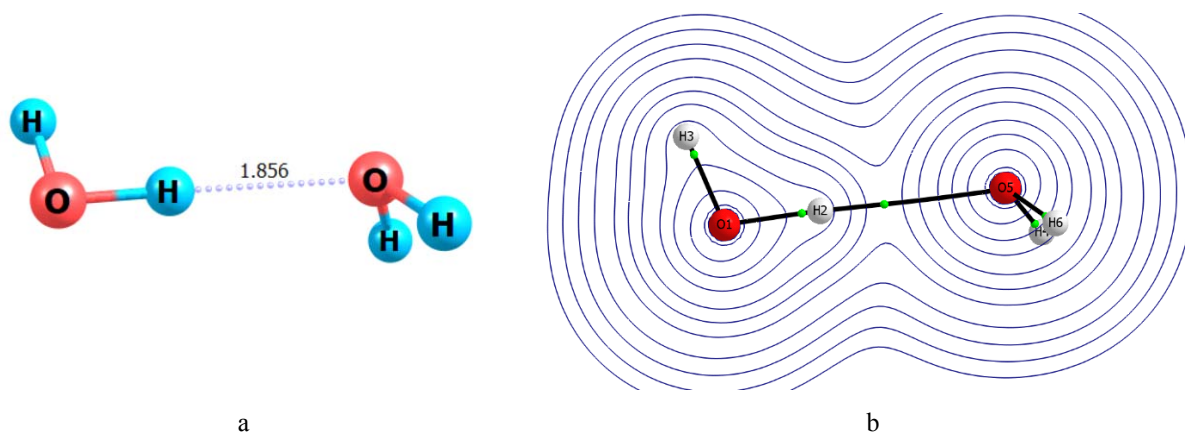


Fig. 8. Calculation results of the optimized state for the dimer $[\text{H}_2\text{O}\cdots\text{H}_2\text{O}]$: (a) – optimized 3d model, and (b) – molecular graph with potential energy density surface in the H3–O1–H2–O5 plane

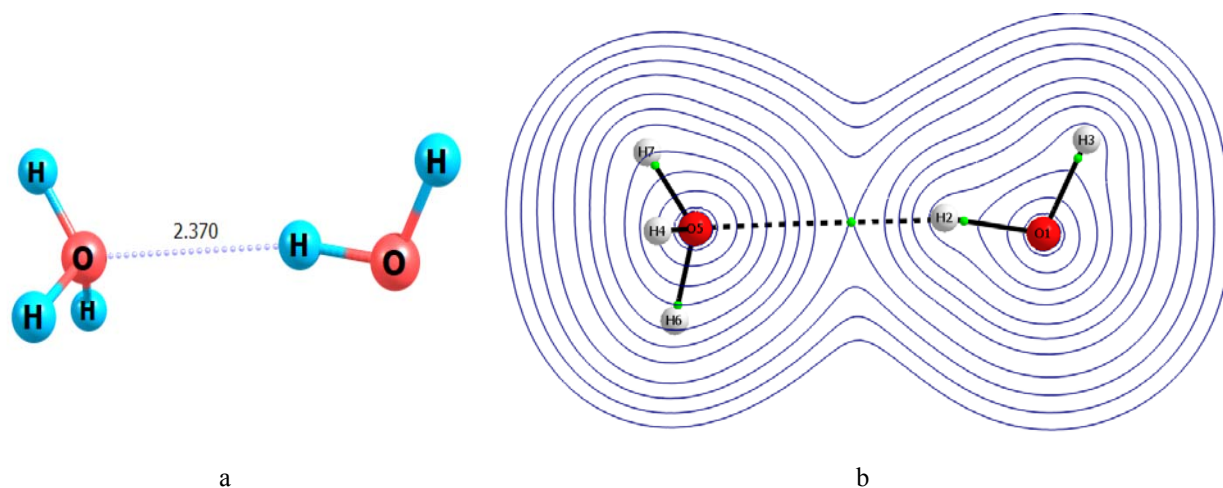


Fig. 9. Calculation results of the optimized state for the $[\text{H}_2\text{O}\cdots\text{H}_3\text{O}^+]$ dimer: (a) – optimized 3d model, and (b) – molecular graph with the potential energy density surface in the H3–O1–H2–O5 plane

The results of the calculations are summarized in Table 2 and Figs. 8 and 9.

Calculations showed that in the $[\text{H}_2\text{O}\cdots\text{H}_2\text{O}]$ dimer, the binding energy for a hydrogen bond according to two polarization methods, PCM and SMD, is quite close: -28.16 and -30.24 kJ/mol, respectively. For comparison, the binding energy for the $[\text{H}_2\text{O}\cdots\text{H}_2\text{O}]$ dimer in a vacuum (i.e. excluding solvation effects) is -22.63 kJ/mol. On the H3–O1–H2–O5 potential energy density plane, an intermolecular critical point (3;–1) is established, where the electron density gradients $\rho(r)$ are zero (shown in green in figures). The optimized hydrogen bond length for the $[\text{H}_2\text{O}\cdots\text{H}_2\text{O}]$ dimer was 1.856 Å.

For the $[\text{H}_2\text{O}\cdots\text{H}_3\text{O}^+]$ dimer, the value of the binding energy for a hydrogen bond using the SMD method was -6.60 kJ/mol with a bond length of

2.370 Å (Fig. 9). In the approximation of the PCM polarization continuum model, the formation of a hydrogen bond is not found: no minimum is recorded on the H3–O1–H2–O5 potential energy density plane. Calculations in a vacuum also showed the impossibility of forming a hydrogen bond in the $[\text{H}_2\text{O}\cdots\text{H}_3\text{O}^+]$ dimer. Calculations using the universal SMD solvation model showed that the addition of a proton to a water molecule leads to a decrease in the negative effective charge on the oxygen atom involved in the formation of a hydrogen bond from -0.626 to -0.142 unit of electron charge. It is also important to note that in the dimer $[\text{H}_2\text{O}\cdots\text{H}_3\text{O}^+]$, there is a violation of linearity among the $-\text{O}\cdots\text{H}-\text{O}-$ atoms and the length of the hydrogen bond increases. All these changes in the electronic structure of the water dimer after the addition of a proton leads to a 4.6-times decrease in the binding energy of the hydrogen bond.

REFERENCES

1. *Current trends in the preparation, characterization and applications of oat starch – a review* // Kaur P., Kaur K., Basha S.J., Kennedy J.F. // *Int. J. Biol. Macromol.* – 2022. – Vol.212. – P.172-181.

2. *Fan Y., Picchioni F. Modification of starch: a review on the application of “green” solvents and controlled functionalization* // *Carbohydr. Polym.* – 2022. – Vol.241. – Art. No. 116350.

3. *Physical, thermal, mechanical, antimicrobial and physicochemical properties of starch based film containing aloe vera: a review* // Nizam N.H.M., Rawi N.F.M., Ramle S.F.M., Aziz A.A., Abdullah C.K., Rashedi A., Kassim M.H.M. // *J. Mater. Res. Technol.* – 2021. – Vol.15. – P.1572-1589.

4. *Adewale P., Yancheshmeh M.S., Lam E. Starch modification for non-food, industrial applications: Market intelligence and critical review* // *Carbohydr. Polym.* – 2022. – Vol.291. – Art. No. 119590.

5. *Amylolysis of amylopectin and amylose isolated from wheat, triticale, corn and barley starches* / Naguleswaran S., Vasanthan T., Hoover R., Bressler D. // *Food Hydrocolloids.* – 2014. – Vol.35. – P.686-693.

6. *Mekhanizm vilugovuvannya amilozy z natyvnoho i termoobroblynykh krokhmaliv u haryachiy nadlyshkoviy void* / Myrhorodska-Terentieva V.D., Nikolenko M.V., Kovalenko I.L., Avdienko T.M. // *Voprosy Khimii i Khimicheskoi Tekhnologii.* – 2023. – No. 1. – P.73-81.

7. *Effect of storage temperature on rice thermal properties* / Zhou Z., Robards K., Helliwell S., Blanchard C. // *Food Res. Int.* – 2010. – Vol.43. – P.709-715.

8. *Resio A.C., Suarez C. Gelatinization kinetics of amaranth starch* // *Int. J. Food Sci. Technol.* – 2001. – Vol.36. – P.441-448.

9. *Ojeda C., Tolaba M., Suarez C. Modeling starch gelatinization kinetics of milled rice flour* // *Cereal Chem.* – 2000. – Vol.77. – P.145-147.

10. *Girenko D.V., Gyrenko A.A., Nikolenko N.V. Potentiometric determination of chlorate impurities in hypochlorite solutions* // *Int. J. Anal. Chem.* – 2019. – Vol.2019. – Art. No. 2360420.

11. *Van der Sman R.G.M., Mauer L.J. Starch gelatinization temperature in sugar and polyol solutions explained by hydrogen bond density* // *Food Hydrocolloids.* – 2019. – Vol.94. – P.371-380.

12. *A new basis set exchange: an open, up-to-date resource for the molecular sciences community* / Pritchard B.P., Altarawy D., Didier B., Gibson T.D., Windus T.L. // *J. Chem. Inf. Model.* – 2019. – Vol.59. – No. 11. – P.4814-4820.

13. *Tomasi J., Mennucci B., Camm R. Quantum mechanical continuum solvation models* // *Chem. Rev.* – 2005. – Vol.105. – No. 8. – P.2999-3094.

14. *Marenich A.V., Cramer C.J., Truhlar D.G. Universal solvation model based on solute electron density and on a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions* // *J. Phys. Chem. B.* – 2009. – Vol.113. – No. 18. – P.6378-6396.

15. *Espinosa E., Molins E., Lecomte C. Hydrogen bond strengths revealed by topological analyses of experimentally observed electron densities* // *Chem. Phys. Lett.* – 1998. – Vol.285. – No. 3/4. – P.170-173.

Received 19.04.2023

ПСЕВДОКАТАЛІТИЧНЕ ПРИСКОРЕННЯ ГІДРОТЕРМІЧНОГО ВИЛУГОВУВАННЯ АМІЛОЗИ З КРОХМАЛЮ В КИСЛИХ СЕРЕДОВИЩАХ

В.Д. Миргородська-Терентьєва, М.В. Ніколенко, І.В. Скар, Є.С. Осокін, О.В. Приловський, О.В. Волнянська, М.О. Мироняк

З метою встановлення закономірностей впливу кислотності розчинів на ефективність вилуговування амілози з крохмалю здійснені кінетичні дослідження за температур 60–70°C з використанням буферних розчинів з рН 3–5. Показано, що кінетичні дані найкраще описуються моделлю Крюгера-Циглера. Встановлено, що зі зменшенням рН розчинів від 5,0 до 3,0 енергія активації процесу вилуговування амілози знижується від 185 до 22 кДж/моль, а її залежність від концентрації іонів водню описується двома лінійними ділянками в інтервалах рН 3,0–3,3 та 3,6–5,0. Ефект зниження енергії водневого зв'язку при приєднанні додаткового протона до молекули води продемонстровано квантово-хімічним моделюванням з використанням програми Gaussian 09. Показано, що протонізація молекули води призводить до зниження ефективного заряду на атомі кисню з –0,626 до –0,142 од. зар. е. При цьому порушується лінійність водневого зв'язку вздовж атомів –O...H–O–, довжина водневого зв'язку збільшується з 1,856 до 2,370 Å, а енергія зв'язування зменшується в 4,6 разів. Таким чином, іони водню можна розглядати як своєрідний псевдодокаталізатор процесу вилучення амілози з крохмальних гранул, оскільки за їх присутності знижується енергія активації процесу та підвищується його швидкість. Зроблено висновок, що процес гідротермічного вилуговування амілози з крохмалю можна інтенсифікувати в результаті його проведення в кислих середовищах без додаткового нагрівання крохмальних суспензій.

Ключові слова: амілоза, вилуговування, рівняння Крюгера-Циглера, енергія активації, водневий зв'язок.

PSEUDOCATALYTIC ACCELERATION OF HYDROTHERMAL LEACHING OF AMYLOSE FROM STARCH IN ACIDIC MEDIA

V.D. Myrhorodska-Terentieva ^{a, *}, M.V. Nikolenko ^a, I.V. Sknar ^a, Ye.S. Osokin ^b, O.V. Prylovskiy ^a, O.V. Volnyanska ^a, M.O. Mironyak ^a

^a Ukrainian State University of Chemical Technology, Dnipro, Ukraine

^b Primus Inter Pares School, Dnipro, Ukraine

* e-mail: mirgorodskaya.viktoria@gmail.com

Kinetic studies were conducted at 60–70°C using buffer solutions with pH 3–5 to establish the effect of solution acidity on the efficiency of amylose leaching from starch. It was shown that the kinetic data are well described by the Kruger-Ziegler model. It was established that as the pH of the solutions decreases from 5.0 to 3.0, the activation energy of amylose leaching process decreases from 185 to 22 kJ/mol, and its dependence on hydrogen ion concentration is described by two linear segments within the pH ranges of 3.0–3.3 and 3.6–5.0. The effect of reducing the hydrogen bond energy upon addition of an additional proton to the water molecule was demonstrated through quantum-chemical modeling using the Gaussian 09 software. It was shown that protonation of the water molecule leads to a decrease in the effective charge on the oxygen atom from –0.626 to –0.142 unit of electron charge. At the same time, the linearity of the hydrogen bond along the –O…H–O– atoms is violated, the length of the hydrogen bond increases from 1.856 to 2.370 Å, and the binding energy decreases by 4.6 times. Thus, hydrogen ions can be considered as a kind of pseudo-catalyst for the process of amylose leaching from starch grains, since in their presence the activation energy of the process decreases and its rate increases. It was concluded that the process of hydrothermal leaching of amylose from starch can be intensified by carrying it out in acidic media without additional heating of starch suspensions.

Keywords: amylose; leaching; Kruger-Ziegler equation; activation energy; hydrogen bond.

REFERENCES

1. Kaur P, Kaur K, Basha SJ, Kennedy JF. Current trends in the preparation, characterization and applications of oat starch – a review. *Int J Biol Macromol.* 2022; 212: 172–181. doi: 10.1016/j.ijbiomac.2022.05.117.
2. Fan Y, Picchioni F. Modification of starch: a review on the application of «green» solvents and controlled functionalization. *Carbohydr Polym.* 2022; 241: 116350. doi: 10.1016/j.carbpol.2020.116350.
3. Nizam NHM, Rawi NFM, Ramle SFM, Aziz AA, Abdullah CK, Rashedi A, et al. Physical, thermal, mechanical, antimicrobial and physicochemical properties of starch based film containing aloe vera: a review. *J Mater Res Technol.* 2021; 15: 1572–1589. doi: 10.1016/j.jmrt.2021.08.138.
4. Adewale P, Yancheshmeh MS, Lam E. Starch modification for non-food, industrial applications: market intelligence and critical review. *Carbohydr Polym.* 2022; 291: 119590. doi: 10.1016/j.carbpol.2022.119590.
5. Naguleswaran S, Vasanthan T, Hoover R, Bressler D. Amylolysis of amylopectin and amylose isolated from wheat, triticale, corn and barley starches. *Food Hydrocolloids.* 2014; 35: 686–693. doi: 10.1016/j.foodhyd.2013.08.018.
6. Myrhorodska-Terentieva VD, Nikolenko MV, Kovalenko IL, Avdienko TM. Mekhanizm vylugovuvannya amilozy z natyvnoho i termoobroblenykh krokhmaliv u haryachiy nadlyshkoviy vodi [The mechanism of amylose leaching from native and heat-treated starches in hot excess water]. *Voprosy Khimii i Khimicheskoi Tekhnologii.* 2023; (1): 73–81. (in Ukrainian). doi: 10.32434/0321-4095-2023-146-1-73-81.
7. Zhou Z, Robards K, Helliwell S, Blanchard C. Effect of storage temperature on rice thermal properties. *Food Res Int.* 2010; 43: 709–715. doi: 10.1016/j.foodres.2009.11.002.
8. Resio AC, Suarez C. Gelatinization kinetics of amaranth starch. *Int J Food Sci Technol.* 2001; 36: 441–448. doi: 10.1046/j.1365-2621.2001.00478.x.
9. Ojeda CA, Tolaba MP, Suarez C. Modeling starch gelatinization kinetics of milled rice flour. *Cereal Chem.* 2000; 77: 145–147. doi: 10.1094/CCHEM.2000.77.2.145.
10. Girenko DV, Gyrenko AA, Nikolenko NV. Potentiometric determination of chlorate impurities in hypochlorite solutions. *Int J Anal Chem.* 2019; 2019: 2360420. doi: 10.1155/2019/2360420.
11. Van der Sman RGM, Mauer LJ. Starch gelatinization temperature in sugar and polyol solutions explained by hydrogen bond density. *Food Hydrocolloids.* 2019; 94: 371–380. doi: 10.1016/j.foodhyd.2019.03.034.
12. Pritchard BP, Altarawy D, Didier B, Gibson TD, Windus TL. A new basis set exchange: an open, up-to-date resource for the molecular sciences community. *J Chem Inf Model.* 2019; 59(11): 4814–4820. doi: 10.1021/acs.jcim.9b00725.
13. Tomasi J, Mennucci B, Camm R. Quantum mechanical continuum solvation models. *Chem Rev.* 2005; 105(8): 2999–3093. doi: 10.1021/cr9904009.
14. Marenich AV, Cramer CJ, Truhlar DG. Universal solvation model based on solute electron density and on a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions. *J Phys Chem B.* 2009; 113(18): 6378–6396. doi: 10.1021/jp810292n.
15. Espinosa E, Molins E, Lecomte C. Hydrogen bond strengths revealed by topological analyses of experimentally observed electron densities. *Chem Phys Lett.* 1998; 285: 170–173. doi: 10.1016/S0009-2614(98)00036-0.