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Modelling the distribution of a_w, pH and ions in marinated beef meat

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ABSTRACT

New beef products from low value cuts could be developed using marinating since this process has been shown to improve meat sensorial properties and shelf life. However, to optimise the process mathematical models are needed to predict evolution of the physicochemical properties that determine biochemical and structural changes. Two major works have been carried out to elaborate comprehensive models: (1) Thermodynamic models were adapted to predict water sorption isotherms and pH of beef meat tissue in presence of salts (NaCl, KCl) and organic acids (acetic, lactic, citric and ascorbic acid), (2) Fickian numerical models were set up to predict the migration of ions within meat cuts using apparent diffusivities previously estimated from 1D experiments. Simulation calculations showed reasonable agreement with measurements and can be used to investigate the effect of marinating conditions, product heterogeneity, dimension and shape.

1. Introduction

Marinating has been shown to improve tenderness and/or cooking yield of beef (Burke & Monahan, 2003; Scanga et al., 2000; Shuming, Yan, Eric, & Herbert, 2009; Wenham & Locker, 1976), pork (Sheard, Nute, Richardson, & Wood, 2005; Sheard & Tali, 2004) and poultry meat (Barbanti & Pasquini, 2005). Offer and Knight (1988) have described the mechanisms underlying water binding to meat proteins including the impact of pH and NaCl and explained the main trends observed in previous studies. Marinating is also known to increase meat products shelf life (Drosinos, Mataragas, Kampani, Kritikos, & Metaxopoulos, 2006). So it is expected that new beef products from low value cuts could be developed using this process. These changes during marinating are promoted by biochemical and histological modifications; for example it was shown that acidic marinating induces oxidation of lipids and proteins, increases protein hydrophobicity and favours the increase in inter cellular spaces (Sharedeh, Gatellier, Peyrin, Astruc, & Daudin, 2011). Acidification of beef meat by citric acid was also observed to increase susceptibility to lipid oxidation and to modify tissue microstructure (Ke, Huang, Decker, & Hultin, 2009).

Great spatial variations of the physical–chemical parameters appear within meat pieces during the marinating process due to ingredients migration. These physical–chemical parameters (water activity, pH and Na^+ and Cl^-) determine the above changes. But, measuring pH and water activity (a_w) is not always possible on a continuous basis since measurements are invasive for the product. Few attempts have been made to predict such measurements or to estimate their changes during a process although this would certainly provide useful information (Lebert & Lebert, 2006). Since pH and a_w are dependent on the constituents that compose foods (water, organic acids, bases, electrolytes, amino acids, peptides and metabolites), models that take these constituents into account are based on the applied thermodynamics approach and solution equilibrium theory. Thus, to optimise the marinating conditions according to meat tissue properties and product shape and dimensions, mathematical models should be elaborated in order calculate the time evolution of the spatial distribution of the local physical–chemical parameters. These parameters are defined as activities in thermodynamics. Activity is linked to the component i concentration by the relation:

$$a_i = \gamma_i c_i \tag{1}$$

where γ_i is the activity coefficient ($l\,mol^{-1}$), a_i the solute activity and c_i the concentration ($mol\,l^{-1}$)

The activity coefficient describes the deviation from ideal solution behaviour, that is, the difference which exists between the component activity and its concentration. Three types of solutions can be distinguished:

- a pure solvent, it is an ideal solution in the sense of Raoult's law with $\gamma_i = 1$;

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- an ideal dilute solution: the solvent is present in excess compared to the solute. Henry's law can be applied to the solute and γ_i approaches unity;
- a real solution: γ_i is different from unity.

When the activity coefficients of all the components in the solution are known, the activity coefficients of water and hydrogen ions can be calculated and used to determine two major parameters: pH and a_w:

$$pH = -\log_{10}\left(a^m_{H^+}\right) = -\log_{10}\left(\gamma^m_{H^+}.m_{H^+}\right) \tag{2}$$

where $\gamma^m_{H^+}, a^m_{H^+}$ are the activity coefficient and the activity of H^+ defined on the molality scale (superscript m) and the molality of H^+ (mol H^+/kg water) defined on the molar fraction scale with standard pure water as a reference state.

$$a_w = \gamma_{H_2O} \cdot x_{H_2O} \tag{3}$$

where γ_{H_2O}, a_w and x_{H_2O} are the activity coefficient, activity and molar fraction of water, respectively.

The deviation from ideal solution behaviour has two consequences:

- on the method to measure pH. pH is defined based on the activity, but it is usually believed that $pH = -\log(c_i)$ where c_i is the proton concentration. In the case of a strong acid, this expression is only valid when the concentration of the mixture is low;
- on the estimation of pH and a_w: as soon as a salt is added to a medium, even at a very low concentration, the salt can greatly modify the chemical equilibrium as indicated by Gibbs–Duhem's law (Prausnitz, Lichtenthaler & de Azevedo, 1999). In media containing non-electrolyte species, deviation from ideality increases when the concentration of a component increases or when the number of the components even at a low concentration increases.

Models that can predict pH and a_w, predict activities and activity coefficients based on behaviour of mixed liquids. Since the early years of physical chemistry, thousands of articles have been written in an effort to understand the behaviour of mixed fluids. While there is not a general theory of liquid mixtures, there is, instead, a variety of restricted theories and models, each useful for a particular type of mixture (Prausnitz et al., 1999). All theories are based on excess partial molar free energy (g^E) and activity coefficient (γ) estimation, parameters that allowed the calculation of physic-chemical properties (Fig. 1). Such a model would make it possible to answer to the expectations of food engineers for the design of equipment and processes. Indeed, a large amount of reliable data on the equilibrium properties of materials is necessary to describe the transformation of raw materials to finished foods or to formulate new foods with defined characteristics. However, the limited availability of experimental data can hardly satisfy such an enormous demand.

To construct a theory of liquid mixture, two kinds of information are required: the structure of liquids (the way the molecules in a liquid are arranged in space) and the intermolecular forces between like and unlike molecules. Unfortunately, information of either kind is inadequate and, as a result, all theories must make simplifying assumptions to overcome this disadvantage (Prausnitz et al., 1999). More theoretical work has been concerned with mixtures of liquids whose molecules are non polar and spherical: for example, the regular solution theory of Scatchard and Hildebrand (Prausnitz et al., 1999) frequently provides a good approximation for mixtures of hydrocarbons. All theories are then extended, often semi-empirically, to more complicated molecules.

Among these theories, predictive activity coefficient methods were initially based on, but are now mostly based on group contribution models: ASOG (Wilson & Deal, 1962) and UNIFAC (Fredenslund, Jones, & Prausnitz, 1975). Indeed, in any group-contribution method, the basic idea is that whereas there are thousands of chemical compounds of interest, the number of functional groups that constitute these compounds is smaller. Extension of the group-contribution idea to mixtures is attractive because, although the number of pure compounds is very large, the number of different mixtures is larger by many orders of magnitude. Millions of multicomponent mixtures of interest in the food industry can be constituted from perhaps 30, 50, or at most 100 functional groups. The fundamental assumption of a group-contribution method is additivity: the contribution made by one group within a molecule is assumed to be independent of that made by any other group in that molecule. This assumption is valid only when the influence of any group in a molecule is not affected by the nature of other groups within that molecule. In consequence, any group-contribution method is necessarily approximate because the contribution of a given group in one molecule is not necessarily the same as that in another molecule.

These methods are daily used in chemical industry and new developments continue to be made in the case of UNIFAC (Gmehling, 1988; Larsen, Rasmussen, & Fredenslund, 1987; Weidlich & Gmehling, 1987) or ASOG (Kojima & Togichi, 1979; Togichi, Tiegs, Gmehling, & Kojima, 1990) improving the range and accuracy of the methods. New methods such as the COSMOS-RS (Eckert & Klamt, 2002; Klamt, 1995), Group Contribution Solvation model (Lin & Sandler, 1999), and

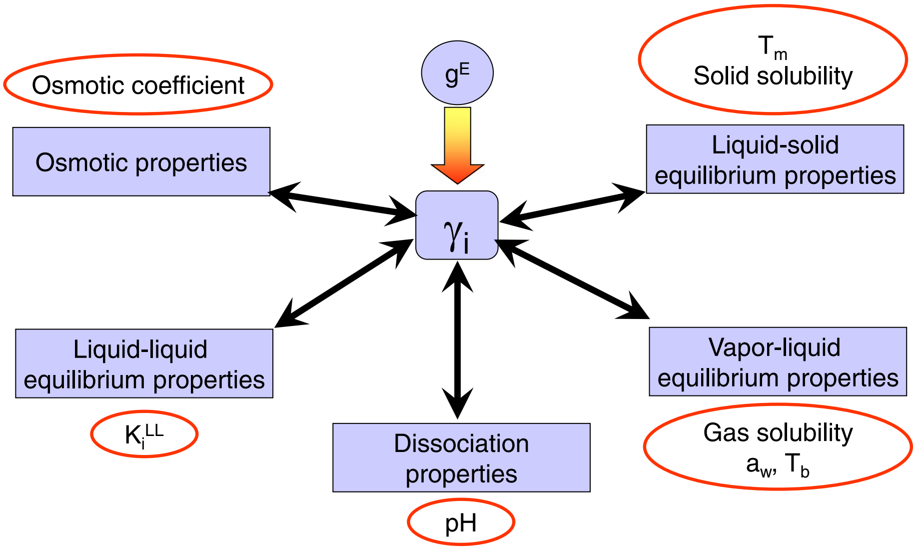

Fig. 1. Relationship between Excess Gibbs Energy (g^E) and physical–chemical properties.