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Effect of electrolytes on the kinetics of thiamine loss in model systems of high water activity

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The influence of different electrolytes (NaCl, KCl and Na_2SO_4) on the kinetics of thiamine degradation in model systems of reduced water activity (a_w = 0·95), at pH values of 4·0 and 5·5 and at different processing temperatures (80°C, 90°C and 100°C) was studied. In all cases a first order reaction kinetics for thiamine degradation was confirmed. The strong influence of temperature and pH on the rates of degradation was evident. The adjustment of a_w with electrolytes, particularly NaCl or KCl, exerts a protective effect on thiamine destruction, compared with a buffer system (without solute addition) or with systems containing non-electrolytes. Activation energies seemed to be independent of the type of solute and ranged from 27 to 29 kcal mole^{-1}.

INTRODUCTION

Food preservation at high water activity (a_w = 0·90 – 0.95) can be achieved by combining a limited decrease in a_w and pH, addition of allowed chemical preservatives and mild heat treatment, among other factors (Leistner & Rödel, 1975). Development of these new processes needs a knowledge of nutrient stability at a_w values above 0·90. Several authors have studied the rates of thiamine destruction in a wide variety of model systems, buffer solutions and foods of high moisture content. A range of conditions, including temperature, pH and a_w have been recently reviewed by Mauri *et al.* (1989). It has been noted that the type of solute used to adjust the a_w influences the rate of degradation.

When a solute is added to water to adjust a_w, it not only modifies macroscopical physical parameters such as density, dielectric constant, refractive index, viscosity, but specific interactions between solvent and solute molecules too (Reichardt, 1979). Particularly, Farrer (1945) working with different buffer solutions ($a_w \geq$ 0.99, i.e. very low ionic media concentration) stated that thiamine was destroyed at different rates. The purpose of present work was to study specific solute (electrolyte) effects on the kinetics of thiamine loss in buffer solutions of water activity adjusted to 0·95 by addition of NaCl, KCl or Na_2SO_4 (electrolyte concentration between 7·7 and 17·2% w/w) in the range 80·0–100·0°C.

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MATERIALS AND METHODS

Model systems

Model systems were prepared with thiamine hydrochloride (0·1 mg/100 ml) and phosphate buffer (KH_2PO_4 and Na_2 $HPO_4 \cdot 2H_2O$, 0·07 M) to maintain a constant pH (4·0 or 5·5) during the runs. Sodium chloride, potassium chloride or sodium sulphate were added to adjust a_w to 0·95. Selected pH values were similar to those usually chosen to preserve 'high moisture' (Sperber, 1983) foods. Contribution of buffer salts to final a_w was obtained from data of Ferro Fontán *et al.* (1979). Electrolyte concentrations to achieve desired a_w were calculated according to Pitzer & Mayorga's expression (1973). a_w of model systems was evaluated using the Ross (1975) equation. A Novasina Thermoconstanter Humidat hygrometer (Novasina AG, Switzerland) was used to check the a_w of the samples as described by Kitic *et al.* (1986). Screw-cap glass tubes were heated at 100°C, 90°C or 80°C in a shaken thermostatic water–glycerol bath. Particular heat treatments at lower temperatures (mainly at 55°C) were performed in a forced convection oven.

Thiamine analysis

Thiamine was analysed by two methods. Every sample was measured by the thiochrome method using mercuric chloride as oxidant (Ryan & Ingle, 1980). Fluorescence was determined with an Aminco-Bowman spectrophoto-fluorometer. The excitation and emission monochromators were set at 365 nm and 435 nm, respectively. For some model systems (pH 5·5; a_w = 0·95; T = 100°C and NaCl or KCl as humectants) thiamine was also measured by high performance liquid chromatography (HPLC). Analysis were carried out on a carbohydrate (10 μm) column (Waters Association) installed in a Micromeritics chromatograph equipped with a solvent delivery system Model 760 and an injector Model 731. The mobile phase was acetonitrile–NH_4HCO_3 (1% w/v), 80:20 v/v and the flow-rate was 1·0 ml/min. The uv/vis detector (Micromeritics, Model 787) was set at 254 nm, and data were acquired from a Spectra-Physics integrator (Model SP 4290). Good correlation between methods was found (relative errors between rate-constants calculated with data from both methods were 10–12%).

Materials

NaCl, KCl, $HgCl_2$ and acetonitrile were from Merck (Darmstadt, West Germany); NaOH, KH_2PO_4, $Na_2HPO_4 \cdot 2H_2O$, Na_2SO_4 and NH_4HCO_3 from Mallinckrodt Chem. Works (St Louis, MO). Thiamine hydrochloride was from Sigma Chem. Co. (St Louis, MO) and fluorescence-free isobutanol was from Sintorgan (Buenos Aires, Argentina).

RESULTS AND DISCUSSION

Figure 1 shows a semilog plot of experimental thiamine retention versus time at 80·0, 90·0 and 100·0°C and pH 5·5 for model systems of a_w adjusted to 0·95 by addition of NaCl, KCl and Na_2SO_4. Similar data are shown for a control system containing buffer and thiamine. Temperature and the presence of different solutes used to adjust a_w influence the rate of thiamine degradation under the conditions analysed. Good straight lines were obtained in all cases confirming a first order kinetics for thiamine loss (Mauri *et al.*, 1989). The same behaviour was obtained at pH 4·0 (results not shown). Rate constants (k) and activation energies (E_a), evaluated by using the Arrhenius model, and corresponding errors, were calculated by regression analysis. Results are shown in Table 1.

For each model system, it can be observed that the decrease in pH results in greater retention of the vitamin. The influence of pH on thiamine degradation was recognized practically since the beginning of the studies about its stability (Farrer, 1955). Dwivedi & Arnold (1973) observed that less thiamine breakdown occurred in a buffer system of this vitamin at pH 3·5 than at pH 5·0 or 6·0, suggesting that the protonated form of thiamine, which predominates at pH >4·8 (pK_1), was less prone to thermal destruction than thiamine. The mechanism appeared to be the same for both forms. These considerations explain the differences of rate constants with pH found in the present work.

Figure 2 shows the effect of temperature on rate constants for model systems of a_w 0·95 adjusted with electrolytes studied, and for the control systems (buffer)

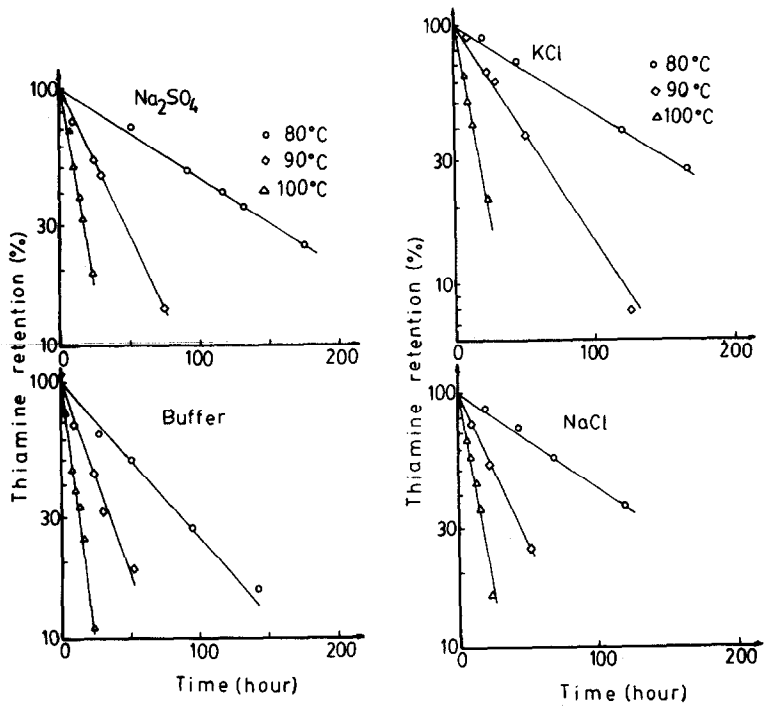

Fig. 1. Kinetics of thiamine retention in model systems (pH = 5·5, a_w = 0·95).

Table 1. Kinetic parameters for thiamine degradation in model systems (a_w = 0·95)

	100°C		90°C		80°C			
	k (h^{-1})	Δk (h^{-1})	k (h^{-1})	Δk (h^{-1})	k (h^{-1})	Δk (h^{-1})	E_a (kcal $mole^{-1}$)	ΔE_a (kcal $mole^{-1}$)
				pH 5·5				
Buffer	0·093	0·004	0·035	0·003	0·014	0·001	27·4	2
NaCl	0·065	0·004	0·027	0·003	0·0087	0·0005	27·4	0·5
KCl	0·067	0·004	0·021	0·001	0·0080	0·0008	27·7	0·4
Na_2SO_4	0·069	0·006	0·0262	0·0009	0·0081	0·0004	28·1	0·3
				pH 4·0				
Buffer	0·047	0·002	0·018	0·003	0·0065	0·0005	29	3
NaCl	0·024	0·001	0·0107	0·0003	0·0031	0·0001	29	1
KCl	0·0281	0·0009	0·0098	0·0005	0·0030	0·0001	29	2
Na_2SO_4	0·044	0·005	0·0170	0·0008	0·0052	0·0002	29	3

without humectant. Figure 2 also shows k values at 55°C (for model systems at pH 5·5) measured in the present work to evaluate temperature effect from 100°C up to accelerated storage conditions, as well as k values at 45°C, 55°C, 60°C and 65°C for model systems containing Na_2SO_4, at pH 5·5 as reported by Fernández (1984). The Arrhenius equation fits the temperature dependence of rate constants for every system in the range of temperatures studied. The quantitative study of the effect of temperature on thiamine loss, applying

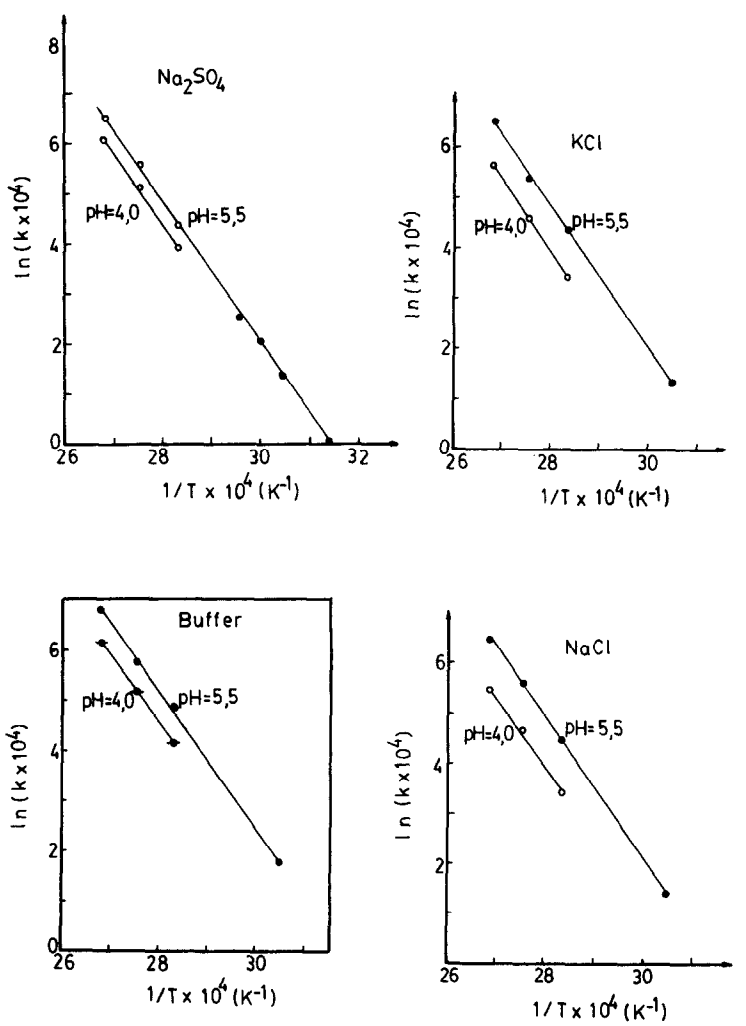

Fig. 2. Effect of temperature on rate constant in model systems of a_w 0·95.

the Arrhenius equation, began with Rice & Beuk (1945) in pork and Farrer & Morrison (1949) in model systems. Mauri *et al.* (1989) summarized and compared activation energy values for thiamine loss in a great variety of foods, buffer solutions and model systems ($a_w \geq 0{\cdot}90$), in a wide range of temperatures. They showed that all E_a values ranged between 20 kcal mole^{-1} and 32 kcal mole^{-1}, most of them being between 26 kcal mole^{-1} and 30 kcal mole^{-1}. Results of the present work vary between 27 and 29 kcal mole^{-1} and are independent of the humectant present in the systems as well as of pH. So, these conclusions would suggest that addition of humectants or a small variation in pH value (important means of preservation by combined techniques) should not change the effect of temperature on thiamine loss.

From Table 1 it can be observed that systems containing electrolytes present lower losses of thiamine than the control system. At pH 5·5, they all have a quite similar rate constant, about 30–40% lower than the k values of the control system (buffer). At pH 4·0, model systems containing NaCl or KCl also present k values 40–50% lower than those of the control system, but when Na_2SO_4 is present, k values are from 6 to 9% below corresponding k values of the buffer system. Since the simple ions have dimensions and bear charges comparable to those of the water molecule, it is to be expected that the structure of water will be considerably modified in ionic solutions (Robinson & Stokes, 1968). Transport properties of water, at low concentrations, may be adequately explained taking into account the magnitude of ionic charge, concentration and dielectric constant of solvent (Debye–Hückel's law). Electrolyte effects in certain processes are not specific up to concentrations of about 0·1 molal and can be expressed in terms of ionic strength (Robinson & Stokes, 1968). At higher concentrations (the present study is such a case) specific ion-solvent effects govern the solution behaviour and it cannot be explained by purely electrostatic considerations. As a result of ion–dipole interactions, solvent molecules reorganize in the ionic solvation sphere. It is important to remember that two kinds of ions exist: the 'structure-breaking' and the 'structure-making' ions (Franks, 1983). 'Structure-making ions (i.e. SO_4^{2-}) possess well ordered hydration spheres, whereas 'structure-breaking' ions (i.e. Cl^-, Na^+, K^+) would not be able to align the water dipoles and to overcome, to any extent, the hydrogen bond interactions that exist in bulk water. This consideration would justify differences between NaCl and KCl systems and the Na_2SO_4 system at pH 4·0. At pH 5·5, though the presence of salts also has a protective effect compared with the control system, there are no appreciable differences between rate constants for systems with different electrolytes. This is possibly due to the participation of different forms of the thiamine molecule ($pK = 4{\cdot}8$) in the reaction, which accelerates the rates of destruction at pH 5·5, decreasing the effect of the solutes 'per se'. Figure 3 compares thiamine retention versus heating time at 100°C and pH 4·0, for model systems of a_w 0·95 adjusted with electrolytes (present work) and with non-electrolytes (Mauri *et al.*, 1990). Systems containing non-electrolytes (glycerol, sorbitol or propylene glycol) present slightly higher losses than the model system of $a_w \cong 1$ (without humectant). Mauri *et al.* (1990) attributed non-electrolyte effects on rate constants principally to changes in solvent polarity. The addition of electrolytes (NaCl, KCl or Na_2SO_4) produces the opposite effect, the alteration in water structure by ionic interactions being responsible for differences observed.

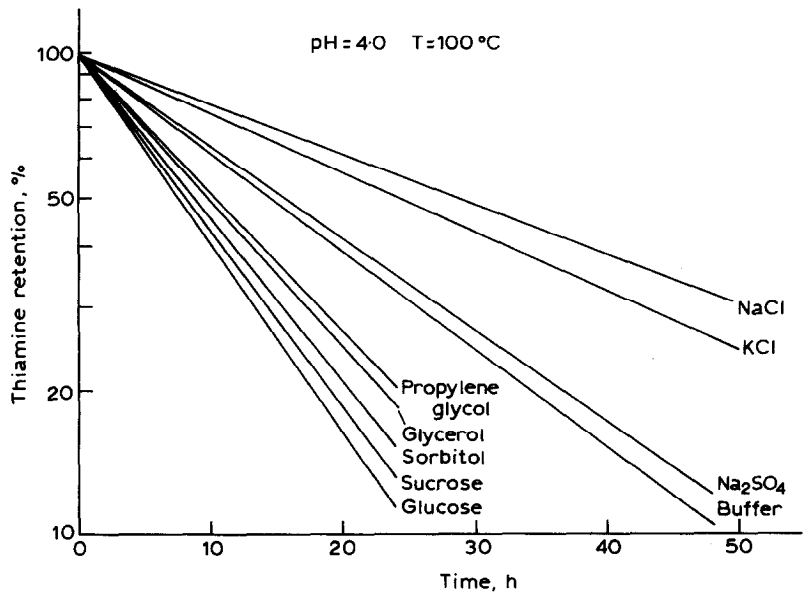

Fig. 3. Effect of humectant on thiamine degradation rate in model systems (pH = 4·0, a_w = 0·95, T = 100°C).

Results achieved in the present work show that, independently of absolute a_w value (0·95), the addition of solutes modifies the reaction media so that the parameter a_w alone is not useful for predicting thiamine stability. The effect of the solute 'per se' must be considered for any future study.

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