MUTUAL DIFFUSION COEFFICIENT OF AQUEOUS SUGAR SOLUTIONS

YUJI SANO* AND SHUICHI YAMAMOTO

*Department of Applied Chemistry and Chemical Engineering,
Yamaguchi University, Ube, 755*

Key Words: Food Chemical Engineering, Mass Transfer, Mutual Diffusion Coefficient, Sugar, Maltodextrin, Aqueous Solution, Drying

The mutual diffusion coefficient of aqueous solutions with sugars of various molecular weight, obtained by drying experiment of the solution, was investigated for the effects of concentration, temperature and molecular weight of sugar.

The mutual diffusion coefficient of dilute solution was correlated using Wilke's diffusion factor. The concentration dependence was presented by linear relation of the logarithm of the diffusion coefficient vs. the sugar mole fraction regardless of temperature. The slopes of the linear relations were expressed by a power function of the molecular weight. From the linear relation, the activation energy was expressed also by linear relation of the sugar mole fraction, in which the slopes were expressed by the other power function of the molecular weight. The resultant estimation equation covers well for the temperature range 298-323 K and for the molecular weight range of sugars, from 180 for glucose to 6100 for maltodextrin.

Introduction

Analysis of the drying process for food materials such as aqueous solutions containing sugars skim milk, coffee extract, etc., and solid foods such as potato, apple tissue macaroni etc., depends on a knowledge of the diffusion coefficients⁴⁾. Sugars are essential in various foods and also play an important role in biochemical and medical products such as dry binder, thickening agents, stabilizing agents for enzymes. In an aqueous solution of sugars the diffusion coefficient usually shows strong concentration dependence.

The mutual diffusion coefficients of aqueous solutions for various sugars have been reported by several investigators, such as those of glucose (Gladden and Dole³⁾) sucrose (Ellerton and Dunlop²⁾), x and y lose and maltose (Uedaira and Uedaira⁸⁾). But most of these data are limited to room temperature, and the dependences on concentration and temperature have not been investigated widely. Systematic surveys of the effect of sugar molecular weight are also few.

The authors¹⁰⁾ measured the diffusion coefficients of various sugars by the capillary cell method in dilute solution and by the drying experiment of aqueous solution in concentrated range. Simple empirical equations for the dependence of concentration and temperature were then derived, without taking account of the effect of molecular weight.

Here, based on the previous data¹⁰⁾, the effect of sugar molecular weight on the mutual diffusion coefficient is surveyed and estimation equations are derived as a function of concentration, temperature and the molecular weight of the sugar.

1. Data of Diffusion Coefficient

The experimental apparatus and the procedures were described in a previous report¹⁰⁾. Sugars investigated in this study are monosaccharide (glucose), disaccharides (sucrose, maltose, lactose) and oligosaccharides (maltodextrin of various *DE* value) as shown in **Table 1**.

The diffusion coefficients in the concentrated range were calculated as a function of concentration from the previous drying rate data obtained for various sugar aqueous solutions, using the direct calculation method for the regular regime given by the authors⁶⁾, assuming zero surface concentration or a certain finite value of surface concentration corresponding to the effective zero drying rate. In the calculating range of concentration (average water content larger than 0.15 kg water/kg sugar for the drying rate), in which the linear relation of $\log D$ vs. X_s was obtained through all sugars investigated as shown later, the calculation assuming zero surface concentration was convenient and satisfactory. The assumption of zero surface concentration corresponds to the supersaturated conditions of the solution near the surface in the early stage of the regular regime. In the drying experiments of the sugar solutions listed in the Table 1, transparency of the solution was maintained and no precipitation was found during drying. The method of calculating the diffusion coefficient proposed by Schoeber⁷⁾ was also tested and close agreement with the results by the method of the authors⁶⁾ was confirmed.

2. Results and Discussion

2.1 The diffusion coefficient in dilute solution

The mutual diffusion coefficient in dilute aqueous solution for the various sugars at 303 K, obtained by the capillary cell method, are shown in Table 1. They are

* Received April 23, 1993. Correspondence concerning this article should be addressed to Y. Sano.

Table 1. Sugars investigated in this study.
 D_0 is the observed value by the capillary-cell method¹⁰⁾

Sugars	M_s [kg/kmol]	D_0 [m^2/s] * 10^{10}
glucose	180	7.0
sucrose	342	6.0
maltose	342	6.0
lactose	342	6.0
maltotriose	504	4.3
maltopentaose	828	3.4
oligotose	570	5.1
maltodextrin (DE = 40)	910	3.8
maltodextrin (DE = 25)	1300	2.9
maltodextrin (DE = 11)	6100	2.2

Fig. 1 D_0 by Eq. (1) in comparison with observed values¹⁰⁾

correlated using the diffusion factor by Wilke and Chang⁹⁾. Molar volume is calculated from the molecular weight of sugar by $V = M_s/d_s$, assuming a constant density of sugars $d_s = 1560$ kg/m³ (density of glucose). An empirical equation with the term of molecular weight of solute M_s is then presented as follows.

$$\frac{T}{D_0 \eta} = 9.5 \times 10^{13} M_s^{1/3} \quad (1)$$

where η is the viscosity of water at temperature T . Eq. (1) presents well the values of D_0 in Table 1 and the values of various sugars in the literatures^{3, 5, 8)}, as shown in Fig. 1.

2.2 Concentration dependence of the diffusion coefficient

In the drying experiment with sugar aqueous solution¹⁰⁾, the temperature of the solution reached the drying air temperature in the later drying stage of the regular regime. The diffusion coefficients were calculated as a function of water content from the regular regime drying-rate curves at the drying air temperature, using the methods by authors⁶⁾ in the range of average water content ($u > 0.15$).

The diffusion coefficient in the concentrated range

Fig. 2 Concentration dependence D vs. X_s for various sugars at 303 K

Fig. 3 Concentration dependence D vs. X_s for various maltodextrins at 303 K

calculated from the drying rate data are correlated with the mole fraction of solute.

$$X_s = \frac{1}{1 + u(M_s/M_w)} \quad (2)$$

The plots of $\log D$ vs. X_s for the various sugar solutions are presented as linear relations in Figs. 2 and 3. The linear relations reached the values of D_0 calculated from Eq. (1) at $X_s = 0$ quite well for the various sugars.

From the fact of the linear relation for the concentration dependence of the diffusion coefficient, the correlation equation is derived using the slope α of $\log D$ vs.

Fig. 4 Correlation of α with molecular weight of sugar at 303 K

Fig. 5 Correlation of β with molecular weight of sugar

X_s .

$$\log(D/D_0) = -\alpha X_s \quad (3)$$

The values of α for various sugar solutions at 303 K are correlated with the molecular weight ratio of solute and solvent (water) as shown in Fig. 4. The correlation equation of α for 303 K is presented as follows.

$$\alpha_{303} = 0.70 (M_s / M_w)^{0.84} \quad (4)$$

2.3 Correlation equation of diffusion coefficient

If the linear relation of $\log D$ vs. X_s by Eq. (3) holds at any temperature, then the slope α_T at temperature T is related to the slope α_{303} at 303 K, using the activation energy as follows.

$$\ln \left(\frac{D_{0,T}}{D_{0,303}} \cdot \frac{D_{303}}{D_T} \right) = 2.303 (\alpha_T - \alpha_{303}) X_s = \frac{\Delta E - \Delta E_0}{R} \left(\frac{1}{T} - \frac{1}{303} \right) \quad (5)$$

The activation energy should be expressed by the following linear relation of the sugar mole fraction X_s , which corresponds to the constancy of the slope α of Eq. (3), regardless of temperature.

$$\Delta E - \Delta E_0 = \beta X_s \quad (6)$$

Fig. 6 Comparison of D , observed and calculated, for various sugars

Using β , α_T is expressed as follows.

$$\alpha_T = \alpha_{303} + \frac{\beta}{2.303R} \left(\frac{1}{T} - \frac{1}{303} \right) \quad (7)$$

The activation energy ΔE_0 for the dilute solution ($X_s = 0$) is evaluated from Eq. (1), using the temperature change of water viscosity as 17.3 kJ/mol.

The values of β for various sugars were calculated by Eq. (7) and correlated with the molecular weight of sugar, as shown in Fig. 5. The correlation equation of β is expressed as follows.

$$\beta = 20.5 (M_s / M_w)^{0.7} \quad (8)$$

Then the activation energy is

$$\Delta E = 17.3 + 20.5 (M_s / M_w)^{0.7} X_s \quad (9)$$

and α at temperature T is

$$\alpha_T = \alpha_{303} + 20.5 \frac{(M_s / M_w)^{0.7}}{2.303R} \left(\frac{1}{T} - \frac{1}{303} \right) \quad (10)$$

From Eqs. (1), (3), (4) and (10), the values of D are calculated and are compared with the experimental values for various sugars at 323 K and reported values in the literature such as those of glucose at 298 K¹⁾ and 323 K⁷⁾ in Fig. 6. The same comparisons are shown for maltodextrins in Fig. 7. The linear lines of $\log D$ vs. X_s , calculated with the slope by Eq. (10) and with the values of D_0 by Eq. (1), fit the experimental values and literature values quite satisfactorily. Thus the estimation equations derived here will be useful in predicting the mutual diffusion coefficient of aqueous sugar solutions, in the concentration range in which the linear relation of $\log D$ vs. X_s holds. The error of estimation will be less than 30 %, as shown in Figs. 2, 3, 6 and 7.

Conclusions

The concentration-dependent mutual diffusion coefficient of sugar aqueous solutions are investigated from glucose to maltodextrin (molecular weight = 6100)

Fig. 7 Comparison of D , observed and calculated, for various maltodextrins

for the temperatures up to 50°C. In the range of water content larger than 0.15 kg water/kg sugar, the concentration dependence is expressed by linear relations of the logarithm of the diffusion coefficient vs. the mole fraction of sugar, regardless of temperature. Using the slope of the linear relation, empirical equations, Eqs. (1), (3), (4) and (10), for estimation of the diffusion coefficient are derived as a function of concentration, temperature and molecular weight of sugar. The error of the estimation may be within 30 % in the range considered.

Acknowledgement

This work was financially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education Science and Culture.

Nomenclature

D	= mutual diffusion coefficient	[m ² /s]
D_0	= D of dilute solution	[m ² /s]
DE	= dextrose equivalent	[-]
ΔE	= activation energy of diffusion coefficient	[kJ/mol]
M_s	= molecular weight of solute	[kg/kmol]
M_w	= molecular weight of solvent	[kg/kmol]
R	= gas constant	8.314×10^{-3} [kJ/molK]
u	= water content	[kg solv./kg solute]
T	= temperature	[K]
X_s	= mole fraction of solute	[-]
α	= slope of $\log D$ vs. X_s	[-]
β	= slope of ΔE vs. X_s	[kJ/mol]
η	= viscosity of water	[Pa·s]

Literature cited

- Chandrasekaran, S.K. and C. Judson King: *AIChE J.*, **18**, p. 513-520 (1972)
- Ellerton, H.D. and P. Dunlop: *J. Phys. Chem.*, **71**, p. 1291-1297 (1967)
- Gladden, J.K. and M. Dole: *J. Am. Chem. Soc.*, **75**, p. 3900-3904 (1953)
- Luyben, K.Ch.A.M., J.J. Olieman and S. Bruin: *Drying '80*, vol. 2, ed. by A.S. Mujumdar, Hemisphere, p. 233-243 (1980)
- Paduano, L., R. Sartorio, V. Vitagliano, J.G. Albright, D.G. Miller and J. Mitchell: *J. Phys. Chem.*, **94**, p. 6885-6888 (1990)
- Sano, Y. and S. Yamamoto: *J. Chem. Eng. Japan*, **23**, p. 331-338 (1990)
- Schoeber, W.J.A.H.: Ph.D. Thesis, Tech. Univ. Eindhoven (1976)/Schoeber, W.J.A.H. and H.A.C. Thijssen: *AIChE Symp. Series*, **73** (163), p. 12-24 (1977)
- Uedaira, H. and H. Uedaira: *Bulletin Chem. Soc. Japan*, **42**, p. 2140-2142 (1969)
- Wilke C.R. and P. Chang: *AIChE J.*, **1**, p. 264-270 (1955)
- Yamamoto, S. and Y. Sano: *World Congress III of Chem. Eng.*, vol. II, 8b-152, p. 564-567, Tokyo (1986)/Sano, Y. and S. Yamamoto: Report of Grant-in-Aid for Scientific Research (C-60550669), (1987)