Modeling Segregation of Solute Material during Drying of Liquid Foods

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Liquid foods consist of many solutes that have very different diffusivities. The binary diffusion coefficient in a dilute aqueous solution can differ up to two orders of magnitude for a low and a high molecular weight component, respectively. During drying the concentration gradients originating from the water transport will induce mass transport of solutes in opposite direction. The transport velocities of the different solutes depend on the concentration gradients and on the values of their diffusion coefficients. Given the large difference in these coefficients, segregation of components can be expected during drying. Meerdink et al. (1988) and Meerdink (1993) have shown that segregation occurs during drying of an aqueous solution of sucrose and sodium caseinate in an agar gel matrix. In these drying experiments, a number of slabs were dried simultaneously and cut in thin slices after different drying times. Analysis of the slices gave the concentration profiles of water, sucrose, and sodium caseinate. All experiments showed that during drying the sodium caseinate/sucrose weight ratio increased near the surface. In the center of the slab the ratio decreased. In experiments with an initial dry solids content of 15.9% on total basis, the sodium caseinate/sucrose ratio in the surface layer increased with time from 0.50 to 0.60, while the ratio in the bottom layer decreased to 0.43. These results agree with our theoretical considerations. The concentration at the surface of the component with the smallest diffusivity (sodium caseinate) is relatively high as compared with the other component (sucrose). For the center the opposite reasoning is valid.

Segregation can in principle influence the product quality, in particular the surface properties. Since liquid foods are commonly dried in spray dryers, segregation can influence powder characteristics in this way.

In the literature on drying, information on segregation during drying of liquid foods is absent, with one important exception: the retention of volatile (trace) components during drying (Chandrasekaran and King, 1972; Kerkhof, 1975; Riede and Schlünder, 1988).

The purposes of our work are to develop a drying model that describes the segregation, and to evaluate the extent of segregation during spray drying using the developed model. The drying model is developed for the ternary food model system used by Meerdink et al. (1988) and Meerdink (1993). The influence of the gel matrix is neglected. The model takes into account the volume shrinkage during drying and the concentration dependence of the diffusion coefficients. The diffusion coefficients are estimated from the results of the drying experiments.

Ternary Drying Model

Model formulation

The ternary drying model is based on the Maxwell-Stefan (MS) equations for multicomponent diffusional mass transfer (Krishna and Taylor, 1986). In a ternary mixture there are two independent MS equations, containing three independent MS multicomponent diffusion coefficients, in this case, D_{ws}^{MS}, D_{wp}^{MS} and D_{sp}^{MS}. An important model assumption is that the volume decrease of the drying system equals the volume of the evaporated water during drying. Consequently the volume flux of water equals the opposite volume flux of the solutes, and hence the volume average velocity is zero. Combining the MS equations with the continuity equations for water and sucrose in a slab, two coupled partial differential equations are obtained describing the unsteady-state transport of water and sucrose:

$$\frac{\partial C_w}{\partial t}=\frac{\partial}{\partial r}E_{ww}\frac{\partial C_w}{\partial r}+\frac{\partial}{\partial r}E_{ws}\frac{\partial C_s}{\partial r} \tag{1}$$

$$\frac{\partial C_s}{\partial t}=\frac{\partial}{\partial r}E_{sw}\frac{\partial C_w}{\partial r}+\frac{\partial}{\partial r}E_{ss}\frac{\partial C_s}{\partial r} \tag{2}$$

where C is the molar concentration, t is the drying time, r is the space coordinate, E is an element of the matrix of transformed diffusion coefficients $[E]$, and the subscripts w and s denote water and sucrose, respectively. The elements of the

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matrix $[E]$ are functions of the three MS diffusion coefficients and the thermodynamic activity coefficients (Krishna and Taylor, 1986).

The initial and boundary equations for these partial differential equations are

$$t=0 \quad 0 \le r \le R_{e,0} \quad C_w = C_{w,0} \quad C_s = C_{s,0} \tag{3}$$

$$t>0 \quad r=0 \quad \frac{dC_w}{dr}=0 \quad \frac{dC_s}{dr}=0$$

$$t>0 \quad r=R_{e,t} \tag{4}$$

$$(E_{ww}E_{ss}-E_{ws}E_{sw})\frac{dC_w}{dr} = -k_g(\rho_{w,i}-\rho_{w,b})[E_{ws}C_sV_w + E_{ss}(1-C_wV_w)] \tag{5a}$$

$$(E_{ww}E_{ss}-E_{ws}E_{sw})\frac{dC_s}{dr} = k_g(\rho_{w,i}-\rho_{w,b})[E_{ww}C_sV_w + E_{sw}(1-C_wV_w)] \tag{5b}$$

where R_e is the external radius, k_g is the external mass-transfer coefficient, ρ_w is the gas-phase water concentration, V_w is the partial molar volume of water, and the subscripts 0, i, and b denote initial, interface and bulk phase, respectively. The boundary Eqs. 5a and 5b are derived from flux equations describing the transport of water and sucrose with respect to the receding surface.

The two partial differential equations are solved numerically. They are transformed using a sodium caseinate centered space coordinate, because of the receding surface. This transformation avoids the movement of the external surface through the space coordinate grid.

The concentration dependence of the diffusion coefficients

Experimental data, and measuring and estimation methods concerning MS multicomponent diffusion coefficients in concentrated aqueous solutions are lacking (Wesselingh and Krishna, 1990). Therefore, the MS diffusion coefficients are estimated from the results of the drying experiments. It is expected that the MS diffusion coefficients strongly decrease at low water concentrations, as found for MS diffusion coefficients in concentrated binary aqueous solutions. The water concentration dependence of each MS diffusion coefficient is described by the next equation:

$$D_{nm}^{\mathrm{MS}} = D_{nm,\infty}^{\mathrm{MS}}(C_wV_w)^{a_{nm}} \tag{6}$$

where a is the exponent describing the concentration dependence, and the subscripts n, m, and ∞ denote components i and j, and the value of the MS diffusion coefficient at infinite dilute aqueous solution, respectively.

The thermodynamic activity coefficients are considered to be independent of the water concentration. This assumption is certainly not valid at low water concentrations. However, there is a lack of thermodynamic models and data that describe the change of the thermodynamic activity coefficients as a function of the water concentration. As a consequence, the estimated concentration dependencies of the MS diffusion coefficients do not only reflect the effect of the decreasing water concentration on the mobility of water and solutes, but also reflect the influence of the thermodynamic nonidealities on the driving force for diffusion, in particular at low water concentrations.

The parameters $D_{nm,\infty}^{\mathrm{MS}}$ and a_{nm} are estimated using the Downhill simplex method developed by Nelder and Mead (Press et al., 1989). The sum of the relative errors between measured and calculated ratio and water concentration profiles is taken as the optimization criterion. The results of drying experiments with different initial solids contents are used. The estimation procedure reveals that there exists a strong correlation between the exponents a_{ws} and a_{wp}, leading even to negative values of a_{ws} or a_{wp}. The literature (Menting, 1970; Luyben et al., 1980; Furuta et al., 1984) shows that a_{ws} and a_{wp} should be positive and by approximation equal. Therefore, it is assumed that the water concentration dependencies of D_{ws}^{MS} and D_{wp}^{MS} are identical.

Results and Discussion

Simulation of the experimental drying data

Figure 1 shows drying model simulations compared with experimental data (Meerdink et al., 1988). The model describes the experimental water concentration and ratio profiles reasonably well. The average relative discrepancy between simulation results and experimental water concentration and ratio profiles used in the optimization is 16%. In particular, the trend in the shape of the calculated profiles agrees well with the experimental profiles. The calculated surface ratios show a strong increase in the first and second part of the drying process (penetration period), whereas in the third part of the drying process (regular regime period) the value remains more or less constant. This phenomenon is caused by the already very low surface water concentration at the end of the second drying period. At this water concentration, the mobility of sucrose with respect to sodium caseinate has become very low. The degree of segregation then attains a "fixed" value. The final value of the calculated surface ratio (1.51) is much higher than the initial ratio (0.50), which indicates that segregation is particularly important at the surface. The physical-chemical surface properties can thus be very different from the properties as determined from the average composition.

Estimated MS diffusion coefficients

One set of estimated equations for the MS diffusion coefficients is given in Table 1. The equations in Table 1 should be interpreted with care. A different set of values for the parameters $D_{nm,\infty}^{\mathrm{MS}}$ and a_{nm} can give equally appropriate descriptions of the experimental drying data, with almost the same value for the optimization criterion. However, in all cases the estimated relations for the water concentration dependence of D_{ws}^{MS} and D_{wp}^{MS} differ from the estimated relation for D_{sp}^{MS} by at least 1 to 2 orders of magnitude.

The estimated behavior of D_{ws}^{MS} and D_{wp}^{MS} is in agreement with the general finding that the water diffusivity in foods decreases strongly at low moisture contents. The values of the estimated diffusion coefficients are in the same order of magnitude as are found in the literature for binary water diffusion coefficients in liquid foods (Menting, 1970; Luyben, et al., 1980; Furuta et al., 1984). The estimated water concentration dependence of D_{sp}^{MS} is more pronounced than for D_{ws}^{MS} or D_{wp}^{MS},

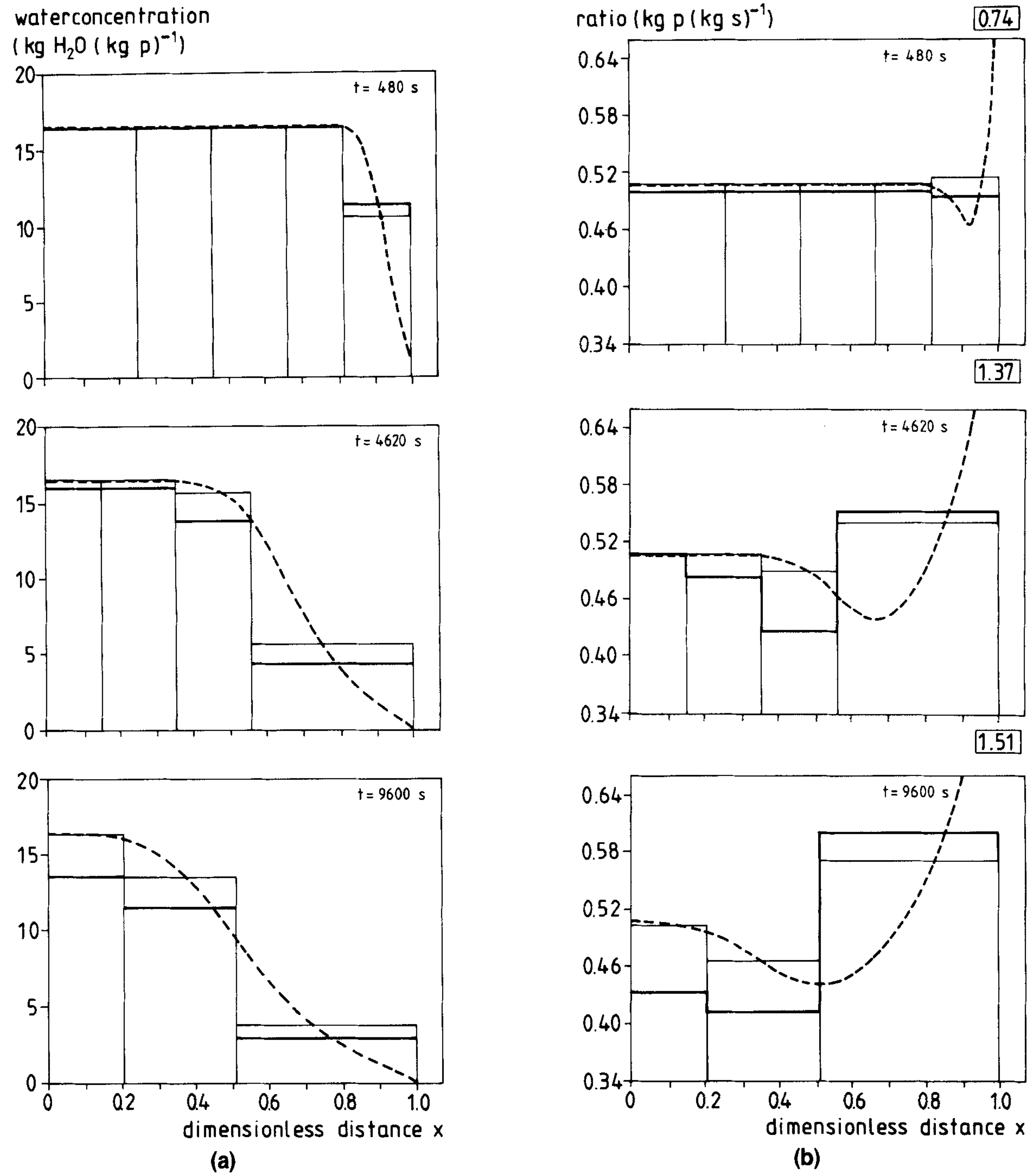


Figure 1. Experimental and simulated profiles at three different drying times.

(a) Water concentration profiles; (b) solute ratio profiles. □: Calculated solute ratio at surface. Initial water content 16 kg H_2O (kg·p)$^{-1}$; initial ratio 0.5 kg·p (kg·s)$^{-1}$; initial layer thickness 1 cm; and external mass-transfer coefficient 1.5 10^{-2} m·s^{-1}; ——: experimental data, average value in a slice is depicted; - -: model simulation, diffusion data Table 1; ——; averaged simulation results. The dimensionless distance X is defined as:

$$X=\int_0^r C_p dr \bigg/ \int_0^{R_e} C_p dr.$$

which is in agreement with the difference in molecular size of water and sucrose. As a result, the mutual mobility of sucrose and sodium caseinate is very low at low water concentrations. Similar results are found for the water concentration dependence of the diffusion coefficients of aroma components in carbohydrate solutions (Menting, 1970; Chandrasekaran and King, 1972; Furuta et al., 1984).

The very low values of $Đ_{sp}^{MS}$ at low moisture contents as compared to $Đ_{ws}^{MS}$ and $Đ_{wp}^{MS}$ indicate that the segregation cannot proceed on the time scale of the drying process at low moisture

Table 1 Estimated Maxwell-Stefan Diffusion Coefficients

$$D_{ws}^{MS} = 4.7 \times 10^{-10} (C_w V_w)^{1.6}\ \mathrm{m^2 \cdot s^{-1}}$$

$$D_{wp}^{MS} = 3.2 \times 10^{-10} (C_w V_w)^{1.6}\ \mathrm{m^2 \cdot s^{-1}}$$

$$D_{sp}^{MS} = 6.7 \times 10^{-12} (C_w V_w)^{3.2}\ \mathrm{m^2 \cdot s^{-1}}$$

concentrations. Consequently, the ratio between the dry solids components attains a fixed value at these moisture concentrations. In particular the surface ratio will attain a fixed value soon after the beginning of the drying process, given the existing low water concentrations, as shown in Figure 1.

Segregation during spray drying

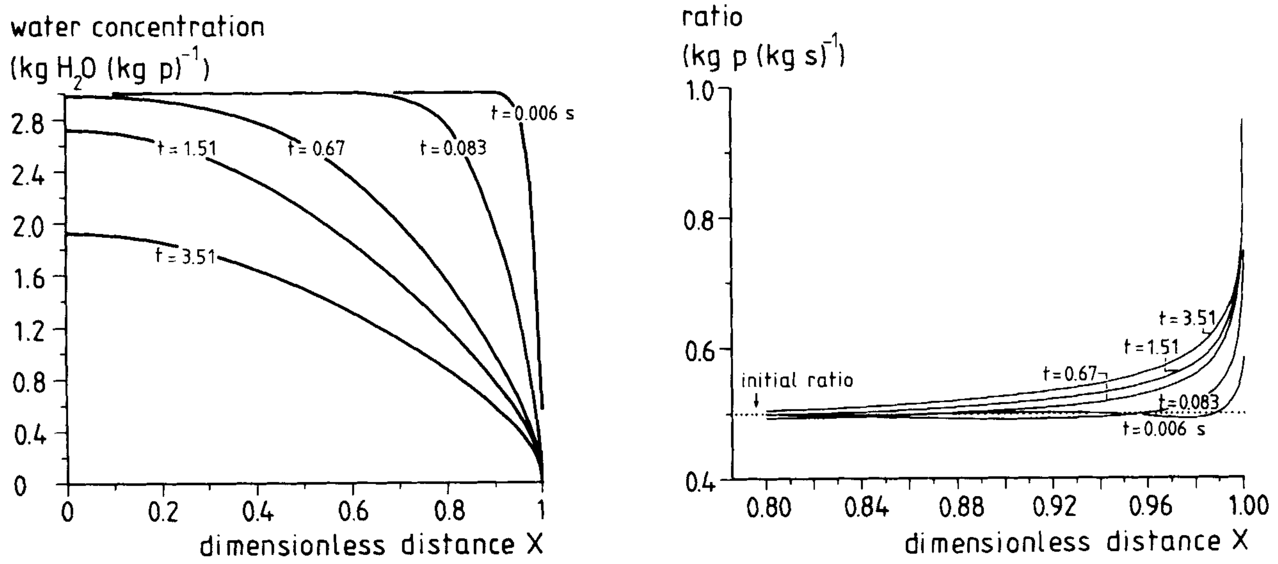
The results of a model simulation under "spray drying"-like conditions with the estimated MS diffusion coefficients are shown in Figure 2. The calculated water concentration profiles show similar behavior as found in spray drying kinetics calculations with drying models based on the unsteady diffusion equation for binary systems (Wijlhuizen et al., 1979). Very steep profiles at the onset of the drying process are followed by a flattening of the profiles. The surface water concentration decreases very rapidly from the initial value to the final moisture content, because internal mass transfer is the rate controlling mechanism. As one can see from the ratio profiles, segregation primarily takes place in the first stage of the drying process. After a drying time of about 3.5 s, the ratio profile is "fixed"; at that stage about 55% of the initial amount of water is evaporated.

The extent to which segregation occurs under spray drying conditions is less than found for the simulated drying experiments (see Figure 1). This difference is not caused by the different time scales, because the Fourier times are comparable, but instead by the difference in initial water content. More precisely, by the increased difference in diffusion coefficients due to the water concentration dependency of the MS diffusion coefficients. The mobility of sucrose (D_{sp}^{MS}) decreases much stronger with decreasing water content than the water mobility (D_{ws}^{MS} and D_{wp}^{MS}) itself. As a consequence, the characteristic time of the segregation process increases faster than the characteristic time of the drying process with decreasing initial water content, and the "overall" degree of segregation will therefore be limited at higher initial solid contents. Model simulations reveal that the calculated surface ratio decreases from 1.41 down to 0.68 when the initial water content decreases from 80% down to 30% on total basis, at an average final water content of 0.2 kg H_2O (kg·ds)$^{-1}$. The simulation results indicate that segregation does occur during spray drying, but the extent depends on the initial water content. The importance for the product quality will depend on the dry solids components involved and the applications aimed at, but effects are possible.

Conclusions

Simulations with a ternary drying model, based on the Stefan-Maxwell equations, resulted in a good agreement between experimental water concentration profiles as well as with experimental solute ratio profiles. Although different sets of relations for the Maxwell-Stefan diffusivities were found, the estimated differences between the water concentration dependencies of the diffusivities agreed with values reported in the literature. The calculated ratio at the surface increased from 0.50- to 1.51-kg sodium caseinate (kg sucrose)$^{-1}$ for an initial moisture of 15.9% on total basis.

Model simulations revealed that during spray drying segregation will occur in the model food, although to a lesser extent than found in the drying experiments. The calculated surface ratios of the dry solids components were decreasing at increasing initial dry solids contents. The extent of segregation can be controlled by applying different initial dry solids contents.



(a) (b)

Figure 2. Calculated profiles during spray drying.

(a) Water concentration profiles; (b) solute ratio profiles. Initial moisture content 3 kgH_2O(kg·p)$^{-1}$; initial ratio 0.5 kg·p (kg·s)$^{-1}$; initial layer thickness 50 μm; and external mass-transfer coefficient 1 m·s^{-1}. Diffusion data Table 1.

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Notation

a = fitting parameter
C = concentration, $\text{mol}\cdot\text{m}^{-3}$
D = diffusion coefficient, $\text{m}^2\cdot\text{s}^{-1}$
$[E]$ = matrix of transformed Maxwell-Stefan diffusion coefficients, $\text{m}^2\cdot\text{s}^{-1}$
ds = dry solids
k_g = external mass-transfer coefficient, $\text{m}\cdot\text{s}^{-1}$
p = sodium caseinate (protein)
R_e = external radius, m
r = space coordinate, m
s = sucrose
t = time, s
V = partial volume, $\text{m}^3\cdot\text{mol}^{-1}$
X = dimensionless distance

Greek letters

ρ = concentration gas phase, $\text{mol}\cdot\text{m}^{-3}$

Superscripts

MS = Maxwell-Stefan

Subscripts

0 = initial
b = bulk phase
i = interface
p = sodium caseinate (protein)
s = sucrose
t = time
w = water
∞ = at infinite dilute aqueous solution

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