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EVALUATION OF ISOTHERMAL KINETIC OF SWEETENER

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The aspartame is an artificial sweetener was discovered accidentally in the United States by J. M. Schlatter in 1965. In this work the kinetic of the thermal decomposition of sweetener, containing aspartame as sweetening agent, by means isothermal TG method was studied. The comparison of thermogravimetric data to the reference profiles of standard aspartame and lactose suggests an interaction between the two components in the sweetener, due to the decrease in the thermal stability of sweetener and of the overlapping processes. In the isothermal kinetic study the sweetener exhibited lower activation energy values, indicating a lower stability corroborating the thermoanalytical data. In case of the sweetener, the lower activation energy can be related to the interactions which took place between its components.

Keywords: *aspartame, kinetic analysis, sweetener, thermogravimetry*

Introduction

Among the existing food additives, the sweeteners provide the sweet taste of the food products. One of the most widely marketed sweetener is NutraSweet®, containing aspartame which was synthesized by chemical and enzymatic methods, as well as by using recombined DNA technology method. However, the most frequently used industrial process is the chemical synthesis [1].

When a solid sample is submitted to heat, it can undergo decomposition. During the thermal decomposition reactions, the crystalline array of solids is remarkably altered, producing new substances, which were absent from the original system.

Decomposition and denaturation of carbohydrates and oxidation of proteins are some of the observed phenomena when the temperature of food is varied. The thermoanalytical techniques are frequently used for the characterization of foods. The kinetic factors, as temperature and time, provoke the decomposition of the components, resulting the formation of new compounds that can be noxious to the health, demonstrating the importance of the study of food products [2–4].

In this work the thermal decomposition kinetic of aspartame sweetener, by means isothermal method was studied.

Experimental

The standards utilized were aspartame hemihydrate and α-lactose monohydrate. The sweetener samples, containing aspartame as sweetening agent, were acquired in the Brazilian local market. The composition of the sweetener is: 38% of aspartame; 57% of lactose (diluent); 2.4% of carboxymethylcellulose sodium (disintegrating agent); 1.5% of polyvinylpyrrolidone (agglutinant); 0.8% of silicon dioxide (antiumectant) and 0.3% of magnesium stearate (lubricant). The samples were stored in desiccator.

Thermogravimetry

The dynamic TG curves were obtained using a Shimadzu TGA-50 thermobalance in air atmosphere, with a flow rate of 20 mL min^{-1}, and at a heating rate of 10 K min^{-1}. The curves were recorded from room temperature up to 900°C, using alumina crucibles with an initial sample mass of 10.00±0.50 mg. The isothermal TG curves were obtained on the base of the dynamic TG profiles. The isothermal experiments have been performed between 80–220°C for 4 h, at a heating rate of 10 K min^{-1}.

Kinetic study

The determination of probable reaction mechanism and the kinetic parameters of the thermal decomposi-

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tion of the samples, using the isothermal method, based on the Arrhenius law. Starting from the equation which describes the reaction mechanism, the rate constants of the thermal decomposition were calculated. The repetition of the experiment at different temperatures allowed to calculate the apparent activation energy and the pre-exponential factor, using the linearized Arrhenius equation [5–8].

Results and discussion

Thermogravimetry

The TG profile of the aspartame hemihydrate exhibited five mass loss steps (Fig. 1). The first is between 30–82°C and the second step appeared between 82–157°C were attributed to the dehydration of aspartame causing 0.77 and 1.97% of mass losses. The third step between 187–218°C was attributed to stoichiometric the decomposition of aspartame through the formation of methanol with a mass loss of 10.55%. The fourth step (219–500°C) was attributed to the stoichiometric decomposition of 5-benzyl-3,6-dioxopiperazineacetic acid (product of the thermal degradation of aspartame) through the evolution of phenylalanine methyl ester corresponding to 55.06% of mass loss. Finally, in the fifth decomposition step between 500–716°C the decomposition of 5-benzyl causing 30.44% of mass loss has completed.

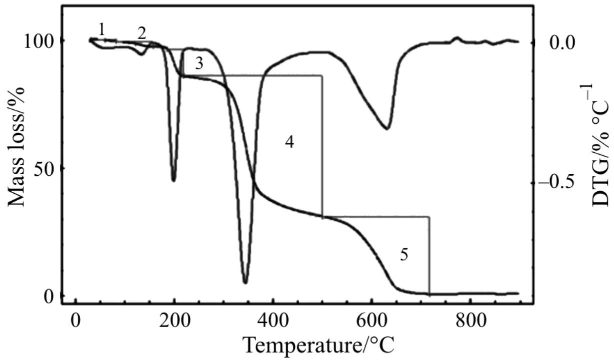

Fig. 1 TG/DTG curves of aspartame

The thermal decomposition profile of the α-lactose monohydrate showed four mass loss steps (Fig. 2). During the first step, between 125–175°C, the lactose lost its crystalline water causing 4.58% of mass loss. In the second one (176–285°C) 27.20% and in the third step (285–394°C) 34.88% of mass losses were observed. Finally, in the fourth step (394–607°C) 32.84% of mass loss was attributed to the secondary decomposition of lactose.

The TG curve of the sweetener exhibited seven mass loss steps (Fig. 3). In the first three steps, between 26–64, 66–86 and 87–109°C 0.9, 1.3 and 1.8% of mass losses were recorded, respectively. They were attributed to the water release (dehydration in part) of the sample. In the fourth step (114–191°C) 11.3% of mass loss was recorded corresponding to the decomposition of aspartame and lactose. In the last three steps (191–308, 309–480 and 482–645°C) 30.8, 20.9 and 31.3% of mass losses were obtained respectively, and were attributed to the secondary decomposition of 5-benzyl-3,6-dioxopiperazineacetic acid (5-benzyl) and lactose.

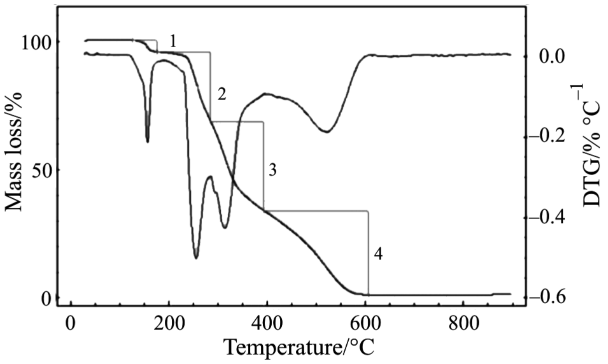

Fig. 2 TG/DTG curves of lactose

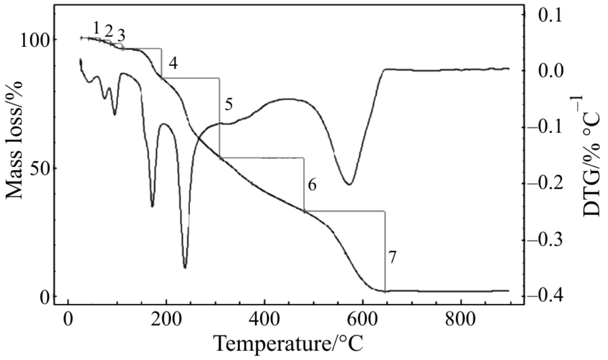

Fig. 3 TG/DTG curves of sweetener

By the comparison of the TG curve of sweetener to the reference TG curves of aspartame and lactose, decrease in the thermal stability of sweetener was observed. It was concluded that some interaction took place between aspartame and lactose in the sweetener.

Kinetic study

The isothermal TG curves of aspartame showed only one mass loss step, due to the evaporation of water between 80–145°C. In 150–200°C temperature range two mass loss steps were presented. The first one was similar (evaporation of water) and the second step corresponds to the decomposition of aspartame (Table 1).

Table 1 Kinetic parameters of aspartame obtained by the isothermal method

Temperature/°C	Rate constant/s^{-1}	Reaction order
80	1.91E-07	2
120	2.08E-07	2
130	2.24E-07	2
140	4.92E-07	2
145	9.19E-07	2
150 (1st step)	1.86E-06	2
150 (2nd step)	1.12E-06	0
155 (1st step)	1.94E-06	2
155 (2nd step)	1.28E-06	0
160 (1st step)	4.92E-06	2
160 (2nd step)	1.93E-06	0
170 (1st step)	6.34E-05	2
170 (2nd step)	5.75E-05	0
180 (1st step)	1.59E-04	2
180 (2nd step)	1.41E-04	0
190 (1st step)	3.60E-04	2
190 (2nd step)	3.09E-04	0
200 (1st step)	6.09E-04	2
200 (2nd step)	5.41E-04	0

Table 2 Kinetic parameters of the sweetener obtained by the isothermal method

Temperature/°C	Rate constant/s^{-1}	Reaction order
80	4.937E-06	2
120	7.37E-06	2
130	9.59E-06	2
140 (1st step)	6.182E-05	2
140 (2nd step)	5.10E-05	0
145 (1st step)	7.98E-05	2
145 (2nd step)	6.41E-05	0
150 (1st step)	9.24E-05	2
150 (2nd step)	8.79E-05	0
155 (1st step)	1.74E-04	2
155 (2nd step)	1.260E-04	0
160 (1st step)	3.69E-04	2
160 (2nd step)	2.26E-04	0
170 (1st step)	5.74E-04	2
170 (2nd step)	3.85E-04	0
180 (1st step)	8.74E-04	2
180 (2nd step)	4.90E-04	0
190 (1st step)	7.80E-03	2
190 (2nd step)	6.07E-03	0
200 (1st step)	8.65E-03	2
200 (2nd step)	7.99E-03	0

The isothermal TG profiles of the sweetener indicated one mass loss step between 80–130°C, which was attributed to the formation and evaporation of methanol. On the contrary, in the 140 to 200°C range, two mass loss steps were noticed. The first one was attributed to the methanol evaporation and the second step was ascribed to the decomposition of 5-benzyl (Table 2).

Comparing the isothermal thermogravimetric curves of aspartame to the ones of the sweetener a decrease in the extent of decomposition was observed due to the presence of excipients in the sweetener.

In the method which applies the Arrhenius law, the isothermal TG data were converted and inserted into the Arrhenius equation. The equation that best describes the thermal decomposition mechanism of the samples was chosen according to its best linear correlation coefficient. The results presented a better linear regression in the graphs of the reciprocal mass ($1/m=1/m_0+kt$) and mass ($m=m_0-kt$) as a function of reaction time [8], indicating that the thermal decomposition reactions of aspartame and of the sweetener follow a second order mechanism in the first step and a zero order mechanism in the second step, respectively.

Therefore, the rate constants (k) of the processes were calculated using the classical Arrhenius equation corresponding to the second order reaction in the first step and to the zero order reaction in the second step. The results are collected in Tables 1 and 2.

A linear correlation was verified between the logarithm of the rate constant ($\ln k$) *vs*. the reciprocal temperature ($1/T$). Thus, the activation energies and the pre-exponential factors of the thermal decomposition reaction of the samples can be calculated by means of the Arrhenius equation (Table 3).

Table 3 Kinetic parameters of the samples obtained by the isothermal method

Kinetic parameters	Asapartame	Sweetener
E/kJ mol^{-1}	171 328	118 140
A/s^{-1}	244E+15 7.41E+34	4.73E+10 1.83E+13
r	0.9897 0.9932	0.9633 0.9698

The reaction order was not the same for the first and the second steps, which suggests that the products of the thermal decomposition can be different.

The kinetic data [9, 10] obtained by isothermal thermogravimetry indicated that aspartame has a larger stability compared to the sweetener. With regard to the first step, the kinetic parameters of the decomposition of aspartame were attributed to the methanol evaporation and to the formation of the 5-benzyl. As for the second step, the kinetic parameters were attributed the decomposition of 5-benzyl.

The rate constants (*k*) increase with the increase of isothermal temperature, allowing the estimation of the rate constant at any temperature of interest [8].

Conclusions

The comparison of TG data of sweetener to the reference TG curves of aspartame and lactose suggests the occurrence of a certain interaction between aspartame and lactose in the sweetener. It was verified by the decrease of the thermal stability of sweetener and by the overlapping decomposition processes.

The isothermal method, which applies the Arrhenius law, indicated that the thermal decomposition reactions of aspartame and of the sweetener follow second order mechanism in the first step and a zero order mechanism in the second step of their decomposition, respectively. The sweetener presented lower activation energy values, indicating a less stability and corroborated the thermal data.

The rate constants obtained by the isothermal method presented an exponential behavior with temperature, allowing the estimation of the rate constant at any temperature of interest. In case of the sweetener, the lower activation energy can be the consequence of interactions took place among its components.

Acknowledgements

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