

PE4.99 Measurement and prediction of pH and aw of meat products 356.00

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Abstract—Marination is commonly used in the processing of meat products (i) to develop organoleptic and texture properties in the final products, (ii) to preserve nutritional qualities and (iii) to prevent growth of pathogenic bacteria and so increase shelf life. In this process, meat is brought into contact with a solution containing various ingredients such as salts, organic acids and flavouring agents. Time course of some physico-chemical properties (pH and aw) of meat was studied during the marinating process. First, an experimental database of sorption curves and titration curves of meat products (gelatine, beef meat juice and beef meat) was set up. The influence of different concentrations of one or two ingredients on the sorption or titration curves was measured. Second, a thermodynamic approach was used to predict sorption and titration curves. It was based on the group contribution concept for short- and long-range interactions, and took into account variable concentration-dependent solvation of ions and molecules. This approach showed that the three media (gelatine, beef meat juice and beef meat) had similar behaviour. Addition of salts (NaCl, KCl) had no effect on titration curves, unlike addition of organic acids (acetic, lactic and citric acid), which strongly modified pH. The prediction of sorption and titration curves of meat products by the thermodynamic approach was satisfactory.

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Index Terms— pH, aw, sorption curve, meat, UNIFAC

I. INTRODUCTION

Besides temperature and pressure, water activity (aw) and pH are major physico-chemical properties in biotechnology and the food industry. They are used to characterise both microbial behaviour and the time course of chemical reactions in aqueous liquid solution. In the aqueous solutions used in pharmaceuticals, biology or microbiology, many solutes can be added to the mixtures, and their concentration can vary from one composition to another. These mixtures, in which the

water is the main component, and so is considered as the solvent, can contain many different solutes at different concentrations. These solutes can be neutral molecules such as sugars or alcohols, or electrolytes such as acids, bases and amino acids. They can be used to depress the water activity, or to modify the pH. Activity is linked to the concentration of component i by the relation $a_i = g_i c_i$, where g_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, i.e., the difference between the component activity and its concentration. The deviation from ideal solution behaviour has two consequences. The first concerns the method used to measure pH. pH is defined based on the activity, but it is usually assumed that $\text{pH} = -\log_{10}(c_i)$, 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. The second consequence concerns the estimation of pH and aw: when a salt is added to a medium, even at a very low concentration, it can greatly modify the chemical equilibrium, as expressed by Gibbs-Duhem's law (Prausnitz et al., 1999). In media containing non-electrolyte species, deviation from ideality increases as the concentration of a component increases or as the number of the components increases, even at low concentrations. To construct a theory of a liquid mixture, two kinds of information are required: the structure of the liquids and the intermolecular forces between like and unlike molecules. Unfortunately, in both cases information is incomplete and so all theories must make simplifying assumptions (Prausnitz et al., 1999). Most theoretical work has been concerned with mixtures of liquids comprising nonpolar spherical molecules: e.g., the regular solution theory of Scatchard and Hildebrand frequently provides a good approximation for mixtures of hydrocarbons. All the theories have been extended, often semiempirically, to more complex molecules. Among these theories, predictive activity coefficient methods are now mostly based on group contribution models: ASOG (Wilson and Deal, 1962) and UNIFAC (Fredenslund et al., 1975). These methods are used daily in the chemical industry and new developments are still being made in

the case of UNIFAC (Larsen et al., 1987) or ASOG (Kojima and Tochigi, 1979), improving the range and accuracy of the methods. Models for electrolyte activity coefficients result largely from that of Debye-Hückel for the long-range ion-ion interaction contribution, such as that of Pitzer (1973). However, in all cases, Robinson and Stokes (1959) and later Achard et al. (1994) clearly identified the need to define the ionic entity in terms of its degree of hydration. Finally, in the food industry, Lebert and Richon (1984), Le Maguer (1992) and Catté et al. (1995) carried out pioneering work on aqueous carbohydrate systems. The UNIFAC equation is also used to predict the retention of aroma compounds by foods (Sancho et al., 1997), and also *aw* and pH of bacterial growth media (Achard et al. 1994, Lebert et al., 2005). This work used a group contribution method (Achard et al., 1994), which, added to the equilibrium properties of water, yielded equilibrium properties of all the components in aqueous solutions, including liquid food solutions, aqueous gelatine gels, meat juice and meat.

II. MATERIALS AND METHODS

A. pH and titration curve

Solution pH was measured using a MP230 pH meter (Mettler Toledo, Viroflay, France) equipped with an Inlab 413 probe (Mettler Toledo) with a built-in temperature sensor. The measuring range was 0-14 with a temperature range of 0-60 °C. Measurement reproducibility was ± 0.001 per pH unit. A TitroLine alpha plus titrator (Schott, Germany) fitted with 20 ml units was used for the titration curves. Dosing error was 0.1% of the total volume. It was equipped with a ScienceLine pH combination probe (Schott). The measuring range was 0-14 with a temperature range of -5 to $+80$ °C. Measurement reproducibility was ± 0.01 per pH unit.

B. *aw* and sorption curve

Two instruments were used to measure *aw*: - an *aw*-meter (sprint TH500 Novasina, Roucaire, France). The temperature inside the measuring cell was controlled in the range 0-50 °C, with a precision of 0.2 °C. The measuring range was 0.05-1.00. Measurement accuracy was ± 0.005 *aw* unit. Calibration was carried out with a six-point reference system: 0.11, 0.33, 0.53, 0.75, 0.90 and 0.98. - an automatic micro-osmometer (type 13/13DR, Autocal Roebing, Germany), which determines the freezing point of aqueous solutions.

Measuring range was 0-2500 mOsm and accuracy was $\pm 0.5\%$. Calibration was performed with pure water and a standard solution at 300 mOsm/kg of water.

C. Gelatine, gelatine gel, meat and meat juice preparation

Gelatine was dissolved in purified water (MilliQ-Plus Water Purification System, Millipore S.A., Molsheim, France). Organic acids (acetic acid, lactic acid, citric acid) and (or) salts (sodium chloride, potassium chloride) were added for titration curves. A pure gelatine gel was prepared by melting gelatine granules (Rousselot, France) in pure distilled water at 58 °C for 45 min with slight agitation. The water content was adjusted to 3 kg of water for 1 kg of anhydrous gelatine (moisture content 75% w/w). This pure gelatine preparation was gelatineized at 4 °C for at least 24 h. Salt or a salt of an organic acid was added for the sorption curve in gelatine gel. Meat and meat juice were from semimembranosus and semitendinosus muscles of young cattle (less than 18 months old). Frozen meat was thawed at ambient temperature, and juice was recovered and used for measurements. Meat was ground for the titration curves.

D. pK determination

The pK of the gelatine was estimated from one experimental titration curve. A dichotomous search (Edgar and Himmelblau, 1988) was used to optimize the pK values.

E. Molar mass determination

The molar mass was determined using the method of Chen (1986), which measures the freezing point depression of a solution water + solute compared with pure water. *aw* was measured with the micro-osmometer and was linked to the molar mass of the solute

F. Sorption curve determination

The fast, accurate method of Baucour and Daudin (2000) was used to measure sorption isotherms of solid gelatine gels in the water activity range 0.6-1.

G. Thermodynamic model

The thermodynamic properties of a mixture depend on the forces that exist between the present species. When electrolytes are considered, the system is characterized by both molecular species and ionic species, resulting in three different types of

interactions: ion-ion, molecule-molecule and ion-molecule. Ion-ion interactions are governed by electrostatic forces between ions, which have a much longer range than other intermolecular forces. Molecule-molecule and ion-molecule interaction forces are known to be short-range. The excess Gibbs energy of systems containing electrolytes can thus be considered as the sum of two terms, one related to long-range forces between ions and the other to short-range forces between all the species. The solution model developed by Achard et al. (1994) was used to estimate the order of magnitude of the deviation for all of the species, charged or uncharged, in relation to an ideal infinitely diluted solution. It is formed by the juxtaposition of three contributions that take into account factors related to the size of the molecules present, electrostatic effects for the charged species and the solvation of some ionic forms, respectively: - the UNIFAC (universal functional group activity coefficients) model modified by Larsen et al. (1987) used to predict the activities of non-ionic molecules in mixtures such as sugars, alcohols, etc., - the Pitzer-Debye model describing long-range interactions between ionic species, based on the Pitzer theory (Pitzer, 1973), and - the solvation of charged species giving clusters, accounted for by 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 all the different species in the solution. These calculations are combined with thermodynamic equilibrium equations using the equilibrium constants (pK) defined at infinite dilution and generally given in reference tables. The detailed composition of the solution (concentrations of different charged species) and the activities of the different solutes are determined by solving the equation system. Activity coefficients give access to properties such as water activity, osmotic pressure, freezing point depression, boiling temperature increase, pH and acidity.

III. RESULTS AND DISCUSSION

A. Gelatine representation

The equivalent molecular mass of gelatine was found to be approx. 2250. Six pKa values were determined: 1.2, 3.0, 3.9, 8.4, 10.6 and 11.6 from the titration curve of a gelatine solution (20 g.l⁻¹). For the breakdown of the molecule into functional groups, CH₂CO and CH₂NH groups were used, as the group CO-NH

(peptide bond) is not found in the thermodynamic databases.

B. Titration curves of gelatine solutions

A database of 22 titration curves was used for the validation of the above gelatine representation. Predictions of titration curves of gelatine solution were made for gelatine, gelatine with a salt (sodium chloride or potassium chloride), gelatine with one organic acid (acetic acid, lactic acid or citric acid) and gelatine with one salt and one organic acid. Figure 1 shows the experimental and calculated titration curves of a solution of gelatine (50 g.l⁻¹). A close agreement can be observed in this case. Similar results were obtained when a salt, an organic acid or a salt and an organic acid were added in varied proportions.

C. Sorption curves of gelatine gels

The model predicts sorption curves of gelatine gel with varied proportions of sodium chloride (Fig. 2). The deviations between experimental and predicted values were less than 0.01 aw unit for gel at aw above 0.90. Deviation was higher (between 0.01 and 0.02 aw unit) for a gel with a measured aw between 0.70 and 0.90. The prediction of sorption curves of a gelatine gel with different salts of organic acids (sodium acetate, sodium lactate, potassium lactate and potassium sorbate) was obtained with the same precision.

D. Extension to meat juice and meat

The above description of gelatine was used (in only one situation: the titration curve of meat juice and meat). A relatively close agreement was obtained (Figure 1), but the results need to be confirmed in more varied conditions, e.g., adding salts or organic acids

IV. CONCLUSION

This study shows that it is possible to calculate, in a satisfactory way, two physico-chemical properties (aw and pH) of gelatine (in solution or in gel). The first results show that extension to meat juice and meat is possible. Thus a thermodynamic model can be a useful tool for the food industry. This model, coupled with heat and mass transfer models, can predict profiles of pH and aw in meat products during the process of marinating and cooking

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Figure 1. Comparison of experimental and calculated titration curves of gelatine solution, meat juice and meat.

Figure 2. Comparison of experimental and calculated sorption curves of gelatine gel with addition of sodium chloride.

Figure 1

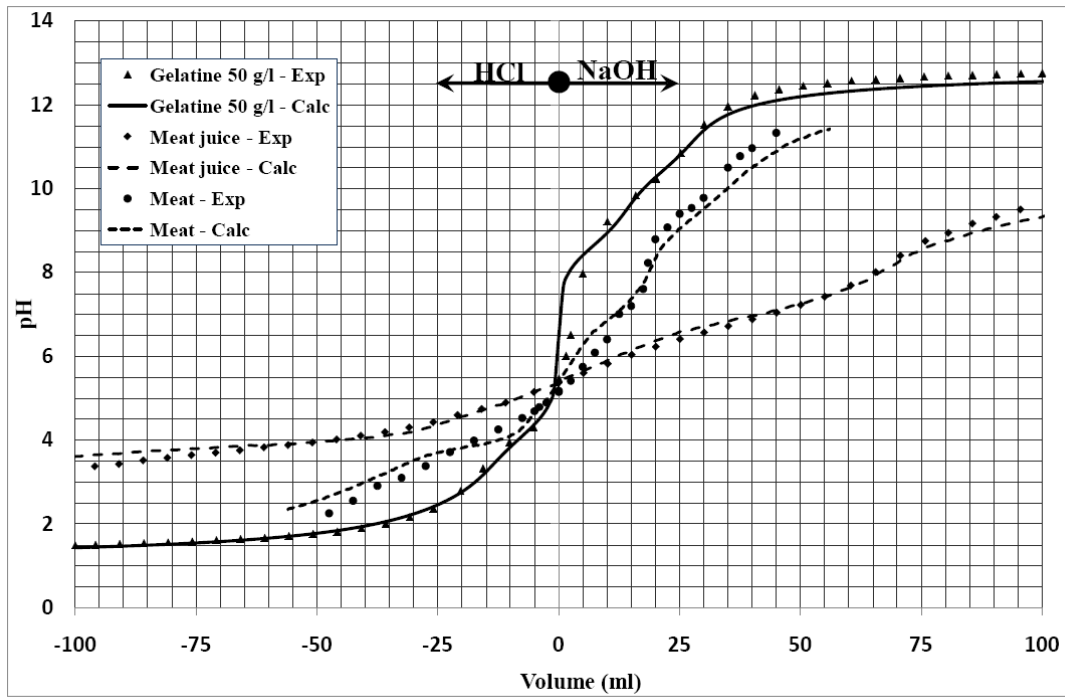


Figure 2

