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Dual mode diffusion and sorption of sodium chloride in pork meats under cooking conditions

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ABSTRACT

This study aims to obtain insight into mechanisms of NaCl diffusion in pork meats under cooking conditions: the loins at 5 (raw), 63 (pre-cooked) and 98 °C (pre-cooked), the mince at 98 °C (pre-cooked), and the filet at 98 °C (pre-cooked). It has been generally presumed that NaCl in any of pork meats diffuses with a constant Fick's diffusion coefficient, D, through liquid water channel imbibed in them. However in the present study, we experimentally obtained skewed bell shape variations of D in all of the above meats with respective maxima at certain low NaCl concentrations. These variations were interpreted in terms of a dual mode sorption and diffusion theory, which had been successfully applied to NaCl diffusion behaviors in Japanese radish and solidified egg white. This interpretation gives a thermodynamic diffusion coefficient, $D_T(p)$ for the partition species of NaCl and another one, $D_T(L)$ for the Langmuir type sorption species, both in the water swollen substrates in the meats. It was found that $D_T(p)$ values are sizably smaller than corresponding $D_T(L)$ values. This difference was ascribed to the lower water content in the p region than that in the L region. With the two D_Ts and additional equilibrium parameters, the theory explained the remarkable decrease of D value with C at 21 °C found by Guiheneuf et al. and nearly constant D values in the higher C range at 5 °C reported by other researchers. Experimentally obtained sorption isotherms of NaCl, which were slightly convex upward in the low C range, were satisfactorily reproduced with the parameters and the fractions of water swollen substrates in the whole meats.

1. Introduction

Diffusion of NaCl in various meats under their cooking conditions has long been studied as one of the most important problems in cooking foods for mankind. In the relevant studies, it has been usual to assume a constant D defined against the concentration gradient in the pertaining substrates. Literature before 1984 is summarized in a review given by Rüegg & Schär, where D values, e.g., for pork loin and cheese, are tabulated for the quick overview (Rüegg & Schär, 1985). The constancy of D in the pork was explicitly rationalized by the high fractions of imbibed water in the substrates, e.g., 73 g/100 g for pork loin, which makes it apparently reasonable to presume perforating continuous channels filled with liquid water (Offer et al., 1989). If this assumption be true, constant D must reproduce the concentration profile in the substrate over the ranges measured, although some variations may be admitted for the decrease of the activity coefficient of NaCl with the concentration (Truesdell, 1968). However in consideration of the practical processes, it has been usual to measure the concentration profiles of NaCl in various meat substrates being contacted with high NaCl solutions like 5 mol/kg, or even with the salt granules. Meticulous examination of some concentration profiles reported for one-dimensional NaCl diffusion, e.g., in Emmental cheese, reveals upward deviation of experimental points from the theoretical line in the concentration range lower than 0.5 mol/kg, which implies an enhancement of D to a certain degree in such a concentration range (Pajonk, Suarel, & Andrieu, 2003). Moreover, at least one pioneering study by ^{23}Na NMR imaging has reported about 81% decrease of D in the range of 0.34–0.84 mol/kg NaCl in pork loin at 21 °C. No credible rationalization for the decrease was presented by the authors (Guiheneuf, Gibbs, & Hall, 1997).

Recently in our two preceding studies, we have reported that experimentally obtained D values of NaCl in Japanese radish and solidified egg white show variations with respective maxima accompanied by gradual decreases over the maximum showing

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Nomenclature

C	concentration of NaCl in total pork (mol/kg)
C_L	concentration of the Langmuir species of NaCl in total pork (mol/kg)
C_p	concentration of the partitioned species of NaCl in total pork (mol/kg)
C_s	concentration of NaCl in the outer solution (mol/kg)
D	Fick's diffusion coefficient (m^2/s)
D_L	Fick's diffusion coefficient of the Langmuir species of NaCl (m^2/s)
D_p	Fick's diffusion coefficient of the partitioned species of NaCl (m^2/s)
D_T	thermodynamic diffusion coefficient (m^2/s)
$D_T(L)$	thermodynamic diffusion coefficient of the Langmuir species of NaCl (m^2/s)
$D_T(p)$	thermodynamic diffusion coefficient of the partitioned species of NaCl (m^2/s)
D_W	diffusion coefficient of NaCl in water (m^2/s)
E_a	activation energy of NaCl diffusion (kJ/mol)
K	K_L/K_p (kg/mol)
K_L	equilibrium constant of Langmuir mode sorption (kg/mol)
K_p	equilibrium constant of partition mode sorption
K_p'	partition coefficient of NaCl in the water swollen protein substrate
S	concentration of Langmuir mode sorption site in total pork (mol/kg)
T	temperature (°K) (°C)
t	diffusion time (s)
x	distance from the surface of pork cross section (m)
α	KS
β	fraction of the weight of the water swollen protein including the swelling water in the weight of total pork
η	$x/2/\sqrt{t}(m/s^{1/2})$
θ	C_L/S
φ_p	volume fraction of polymer component in the water swollen substrate (the liquid water contained in the pork being set aside)

concentrations (Hashiba, Gocho, & Komiyama, 2008; Hashiba, Komiyama, Nakanishi, & Gocho, 2007). According to these observed facts, we redefine here D as a variable with C in foodstuff substrates. The theory applied was the dual mode diffusion and sorption one which had been first proposed by one of the present authors for the diffusion of anionic dyes in Nylon (Komiyama & Iijima, 1974). The theory is based on the formulation of solute diffusion in terms of the chemical potential gradient (Onsager & Fuoss, 1932) and assumes a rapid equilibrium between the two species of NaCl in p and L modes in the water swollen substrate. Here the word 'water swollen substrate' means 'the weight of water containing meat minus the weight of liquid water imbibed in the meat'. The diffusion of NaCl partitioned in the imbibed liquid water was found not to participate in the rate determining step of the diffusion (Hashiba et al., 2007, 2008). The p type sorption species assigned is that in the water swollen uncharged region in the substrate and the L type sorption species is that in the water swollen charged region of the substrate. Two constant thermodynamic diffusion coefficients, $D_T(p)$ and $D_T(L)$ in the respective regions, which stand for solely the mobilities of NaCl, were estimated by the analysis of the maximum showing variations of D. It was found that $D_T(L)$ values are larger than $D_T(p)$ by a few to several times. We ascribed the reason to the higher water content of the charge containing L region than that of the uncharged p region. Some equilibrium parameters were also obtained by analyzing the variations of D. As far as we know, solely this theory can quantitatively explain such variations of D of NaCl with C in water containing foodstuffs. It must be quite interesting to extend the application of the theory to the diffusion behaviors of NaCl in other kinds of foodstuffs, many of which we presume to await clarification in the mechanism.

Among the seasoning processes of various foodstuffs with NaCl, those of various meats are undoubtedly the most important ones. Pork meats have long been brined under a wide variety of conditions with respect to temperature, time and the heating methods like boiling, steaming and so on. Meats or the muscles of various animals, comprise largely proteins like actin and myocin and various lipids. These materials comprise accumulated uni-directional bundles of fibers to form blocks.

In the present study, we focus on the diffusion of NaCl in pork meats under representative cooking conditions. For comparison purpose, minced pork loin and the filet block are included in the object of the investigation. As a model process for stewing, pork loin block pretreated at 98 °C is cooked in the salt solution at 98 °C. One-dimensional diffusion of NaCl is studied in the direction parallel to the muscle fiber axis. In reference to the diffusion process of NaCl in preparing loin roll, the loin pretreated at 63 °C is brined in the salt solution at 63 °C. For preparing raw ham, the loin is treated in the salt solution at 5 °C. The last treatment takes fairly long time of about 10 h. Minced loin and filet block are salted at 98 °C to compare with pork loin block in NaCl diffusion behaviors. We expect that the diffusion behaviors of NaCl under these conditions are reasonably interpreted with the dual mode diffusion and sorption theory, if the modifications of the meats by the pretreatments are properly taken into account.

2. Theory and the application

The theory applied to NaCl diffusion in foodstuffs was fully described in the preceding study on Japanese radish (Hashiba et al., 2007). We excerpt some basic assumptions, the meanings of the parameters used in the theory and the iterative method to estimate the parameters. The theoretical curve drawn with the parameters for $C < 0.5$ mol/kg is extended for $C > 0.5$ mol/kg, to compare with experimentally obtained (constant) D values which have been reported by other researchers.

2.1. Organization of foodstuffs pertinent to salt diffusion

Any foodstuffs under cooking conditions comprise two regions mentioned in the introduction: water swollen substrate region and liquid water region. NaCl passes through these two regions in ways determined by the geometries of the two regions. As instances, NaCl must pass through the cell walls and liquid water in Japanese radish (Hashiba et al., 2007) and passes through coagulated three-dimensional protein networks and liquid water in solidified egg white (Hashiba et al., 2008). For pork loin and filet, NaCl must pass through directional bundles of muscle fibers and liquid water. The arrangements of the two regions may lead to different combinations of the resistances to overall NaCl diffusion. Here we adopt the most simple series combination of the two resistances for the organized muscle structure (Offer et al., 1989). On that assumption, if we further assume that the resistance of the water swollen substrate