A Diffusion Model with a Concentration-Dependent Diffusion Coefficient for Describing Water Movement in Legumes During Soaking

KENNETH H. HSU

ABSTRACT
A mathematical model based on Fick's diffusion equation with a concentration-dependent diffusion coefficient was proposed to describe the absorption of water by legumes. The equation was solved by using a numerical scheme. Parameter study was performed. The model is capable of predicting sigmoidal-shaped water uptake curves common to many legumes. Differences are discussed between the surface resistance boundary condition used in this study and the radiation boundary condition widely used for dehydration calculations. The validity of using the proposed model to describe the water uptake of legumes was verified by the good fit between the experimental and theoretical curves.

INTRODUCTION
PROCESSING OF CEREALS and legumes often requires that the seeds be hydrated first to facilitate the consecutive extraction or cooking. Thus penetration of water into these materials is of theoretical and practical interest to processing industries.

Mechanism of water penetration into seeds was the subject of many autoradiographic studies (Butcher and Stenvert, 1973; Jackson and Varrian-Marston, 1980; Moss, 1977; Stenvert and Kingswood, 1976, 1977). It had been demonstrated that diffusion in the solid endosperm is the main mechanism that controls the rate of absorption in seeds regardless of the mode of entry of the moisture. Quantitative analysis of water diffusion in seeds, under the absorption condition, was first performed by Becker (1959, 1960), utilizing a simplified solution for solids of arbitrary shape, which he derived from Fick's diffusion equation. The uptake of water in the initial period of tempering of wheat can be described by the solution he introduced, and the diffusivity in this period can be considered constant. Chung et al. (1961) and Fan et al. (1962), by analogy, extended the equation derived by Becker to represent the volume increase of wheat, corn and sorghum during steeping. With slight modification, Becker's equation also had been applied to describe the kinetics of hydration for paddy rice during soaking (Bandyopadhyay and Ghose, 1965) and parboiling (Bandyopadhyay and Roy, 1976). Bakshi and Singh (1980) modified Fick's diffusion equation for a spherical body to incorporate a reaction term for the prediction of water uptake during the parboiling of rice. In all these cases, a constant diffusion coefficient was used without introducing too great an error in their results.

Other work, however, had shown that the diffusivity of water in cereals and oil seeds often are dependent upon the moisture content of the seeds. Chittenden and Hustrulid (1966) reported that the mean diffusivity of shelled corn varied linearly with the initial moisture content; they concluded that the actual diffusivity should depend also on moisture content at any point within the kernel. Shakewich and Williams (1971) found that water diffusivity of rape seeds increased drastically with the time of immersion in water. Hsu (1981) demonstrated that, during the soaking of soybeans, the water diffusivity is strongly dependent upon the moisture content of the seeds and that the diffusion equation with constant diffusivity is inadequate in describing the water absorption curve. The applicability of diffusion equation with a constant diffusion coefficient to the sorption of soybeans also was questioned by others (Singh, 1972).

Quantitative analysis of water diffusion in cereals and legumes having concentration-dependent diffusion coefficient is scarce. Whitaker et al. (1969), using the technique of finite-difference, introduced a scheme for the solution of a nonlinear diffusion equation. They solved the equation for the case where the diffusion coefficient is a linear function of the concentration and tested the results over a model system under dehydration conditions with some success. The acceptability of this solution to the water uptake of cereals or legumes, however, was not tested.

It is, thus, the purpose of this study to theoretically develop a model for the prediction and analysis of water uptake in seeds where the diffusivity is concentration dependent and to verify this model experimentally.

THEORY
BY ASSUMING that (1) the seeds are spherical, (2) diffusion takes place only in the radial direction, and (3) the effect of volume change due to absorption is negligible, one can use the diffusion equation in spherical coordinates provided by Crank (1975):

$$\frac{\partial C}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 D \frac{\partial C}{\partial r} \right)$$

where $D$ is dependent only on concentration $C$.

Previous results (Hsu, 1981) on the absorption of water by soybeans had indicated that the diffusivity may vary exponentially with the moisture content of the seeds; thus, it could be taken that:

$$D = D_0 e^{kC}$$

We will assume that the moisture is evenly distributed in the seeds, initially, or

$$C = C_0 \text{ for all } r \text{, } t = 0$$

and the boundary conditions are:

$$\frac{\partial C}{\partial r} |_{r = 0} = 0 \text{ at } t = 0, \text{ } t > 0; \text{ and}$$

$$C = (1 - e^{-2t})C_1 + C_0 e^{-at} \text{ at } r = 1, \text{ } t > 0$$

where $C_1$ is the saturation concentration.

The first boundary condition represents the symmetry of the system, and the second boundary condition defines the concentration change on the surface of the seed to be a first order process with a rate constant $g$. Preliminary studies assuming instantaneous saturation at the surface upon the immersion of seeds in water (i.e., $C = C_1$ at $r = a$) had produced absorption curves that overpredict the amount of uptake in the initial stages of soaking of soybeans. Most legumes and oilseeds contain waxy materials on their seed coats, which act as barriers to moisture movement. Varriano-Marston and Jackson (1981) also have shown that most water enters black beans at the hilum and is transported to the periphery of the cotyledon. If this mode of water penetration were common to other legumes, the assumption of instant surface saturation might not be realistic. Eq. (5) describes a condition in which the surface concentration is allowed to increase from $C_0$ to $C_1$ over time. On writing this expression, we are assuming that the surface concentration

Author Hsu is affiliated with the Dept. of Food Technology, Iowa State Univ., Ames, IA 50011.
change can be rapid but not instantaneous. The rate at which this change is accomplished is directly proportional to the value of the parameter $\beta$, as is shown in Fig. 1. Similar boundary conditions were used successfully to describe diffusion of organic vapors in glassy polymers (Long and Richman, 1960).

By making the following substitutions:

$$
C^* = \frac{C - C_0}{C_1 - C_0}; \quad R = \frac{r}{a}
$$

$$
T = \frac{D_0 t}{a^2}; \quad D = \frac{D}{D_0}
$$

$$
D_0 = D_0 e^{k c C_0}; \quad k = \kappa (C_1 - C_0)
$$

(6)

Eq. (1) to (5) can be expressed in dimensionless forms as:

$$
\frac{\partial C^*}{\partial T} = \frac{\partial}{\partial R} \left( D \frac{\partial C^*}{\partial R} \right) + \frac{2}{R} \frac{\partial C^*}{\partial R};
$$

(7)

$$
D = e^{k C^*}
$$

(8)

$$
C^* = 0, \text{ for all } R, \text{ at } T = 0;
$$

(9)

$$
\frac{\partial C^*}{\partial R} = 0, \text{ at } R = 0; \text{ and}
$$

(10)

$$
C^* = 1 - e^{-BT}, \text{ at } R = 1;
$$

(11)

respectively. On introducing

$$
S = \int_{0}^{C^*} D dC^* = \frac{1}{k} (D - 1) = \frac{1}{k} (e^{k C^*} - 1)
$$

(12)

Eq. (7) is further simplified to

$$
\frac{\partial S}{\partial T} = \frac{\partial^2 S}{\partial R^2} + \frac{2 \partial S}{\partial R} R
$$

(13)

with initial and boundary conditions:

$$
S = 0, \text{ for all } R, \text{ at } T = 0
$$

(14)

$$
\frac{\partial S}{\partial R} = 0, \text{ at } R = 0; \text{ and}
$$

(15)

$$
S = \frac{1}{e^{k (1 - e^{-BT}) - 1}}, \text{ at } R = 1
$$

(16)

Eq. (13) is nonlinear and can best be solved numerically.

**SOLUTION**

**NUMERICAL METHODS** for the solution of nonlinear diffusion equations along with some calculated results were discussed by Crank (1975). In this study, a finite-difference method will be employed to solve the concentration-dependent form of the diffusion equation. One can visualize the sphere as being made up of $n$ spherical shells with equal thickness, SR. The concentrations at the interfaces of these shells will be designated as $S_i$ ($i = 1, \ldots, n+1$), with $S_1$ at $R = 0$ and $S_{n+1}$ at $R = 1$. Thus,

$$
\delta R = \frac{1}{n} \text{ and }
$$

$$
R_i = (i - 1) \delta R, \quad i = 1, \ldots, n+1
$$

Discretization of the diffusion equation can be achieved by making the following approximations for the first- and second-order derivatives (Crank, 1975).

$$
\frac{\partial S}{\partial R} \approx \frac{S_{i+1} - S_i}{\delta R}
$$

(17)

$$
\frac{\partial^2 S}{\partial R^2} \approx \frac{S_{i+1} - 2S_i + S_{i-1}}{\delta R^2}
$$

(18)

with these substitutions, as well as that of Eq. (12), Eq. (13) becomes

$$
\frac{dS_i}{dT} = (kS_i + 1) \left[ \frac{S_{i+1} - 2S_i + S_{i-1}}{\delta R^2} + \frac{2}{(i - 1)\delta R} \frac{S_{i+1} - S_i}{\delta R} \right]
$$

(19)

with the initial and boundary conditions:

$$
S_i = 0, \text{ for all } R, \text{ at } T = 0, i = 1, \ldots, n+1;
$$

(20)

$$
S_1 = S_2, \text{ @ } R = 0; \text{ and}
$$

(21)

$$
S_{n+1} = \frac{e^{k (1 - e^{-BT}) - 1}}{k}, \text{ @ } R = 1
$$

(22)

Eq. (19) is descriptive for any $i$th position except the two extremes; i.e., $R = 0$, and $R = 1$. At the center of the sphere, the symmetry of the system required that the two terms in the square brackets be zero; thus,

$$
\frac{dS_1}{dT} = 0
$$

(23)

At the surface, $dS_i/dT$ can be obtained simply by differentiating Eq. (23) with respect to $T$.

$$
\frac{dS_{n+1}}{dT} = Be^{k(1 - e^{-BT}) - BT}
$$

(24)

There is now a set of $(n+1)$ ordinary differential equations, as the result of discretization, which need to be solved simultaneously. The widely available software package GEAR (Hindmarsh, 1974) can be used for such calculations.

Actual concentration at a given position, $C_i$, can be determined from the calculated $S_i$ according to Eq. (12). This concentration, however, is difficult to measure in the laboratory. An experimentally more verifiable quantity (i.e., fraction of total absorption, $M_i/M_0$) will be used as a measure of the extent of diffusion. This quantity, $M_i/M_0$, is defined as:

$$
M_i = \int_0^R C^* 4\pi R^2 dR
$$

$$
M_0 = \int_0^R 4\pi R^2 dR
$$

(25)

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and it is evaluated by the application of Simpson’s rule:

\[ \frac{M_t}{M_0} = \left( \frac{6R}{m} \right)^3 \left( \frac{\sum_{i=1}^{m} C_{2i}^m (2i-1)^2 + 2C_{2i-1}^m (2i-1)^2 + C_{2m+1}^m (2m)^2}{1} \right) \]

where \( m = n/2 = 10 \)

(26)

**MATERIALS & METHODS**

**Beans**

Soybeans used were of Amsoy 71 cultivar produced as certified seeds from the 1974 crop. Faba beans were from Kuwait; they were screened first to obtain a relatively uniform size. The average diameter of each bean was determined as the arithmetic mean of the longest and shortest dimensions. For soybean, the average diameter was determined to be 0.714 cm; and for faba bean, it was 1.07 cm.

**Water absorption**

Ten grams of beans were placed in a water-proof plastic sample pouch and left to equilibrate in a temperature-controlled water bath to the test temperature. Beans were then transferred to a strainer and immersed into the water. After a preset time period, they were removed from water, superficially dried with facial tissues, and weighed. The weight gain was calculated as the difference between the measured weight at a given time and the original weight. Solids lost during soaking were ignored in this study because (1) the soaking time was relatively short, and (2) the amount of water absorbed was much greater than the amount of solid leached. Fractional absorption, \( M_t/M_0 \), was determined as:

\[ \frac{\text{weight gain after time } t}{\text{total weight gain}} \]

**RESULTS & DISCUSSION**

CALCULATIONS were performed by using the following values for constants: \( k = 1.0 \) and \( B = 286.2 \); time increment of \( 1 \times 10^{-4} \) and spacial mesh of \( 20 (n = 20) \) were used also. The concentration profiles are shown in Fig. 2 with the dimensionless time, \( T \), as the parameter. With the given constants, the concentration at the surface was shown to increase as time increased and came within 1% of saturation concentration at \( T = 0.02 \). Concentration at the center did not reach any significant level until time passed \( T = 0.03 \), that means a core should be evident up to this instant. As time progressed, the center concentration continued to increase, and the concentration gradient should continually decrease.

The effects of parameters \( D_0, k, \) and \( \beta \) on the shape of the absorption curve are depicted in Fig. 3, 4, and 5, respectively, for the case in which the initial concentration is zero \( (C_0 = 0) \). The saturation concentration and the radius used for this parametric study are 1.00 g/g solid and 0.535 cm, respectively.

**Fig. 2**—Concentration profiles during the absorption of water. Numbers on curves are values of dimensionless time, \( T \).

**Fig. 3**—Effect of parameters \( D_0 \) on the water absorption rate, at constant \( k \) and \( \beta \) values. Numbers on curve are values of \( D_0 \).

**Fig. 4**—Effect of parameter \( k \) on the water absorption rate, at constant \( D_0 \) and \( \beta \) values. Numbers on curves are values of \( k \).

**Fig. 5**—Effect of parameter \( \beta \) on the water absorption rate, at constant \( D_0 \) and \( k \) values. Numbers on curves are values of \( \beta \).
Since the diffusion coefficient is dependent both on the parameters $D_0$ and $\kappa$ as described in Eq. (2), any increase in their values will bring about an increase in the rate of uptake and, hence, a reduction of time required in reaching the maximum absorption. This effect is well demonstrated by the shift of the absorption curves to the left in Fig. 3 and 4. The effect of the parameter $\kappa$ on the absorption curve is in addition to that due to the parameter $D_0$. At $\kappa = 0$, the system reduces to one of constant diffusivity, and rate of absorption is determined solely by the parameter $D_0$.

However, as $\kappa$ takes on a positive value, the diffusion coefficient increases from its original $D_0$ value exponentially as absorption progresses, achieving high rates of uptake even into regions of low concentration driving force. This extended high uptake rate increases the steepness of the absorption curve. It could be expected that as the value of $\kappa$ increases the steepness of the absorption curve will increase accordingly, as is shown in Fig. 4.

The effect of parameter $\beta$ on the absorption curve is shown in Fig. 5. At high values, surface concentration approaches saturation very quickly (Fig. 1), and the absorption curve should approach that for the case of instant surface saturation. This is verified by Fig. 5; at $\beta = 100$, the absorption curve actually overlapped that for instant surface saturation. As value of $\beta$ decreases, the delay of saturation at the surface further restricts the movement of water into the beans, which is reflected by the reduction of uptake of water in the initial stage of soaking. However, as time progresses, the surface becomes increasingly saturated, and the diffusion inside of the solid again becomes the only resistance to absorption. This means that the effect of $\beta$ on the absorption curve should be more pronounced at the initial stage rather than at the later stages of absorption.

As a result, inflection points will appear on the absorption curves, particularly at low $\beta$ values (Fig. 5), and the curves will become sigmoidal.

The boundary condition (Equation 11) used in this study differs from the radiation boundary condition (i.e., $\text{Bi} = \frac{\text{C}_0}{\text{C}_s}$), widely used under drying conditions, in that the surface concentration is strictly a function of time and not dependent upon the concentration gradient at the surface. Figure 6 shows the change of surface concentration with time for the two cases in discussion. Initially, the surface concentrations are increasing at relatively the same rate. As more water diffuses into the beans, the concentration gradient at the bean surface decreases, and the difference in the rate of surface concentration change becomes evident. It becomes increasingly more difficult for the gradient-dependent surface concentration to attend saturation as diffusion progresses. Fig. 7 shows the resultant absorption curves for the two cases in which the surface conditions are as presented in Fig. 6. After one hour of soaking, the water uptake predicted by using Eq. (11) as a boundary condition is higher than that predicted by employing the radiation boundary condition. Also, the absorption curve simulated by using the radiation boundary condition does not show any point of inflection, which has been observed in the water absorption curve of various legumes. At very high values of either $\beta$ or $\text{Bi}$, the absorption curves approach that for instant surface saturation, as can be expected.

The proposed model could be verified by comparing the actual and predicted absorption curves. The diffusion model was programmed in a computer to simulate water uptake of legumes. It is obvious that, to simulate water uptake, the surface concentration changes were determined by the radiation boundary condition.

![Fig. 6—Changes in surface concentration with time, as specified by the radiation boundary condition and Eq. (11).](image)

![Fig. 7—Theoretical absorption curve simulated by using the boundary conditions as specified in Fig. 6.](image)

<table>
<thead>
<tr>
<th>Table 1—Values of the diffusion model parameters for various legumes</th>
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<tr>
<td>soybean</td>
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<td>faba bean</td>
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<td>Calif. small white bean$^c$</td>
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$^a$ C can be expressed as g/g solid since volume change was assumed negligible.

$^b$ Error sum of squares; 10 observations for each calculation.

$^c$ Data taken from Fig. 1 of Kpn (1979).

$^d$ These values represented $D_0$ and $\kappa$, respectively. Because the initial moisture content for the Calif. small white bean was not provided, true values for $D_0$ and $\kappa$ could not be calculated.

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absorption, some estimates of the parameters \( k \), \( D_0 \) and \( \beta \) are needed. The best estimates of these parameters could be obtained by employing a sequential pattern search method to locate a set of parameters that would provide a minimal error sum of squares between the experimental and theoretical curves. In this study, the simplex search method (Fan et al., 1969; Spendley et al., 1962) was utilized. The values of parameters determined by the procedure were summarized in Table 1 for soya, faba, and California small white beans. The theoretical and actual absorption curves for these legumes were depicted in Fig. 8 for comparison. It could be seen that the theoretical curves fitted the experimental ones very well, indicating the accuracy with which the proposed diffusion model could predict the water uptake of legumes. This observation was supported by the low error sum of squares as shown in Table 1.

Water can penetrate more readily through the hull of soybean than it can that of faba- or California small white bean. This slow surface penetration of faba- and California small white beans by water, as indicated by their sigmoidal absorption curves, was accurately reflected in low \( \beta \) values for these legumes. Food scientists who work with legume processing have long realized that beans with high moisture content hydrate more rapidly than those with low moisture (Smith and Nash, 1961; Crean and Haisman, 1963). Results of this investigation substantiated those reported observations. According to Eq. (2), water diffusivity, and hence rate of water uptake, increases with the water content of the bean if the parameter \( \kappa \) is positive. Table 1 shows that values of \( \kappa \) for all beans studied were indeed positive. The results also indicated that the diffusion coefficient of California small white bean was more dependent on the moisture content than either that of soya- or faba bean.

CONCLUSION

1. Concentration dependence of the diffusion coefficient of some legumes can be adequately expressed in exponential forms.
2. The boundary conditions to the diffusion equation introduced in this study can better describe the surface concentration changes under the absorption condition.
3. The proposed model has been demonstrated to be accurate in describing the water absorption of various legumes.

REFERENCES


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