A THEORETICAL TOOL FOR THE PREDICTION OF PHYSICAL-CHEMICAL PROPERTIES (a_w, pH) OF BIOLOGICAL MEDIA AND FOODS

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Abstract – The development of process simulators is actually limited by the absence of tools predicting the evolution of the physical-chemical properties that determine biochemical, microbiological and structural changes. A work have been carried out to elaborate a thermodynamic model to predict water sorption isotherms and pH of biological media and foods tissue in presence of different additives such as salts or organic acids. The model can predict pH and a_w of beef and pork meat with or without preservatives such as salts or organic acids

Key Words – pH, water activity, modeling

I. INTRODUCTION

The knowledge of physical-chemical properties of foods is essential for scientists and engineers who have to solve the problems in food preservation, processing, storage, marketing, consumption, and even after consumption (Rahman, 2009). In a general way, transformation and preservation processes modify physical-chemical processes. It appears essential for food researchers and engineers to develop food and biotechnology industry effective simulation tools permitting to increase nutritional and safety qualities in the transformed products as well as to assure a better homogeneity of the production and a cost allowing an increased competitiveness for the companies.

To achieve this goal, it requires the use of numeric simulation. This is a method that consists in analysing a phenomenon, a process or the behaviour of a system through a mathematical model that describes correctly the reactions of the studied object. However, to describe the transformation of an agricultural product in a food, it is necessary to describe according to the time and the space the heat and mass transfers that occur between the product and its environment or inside the product, the chemical, biochemical or microbiological kinetics that have place on the surface or in the product, the local modifications of chemical composition that are led and the evolution of the mechanical linked to structure, nutritional, microbial and sensory properties of the product according to the transfers and the kinetic.

Water activity (a_w) and pH are, with temperature, the major physical-chemical properties in biotechnology and food industry: they are used to characterise the microbial behaviour as well as the evolution of chemical reactions in aqueous liquid solution. Somewhere, foods are complex media which can be liquid or solid. Food constituents are diverse in size and molecular behaviour: water, organic acids, bases, electrolytes, amino acids, nucleic acids and metabolites. By characterising the types of interactions occurring between these constituents and by considering the dissociation reactions in complex aqueous mixture and the thermodynamic theories of solutions, researchers have developed models that predict the physico-chemical properties of such mixtures (pH, a_w, concentration of the constituents) (Achard et al., 1994 and Sereno et al., 2001). These models determine the activity coefficient – in a molar scale - of each constituent present in the solution and calculate the activity using equation 1:

$$a_i = \gamma_i . x_i \quad \text{Equation 1}$$

where γ_i is activity coefficient; a_i is solute activity; x_i is molar fraction of the component i in the medium determined from the medium composition.

The aim of this work was to test the accuracy of thermodynamic models to predict water activity and pH from the local composition within pork and beef meat.

II. MATERIALS AND METHODS

II.1. Samples preparation

Beef meat samples amples were excised from *Semimembranosus* (SM) muscles of heifers. Pork samples were excised from boneless loins. Meat was maturated during 10 days at 4°C, then vacuum-packed and frozen at -20°C. The samples were prepared after thawing at 4°C until meat temperature reached 1°C.

II.2. Measurements

The pH was measured with an MP230 pH meter (Mettler Toledo, Viroflay, France) equipped with an Inlab 413 (Mettler Toledo) probe with a built-in temperature sensor. The measuring range was from 0 to 14 with a temperature field of 0 to 60°C. Measurement reproducibility was +/- 0.001 per pH unit. To determine the pH profiles within meat samples 0.5 g in weight were taken and their pH were measured after mincing with 0.5 mL of deionized water.

Water content was assessed from oven drying at 104°C for 24 h.

An a_w-sprint TH500 was used for measuring water activity (Novasina, Roucaire, France). The temperature inside the measuring cell was controlled from 0°C up to 50°C, with a precision of 0.2°C. Measuring range was from 0.05 up to 1.00. Measurement accuracy was +/- 0.005 aw unit. Calibration was made with a six reference points system: 0.11, 0.33, 0.53, 0.75, 0.90 and 0.98.

II.3. Experiments

II.3.1. Molar mass determination

The apparent molar mass was determined using the method of Chen (1986) which measures the freezing point depression of a solution water + solute while compared to pure water.

II.3.2. Titration curves

For titration curve, 30 g of food product were crushed. If necessary, a salt or an organic acid or a salt of organic acid was added. Titration curves of beef meat were obtained by adding 5% (w/w) salt (NaCl) or 1%, 3% or 5% (w/w) organic acid (acetic acid, lactic acid or citric acid) or both salt and organic acid.

II.3.3. Water activity and water sorption curves

Water sorption isotherms of beef or pork meat, with or without additives, were obtained by placing samples in dehydration cells at 25°C then measured with Novasina apparatus. For each experiment 3 thin slices - 1 g each – of the same sample were placed in the dehydration cells: equilibrium time was less than 24 h. Specific water activity determinations were also made with the Novasina apparatus for beef meat with addition of one additive.

II.3.4. pK determination

The pK of meat were estimated from experimental titration curves. A dichotomous search (Edgar and Himmelblau, 1988) was used to optimise the pK. The sum square error (SSE) between experimental and predicted values was calculated for each pK tested. When the difference between two successive values pK_1 and pK_2 were less than a defined ΔpK, the calculations were stopped. The average was chosen as the parameter value, giving a precision of $\Delta pK/2$.

II.4. Thermodynamic model

The the UNIFAC (Universal Functional Group Activity Coefficients) model modified by Larsen et al. (1987) was used to predict the activities of non-ionic molecules in mixtures such as sugars, alcohols, etc ($g^{E,SR}$). This model is based on the concept of group contributions.

The model describing long-term interactions between ionic species is based on the Pitzer-Debye-Hückel (PDH) theory (Pitzer, 1973). Ions are considered as UNIFAC independent groups ($g^{E,LR}$).

Solvation of charged species giving clusters was taken into account by means of a hydration number for each ion at infinite dilution.

The combination of these three contributions is the basis of the solution model. It makes it possible to calculate the activities of different species. These calculations are combined with thermodynamic equilibrium equations that use the equilibrium constants (pK) defined at infinite dilution and generally provided in the reference tables. The software manages several types of data (Figure 1) that allow the predictions of pH and aw of aqueous mixtures

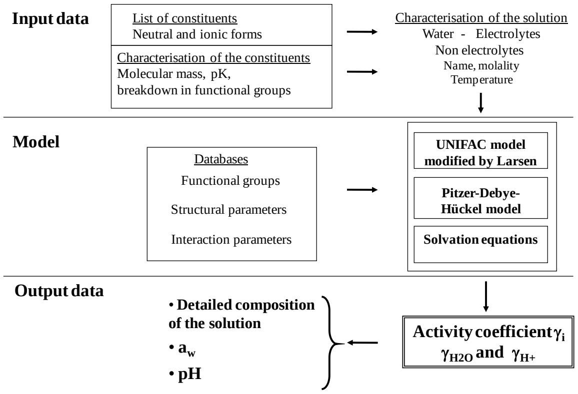

Figure 1.Structure of the thermodynamic model

Meat is complex media with a very large number of compounds that are not necessarily identified or well-characterized. The thermodynamic model can be used when a description of the medium can be done in terms of molecules. To used the thermodynamic model to such complex media, a virtual molecule having the same behaviour that the complex media have been created. It was been necessary to determine the equivalent molecular weight, the functional groups and the pKa's.

III. RESULTS AND DISCUSSION

III.1. Modeling beef and pork meat

It is possible to propose a decomposition of meat into functional groups. From one titration curve of beef meat several pK's of a virtual molecule were calculated and its apparent molar mass estimated by the method of Chen (1986). For meat, a chemical compound - equivalent molecular mass of 2 230 and 6 pKa's - was found to have in many conditions the same behaviour than pork and beef meat. Table 1 gives the estimation of theses parameters beef meat. The virtual molecules were then break down into functional groups with the respect of some conditions:

- the sum of the molar mass of the different groups is equal to the molar mass of the virtual molecule
- there are at least the same number of $COOH/COO^-$ and NH_2/NH_3^+ groups than pKa's
- to take account of the peptidic bonds, CH_2CO and CH_2NH groups were introduced because the group CO-NH does not exist in the UNIFAC model

Table 1: Characteristics of equivalent molecule of beef and pork meat

Mean apparent mass	2230
Decomposition	15 CH_3, 18 CH_2, 15 CH, 14 NH_2, 1 NH_3^+, 14 COOH, 1 COO^-, 9 CH_2CO, 9 CH_2NH
pKa	2.5 – 3.5 – 3.9 – 7.0 - 9.0 – 11.6

III.2. Prediction of sorption and titration curves

The model predicts the pH and the a_w of meat with or not addition of different additives (salts or organic acids or salts of organic acids).

Excellent predictions are obtained for titration curve of meat : the deviations between experimental and predicted values are less than 0.2 pH unit in the pH domain from 2.0 up to 10.0 (Figure 2).

Good results are obtained when organic acids are added: the average error is equal to of 0.3 pH unit and the maximum error is less than 0.6 pH unit.

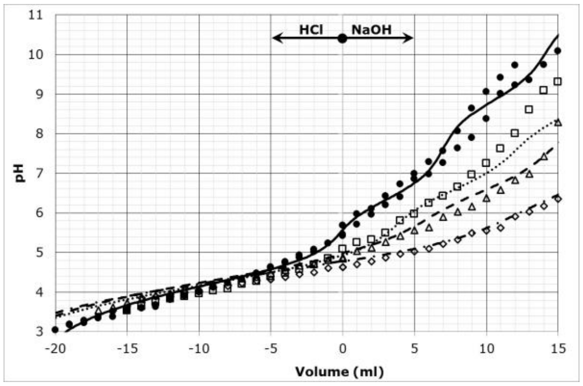

Figure 2. Comparison between experimental and calculated titration curves of meat and meat with one organic acid at 25°C (symbols = measurement – lines = prediction). (● = Beef meat - ◇ = 5% citric acid - ☐= 5% lactic acid - △ 5% acetic acid)

Sorption curves are also correctly predicted for meat with or without addition of different salts (Figures 3). The deviations between experimental and predicted values are less than 0.01 a_w unit for at a_w below 0.95. Deviation was higher (between 0.01 and 0.02 a_w unit) for a meat product having a measured a_w above 0.95.

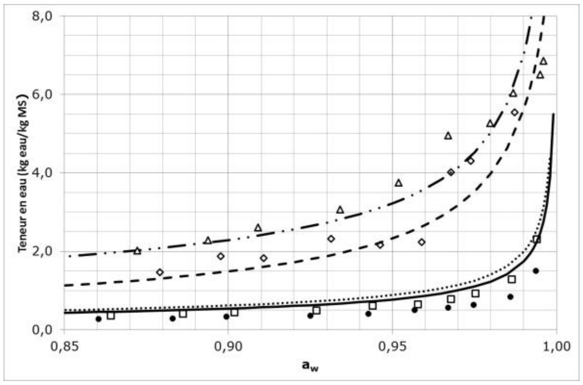

Figure 3. Incidence of sodium chloride content on meat sorption curves measured at 20°C (symbols) and predicted using the thermodynamic model (lines): meat (●, ▬▬▬), meat + 0.5% NaCl (☐, ▪▪▪▪▪▪), meat + 5 % NaCl (◇, ▬ ▬), meat + 10 % of NaCl (△, ▬▬ ▪)

IV. CONCLUSION

Some mathematical tools now exist to calculate a priori the physical-chemical properties of complex liquid solutions understanding numerous molecules of biologic interest (salts, organic acids, amino acids, peptides, sugars). This work demonstrates that they can be applied to meat tissue and in the future, the thermodynamic model predictions becomes to be extended to other food products (chicken meat, fish meat, cheese, fruits, …) and to other properties such as redox potential (Eh) which is linked to the electron activity. Calculations with thermodynamic model are very long but the use of neural networks would be an alternative to speed up the calculations while including those models into process simulators. This thermodynamic model should be an interesting tool for helping companies to formulate new products with new nutritional constraints such as low salt content, low sugar content and low fat content

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