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Chemical Engineering Journal 86 (2002) 179–184

Chemical Engineering Journal

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Drying of gelled sugar solutions—water diffusion behavior

Shuichi Yamamoto*, Takashi Saeki, Tomohide Inoshita

Department of Chemical Engineering, Yamaguchi University, Tokiwadai, Ube 755-8611, Japan

Abstract

As various types of gels or gelled solutions are important in food industries, mass transport phenomena in sugar solutions gelled with polysaccharides such as agar, pectin, sodium alginate and a protein (gelatin) were investigated. Water diffusivities from the isothermal regular regime drying curves, desorption isotherms, viscosities, and electroconductivities were determined for gelled sugar solutions.

Gels tested were divided into two types (I and II). Type I gels (agar and sodium alginate) did not affect the transport properties (water diffusivities) of sugar solutions although the viscosities changed very much. The water diffusivities of Type II gels (gelatin and pectin) were much lower than those for Type I gels, especially at low water contents. The desorption isotherms of Type I and Type II gels were similar. Although the electroconductivities decreased with increasing sugar concentration, they did not change when the solutions were gelled. It is suggested that Type I gel network was quite uniform during drying while a rather dense gel network was formed near the surface of Type II gels after a certain period of drying. This kind of hard skin layer might govern the water diffusivity (and the drying rate). © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Water diffusivity; Drying rate; Gel; Desorption isotherm; Viscosity; Electroconductivity

1. Introduction

Various types of gels or gelled solutions are important in food and pharmaceutical industries [1]. For example, a gelatin (protein gel) solution is dried to produce pharmaceutical capsules. Agar, pectin, sodium alginate and some other polysaccharide gels are added to liquid foods to be dried.

By experience we know that adding certain types of gels does not affect significantly the transport properties of small molecules in the gels while some gels change such properties to a great extent. Unfortunately, quantitative and systematic studies on drying of gelled solutions as well as mass transport phenomena in the gels are not satisfactory.

In this study mass transport phenomena in various types of gelled sugar solutions were investigated. Sugar (sucrose, trehalose and maltodextrin) solutions gelled with polysaccharides such as agar, pectin, sodium alginate, and a protein (gelatin) were used as model gel systems.

The measured items are: (i) isothermal drying curves to determine water diffusivities which decrease sharply with decreasing water content on the basis of the regular regime (RR) drying curve [2–9]; (ii) desorption isotherms to know the state of water in the gels; (iii) rheological properties such as viscosity; and (iv) electroconductivities to know the mass transport properties in viscous solutions (sols) and gels.

The drying rates and desorption isotherms of semi-solid foods (pasta-like foods) were measured for comparison.

2. Experimental

2.1. Materials

Sugars (carbohydrates) employed in this study are disaccharides [sucrose (Wako Pure Chemical, Japan) and trehalose (Trehaose, Hayashibara, Japan)] and oligosaccharides [maltodextrin of dextrose equivalents (DE) = 11, molecular weight ca. 6000 (Pinedex #2, Matsutani Kagaku Kogyo, Japan), a maltotetraose-rich maltodextrin (DE = 39, Tetrup-H, Hayashibara), a maltopentaose-rich maltodextrin (DE = 39, Pentrup, Hayashibara)]. Gel-forming agents (agar-agar, sodium alginate, gelatin and pectin) were purchased from Wako Pure Chemicals. Japanese noodle (Kishimen) and pasta (fettuccine) were boiled for 15–20 min and used for the drying and the desorption experiments.

2.2. Gel preparation

Sugar solutions (ca. 40 wt.%) were heated with agar-agar (1–4 wt.%), sodium alginate (1–4 wt.%), pectin (1–4 wt.%), or gelatin (1–4 wt.%) to dissolve solids, and injected into an aluminum dish (diameter = 50 mm, depth = 1 or 3 mm) to prepare slab shaped samples.

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* Corresponding author.
E-mail address: shuichi@po.cc.yamaguchi-u.ac.jp (S. Yamamoto).

PII: S1385-8947(01)00286-8

Nomenclature

A	effective area for drying (m^2)
A_W	water activity (–)
d_s	density of pure solid (kg/m^3)
D	diffusion coefficient (m^2/s)
D_a	apparent diffusion coefficient ($kg^2/(m^4\,s)$)
D_s	diffusion coefficient in concentrated solutions (m^2/s)
D_0	diffusion coefficient in infinite dilute solutions (m^2/s)
F	Faraday constant (C/mol)
F'	normalized isothermal drying rate $= -d\bar{u}/d\tau' = -(R_s d_s)^2 (d\bar{u}/dt)$ ($kg^2/(m^4\,s)$)
n_A, n_C	transport numbers of anion and cation, respectively (–)
R	gas constant ($J\,mol^{-1}\,K^{-1}$)
R_s	slab thickness or half thickness of the film in the absence of water (m)
Sh	Sherwood number (–)
t	time (s)
T	absolute temperature (K)
u	water content (kg water/(kg solid))
$\bar{u}$	average water content (kg water/(kg solid))
W_s	solid weight $= AR_s d_s$ (kg)
Greek symbols	
η	viscosity (Pa s)
Λ_s	equivalent conductivity of electrolyte in concentrated solutions ($m^2\,mol^{-1}\,S$)
Λ_0	equivalent conductivity of electrolyte in dilute solutions ($m^2\,mol^{-1}\,S$)
ρ_s	mass solid concentration (kg solid/m^3)
$\tau' = t/(d_s R_s)^2$	($m^4\,s/kg^2$)

2.3. Drying experiment

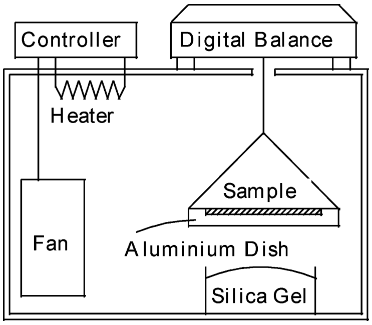

Fig. 1. Experimental setup for the isothermal drying experiment.

Isothermal drying experiments with a gelled slab were performed in a constant-air temperature box as shown in Fig. 1. Silica gels were placed in the box as desiccants. The air temperature was controlled so that the sample temperature is maintained at an assigned temperature. The air temperature in the drying box was somewhat higher than the assigned value at the beginning of the experiment, and then, lowered gradually with the progress of the drying. Such temperature control programs were not employed for the drying of samples in a vacuum drying setup on the basis of a Cahn 2000 balance (Cahn Instruments, USA) shown in Fig. 2. The weight of the film was continuously measured by the Cahn balance and stored in a personal computer. The drying rates for the average water content $\bar{u} > 0.2$–0.3 were measured by the setup shown in Fig. 1 and those for low water contents $\bar{u} < 0.2$–0.3 by the setup shown in Fig. 2. The weight and the temperature measurements were done separately in both setups.

In addition to these two setups, a versatile setup for measuring adsorption/desorption rates at atmospheric pressure or under vacuum was developed on the basis of a magnetic suspension balance (Rubotherm, Germany) as shown schematically in Fig. 3.

2.4. Desorption isotherm

Samples (gels) were stored in a sealed container in the presence of saturated salt solutions of known water activities. The samples were weighed periodically until the weight loss became less than 2% per 12 h (usually 2–3 days).

2.5. Water diffusivity

The diffusion coefficient of water in liquid foods $D(u)$ which depends strongly on the water content u can be determined from the RR isothermal drying curve [2–7]. When the isothermal drying rate $-d\bar{u}/dt$ is converted to $F' = -(R_s d_s)^2 (d\bar{u}/dt)$ and plotted against the average water content $\bar{u}$, the so-called "RR" master curve is obtained. Although $D(u)$ can be determined from the RR curve by several methods including our simple method [7], the experimental data in this paper are shown as apparent diffusion coefficients $D_a(u)$ defined by Eq. (1) as the purpose of

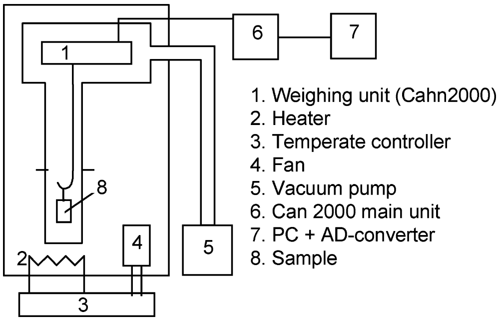

Fig. 2. Experimental setup for the vacuum isothermal drying.

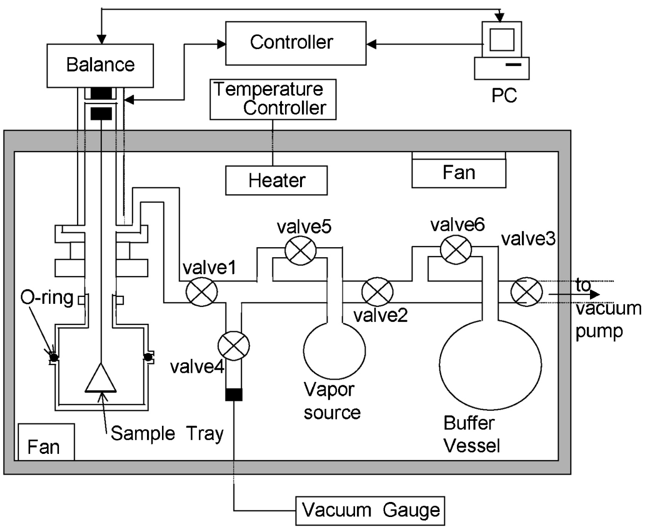

Fig. 3. Experimental setup for the drying and the adsorption with a magnetic suspension balance.

this paper is not to present precise $D(u)$ values as physical transport properties but to examine the effect of the gel properties on the water diffusion in gelled sugar solutions.

$$D_a = \left(\frac{4}{\pi^2}\right)\left(\frac{F'}{\bar{u}}\right) \tag{1}$$

2.6. Electroconductivity measurement

It is well known that the mobility of ions in aqueous solutions can be related to the electroconductivity as follows [10]:

$$D = \left(\frac{2RT}{F^2}\right) n_A n_C \Lambda \tag{2}$$

where R is the gas constant, T the absolute temperature, F the Faraday constant, n_A the transport number of anion, n_C the transport number of cation, and Λ the equivalent conductivity of electrolyte. If this equation is assumed to be valid in concentrated solutions, the ratio of the diffusion coefficient in concentrated solutions D_s to that in infinite dilute solutions D_0 can be given by

$$\frac{D_s}{D_0} = \frac{\Lambda_s}{\Lambda_0} \tag{3}$$

This equation means that the ratio of the diffusion in concentrated solutions to that in dilute solutions is proportional to the ratio of the equivalent conductivity of electrolyte in concentrated solutions, Λ_s to that in dilute solutions, Λ_0. Hoshino [11] is the first who measured the electroconductivities of salts in electrostatically neutral polymer solutions to investigate the applicability of Eq. (3). We measured the electroconductivities of NaCl in various sugar solutions as a function of sugar concentration by Horiba conductivity meter (9382-10D, Kyoto, Japan). The micro-viscosity η_{micro} which governs the diffusion [11] is then given by

$$\eta_{\text{micro}} = \frac{\eta_0 \Lambda_0}{\Lambda_s} \tag{4}$$

2.7. Viscosity measurement

Viscosity (macro-viscosity) values of sugar solutions of various concentrations were measured by a cone and plate viscometer (Tokimec, Tokyo) at 303 and 323 K.

3. Results

3.1. Effect of gel concentration

The apparent water diffusion coefficients (D_a) for gelled sucrose, trehalose and maltodextrin solutions of various agar concentrations are shown in Figs. 4–6. Although the D_a values depended strongly on water concentration, they were not influenced by the agar concentration (1–4%). Similarly, D_a values for sodium alginate gelled sucrose solutions did not depend on the gel concentration (data not shown). On the contrary, D_a values for gelatin gels were affected by the gel concentration as shown in Fig. 7.

3.2. Effect of type of gel

The D_a values for sucrose solutions gelled with various types of gels are shown in Fig. 8. As mentioned previously, the D_a values at high water contents ($0.6 < u < 1.0$) are similar. At low water contents ($u < 0.5$), the D_a values for the gelatin and pectin gels became lower than those for the agar, and the alginate gels. The D_a values for the gelatin sugar gels are compared with those for pure gelatin gels (without sugars) in Fig. 9. At low water content regions ($u < 0.4$), the D_a values with or without sugar are similar.

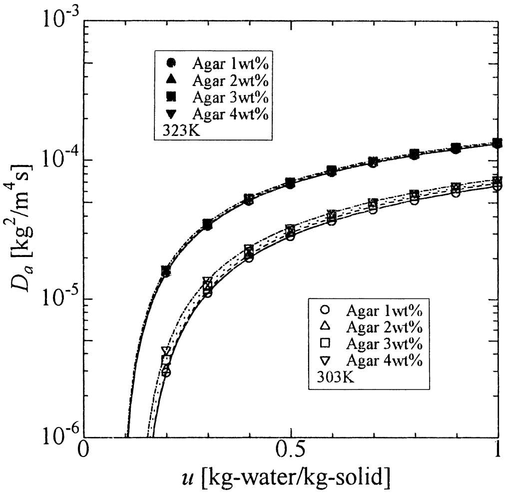

Fig. 4. Apparent water diffusion coefficient in gelled sucrose with agar vs. water content.

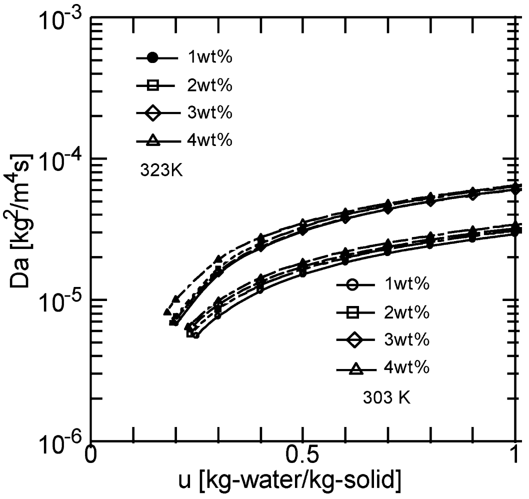

Fig. 5. Apparent water diffusion coefficient in gelled maltodextrin with agar vs. water content.

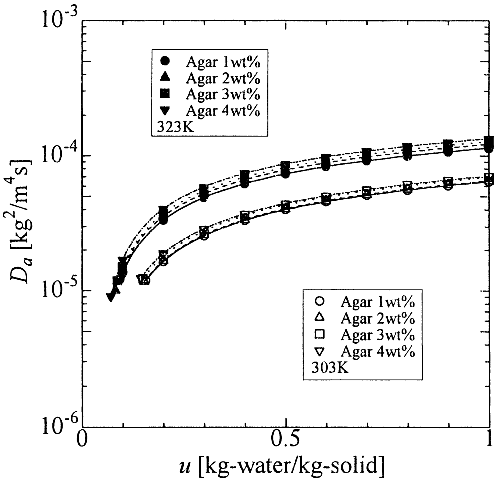

Fig. 6. Apparent water diffusion coefficient in gelled trehalose with agar vs. water content.

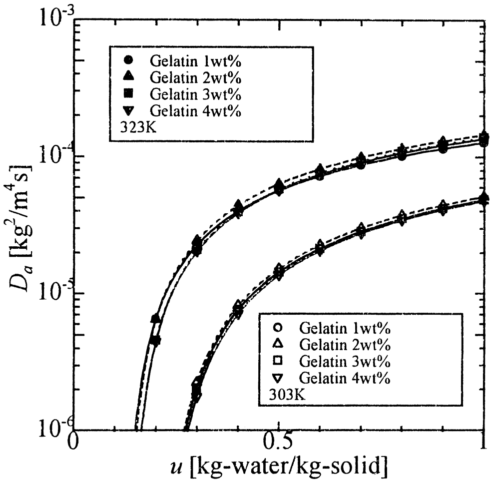

Fig. 7. Apparent water diffusion coefficient in gelled sucrose with gelatin vs. water content.

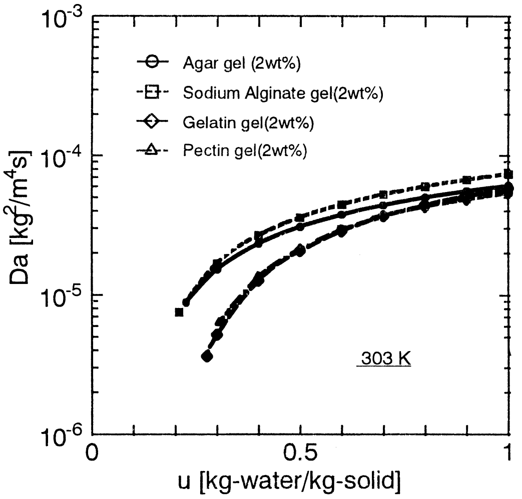

Fig. 8. Apparent water diffusion coefficient in sucrose gelled with various types of gels vs. water content.

Namely, the water diffusion (and the drying rate) is governed by the mass transfer in the gelatin gel layer at low water contents whereas the agar and the alginate gels do not affect the water diffusion in sugar solutions. The dried surfaces of gelatin and pectin sugar gels after the drying experiments were smooth compared with those of the other gels. In order to obtain quantitative information on the surface properties, the dried gel surfaces were analyzed by atomic force microscopy (AFM). Unfortunately, AFM did not show the surface properties clearly.

Although it is not easy to define a "gel", the isothermal drying rates of several pasta-like foods [Japanese noodle (Kishimen) and pasta (fettuccine)] were determined to obtain the water diffusivity. As shown in Fig. 10, the D_a values for various cooked pasta-like foods are similar and much higher at low water contents than those for sucrose and maltodextrin gels.

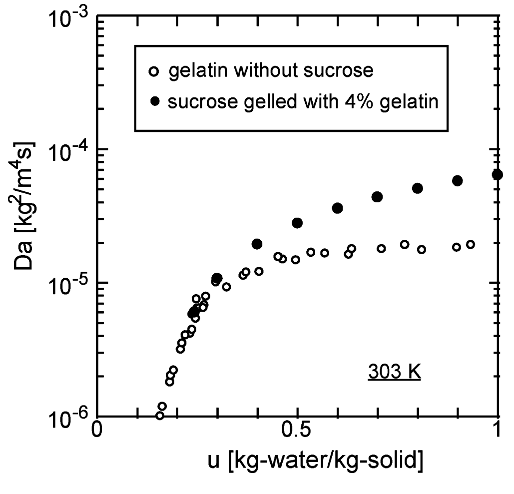

Fig. 9. Apparent water diffusion coefficient in gelatin and sucrose gelled with 4% gelatin vs. water content.

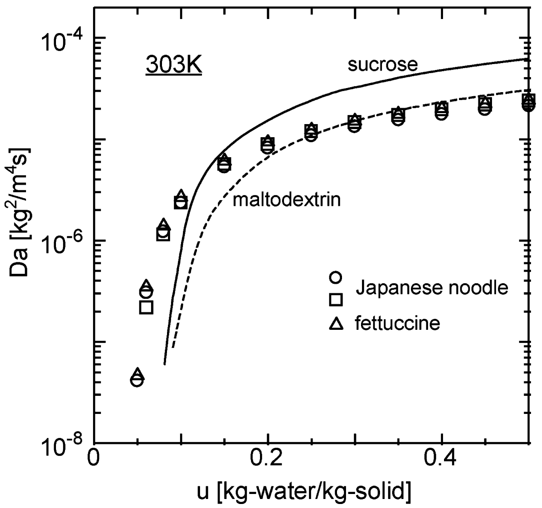

Fig. 10. Apparent water diffusion coefficient in pasta-like foods vs. water content.

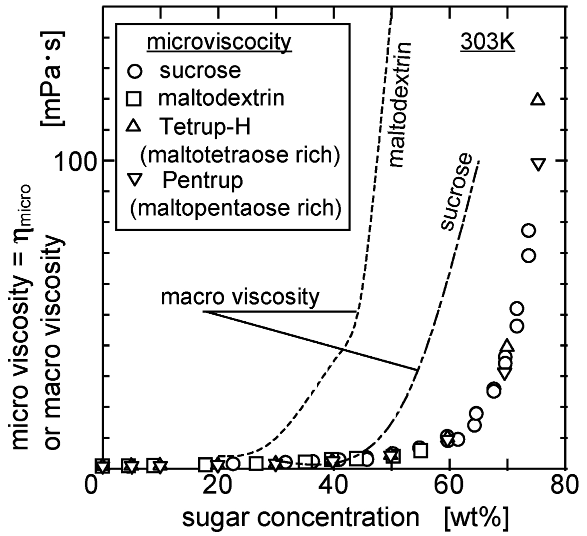

Fig. 12. Macro- and micro-viscosity vs. sugar concentration.

3.3. Desorption isotherm

Desorption isotherms for various gels are shown in Fig. 11. Unlike the water diffusivity–water content relationships, the desorption isotherm curves for various sucrose gels and gelatin are similar. The equilibrium water content at a given water activity A_w for the pasta-like foods are lower than those for the sugar solutions. This suggests that as the water in the pasta-like foods was not strongly bound to the solid even at low water contents the water diffusivities were higher than those in sugar and sugar gels.

3.4. Macro- and micro-viscosity

Fig. 12 shows the rheological property of sugar solutions—viscosity values measured by a cone and plate viscometer (macro-viscosity). The macro-viscosity values of sucrose and maltodextrin increased very sharply with increasing solid concentration, and the values of maltodextrin were much higher than those of sucrose.

On the contrary, the micro-viscosities from the electroconductivity measurement were very similar for sucrose, maltodextrin, Tetrup and Pentrup even at very high solid concentration (>70%) where the solutions were supersaturated solutions of very high macro-viscosities.

The relative water diffusivities (D/D_0) were plotted against the inverse of the relative micro-viscosities $\eta_0/\eta_{\mathrm{micro}} = \Lambda_s/\Lambda_0$ as shown in Fig. 13. Although the absolute values of the apparent water diffusion coefficients were different as shown in Figs. 4 and 5, the values normalized

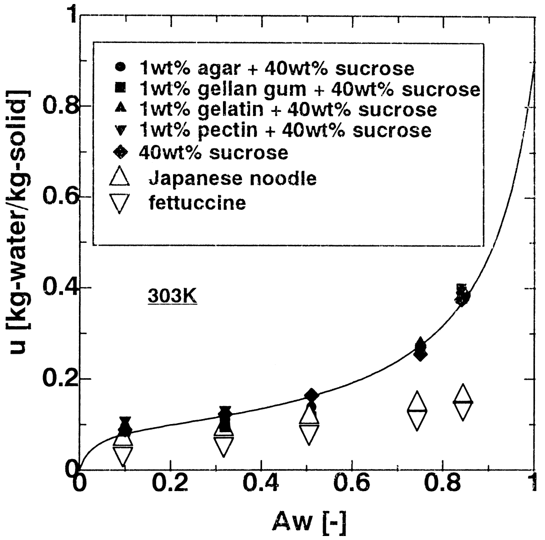

Fig. 11. Desorption isotherms for sucrose gels and gelatin without sucrose and pasta-like foods.

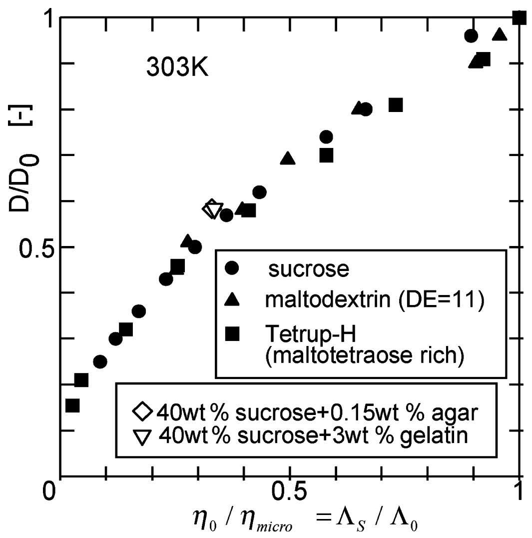

Fig. 13. Relative water diffusivity vs. relative electroconductivity.

with the diffusion coefficient in dilute solutions (molecular diffusivity) were well correlated with the relative electro-conductivities. Namely, the diffusion of small molecules is governed by the viscosity in the network of concentrated and/or gelled solutions and is not directly related to the (macro)viscosity determined by the conventional viscometer. The values for gelled solutions were also well correlated. These results suggest a possibility for determining the water diffusivity in concentrated sugar solutions. One restriction is that it is only suited for electrostatically neutral sugars and other food materials. If the solid contains some fixed charges and/or some free small ions, additional corrections must be needed, which might cause some difficulties in determining the diffusivities.

4. Discussion

Adding a small amount of polysaccharides to sugar solutions increases the solution viscosity significantly, and might result in a gel formation. However, the mass (water) transport in the gel is not always hindered very much. Agarose, a component extracted from agar-agar is widely used as a matrix for chromatography packing materials and for electrophoresis. A large number of papers have been already published on the diffusion and the partition of solutes in the agarose gel [12,13]. These papers have shown that the partition and the diffusion of solute decrease with increasing solute size and/or increasing gel concentration. However, the diffusion of small molecules such as sodium chloride is not affected by the agarose gel net work even when the agarose concentration is 6 wt.%. So, it is easily expected that the diffusion of water molecule in the agarose gel is not hindered by the gel network.

However, this is for the gel which is completely swollen in water. It is not clear whether the effective pore diameter of the agar gel changes when the water content of the gel is decreased. Our experimental results indicate that the dense surface gel net work of gelatin was likely to be formed soon after the drying of gelatin gelled sugar solutions, which results in lowering of the water diffusion coefficient at low water contents.

Another interpretation of these findings is segregation during drying [8] and/or phase separation of gelatin from sugar solutions [14]. Further research is needed to clarify the mechanism involved in this lowering of the water diffusion coefficient, which affects not only the drying behavior [9] but also the flavor (aroma) retention during drying [2,4,15].

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