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Determining concentration-dependent diffusivity in food materials

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1. SYNOPSIS

Methods for determining concentration (water concentration or moisture content)-dependent diffusivity in food materials from the drying rate are briefly reviewed. A simple method was developed on the basis of the power-law diffusion model. The method was first tested on the drying rate generated from the numerical solution of the diffusion equation with a known form of moisture content dependent diffusivity. Then, the drying rates for various sugar solutions obtained experimentally were analyzed on the basis of the present method to determine the moisture content-dependent diffusivities.

NOTATION

D	diffusion coefficient	m^2/s
D_a	apparent diffusion coefficient	$\text{kg}^2/(\text{m}^4\text{s})$
d_s	density of pure solid	kg/m^3
E	$= 1 - \bar{u}/u_0$, efficiency	-
F	$= dE/d\tau$, dimensionless desorption rate	-
F'	$= -(d_s R_s)^2 (d\bar{u}/dt)$, desorption rate	$\text{kg}^2/(\text{m}^4\text{s})$
r	space coordinate	m
R	diffusional distance from $r=0$ to the surface	m
R_s	slab thickness in the absence of water	m
Sh	Sherwood number	-
t	time	s
u	water (moisture) content	$\text{kg-water}/\text{kg-dry solid}$
W	$= u/(1+u)$, water concentration (mass fraction)	$\text{kg-water}/\text{kg-total}$
z	$= \int_0^r \rho_s dr$, space coordinate in the shrinking system	kg/m^2
Z	$= \int_0^R \rho_s dr$	kg/m^2
ρ_s	mass concentration	$\text{kg-solid}/\text{m}^3$
τ	$= t(D_0 \rho_{s0}^2)/(d_s R_s)^2$, dimensionless time in the shrinking system	-

subscript 0 = value at $t = 0$, subscript a = apparent value. overbar = average value

2. INTRODUCTION

Drying is a very important unit operation in the food and pharmaceutical industries, which is performed for volume reduction suitable for distribution and storage and for product stabilization. Carbohydrates and proteins are typical constituents of foods and are also good stabilizing additives for pharmaceuticals. When carbohydrate or protein solutions are dried by hot-air in convective drying, the drying rate is governed by the water diffusion inside the solution, which depends greatly on the water concentration (moisture content), u , and the temperature, T , i.e., $D(u, T)$. Although various methods have been proposed for measuring $D(u, T)$ [for example, Ref.(1)], most of them are not suitable for liquid foods such as carbohydrate solutions because of the strong concentration dependence and high viscosities of concentrated solutions. As shown later in this paper, the determination of

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D from the drying (desorption) rate is very attractive.

The purpose of this paper is to present a simple yet accurate method for determining $D(u)$ from the drying rate. Previous methods are briefly reviewed. A method based on the power-law diffusion model is developed. The desorption data from the numerical solution of the diffusion equation with a known $D(u)$ is analyzed by the method. The $D(u)$ determined by the present method was compared with the one that used for the numerical solution to check the accuracy and the validity. Then, the method was applied to the experimental drying curves of several carbohydrate and protein solutions to determine $D(u)$ values.

3. THEORY

The isothermal drying of (desorption of water from) aqueous carbohydrate or protein solutions can be represented by the following diffusion equation with solute-fixed coordinate which is introduced to avoid the moving boundary problem due to shrinkage of the material(2,3).

$$\frac{\partial u}{\partial \tau} = \frac{\partial}{\partial z} \left(D \rho_s^2 \frac{\partial u}{\partial z} \right) \quad (1)$$

$$\tau = 0, 0 \leq z \leq Z, u = u_0; \tau > 0, z = 0, D \rho_s^2 (\partial u / \partial z) = 0; \tau > 0, z = Z, u = 0 \quad (2a, b, c)$$

The boundary and initial conditions Eqs.(2a)-(2c) imply that the sample having a uniform water concentration initially is dried with desiccated air so that the surface concentration of the sample is equal to zero.

In most cases the solution to Eq.(1) with Eq.(2abc) can only be obtained numerically. However, the numerical solutions can be divided into two regions. At the beginning, only the moisture near the surface is desorbed so that the process can be regarded as a diffusion in a semi-infinite solid(1,2). The apparent diffusivity calculated from the initial desorption rate in this period ("penetration period (PP)") is very often assumed to be the integral average diffusivity in determining $D(u)$ in polymer-solvent systems(1). Because the initial desorption rates at various initial moisture contents are needed for determining $D(u)$, it is not suited for sugar solutions as the desorption experiment with a film shaped sample is not readily made.

After the PP, the so-called regular regime (RR) starts, provided that $D(u)$ is a monotonous decreasing function(2). There are some empirical approaches to obtain a single effective diffusivity from the RR data(1). However, for most aqueous carbohydrate and protein solutions these approaches are not valid as D decreases very considerably with decreasing u . The RR concept developed by Schoeber(2) is based on the observation that the desorption rate F in the RR is not dependent on the initial moisture content u_0 or the initial drying flux. Once the $F - \bar{u}$ curve in the RR is obtained, the corresponding $D - u$ can be derived according to the following procedure.

1. Obtain $d \ln F / d \ln(1 - E) = d \ln F' / d \ln \bar{u}$ as a function of u from the $F - \bar{u}$ curve
2. Determine Sh from $Sh = 4.935 + 2.456 \frac{d \ln F / d \ln(1-E) - 1}{d \ln F / d \ln(1-E) + 1}$
3. Calculate $\int_0^u D \rho_s^2 du = 2F' / Sh$
4. Determine D from $D = \rho_s^{-2} [d(2F' / Sh) / du]$

Schoeber's method does not require any *a priori* information on the type of the diffusion equation. Although this is a big advantage, because of three numerical differentiations

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involved it is sometimes difficult to determine $D(u)$ from scattered experimental data. There are also several different methods which use the RR curve (3,4). However, they also have similar disadvantages.

If the type of diffusivity $D(u)$ is assumed, more simplified procedures can be developed (5). Many $D(u)$ in the carbohydrate-water systems can be described by the power-law equation.

$$D\rho_s^2 = D_0\rho_{s0}^2(u/u_0)^a \quad (4)$$

A major drawback in this method is that assuming a constant a value sometimes fails to describe D over a wide range of u . It is therefore assumed that a is also a function of u , i.e., $a(u)$. From the $D_a - u$ curve, the $D(u)$ can be determined as follows.

$$a = \ln(D_{a1}/D_{a2})/\ln(u_1/u_2) ; D_a = (4/\pi^2)(F'/\bar{u}) \quad (5)(6)$$

$$D|_{u=u_1} = (a+1)\pi^2 D_{a1}/(2Sh\rho_{s1}^2) ; Sh = 4.935 + 2.456a/(a+2) \quad (7)(8)$$

where subscripts 1 and 2 indicate two arbitrary adjacent data points, (u_1, D_{a1}) and (u_2, D_{a2}) ($u_1 > u_2$).

4. RESULTS

This procedure was first tested on the desorption rates generated from the numerical solution of Eqs.(1) and (2abc) with the following fictitious diffusivity(6) (see Fig.1).

$$\ln D = \ln D_2 - (\ln D_2 - \ln D_1)/(1 + bu) \quad (9)$$

where $D_1 = 1.4 \times 10^{-15}$, $D_2 = 1.3 \times 10^{-9}$, $b = 6.74$

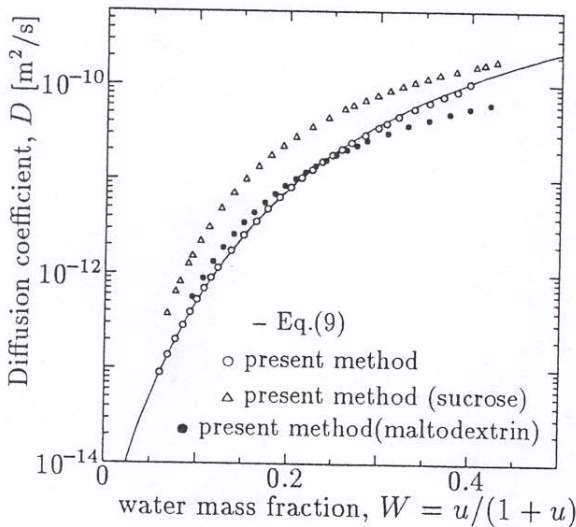


Fig.1 Diffusion coefficients determined from the isothermal drying rates by the present method (symbols). The experiments were made at 30 °C.

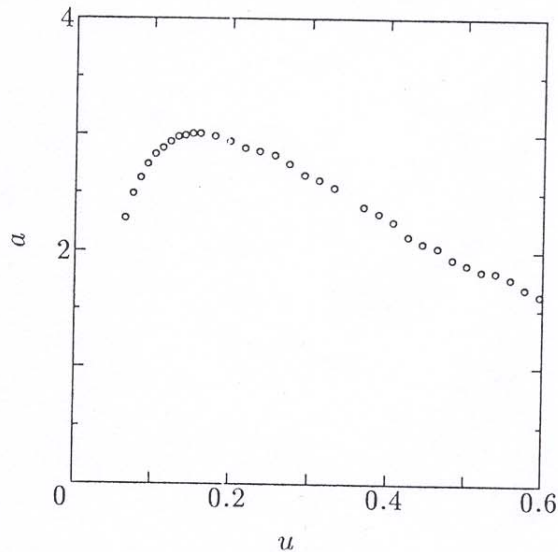


Fig.2 Values of a determined by the present method from the drying rates calculated numerically with Eq.(9)

The values of $D(u)$ determined from the above procedure using Eqs.(5)-(8) agreed closely with Eq.(9) as shown in Fig.1. The a values determined are shown in Fig.2 as a function of u . The D values determined from the experimental drying curves for two carbohydrates

by the present method are also shown in Fig.1.

5. DISCUSSION

There are several important assumptions which have to be carefully examined. The sample solution must be a single homogenous phase. Namely, there are no separate phases such as surface crusts or crystals. Many sugar solutions have a very high solubility in water. When such solutions are to be dried under high external mass-transfer rate conditions (rapid drying), they can form a stable supersaturated solution because of very high viscosities. Consequently, the surface of the sample becomes amorphous sugar without moisture soon after the start of the drying experiment. The sample solution must shrink uniformly in the $-r$ direction. Most sugar solutions gelled with agar-agar show such ideal shrinkage behavior.

The present method has not yet been tested on other food materials such as porous tissues (fruits, vegetables, *etc.*) and low-moisture, solid foods (pasta, *etc.*). In some cases the diffusivity may not be a smooth function like that shown in this paper. Some physical and/or (bio)chemical changes may occur during drying. These subjects will be examined in our future work.

Although the method presented in this paper is highly simplified compared with previous methods, numerical differentiation is still needed to obtain the drying rate. Simple equations which can fit the experimental $\bar{u} - t$ results from which the drying rate or similar information is directly calculated deserve to be investigated.

There are several methods for determining the diffusivity(1). A pulsed field NMR technique is a relatively new and sophisticated method by which the concentration-dependent diffusivity can be measured directly. However, this advanced technique is expensive, and is not available for most food engineers. On the other hand drying experiments which usually use an electronic balance are simple, inexpensive and easy to do. It is also possible to obtain the drying rate from the water vapor concentration of the drying medium determined from its thermal conductivity or by pressure sensor. Although the direct determination of the drying rate without the numerical differentiation involved in this method is attractive, it may be less accurate especially when the diffusion coefficient is extremely small (low water vapour concentrations due to low drying rates).

There are also questions as to the concentration-dependent diffusion mechanism. Interpretation of the water-concentration dependence of the diffusivity, for example, in terms of the glass transition, may also be an interesting subject.

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