Thermodynamic description of the chemical leavening in biscuits

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ABSTRACT

In this paper we describe the chemical reactions of leavening agents in baking biscuits on a sound thermodynamic basis. The model is part in a sequel targeted at physical understanding of biscuit baking with the purpose of reformulation of biscuits with respect to sucrose and sodium levels. The chemical leavening gases, CO2 and NH3, originate from the dissociation of sodium and ammonium bicarbonate. Next to water vapour, these produced gases create gas bubbles in the biscuit dough. The concentrations of the leavening agents and added salt lead to high ionic strength. Consequently, the activities of ions participating in the leavening reaction deviate strongly from ideality. The non-idealities are described using the Pitzer equations. The values of many parameters of the Pitzer model and equilibrium constants are obtained from the strong developed field of CO2 sequestering in ammonia solutions. The model describing the chemical reactions is coupled to a cell model describing the expansion of gas bubbles. Model simulations show that most of the produced gas originates from the bicarbonate, and the ammonium contributes significantly less. The functionality of ammonium as leavening agent is not quite clear, but it may help in reducing sodium levels.

1. Introduction

We are involved in a research program involving the understanding of the baking process of biscuits, and in particular the function of ingredients regarding resulting microstructure, in order to develop reformulation strategies (van der Sman and Renzetti, 2019). Biscuits are high in sugar and sodium levels, with sodium contributed by added salts and leavening agents. Sound reformulation strategies must be based on good understanding of the functionality of ingredients. In an earlier paper we have reviewed the many functions of sucrose in biscuits (Kweon et al., 2009), which we use as a model biscuit in our research. The leavening agents, sodium and ammonium bicarbonate, are involved in a complex of chemical reactions. The function of leavening agents is to generate CO2 gas, which allows (together with the evaporation of moisture) gas bubbles to be formed during baking. For a good understanding of the leavening action, we aim to develop a multiscale simulation, which is based on a sound thermodynamic description of the driving forces for bubble formation, similar to our previous study on expanding starchy snacks (van der Sman and Broeze, 2014).

In food science the chemical reactions of leavening agents are hardly investigated. In a larger review paper (Kweon et al., 2014) have made some remarks on the functionality of leavening agents, but without a detailed description of experiments. Leavening in bread dough via CO2 from yeast or chemical leavening agents is better investigated, which is shortly reviewed below.

The studies (Bellido, 2007; Bellido et al., 2008) have investigated the action of chemical leavening agents in bread dough. Leavening agents produce gases via a reaction of a base like sodium bicarbonate and a weak organic acid, as lactic acid, citric acid, or tartaric acid. The sodium bicarbonate reacts quickly with the weak acid. For more slow release of gases one uses also ammonium bicarbonate, which produces both CO2 and NH3. Maximal gas production is assumed at \( T = 59^\circ\text{C} \). Its use is limited to low moisture products like cookies, where one expects maximal decomposition, because residues give off-tastes after baking.

The dissolution of CO2 in dough is investigated in bakery products leavened by yeast. Earlier models have assumed that during proofing the bread dough is saturated with CO2 (Shah et al., 1998; Fan et al., 1999). Distinct liquid and gas phase are assumed, exchanging CO2 and H2O. During baking the temperature will rise, and the solubility of CO2 reduces - which is released as gas in the expanding bubble. One assumes no extra generation of CO2 by yeast. Later models incorporated the action of yeast, but the hydration of CO2 is not included (Chiotellis and Campbell, 2003; Narasimhan, 2014).

(Aissa et al., 2015) have given a quantitative description of yeast leavening including the hydration of CO2 solubility. In their model they account for 1) the presence of both a liquid and gas phase, 2) the
hydration of CO2 into (b)carbonate, and 3) the ionic strength of the dough (due to added salts). Data is given of CO2 solubility as function of NaCl, showing that salt reduces the solubility of CO2. Dissociation constants for bicarbonate is given as function of temperature, and ionic strength. For the vapour-liquid equilibrium of CO2 they have considered a temperature dependent Henry constant. We intend to develop a similar model for chemical leavening agents, but one which is based on first principles and sound thermodynamics.

In chemical engineering the inverse reaction, the solubilization of CO2 and NH3 gases in water, is a strongly developed field. Currently, the problem of CO2 sequestering is driving this field (Wang et al., 2011; Zhao et al., 2012). It follows that the gases are produced via a complex network of chemical reactions. Furthermore, the high ionic strength requires the use of the Pitzer equation for the computation of the ion activities (Edwards et al., 1978), which enter the expressions for the equilibrium constants. In several (de) protonation reactions water is involved, requiring knowledge of the water activity. Also for the biscuit the water activity must be known, as the moisture content of the biscuit is low, and the sugar content is high. Consequently, the water activity will be considerably lower than unity, which influences the chemical equilibrium of fast reactions.

Wang et al., (2011) have studied the sequestering of CO2 in ammonia solutions. They show a convenient representation of the reaction network, with 3 axes showing 1) proton-transfer, 2) OH transfer, and 3) NH3 transfer. Reactions involving NH3 transfer is the least likely, implying very slow reaction kinetics. Hence, there is a wide separation of time scales of the reaction kinetics, making it a numerical stiff problem, which is very challenging to solve. It will be too demanding to incorporate the full model into a biscuit baking model. Hence, we will also investigate the model reduction of this chemical system.

The paper is organized as follows. We start with a comprehensive model description, entailing a) the thermodynamics of chemical reactions, b) the Pitzer model, c) the bubble expansion model, and d) the model reduction. As experimental data on the action of leavening agents in food is very scarce, model validation will be performed on subproblems from chemical engineering. Subsequently, we present the simulation results for the leavening of biscuits, before we end with conclusions.

2. Model description

2.1. Reaction scheme

The leavening system of the AACC 10–53 biscuit, based on sodium and ammonium bicarbonate, reacts according to the following reaction scheme:

\[ \text{CO}_2(aq) + H_2O \leftrightarrow HCO_3^- + H^+ \]
\[ HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \]
\[ H_2O \leftrightarrow OH^- + H^+ \]
\[ \text{NH}_3(aq) + H_2O \leftrightarrow NH_4^+ + OH^- \]
\[ NH_2COO^- + H_2O \leftrightarrow NH_3(aq) + HCO_3^- \]  
(1)

The above set of reactions is identical to that of the CO2-NH3-H2O system, which is well investigated in the field of chemical engineering (Edwards et al., 1978; Wang et al., 2011). NH2COO− is the carbamate ion. In studies of CO2 sequestering it is shown during solubilization of NH3 and CO2 in water, more carbamate is formed than ammonium (Wang et al., 2011). Only if CO2 is depleted more ammonium than carbamate is formed.

The following equilibrium constants are defined:

\[ K_i = \frac{a_\text{aBac}}{a_\text{aCO}_2} \]
\[ K_2 = \frac{a_\text{CO}_2a_\text{H}}{a_\text{aCO}_3} \]
\[ K_3 = \frac{a_\text{aH}a_\text{H}}{a_\text{aNH}_3} \]
\[ K_4 = \frac{a_\text{NH}_4a_\text{OH}}{a_\text{aNH}_2\text{COO}^-} \]
\[ K_5 = \frac{a_\text{aOH}a_\text{aH}}{a_\text{aNH}_2\text{COO}^-} \]  
(2)

with \( a_i = \gamma_m a_i \) is the activity of component \( i \), which will be expressed in terms of the molality \( m_i \) and the activity coefficient \( \gamma_i \).

The temperature dependency of the equilibrium constants has been investigated in multiple papers (Edwards et al., 1978; Bieling et al., 1989), which all follow the generalized relation:

\[ \log(K) = A_i/T + A_i \log(T) + A_4 + A_4/T \]  
(3)

In Table 1 we have listed the values of \( A_i \) that we have used together with references to their source.

2.2. Pitzer model for multiple electrolyte solutions

We use the Pitzer model as used in the study of (Edwards et al., 1978). In the AACC 10–53 system the total ionic strength is of order unity, and consequently the ternary terms of the Pitzer model are not required.

Hence, the activity coefficient of ion \( a \) is defined by:

\[ \log(\gamma_a) = -z_a^i F(I) + 2 \sum_m m_i B_{ac} - z_a^i \sum_m m_i m_j B_{ac} \]

(4)

In Eq. (4) the subscripts \( ac \) represent any anion/cation pair, while \( a/c \) represent anion/cation pairs with \( a \neq a \). \( B_{ac} \) are called the binary ion-ion parameters.

\( I \) is the ionic strength, computed as:

\[ I = \frac{1}{2} \sum_i z_i^2 m_i \]  
(5)

and \( z_i \) the valency of the ion.

The first term is the Debye contribution with:

\[ F(I) = -A_p \left[ \sqrt{I} + \frac{2}{b} \ln \left( 1 + b \sqrt{I} \right) \right] \]

with \( A_p = 0.392 \), and \( b = 1.2 \) (Edwards et al., 1978).

The binary Pitzer coefficients are a function of the ionic strength, via:

| \( K_i \) | \( A_1 \) | \( A_2 \) | \( A_3 \) | \( A_4 \) | \( A_5 \) | \( \text{ref.} \) |
|---------|---------|---------|---------|---------|---------|---------|
| \( K_1 \) | -12092 | -36.8   | 0.0     | 235     |         | (Edwards et al., 1978) |
| \( K_2 \) | -12431 | -35.5   | 0.0     | 220     |         | (Edwards et al., 1978) |
| \( K_3 \) | -13446 | -22.5   | 0.0     | 26.9    |         | (Edwards et al., 1978) |
| \( K_4 \) | -3336  | 1.497   | -0.03706| 2.76    |         | (Edwards et al., 1978) |
| \( K_5 \) | -2900  | 0.0     | 0.0     | 8.6     |         | (Edwards et al., 1978) |
\[ B_{ai} = \beta_{ai}^{(0)} + 2\beta_{ai}^{(1)} \frac{1 - (1 + \alpha \sqrt{T}) \exp(-\alpha \sqrt{T})}{\alpha T} \]  
and  
\[ B_{ai}' = \frac{1 - (1 + \alpha \sqrt{T}) \exp(-\alpha \sqrt{T})}{\alpha T} \]  

The constant is \( \alpha = 2 \).

The water activity in multicomponent electrolyte solution is related to the osmotic coefficient \( \psi \), which is given by (Pitzer, 1973; Edwards et al., 1978):

\[ (\psi - 1) \sum_{i} m_i = -A \frac{2\sqrt{T}}{1 + B\sqrt{T}} \]  

\[ + \sum_{i} \sum_{a} m_i \beta_{ai}^{(0)} \left( \beta_{ai}^{(1)} + \beta_{ai}^{(1)} \exp(-\alpha \sqrt{T}) \right) \]  

The water activity is computed via:

\[ \psi = \frac{\log(a_\psi)}{M_\psi \sum m_i} \]  

with \( M_\psi \) the molar mass of water.

Data on interaction coefficients \( \beta_{ai}^{(0)} \) are shown in Table 2, which are taken from (Kim et al., 1993; Meng et al., 1995).

### 2.3. Relaxation scheme

The full model is solved via a relaxation scheme. We have defined pseudo reaction rates:

\[ r_1 = k_1(-K_1 a_{CO_2} a_{H_2O} + a_{HCO_3} a_{H}) \]  
\[ r_2 = k_2(-K_2 a_{HCO_3} + a_{CO_2} a_{H}) \]  
\[ r_3 = k_3(-K_3 a_{H_2O} + a_{H} a_{OH}) \]  
\[ r_4 = k_4(-K_4 a_{H_2O} a_{HCO_3} + a_{H} a_{OH} a_{OH}) \]  
\[ r_5 = k_5(-K_5 a_{HCO_3} a_{H_2O} + a_{HCO_3} a_{H}) \]  

This renders the following relaxation scheme:

\[ \partial_t m_{CO_2} = -r_1 \]  
\[ \partial_t m_{H} = -r_1 + r_3 \]  
\[ \partial_t m_{OH} = +r_4 \]  
\[ \partial_t m_{HCO_3} = -r_3 \]  

### Table 2

Pitzer interaction coefficients (Kim et al., 1993; Meng et al., 1995).

| Ion-pair          | \( \beta^{(0)} \) | \( \beta^{(1)} \) |
|-------------------|-------------------|-------------------|
| NaCl              | 0.0765            | 0.2664            |
| NaHCO_3           | 0.0399            | 1.389             |
| NaOH              | 0.0277            | 0.0411            |
| NaHCO_3           | 0.0864            | 0.253             |
| NH_3HCO_3         | -0.0038           | 0.070             |
| (NH_3)_2CO_3      | -0.105 + 0.000375 T | 0                |
| NHCl              | 0.0457            | 0.204             |
| NH_3HCO_3         | 0.4162-0.00125 T  | 0                 |
| HCl               | 0.1775            | 0.2945            |

### Table 3

Temperature dependency of Henry constants \( K_{iH} \) (Kawazuchi and Prausnitz, 1987).

| Gas         | \( B_1 \) | \( B_2 \) | \( B_3 \) | \( B_4 \) |
|-------------|----------|----------|----------|----------|
| CO_2        | -17066   | -68.3    | 0.0660   | 430      |
| NH_3        | -7579    | -13.6    | 0.0086   | 96.2     |

Not all equations need to be solved, as there are three algebraic equations for the balance of carbon, nitrogen and charge. The two mass balances for total nitrogen and total carbon in the liquid phase hold:

\[ N_T = m_{NH_3} + m_{NH_4} + m_{NH_2COO} \]  
\[ C_T = m_{CO_2} + m_{HCO_3} + m_{H_2COO_3} + m_{CO_3} \]  

and the electroneutrality condition is:

\[ m_{NH_4} + m_{NH_3} = 2m_{CO_2} + m_{OH} + m_{H_2COO_3} \]  

\[ m_{NaHCO_3} \text{ and } m_{NaOH} \] are computed via the nitrogen balance, carbon balance, and electroneutrality condition.

The relaxation scheme needs initial conditions for its solution. For the biscuit system the amount of water, the amounts of bicarbonate \( m_{HCO_3} \) and ammonium \( m_{NH_3} \) are given, rendering also the values for \( C_T \) and \( N_T \). \( m_{H} \) and \( m_{OH} \) follow from the assumption of neutral pH. The initial value of other compounds is assumed to be zero.

### 2.4. Bubble formation

During baking there is growth of bubbles due to released gases from the leavening agents. The amount of CO2 and NH3 in the gas bubble are extracted from solution phase, which is accounted for in the carbon and nitrogen balance. The sum in the nitrogen and carbon balance \( C_T \) and \( N_T \) account for the compounds in the solution phase.

Assuming that the biscuit dough behaves as a viscous liquid before thermosetting, the growth of gas bubbles can be described by the Amon and Denson cell model (Amon and Denson, 1984; van der Sman and Broeze, 2014):

\[ p_{gas} - p_0 = \frac{4\eta(1 - \varphi_{por})}{R_b} \frac{dR_b}{dt} \]  

\( \eta \) is the dough viscosity, \( \varphi_{por} \) is the porosity of the dough, and \( R_b \) is the bubble radius. Initially the air bubble is of order \( R_0 = 0 \). We assume a linear ramp of temperature, representing baking conditions - up to the point of gluten thermosetting (95°C). Biscuit dough viscosity in the temperature range 20 – 40°C is about \( \eta = 1 - 5 \times 10^4 \) P.s (Charun et al., 2000). The number of bubble nuclei \( N_0 \) is computed from the assumed initial bubble radius and initial porosity. The gas contains CO2, NH3, H2O, and air:

\[ p_{gas} = p_{CO_2} + p_{NH_3} + p_{H_2O} + p_{air} \]  

The partial pressures of CO2 and NH3 follow Henrys law, cf. (Kawazuchi and Prausnitz, 1987):

\[ p_{gas} = K_{iH} \sigma_{iH} \frac{\varphi_{por}}{\varphi_{por}} \]  

with its temperature dependency following:
Because Eq. (15) can imply explosive growth of the bubble if damped. This damping is also required from a numerical point of view, which includes the effects of salt and sugar:

$$p_{N2O} = a_{N2O}P_{sat}(T)$$

with $P_{sat}$ the temperature dependent saturated vapour pressure. We use the Teten relation:

$$P_{sat}(T) = p_{ref} \exp \left( \frac{17.27 (T - T_{ref})}{T - 35.86} \right)$$

with $T_{ref} = 273.15$ K, and $p_{ref} = 610$ Pa.

To compute the partial gas pressures, we have 3 mass balances describing the change in amount of gas molecules in the gas phase:

$$\frac{\partial n_{CO2}}{\partial t} = \frac{K_{aCO}m_{CO2} - P_{CO2}}{\tau_{gas}}A_{gas}$$

$$\frac{\partial n_{NH3}}{\partial t} = \frac{K_{aNH3}m_{NH3} - P_{NH3}}{RT}A_{gas}$$

$$\frac{\partial n_{H2O}}{\partial t} = \frac{a_{H2O}P_{sat}(T) - P_{H2O}}{\tau_{gas}}A_{gas}$$

with $n_i = p_i/RT$ the molar concentration of gas $i$ in the gas phase. $A_{gas}$ the surface area of all gas bubbles, $\tau_{gas}$ is a relaxation constant, representing the rate of mass transport in the dough matrix. In this simple model we keep it fixed to a small value, such that the gas pressures remain close to the equilibrium values, but fast expansion of the gas bubble will be damped. This damping is also required from a numerical point of view, because Eq. (15) can imply explosive growth of the bubble if $P_{gas} \gg p_0$ at too small values of $\tau_{gas}$ (van der Sman and Broeze, 2014). Hence, the value of $\tau_{gas}$ is determined via trial simulations. The amount of air molecules remains equal to the initial amount: $n_{air}RT_0 = p_0V_{gas}$, with $V_{gas}$ the total volume of the gas phase, and $T_0$ the initial temperature.

The Amon-Denson cell model is solved numerically using a simple explicit time integration scheme, but with an adaptive scheme for the time step. The time step will be proportional to $\Delta t < (1 - \phi_{gas})/(p_r/(p_r + P_{gas} - p_0))$, with $p_r$ a reference over-pressure of $O(100)$ Pa. It follows that for $\Delta t/\tau_{gas} = 0.01$ stable numerical simulations are obtained. For values larger than $\Delta t/\tau_{gas} \geq 0.025$ we obtain unstable simulations with numerical oscillations in bubble size.

2.5. Model reduction

Preliminary simulations have shown that proton transfer reactions are very fast. Some effective reactions are quite slow, which becomes apparent after elimination of the fast proton transfer:

$$2HC03^- \rightarrow CO2 + CO3^{2-} + H2O$$

$$NH4^+ + CO3^{2-} \rightarrow NH2COO^- + H2O$$

$$NH4^+ + NH2COO^- \rightarrow 2NH3 + CO2$$

Their effective equilibrium constants are:

$$K_a = \frac{K'_2}{K'_1} = \frac{a_{NH3}a_{CO2}}{a_{H2O}^2}$$

$$K_b = \frac{K_3}{K_2} = \frac{a_{NH4}a_{CO2}}{a_{H2O}a_{COO}}$$

$$K_c = \frac{K_{15}}{K_{14}} = \frac{a_{NH4}a_{CO2}}{a_{H2O}a_{NH3COO}}$$

The equilibria of these reactions will be computed using a similar relaxation scheme as used for the full model. Again balances hold for the total carbon, total nitrogen and charge. Effectively, we solve the reduced model via relaxation for $m_{CO2}$, $m_{NH3}$, $m_{NH2COO}$ and $m_{COO}$:

$$\frac{\partial m_{CO2}}{\partial t} = r_c + r_e$$

$$\frac{\partial m_{NH3}}{\partial t} = 2r_c$$

$$\frac{\partial m_{NH2COO}}{\partial t} = r_b - r_c$$

$$\frac{\partial m_{COO}}{\partial t} = r_b - r_c$$

$$r_c = k_c(K_{aNH4}a_{CO2} - a_{NH4}a_{CO2})$$

$$r_b = k_b(K_{aNH4}a_{CO2} - a_{NH4}a_{COO})$$

$$r_e = k_e(K_{aNH4}a_{CO2} - a_{NH4}a_{COO})$$

3. Biscuit leavening system

We perform our calculations for the AACC-10-53 biscuit system (Kweon et al., 2009), which is often taken as a reference system for

| Compound                      | Weight (g) |
|-------------------------------|------------|
| Soft Wheat Flour (13% moisture) | 225        |
| Sucrose                       | 94.5       |
| Shortening                    | 90.0       |
| High-fructose corn syrup (42%) | 3.4        |
| Skimmed milk                  | 2.3        |
| NaCl                          | 2.8        |
| Sodium Bicarbonate            | 2.3        |
| Ammonium bicarbonate          | 1.1        |
| Total water                   | 49.5       |

Fig. 1. Henry constant for $CO2$ and $NH3$ as function of temperature, cf. (kawazuishi and Prausnitz, 1987).
biscuits in scientific literature. Hence, a significant amount of data is available for this system. The to-be-developed biscuit baking model will be based on this same system.

The composition of the AACC-10-53 biscuit system is shown in Table 4. Given the molarm weights of NaCl (58.4 g/mol) NaHCO3 (84.0 g/mol), and NH4 HCO3 (79.0 g/mol) and the amount of water available in the formulation, we can compute the following molalities: m\(_{\text{NaCl}}\) = 0.61 M, m\(_{\text{NaHCO3}}\) = 0.35 M, and m\(_{\text{NH4 HCO3}}\) = 0.18 M. If the leavening agents fully dissociate, 0.18 M of NH3 and 0.35 M of CO2 will be produced. Given the weight of water and the amount of moles of gas produced, using the ideal gas law and assuming the gas is at atmospheric pressure \(p_0\), we can compute the volume of gas, \(V_{\text{gas}} = \frac{n_g p_0}{R T}\). The amount of dry matter in the biscuit dough is about 450 g, which is assumed to have the same density as polysaccharides \(\rho = 1550\text{ kg/m}^3\) (van der Sman and Meinders, 2011). Consequently, we expect that the maximal porosity of the biscuit will be about 0.8.

The amount of sugar will also lower the water activity, which can be computed using the Flory-Huggins theory (van der Sman and Renzetti, 2019). However, they are thought to absorb water in the biscuit dough, which is due to the high sugar concentrations (Kweon et al., 2014; van der Sman and Renzetti, 2019). Consequently, we expect that the maximal porosity of the biscuit will be about 0.8.

The water activity of salts \(a_w\) and mean activity coefficient \(\gamma\) for NaCl at room temperature. We have used the model from the above section, and the listed parameter values. Results are shown in Fig. 2, where it is shown that the Pitzer model indeed describes the experimental data quite well, and even beyond the concentration range, that is relevant for biscuits (where \(m \leq 1\) mol/kg) (Chirife and Resnik, 1984), have shown that \(a_w\) is quite independent of temperature in the range of 15–60°C. We also assume that this holds for the activity coefficients.

4.1. Test of Pitzer model on NaCl

The Pitzer model is tested against experimental data on water activity \(a_w\) and mean activity coefficient \(\gamma\) for NaCl at room temperature. We have used the model from the above section, and the listed parameter values. Results are shown in Fig. 2, where it is shown that the Pitzer model indeed describes the experimental data quite well, and even beyond the concentration range, that is relevant for biscuits (where \(m \leq 1\) mol/kg) (Chirife and Resnik, 1984), have shown that \(a_w\) is quite independent of temperature in the range of 15–60°C. We also assume that this holds for the activity coefficients.

4.2. Dissolution of CO2 in salt solutions

A further test of the model is the dissociation of solubilized CO2 in saline water. Experimental data is available by Thurmond and Millero (1982). Their data are expressed in stoichiometric (dis)association constants:

\[
K_1^* = \frac{[\text{HCO}_3^-][\text{H}]}{[\text{CO}_2]}
\]

\[
K_2^* = \frac{[\text{CO}_3^3^-][\text{H}]}{[\text{HCO}_3^-]}
\]

\(pK_1^* = -\log(K_1^*)\) and \(pK_2^* = -\log(K_2^*)\) values are given for different molalities of NaCl. For the dataset of Thurmond and Millero (1982) holds that the total amount of carbon is small: \(C_T \ll 1\).

We will compare the Pitzer model against these datasets, using the same conditions as in the previous section. The results are shown in Fig. 2, where it is shown that the Pitzer model indeed describes the experimental data quite well, and even beyond the concentration range, that is relevant for biscuits (where \(m \leq 1\) mol/kg) (Chirife and Resnik, 1984), have shown that \(a_w\) is quite independent of temperature in the range of 15–60°C. We also assume that this holds for the activity coefficients.

Fig. 2. a) Water activity \(a_w\) and b) Mean activity coefficient \(\gamma\) of NaCl solution at \(T = 25^\circ\text{C}\) as function of molality \(m\), with predictions made by Pitzer model (solid lines). Symbols represent experimental data by Robinson and Stokes (2002).
with the activity coefficients computed using the Pitzer model, and the given interaction coefficients. We assume $\omega_i$ is fully determined by NaCl.

We have performed calculations with $C_T = 10^{-1} \text{M}$, for which holds that $K_{CO_2} \approx 1$. Results are given in Fig. 3. For the range of salt concentrations relevant to biscuit system ($m_{NaCl} \leq 1 \text{ M}$), the model predictions are well in line with the experimental data.

### 4.3. Speciation of ions in the NH3, CO2, water system

A final check of our model is the dissociation of dissolved CO2 and NH3 gases in ions. This problem has been investigated in chemical engineering for CO2 sequestering via Raman spectroscopy (Wen and Brooker, 1995; Zhao et al., 2011; Halstensen et al., 2017). In these systems carbamate ($NH_2COO^-$) will be formed, next to bi-carbonate ($HCO_3^-$) and carbonate ($CO_3^{2-}$) ions. We have compared our simulation results of the full Pitzer model with experimental data from Ref. (Halstensen et al., 2017), as shown in Fig. 4. While using values for all parameters from literature, we observe that the Pitzer model still captures the experimental data reasonably well. Given the many binary interaction coefficients required in the full model, see Table 2, it can be expected that some of these parameters are not very accurate, and explain the discrepancy between predictions and experimental data. Furthermore (Edwards et al., 1978), have stated that their model is not very sensitive to the value of $K_5$, which has been fitted simultaneously with some binary coefficients like $\beta_{NH_2COO}^{(i)}$. We expect further experimental analysis for increasing the accuracy of $\beta_{NH_2COO}^{(i)}$ would increase the accuracy of our model.

### 5. Gas leavening in biscuit dough

After having validated the full model, as discussed in the previous section, we have performed trial simulations with the full model using initial conditions as stated in the biscuit formulation, as shown in Table 4.

Fig. 3. Effective $pK_1$ and $pK_2$ of aqueous solutions at 25 °C with 0.1M NaHCO3 and NaCl at molality $m_{NaCl}$. Symbols represent data from (Thurmond and Miller, 1992), and lines are predictions using the Pitzer model.

From the trial simulations we have learned that there are three dominant (slow) reactions, which can be constructed from the full model via elimination of the very fast proton transfer reactions. This has lead us to the reduced model, as given in section 2.5. The reduced model is coupled to the gas bubble model of Amon and Denson, as given in section 2.4.

We have made some simplifying assumptions, as the main focus of this study has been the development of a model describing the chemistry of the leavening agents, using a sound thermodynamic basis. Our assumptions are:

- the dough temperature rises linear in time, from 30°C to 95°C in 5 min,
- the viscosity of the dough remains constant at $\eta = 5 \times 10^3$ Pa.s,
- air pockets are already present in the dough, as a consequence of the dough mixing,
- gas bubbles will grow from these initial air pockets, having an initial radius of $R_{\text{init}} = 1 \mu$m and initial porosity of $\phi_{\text{gas}} = 0.002$,
- there is no leavening gas escaping from the dough (also there is negligible evaporation), and
- the expanding bubbles do not rupture.

We will perform simulation up to the point that the gas bubbles will rupture, which is due to the thermosetting of gluten. Before rupture of the bubble, the escape of the gases to the baking oven is negligible, compared to after rupturing. After rupturing the structure can be assumed to be fixed, which is an open foam structure allowing easy escape of the leavening gases. At the end of baking oven it can be assumed that the chemical leavening agents have fully dissociated, and little gas is dissolved in the remaining moisture, which is also present in low amounts. Development of the model after bubble rupture will be pursued in future research.

In Fig. 5 we show how the molalities of various compounds change during heating of the biscuit dough. Note that the changes in the molalities are due to several effects: 1) the temperature dependency of the equilibrium constants, 2) the temperature dependency of the solubility of dissolved gases, 3) the slow dynamics in the bubble growth via the high viscosity, and 4) the extraction of dissolved gases via the expanding bubble. In Fig. 6 we show how the partial gas pressures and porosity change during heating.

Our simulations show a clear leavening of the biscuit, leading to a final porosity of about $\phi_{\text{gas}} = 0.9$, which is slightly larger than our estimated value of the maximal porosity ($\phi_{\text{gas}} = 0.8$). This discrepancy is due to the facts 1) that we have not taken into account the contribution of the evaporated water to the gas phase, and 2) that more than half of the bi-
carbonate has dissociated. A significant amount of carbon in the liquid phase is present as carbamate (\(\text{NH}_2\text{COO}^-/\text{CO}_3^-\)) instead of carbonate (\(\text{CO}_3^-\)). Their difference in charge allows more \(\text{CO}_2\) to be produced. We observe that most of the ammonium ions are dissociated, but the solubility of \(\text{NH}_3\) is still quite high near the thermosetting temperature. Hence, little \(\text{NH}_3\) has entered the gas phase, as evidenced its low partial pressure.

The computed porosity is also higher than found in literature. The study of (Pareyt et al., 2009) shows a porosity of about 45%, as obtained via X-ray tomography. In the study of (Fustier et al., 2009) the AACC 10–53 formulation has been used, showing a porosity in the order of 50–60%. These lower values are likely due to the fact that the leavening gases also escape to the environment during heating, which is not taken into account in the current model. Gas escape is particularly significant if the bubble wall ruptures. In the current model all gas bubbles would rupture simultaneously, leading to an abrupt change in porosity. In reality, the bubble rupture would be more distributed over time, leading to a gradual decrease in porosity at the end of baking. If the dough viscosity is higher than estimated, the bubble growth will be slower than predicted by the current model, and the porosity at the end of baking would also be slower. The model definitely needs improved in this aspect, but our objective of the model was to provide the thermodynamic framework of the leavening agents, and how it can be coupled to gas expansion models. Hence, improvements of the prediction of porosity is for future versions of the model.

Up to \(T = 350\) K most of the gas in the bubbles originates from the bicarbonate, as indicated by the high partial gas pressure of \(\text{CO}_2\). At higher temperatures the partial pressure of \(\text{CO}_2\) drops, while that of \(\text{H}_2\text{O}\) and \(\text{NH}_3\) increases. The total gas pressure remains around atmospheric values during the whole simulation. From our simulation results it follows that the functionality is of ammonium bicarbonate as leavening agent is not clear. The bicarbonate-ions do contribute to the production of leavening gas, but the ammonium ions do not. The use of ammonium ions helps to reduce the level of sodium ions, if compared to the case where bicarbonate is provided purely by \(\text{NaHCO}_3\).

To get better insight in the latter case we have performed simulations with biscuit dough having a different composition for leavening agents, namely 0.50 M sodium bicarbonate and 0.02 M ammonium bicarbonate (corresponding with 3.3g sodium bicarbonate and 0.1g ammonium bicarbonate added to a modified AACC 10–53 recipe). Results are shown in Fig. 7. The simulation shows that of course less \(\text{NH}_3\) gas is produced, but the final value of the porosity is lower (0.7) than in the case of the AACC 10–53 biscuit. The temporal evolution of leavening gases is somewhat different, with the gas production delayed until \(T = 340\) K, while in the AACC 10–53 biscuit the leavening start more or less immediately. Due to the late start of the gas production the final porosity is lower at gluten thermosetting temperature, \(T = 95\) C.

6. Conclusions

We have developed a thermodynamic model for the action of leavening agents in biscuits. The level of ions in biscuits demands the use of thermodynamic theories like the Pitzer model to compute the deviations of the compounds activities from ideality. The studied leavening agents, sodium bicarbonate and ammonium bicarbonate, are involved in a complex network of chemical reactions. Fortunately, these reactions are also occurring in \(\text{CO}_2\) sequestering, which is widely studied in the field of chemical engineering. This has allowed us to construct a sound thermodynamic model with known model parameters, describing the complete set of chemical reaction.

The full model has been validated against experimental data available.
from the field of chemical engineering. Subsequently, the full Pitzer
model has been reduced in complexity via elimination of the fast proton
transfer reactions. The reduced model is coupled to the Amon-Denson
model, which describes the expanding gas bubble in the biscuit
dough. This coupled model shows how the chemical equilibria shifts with
temperature and expanding gas phase. A final porosity of about 90% is
developed in the biscuit dough.

The low level of NH3 in the gas phase puts question marks at the
functionality of ammonium bicarbonate as leavening agent. In the
stage before bubble rupture, it is only the bicarbonate ion that contributes to
the produced gas. Ammonia gas escapes from the biscuit only after
bubble rupture, but the escape will be complete at the end of baking. The
synthesis of carbamate makes the leavening gas production already start
at the initial temperature, and it is more evenly distributed over time.
From a personal communication with Harry Levine, a well-known expert
in biscuit manufacturing (Kweon et al., 2009), it follows that ammonium
bicarbonate is also well appropriate for fine-tuning the spreading of the
biscuit, such that they well fit into the prescribed packaging.

The use of ammonium bicarbonate might also be functional from the
viewpoint of the reduction of sodium level. In literature as ammonium
chloride has been proposed as salt replacer (Batenburg and van der
Velden, 2011; Busch et al., 2013; Israr et al., 2016), but there is a poten-
tial of off-odours and off-taste. Also the impact of the compound to
acrylamide needs to be evaluated in this issue of sodium replacement in
bakery products (Amrein et al., 2006).

The developed framework of the Pitzer model coupled to the Amon-
Denson cell model is general enough to encompass biscuit systems con-
taining other leavening agents, for example with reduced sodium levels
using potassium bicarbonate instead of sodium bicarbonate. As sodium is
not involved in the reaction, the model is easily adapted to capture the
interaction coefficients between potassium and the other ions in the
leavening formulation, which can be found in literature (Roy et al.,
1984).

In other biscuit formulations the leavening contains only sodium bi-
carbonate, or sodium bicarbonate with a weak organic acid, such as so-
dium acid pyrophosphate, calcium phosphate, lactic acid, citric acid or
tartaric acid. For several of these weak acids the dissociation equilib-
rium is known (Achard et al., 1994; Velezmoro and Meirelles, 1998; Corey,
2003). Furthermore, it can be also be used to describe the dissolution of
CO2 produced by yeast in other bakery systems cf. (Aissa et al., 2015),
provided that the gas production by the yeast is known.

In a subsequent study we will couple the presented model to heat and
mass transfer at the product level, making it a multiscale model, as we
have developed for expanded snacks (van der Sman and Broeze, 2014).
For this model the thermodynamics needs to be extended towards the
effect of moisture removal on water activity, and the thermosettting of
gluten. For the latter we will apply our theory of effective solvents for
biopolymer melting (van der Sman, 2016), due to the high content of
succrose in biscuits. This multiscale model will be the vehicle to further
pursue reformulation strategies, regarding both sugar and sodium levels.

CRediT authorship contribution statement

R.G.M. van der Sman: Writing – original draft, As the sole author, I
have written the paper, and developed the model and performed the
simulations.

Declaration of competing interest

The author declares there is no conflict of interest.

References

Achard, C., Dussap, C.G., Gros, J.B., 1994. Prediction of pH in complex aqueous mixtures
using a group-contribution method. AIChE J. 40 (7), 1210–1222.
Aissa, M.F.B., Bahloul, S., Monteau, J.Y., Le-Bail, A., 2015. Effect of temperature on the
solubility of co2 in bread dough. Int. J. Food Prop. 18 (5), 1097–1109.
Amon, M., Denson, C.D., 1984. A study of the dynamics of foam growth: analysis of the
growth of closely spaced spherical bubbles. Polym. Eng. Sci. 24 (13), 1026–1034.
Amrein, T.M., Andres, L., Manzano, G.G.G., Amadio, R., 2006. Investigations on the
formation of ammonium hydrogencarbonate on the formation of acrylamide in
model systems. J. Agric. Food Chem. 54 (26), 10253–10261.
Batenburg, M. and R van der Velden. Saltiness enhancement by savory aroma compounds.
J. Food Sci., 76(5), 2011.
Bellido, G.G., 2007. Creation, Growth and Stability of Aerated Structures in Chemically
Leavened Wheat Flour Dough Systems and Relationships to Mechanical Properties
Assessed with Low-Intensity Ultrasound. Ph.D. thesis. Univ. Manitoba.
Bellido, G.G., Scanlon, M.G., Sapirstein, H.D., Page, J.H., 2008. Use of a pressuremeter to
measure the kinetics of carbon dioxide evolution in chemically leavened wheat flour
dough. J. Agric. Food Chem. 56 (21), 9855–9861.
Bieling, V., Rumpf, B., Strepp, F., Maurer, G., 1989. An evolutionary optimization method
for modeling the solubility of ammonia and carbon dioxide in aqueous solutions.
Fluid Phase Equil. 53, 251–259.
Busch, J.L.H.C., Fys, Yong, Goh, S.M., 2013. Sodium reduction: Optimizing product
composition and structure towards increasing saltiness perception. Trends Food Sci.
Tech. 29 (1), 21–34.
Charun, E., Abecasis, J., Contantine, A.S., Rouland, T.M., Vergnes, B., Morel, M.H.,
2000. Effects of temperature and mechanical input on semisweet biscuit (cookie)
quality and dough characteristics. Cereal Chem. 77 (3), 265–271.
Chiostella, E., Campbell, G.M., 2003. Proving of bread dough: modelling the evolution of
the bubble size distribution. Food Bioprod. Process. 81 (3), 194–206.
Chirife, J., Resnik, S.L., 1984. Unsaturated solutions of sodium chloride as reference sources of water activity at various temperatures. J. Food Sci. 49 (6), 1486–1486.

Edwards, T.J., Maurer, G., Newman, J., Praunzit, J.M., 1978. Vapor-liquid equilibria in multicomponent aqueous solutions of volatile weak electrolytes. AIChE J. 24 (6), 966–976. 

Fan, J., Mitchell, J.R., Blanshard, J.M.V., 1999. A model for the oven rise of dough during baking. J. Food Eng. 41 (2), 69–77.

Fustier, P., Castaigne, F., Turgeon, S.L., Biliaderis, C.G., 2009. Impact of commercial soft wheat flour streams on dough rheology and quality attributes of cookies. J. Food Eng. 90 (2), 228–237.

Halstensen, M., Jilvero, H., Jinadasa, W.N., Jens, K.J., 2017. Equilibrium measurements of the nh3-co2-h2o system: Speciation based on Raman spectroscopy and multivariate modeling. J. Chem. 2017.

He, Corey, 2003. Stewart and beyond: new models of acid-base balance. Kidney Int. 64 (3), 777–787.

Ismar, T., Rakha, A., Sohail, M., Rashid, S., Shehzad, A., 2016. Salt reduction in baked products: strategies and constraints. Trends Food Sci. Technol. 51, 98–105.

Kawuzishi, K., Prausnitz, J.M., 1987. Correlation of vapor-liquid equilibria for the system ammonia-carbon dioxide-water. Ind. Eng. Chem. Res. 26 (7), 1482–1485.

Kim, Y.P., Seinfeld, J.H., Saxena, P., 1993. Atmospheric gas-aerosol equilibrium i. thermodynamic model. Aerosol. Sci. Technol. 19 (2), 157–181.

Kweon, M., Slade, L., Levine, H., Martin, R., Souza, E., 2009. Exploration of sugar functionality in sugar-snap and wire-cut cookie baking: Implications for potential sucrose replacement or reduction. Cereal Chem. 86 (4), 425–433.

Kweon, Meera, Slade, Louise, Levine, Harry, Gannon, Diane, 2014. Cookie-versus cracker-functionality requirements explored by src and alveography. Crit. Rev. Food Sci. Nutr. 54 (1), 115–138.

Meng, Z., Seinfeld, J.H., Saxena, P., Kim, Y.P., 1995. Atmospheric gas-aerosol equilibrium: iv. thermodynamics of carbonates. Aerosol. Sci. Technol. 23 (2), 131–154.

Narsimhan, G., 2014. A mechanistic model for baking of leavened aerated food. J. Food Eng. 143, 80–89.

Parrey, B., Talhaoui, F., Kerkhofs, G., Irijs, K., Goesaert, H., Wevers, M., Delcour, J.A., 2009. The role of sugar and fat in sugar-snap cookies: Structural and textural properties. J. Food Eng. 90 (3), 400–408.

Pitzer, K.S., 1973. Thermodynamics of electrolytes. I. theoretical basis and general equations. J. Phys. Chem. 77 (2), 268–277.

Robinson, R.A., Stokes, R.H., 2002. Electrolyte Solutions. Courier Corporation.

Roy, Rabindra N., James, J Gibbons, Williams, Rick, Godwin, Lehman, Baker, Gigi, Simonson, John M., Pitzer, Kenneth S., 1984. The thermodynamics of aqueous carbonate solutions ii. mixtures of potassium carbonate, bicarbonate, and chloride. J. Chem. Therm. 16 (4), 303–315.

Shah, P., Campbell, G.M., McKee, S.L., Rielley, C.D., 1998. Proving of bread dough: modelling the growth of individual bubbles. Food Bioprod. Process. 76 (2), 73–79.

Thurmond, V., Millero, F.J., 1982. Ionization of carbonic acid in sodium chloride solutions at 25 c. J. Solut. Chem. 11 (7), 447–456.

van der Sman, R.G.M., 2012. Thermodynamics of meat proteins. Food Hydrocolloids 27 (2), 529–535.

van der Sman, R.G.M., 2016. Sugar and polysol solutions as effective solvent for biopolymers. Food Hydrocolloids 56, 144–149.

van der Sman, R.G.M., 2017. Predicting the solubility of mixtures of sugars and their replacers using the floory–huggins theory. Food & function 8 (1), 360–371.

van der Sman, R.G.M., Broone, J., 2014. Multiscale analysis of structure development in expanded starch snacks. J. Phys. Condens. Matter 26 (46), 464103.

van der Sman, R.G.M., Meinders, M.B.J., 2011. Prediction of the state diagram of starch water mixtures using the floory–huggins free volume theory. Soft Matter 7 (2), 429–442.

van der Sman, R.G.M., Renzetti, S., 2019. Understanding functionality of sucrose in biscuit for reformulation purposes. Crit. Rev. Food Sci. Nutr. 59 (14), 2225–2239.

Velezmoro, C.E., Metrelles, A.J.A., 1998. Water activity in solutions containing organic acids. Dry. Technol. 16 (9–10), 1789–1805.

Wang, X., Conway, W., Fernandes, D., Lawrance, G., Burns, R., Puxty, G., Maeder, M., 2011. Kinetics of the reversible reaction of co2 (aq) with ammonia in aqueous solution. J. Phys. Chem. 115 (24), 6405–6412.

Wen, N., Brooker, M.H., 1995. Ammonium carbonate, ammonium bicarbonate, and ammonium carbonate equilibria: a Raman study. J. Phys. Condens. Matter 7 (27), 3765–3776.

Wen, N., Brooker, M.H., 1995. Ammonium carbonate, ammonium bicarbonate, and ammonium carbonate equilibria: a Raman study. J. Phys. Condens. Matter 7 (27), 3765–3776.

Zhao, Q., Wang, S., Qin, F., Chen, C., 2011. Composition analysis of co2- nh3- h2o system based on Raman spectra. Ind. Eng. Chem. Res. 50 (9), 5316–5325.

Zhao, B., Su, Y., Tao, W., Li, L., Peng, Y., 2012. Post-combustion co2 capture by aqueous ammonia: a state-of-the-art review. International Journal of Greenhouse Gas Control 9, 355–371.