DRYING MECHANISM OF COATED FILM OF POLYMER SOLUTION*

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Drying of coated film of polyvinylalcohol (PVA) aqueous solution is studied theoretically and experimentally, focusing on the diffusion process of water and the volumetric shrinkage of film occurring by evaporation of water. The diffusion coefficients were measured over the whole range of concentration by three methods, and drying experiments of coated films using hot air were performed. Numerical solutions were obtained from a set of transport equations for water using the observed diffusion coefficients and were compared with the experimental results.

Introduction

In the manufacture of photographic films, synthetic fibers and many kinds of polymer products, the drying of polymer solution plays an important role. It significantly affects the qualities of the products because it is the final process in their manufacture. The histories of solvent concentration distributions and temperature are more important than the overall drying rate, however many problems are still unsolved owing to the complicated behavior of polymer solutions.

Otake *et al.*⁹⁾ studied the drying of cellulose-acetateacetone solution and explained the mechanism of the process by dividing it into two periods, namely the period of forming solid skin and that of decreasing drying rate. Sano and Nishikawa¹²⁾ performed drying experiments on a drop of polyvinylalcohol aqueous solution. They solved the diffusion equation taking into account the dependency of polymer concentration on the equilibrium vapor pressure of water. However, volumetric shrinkage which takes place during the drying and the concentration dependency of the diffusion coefficient were not considered in those studies.

The purpose of the present work is to study the drying mechanism of coated film of PVA aqueous solution and to simulate the process of drying, considering the following three points of views:

- 1. The concentration dependency of diffusion coefficient.
- 2. The concentration dependency of equilibrium vapor pressure of water.
- 3. The effect of volumetric shrinkage of film accompa-

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nied by evaporation of water.

1. Measurement of Mutual Diffusion Coefficients

Diffusion coefficients in polymer-solvent systems have been measured by several workers⁵⁾, but most previous data reported refer to extremely dilute solutions or nearly dried films, and there are few available data for the medium-concentration range. Therefore the diffusion coefficients for almost the whole concentration range were measured to study the drying process of PVA-water solution, using the following three methods. These were the "micro-interferometric method" for dilute concentrations, "film desorption method" for the nearly dried state and "modified micro-interferometric method" for medium concentrations.

1.1 Diffusion coefficients for low concentrations of PVA

Experimental Although there are several methods to measure the diffusion coefficients in low polymer concentrations, the micro-interferometric method developed by Robinson¹¹) and by Crank and Robinson⁶) was adopted in the present study because of the simplicity of the apparatus and the remarkable saving of time.

The apparatus consisted of an optical assembly, an optical wedge (diffusion cell) and a microscope. The e-line ray (5461 Å) was used for interference. The diffusion cell was an optical wedge consisting of two partially-reflecting microscope slides.

Since an interference fringe produced in the cell represents a contour line of constant optical path in the wedge, the refractive index gradient is easily determined. There is a linear relationship between the refractive index and the concentration of PVA aqueous solution, so one can easily obtain the concentration gradient. The details of this method have been treated elsewhere^{7,8)}.

^{*} Received on June 25, 1973 Presented at the 1st Pacific Chemical Engineering Congress, at Kyoto, 13th October 1972

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The mutual diffusion coefficient is defined by the following equation¹:

$$j_A = -\rho D \frac{\partial \omega_A}{\partial z} \tag{1}$$

The diffusion coefficient D(c) as a function of concentration may be calculated from the concentration gradient curve, as shown in **Fig. 1**, by Boltzmann's equation (2);

$$D = -\frac{1}{2t} \left(\frac{dz}{d\Omega} \right) \int_{0}^{a} z d\Omega$$
 (2)

in which the origin of z-axis must be chosen to establish the following equation:

$$\int_{0}^{1} z d\Omega = 0 \tag{3}$$

where

$$\Omega = (\omega_A - \omega_{A2}) / (\omega_{A1} - \omega_{A2}) \tag{4}$$

 ω_{A1} and ω_{A2} are the concentrations of the two contacting solutions, respectively.

Results The sample of PVA employed was a commercial grade having a viscosity-average molecular weight of 21,000 and a polymerization degree of 480. Linear relationships between refractive index n and concentration ω_B , as well as between specific volume and concentration, were obtained in the concentration range from pure solvent to $\omega_B \doteq 0.6$.

The data obtained are shown in **Fig. 2**. Measurement was carried out at 25 °C and 35 °C. At both temperatures the coefficient is almost independent of concentration in the range from $\omega_B = 0.15$ to 0.30, and increases with increasing temperature. The Arrhenius activation energy is estimated to be about 5.6 kcal/mol. **1.2 Diffusion coefficients for intermediate concentrations of PVA**

Experimental Though several attempts have been made, it can be said that there has not been established a reliable method to measure the diffusion coefficient of polymer solution in the intermediate concentration range. Thus the micro-interferometric method was modified for use in such a concentration range.

The apparatus used was the same as mentioned above. A solution was put in the diffusion cell, made of



Fig. 4 Interference fringe



Fig. 5 Gradient of refractive index



Fig. 6 Drying layer of polymer solution

two partially-reflecting microscope slides so as to be U-shaped, as shown in **Fig. 3**. Then the evaporation rate from the interior surface, **A** in Fig. 3, was suppressed, so that the solution could flow freely to the outer surface during the observing time. By means of this device the growth of a meniscus formed on the surface at **B** shown in Fig. 3, where the interference fringes were observed, was avoided. Solvent evaporation occurred at the outer surface and the concentration gradient was formed there.

Figure 4 shows the observed interference fringes. Polymer solution is shown at the right, air at the left and the meniscus, whose width was about $10-20\mu$, in the middle.

The calculation procedure of concentration gradiients from the interference fringes is as follows. In **Fig. 5**,

$$n_1d_1 = nd$$
 (5)

$$d_1 \doteq d + x\theta \tag{6}$$

because angle θ is very small (θ =0.008 radian). When there is a linear relationship between refractive index and concentration, Eqs.(5) and (6) give the relation

$$n = n_1 / (1 - x\theta/d_1) \tag{7}$$

whereas

$$d_1 = L\theta \tag{8}$$

Therefore

$$n = n_1 / (1 - x/L)$$
 (7')

As a result, the refractive index gradient is easily determined from x and L by using Eq.(8).

$$\frac{\partial \rho_A}{\partial t} + \frac{\partial (\rho_A v)}{\partial z} = \frac{\partial}{\partial z} \left(\rho D \frac{\partial \omega_A}{\partial z} \right) \tag{9}$$

$$\frac{\partial \rho_B}{\partial t} + \frac{\partial (\rho_B v)}{\partial z} = \frac{\partial}{\partial z} \left(\rho D \frac{\partial \omega_B}{\partial z} \right) \tag{10}$$

Assuming volumetric additivity between PVA and water,

$$(\rho_A / \rho_A^{\circ}) + (\rho_B / \rho_B^{\circ}) = 1$$
 (11)

From Eqs.(9)-(11) one can obtain the following set of



transfer equations.

$$\frac{\partial v}{\partial z} = \frac{\partial}{\partial z} \left(\frac{D}{\omega_A + \hat{\omega}} \cdot \frac{\partial \omega_A}{\partial z} \right)$$
(12)

$$\frac{\partial \omega_A}{\partial t} - (\omega_A + \hat{\omega}) \frac{\partial v}{\partial z} + v \frac{\partial \omega_A}{\partial z} = 0$$
(13)

where v is the velocity of the mass center and

$$\hat{\omega} = \rho_A^{\bullet} / (\rho_B^{\bullet} - \rho_A^{\bullet}) \tag{14}$$

Now let us consider a layer of polymer solution drying from one side, as shown in **Fig. 6**. The origin of z-axis is fixed at the evaporating surface. The volumetric shrinkage of the layer may occur as drying proceeds, and its amount is equal to the volume of the solvent evaporated. Let us represent the shrinkage as an advance of the bottom surface. The shrinkage σ is represented as

$$\sigma \rho_{A}^{*} + \int_{0}^{s} \rho_{A} dz = \int_{0}^{s_{0}} \rho_{A}|_{t=0} dz$$
 (15)

Where s_0 is the initial thickness and s is that at an arbitrary time. The initial distribution of concentration is everywhere uniform. When one puts an imaginary initial bottom plane far away from the evaporation surface, the concentrations near the imaginary bottom plane are uniform and do not change appreciably. Then one obtains the following equations.

$$\sigma \doteq (1/\rho_A^{\circ}) \left\{ \int_0^{s_0} (\rho_A|_{t=0} - \rho_A) dz + \rho_{A0} \sigma \right\}$$
(16)

Then

$$\sigma \doteq \{1/(\rho_A^{\circ} - \rho_{A0})\} \int_0^{s_0} (\rho_A|_{t=0} - \rho_A) dz \qquad (17)$$

Therefore, one can determine s from Eq.(18).

$$s \doteq s_0 - \{1/(\rho_A^{\circ} - \rho_{A0})\} \int_0^{s_0} (\rho_A|_{t=0} - \rho_A) dz \qquad (18)$$

In applying Green's theorem to Eq.(9) with the boundary condition with respect to domain B on the t-z plane, as shown in **Fig. 7**,

$$\begin{array}{c} 0 \le t \le T \\ Z \le z \le s(t) \end{array} \right\}$$
 (19)

one can obtain

$$D = \iint_{B} \left\{ \frac{\partial}{\partial z} \left(\rho_{A} v - \rho D \frac{\partial \omega_{A}}{\partial z} \right) + \frac{\partial \rho_{A}}{\partial t} \right\} dz dt \quad (20)$$

$$= -\int_{C} \left\{ \left(\rho_{A} v - \rho D \frac{\partial \omega_{A}}{\partial z} \right) dt - \rho_{A} dz \right\}$$
(21)

There is scarcely any concentration gradient at the imaginary bottom plane, so that changing T, Z to t, z, respectively, and differentiating Eq.(21) by t give





$$0 = -\frac{\partial}{\partial t} \int_{z}^{s_{0}} \rho_{A}|_{t=0} dz + \frac{\partial}{\partial t} \int_{z}^{s} \rho_{A} dz + (\rho_{A}v)|_{z=s} -\rho_{A}v + \rho D \frac{\partial \omega_{A}}{\partial z}$$
(22)

By integrating Eq.(12), we obtain the equation

$$v = \frac{D}{\omega_A + \hat{\omega}} \cdot \frac{\partial \omega_A}{\partial z} + v|_{z=s}$$
(23)

Substituting Eq.(23) to Eq.(22), D is given as

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$$D = -\left(1 + \frac{\omega_A}{\hat{\omega}}\right) \left\{ 1 \left/ \left(\rho \frac{\partial \omega_A}{\partial z}\right) \right\} \times \left\{ \frac{\partial}{\partial t} \int_{z}^{s} \rho_A dz + (\rho_A|_{z=s} - \rho_A) v|_{z=s} \right\}$$
(24)

On the other hand, the concentration gradient at z = s(t) is always equal to zero, therefore

$$v|_{z=s} = \frac{d\sigma}{dt} = -\left(\frac{d}{dt}\int_{0}^{s} \rho_{A} dz\right) / \rho_{A}^{*}$$

$$D = -\left(1 + \frac{\omega_{A}}{\hat{\omega}}\right) \left\{ 1 / \left(\rho \frac{\partial \omega_{A}}{\partial z}\right) \right\}$$

$$\times \left\{ \frac{\partial}{\partial t} \int_{z}^{s} \rho_{A} dz - (\rho_{A}|_{z=s} - \rho_{A}) \left(\frac{d}{dt} \int_{0}^{s} \rho_{A} dz\right) / \rho_{A}^{*} \right\}$$

$$(26)$$

One can determine the diffusion coefficients from the changes of concentration distribution curve with time by using the above equation.

Results The distribution curves of concentration obtained are shown in **Fig. 8**. **Figure 9** shows the diffusion coefficients calculated from Eq.(26). During the time of measurement, $v|_{z=s}$ was approximately constant and equal to about -3×10^{-6} cm/sec. The shrinkage of thickness of the imaginary layer was several percent relative to s_0 . It may be attributed to the complicated





calculation that there was a rather large scattering of data. However, we may rely on the results obtained by the above method, because they join those obtained in the low concentration ranges.

1.3 Diffusion coefficients for high concentrations of PVA

Experimental The sorption method was applied to measure the diffusion coefficient in the high-concentration range. It has been reported that there is hysteresis between an adsorption process and a desorption. Thus the desorption method might be favorable for application to the present purpose. The details of this method are described elsewhere^{4,5,10}.

If the concentration just within the surfaces of a plane sheet of thickness 2b is maintained constant, the amount of diffusant M_t taken up from the sheet in time t is given by the equation*

$$\frac{M_t}{M_{\infty}} = 2\sqrt{\frac{Dt}{b^2}} \left\{ \frac{1}{\sqrt{\pi}} + 2\sum_{n=0}^{\infty} (-1)^n \text{ierfc} \frac{nb}{\sqrt{Dt}} \right\} (27)$$

The downtake is considered to be a diffusion process controlled by a constant diffusion coefficient D, and M_{∞} is the equilibrium sorption attained theoretically after infinite time. The value of D can be deduced from an observation of the initial gradient of a graph of M_t/M_{∞} as a function of $\sqrt{t/b^2}$.

For systems in which the diffusion coefficient is concentration-dependent, the initial gradient of each desorption curve yields some mean value, \overline{D} , say, of the

Table 1 Drying conditions of coated film

Run No.	Coated amount [g/cm²]	Initial conc. of coated soln. ω_{A0} [g-water/g-soln.]	Initial thick- ness of film s ₀ [cm]	Constant drying rate R _c [g/cm ² ·sec]
110	0.0985	0.799	0.0943	2.86×10 ⁻⁵
112	0.127	0.799	0.122	2.86×10^{-5}
117	0.0464	0.799	0.0444	2.86×10^{-5}

All the experiments were carried out at the following conditions of hot air. Temperature: 42.0 °C, Humidity: 0.0047 g-water/g-dry air, velocity: 2.7 m/sec

integral diffusion coefficient. Crank³⁾ has shown that \overline{D} provides a reasonable approximation to

$$\overline{D} = (1/\omega_{A0}) \int_{0}^{\omega_{A0}} D(\omega_A) d\omega_A \tag{28}$$

where 0 to ω_{A0} is the concentration range existing in the sheet during the experiment. By calculating values of \overline{D} for each of a series of sorption experiments, a graph showing $\overline{D}\omega_{A0}$ as a function of ω_{A0} can be drawn, and graphical differentiation with respect to ω_{A0} gives a first approximation to the relationship between D and ω_A . This first approximation was adopted in the present work.

<u>Results</u> The cast films used for desorption measurements were made by the evaporation of PVA solution films on mercury. They were about $5 \text{ cm} \times 12 \text{ cm}$ in scale and $10^{-2}-5 \times 10^{-3}$ cm in thickness. From the desorption curves observed, the diffusion of the PVA-aqueous solution is of Fickian type. The deduced values of D are shown in **Fig. 10** as well as those of \overline{D} .

The temperature dependency of D for the high concentration range is somewhat larger than that for the low concentration range. The activation energy was estimated to be about 7.3 kcal/mol.

2. Drying Experiments of Coated Film of PVA Aqueous Solution

Experimental The measuring part of the apparatus used is shown in Fig. 11. Hot air of constant temperature and humidity was fed through the rectangular duct on which an assembly of coated film was put, as shown in Fig. 11. The deflection of the cantilever, 4, caused by the weight change of coated film was converted to an electrical signal by a differential transformer and was recorded continuously. The oil damper was set to minimize the influence of vibration of the static pressure on the weighing. The coating plate, as shown in Fig. 12, was carefully thermal-insulated by keeping the temperature of the upper aluminum plate equal to that of the coated film during the time of drying by an electronic thermo-regulator within a temperature difference of ± 0.1 °C. The base plate for coating of PVA-solution was made of polymethylmethacrylate. The measuring error on weighing the film was within +10 mg.

Results The experimental conditions are listed in **Table 1**. An example of changes of weight and temper-

^{*}The diffusion flux of solvent and then v in Eq.(9) are usually very small in the sorption method. The 2nd term of left hand side of Eq.(9) was neglected in the derivation of Eq.(27).



ature is shown in **Fig. 13**. **Figure 14** shows the drying characteristic curves observed. The drying process can be divided into two periods, that is, the constant and the decreasing drying rate period. With regard to the drying rate characteristic curve during the decreasing period, it can be recognized that the curve changes from convex for a thinner film to concave with increasing film thickness, irrespective of the same initial concentrations.

3. Discussion of Drying Mechanism

Formulation of drying equations Let us consider the drying process of film as shown in **Fig. 15**, where the origin is taken at the bottom of the film. Assuming that the temperature distribution is negligibly small because of the film being very thin and that there is no convective flow in the film because of the high viscosity of the solution, we can obtain the following set of equations to represent the drying process of coated film.

Elimination of v from Eqs.(12) and (13) gives the following mass transfer equation.

$$\frac{\partial \omega_A}{\partial t} + \frac{2D}{\omega_A + \hat{\omega}} \left(\frac{\partial \omega_A}{\partial z}\right)^2 = \frac{\partial}{\partial z} \left(D \frac{\partial \omega_A}{\partial z}\right) \quad (29)$$

Initial conditions:

at
$$t=0$$
, any $z: \omega_A = \omega_{A0} = \text{const.}$ (30)

at
$$t=0$$
 : $s=s_0$ (31)

Boundary conditions:

at
$$z=0$$
 (bottom), any $t: \frac{\partial \omega_A}{\partial z}=0$ (32)

at
$$z=s(t)$$
 (surface), any t :

$$-\frac{\rho D\hat{\omega}}{\omega_{A}+\hat{\omega}}\cdot\frac{\partial \omega_{A}}{\partial z}=k_{g}(p-p_{a}) \qquad (33)$$

$$-\frac{\rho D\hat{\omega}}{\omega_A + \hat{\omega}} \cdot \frac{\partial \omega_A}{\partial z} = -\rho_A^* \frac{ds}{dt}$$
(34)

where

$$D = D(\omega_A, \theta) \tag{35}$$

$$p = p(\omega_{A}, \theta) \tag{36}$$

Eq.(33) is derived by applying Green's theorem to Eq.(9), taking account of Eq.(32), and setting v=0 at t=0.

On the other hand, the heat transfer equation de-

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Fig. 14 Drying characteristic curves of coated film



Fig. 15 Drying model of coated film

termining the temperature of the film is given as

$$\{W_s c_s + W(c_p + c_A w)\} \frac{d\theta}{dt} - r_A W \frac{dw}{dt}$$

$$= h_g(\theta_a - \theta)$$
(37)

The following replacements

$$\begin{array}{l} x = z/s, y = (\omega_{A} - \omega_{Ae}) / (\omega_{A0} - \omega_{Ae}), S = s/s_{0} \\ K = D/s_{0}^{2}, V = v/s_{0}, \hat{y} = (\hat{\omega} + \omega_{Ae}) / (\omega_{A0} - \omega_{Ae}) \end{array} \right\}$$
(38)

convert Eqs.(29)-(34) and (37) to Eqs.(39)-(45).

$$\frac{\partial y}{\partial t} - \frac{x}{S} \cdot \frac{dS}{dt} \cdot \frac{\partial y}{\partial x} + \left(\frac{2K}{y+\hat{y}}\right) \frac{1}{S^2} \left(\frac{\partial y}{\partial x}\right)^2 = \frac{\partial}{\partial x} \left(K \frac{\partial y}{\partial x}\right)$$
(39)

Initial conditions:

at
$$t=0$$
, any x : $y=1$ (40)

at
$$t=0$$
: $S=1, \quad \theta=\theta_w$ (41)

Boundary conditions:

а

at
$$x=0$$
, any t : $\frac{\partial y}{\partial x}=0$ (42)

$$t x =$$
, any t :

$$-\frac{\hat{\omega}\rho K}{(y+\hat{y})S} \cdot \frac{\partial y}{\partial x} = \frac{k_g}{s_0} (\rho - p_a)$$
(43)

$$\frac{k_g}{s_0}(p - p_a) = -\rho_A^{\circ} \frac{dS}{dt}$$
(44)

$$\{W_{s} c_{s} + c_{p} s_{0}(\rho_{0} - \rho_{A0}) + c_{A} s_{0}(\rho_{A0} - \rho_{A}^{\circ})$$

$$+c_A s_0 \rho_A^{\circ} S\} \frac{d\theta}{dt} - r_A \rho_A^{\circ} s_0 \frac{dS}{dt} = h_g(\theta_a - \theta) \quad (45)$$

Numerical solution Eqs.(39) and (45) were solved

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Fig. 16 Diffusion coefficients of PVA aqueous solution

simultaneously with the boundary conditions, Eqs. (40)–(44), to give the calculated results of the drying process of the coated film, as described below.

Figure 16 shows the diffusion coefficients observed at 25 °C in the whole concentration range. The $\ln D$ was represented by a polynomial expression of 7th degree with respect to concentration, ω_A (see **Appendix**). The Arrhenius equation having $\Delta E = 7.3$ kcal/mol was adopted to estimate the temperature dependency of the coefficients.

The equilibrium vapor pressure of water on the PVA aqueous solution was expressed by the formula

$$p(\omega_A, T) = p_{s,T} \cdot a(\omega_A) \tag{46}$$

Where $a(\omega_A)$ is the activity at the concentration of ω_A and approximately assumed to be independent of temperature over a small range of temperature, and was numerically represented by a polynomial expression of 6th degree with respect to concentration by using Sano and Nishikawa's data¹² (see **Appendix**). $p_{s,T}$ is the saturated vapor pressure of water.

The numerical calculation was done by the finitedifference method, in which Δt and Δx were 2.5–5.0 sec and 0.1, respectively. The numerical solutions of the set of equations are shown in Figs. 13, 14 and 17. An example of the calculated results representing the changes of water content distribution and film thickness with time are shown in Fig. 17 for Run 117. As shown in Fig.13, calculated film temperature and weight were in fairly good agreement with the values observed. Values for critical water content coincided with each other too, but there were somewhat appreciable discrepancies between those of the characteristic drying rate curve, as shown in Fig. 14. These discrepancies, especially in the low water content range, may be due partly to the crystallization occurring in the high concentration range of polymer, which may affect both diffusion coefficient and equilibrium vapor pressure of solvent, although these effects could not be quantitatively estimated yet, and partly to the measuring methods of diffusion coefficient mentioned at 1.3, which neglect the influence of volumetric shrinkage assuming a small change of concentration of the system. In spite of these



Fig. 17 Calculated distributions of water concentration

discrepancies, the calculated curves were similar to the observed ones as a whole.

Conclusion

Drying of coated film of polyvinylalcohol aqueous solution was studied experimentally and theoretically to determine the change of distributions of local solvent concentration and temperature of film during drying.

Measurements of diffusion coefficient of the PVAwater system were performed in the whole range of concentration. A new method for measurement in the middle range is proposed.

A set of drying equations taking account of the volumetric shrinkage accompanying the evaporation of solvent was formulated and numerically solved using the observed diffusion coefficients.

The calculated results were compared with the experimental ones obtained from drying experiments of coated film of PVA aqueous solution.

The agreement between them shows the reliability of the diffusion coefficient observed and the theoretical treatment proposed in the present work.

Appendix

Diffusion coefficient

$$D_{25^{\circ}\mathrm{C}}(\omega_A) = \exp\left\{\sum^{\circ} (1 - \omega_A)^{n-1} F_n\right\}$$
(A-1)

 $F_n(n=1, 2, ..., 8): -14.20662, 0.7050937, -92.66516, 718.8218, -2233.989, 3310.831, -2341.191, 627.7167$

Activity of water vapor pressure

at
$$\rho_B / \rho_B^{\circ} \le 0.572$$
 : $a = 1$ (A-2)

at
$$\rho_B/\rho_B^{\circ} > 0.572$$
 : $a = \sum_{n=1}^{l} (\rho_B/\rho_B^{\circ})^{n-1} F'_n$ (A-3)

 $F'_n(n=1, 2, ..., 7): -6.000924, 33.63109, -51.77314, 31.54351, -36.5868, 64.65406, -35.46261$

Acknowledgment

The authors are grateful to Mr. Mamoru Tamai and Mr. Toshiteru Izumi for their assistance in the experimental work, and to Kuraray Co., Ltd. for supplying samples of polyvinylalcohol. Numerical calculations were done in the Data Processing Center of Kyoto University, and partially supported by Grant-in-Aid for Scientific Research from the Ministry of Education, Japan.

Nomenclature

b	= one half of film thickness	[cm]
с	= heat capacity	$[cal/g \cdot ^{\circ}C]$
D	= mutual diffusion coefficient in PVA-water	system
		$[cm^2/sec]$

D	= integral diffusion coefficient [cm ² /sec]
d	= interval distance between optical wedge [cm]
h_g	= heat transfer coefficinet at film surface
	$[cal/cm^2 \cdot sec \cdot °C]$
K	$= D/s_0^2$ [1/sec]
k_g	= mass transfer coefficient at film surface
	$[g/cm^2 \cdot sec \cdot mmHg]$
L	= distance from head of wedge to observed point
	(cf. Fig. 8)
M_t	= amount of diffusant at time t [g]
M_{∞}	= amount of diffusant in equilibrium state [g]
n	= refractive index of PVA solution [—]
þ	= partial pressure of water vapor at film surface
	[mmHg]
p_a	= partial pressure of water vapor in hot air [mmHg]
R	= 1.987 (gas constant) [cal/g-mole·°K]
rA	= latent heat of vaporization of water [cal/g]
S	= dimensionless thickness of film, s/s_0 []
5	= thickness of film [cm]
T	= absolute temperature or time $[^{\circ}K]$, [sec]
t	= time [sec]
V	$= v/s_0 $ [1/sec]
v	= velocity of mass center [cm/sec]
W	= mass of dried-up film [g]
W_{s}	= mass of coating plate [g]
w	= averaged water content of film [g-water/g-polymer]
x	= dimensionless distance, z/s [—]
y	= dimensionless mass fraction of solvent
	$(\omega_A - \omega_{Ae}) / (\omega_{A0} - \omega_{Ae}) \qquad []$
ŷ	$= (\mathbf{\omega} + \mathbf{\omega}_{Ae})/(\mathbf{\omega}_{A0} - \mathbf{\omega}_{Ae}) \qquad []$
z	= distance [cm]
θ	= temperature or wedge angle [°C], [radian]
Ω	= dimensionless mass fraction
	$(\omega_A - \omega_{A2})/(\omega_{A1} - \omega_{A2}) \qquad \qquad []$
ρ	= density [g-solution/cm ³ -solution]
	· •••; · · · •

 ρ_A , ρ_B = concentration of solvent, polymer respectively

 $\begin{array}{ll} \left[g/cm^{3}\text{-solution} \right] \\ \rho_{A}^{\bullet}, \ \rho_{B}^{\bullet} & = \text{density of pure solvent, polymer respectively } \left[g/cm^{3} \right] \\ \sigma & = \text{length of shrinkage of film} & [cm] \\ \omega & = \text{mass fraction} & [--] \\ \hat{\omega} & = \rho_{A}^{\bullet} / (\rho_{B}^{\bullet} - \rho_{A}^{\bullet}) & [--] \end{array}$

<Subscripts>

	1
\boldsymbol{A} .	= solvent (water)
а	= hot air
В	= polymer (PVA)
е	= equilibrium
Þ	= polymer (PVA)
5	= coating plate
w	= wet bulb temper

w = wet bulb temperature 0 = initial value

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ESTIMATION OF THE RESIN PHASE DIFFUSIVITY IN ISOTOPIC ION EXCHANGE^{*}

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Resin-phase diffusivity in isotopic ion exchange was measured by the single-particle method.

The effect of resin diameter, the degree of crosslinking and the concentration and valence of ionic species on resin-phase diffusivity were studied with a macroscopic model by which the diffusivity may be predicted. From these results, the estimating equation of resin-phase diffusivity for sulfonated styrene type resin in the range of the degree of crosslinking 3–16% was obtained.

1. Introduction

The diffusivity in an ion exchange resin phase is an important physical property when the rate of isotopic ion exchange or ion exchange between different ions is predicted.

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Measurements of resin-phase diffusivity have been made by many investigators^{1-4,6-10}. However, the results obtained are different, even in the case of the same sulfonated polystyrene resin, and the estimating equations^{8,10} for resin-phase diffusivity which have been reported are limited in applicability and flexibility. Accordingly, at the present stage it is very difficult to estimate resin-phase diffusivity.

In this work, to establish an estimating method for resin-phase diffusivity, the diffusivities of several ionic species were measured in experiments of isotopic ion exchange conducted by the single-particle method⁵⁾.

^{*} Received on May 7, 1973

Presented at the 34th Annual Meeting at Tokyo, 1969 and the 38th Annual Meeting of The Soc. of Chem. Engrs., Japan, at Tokyo, 1973 〒591 堺市百舌烏梅町4丁