

PHYSICAL ABSORPTION OF OXYGEN IN LAMINAR FALLING FILMS OF DILUTE POLYMERIC AQUEOUS SOLUTIONS

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Abstract— Diffusion coefficients of oxygen in three dilute polymeric aqueous solutions (sodium carboxymethyl cellulose, hydroxyethyl cellulose, polyvinyl alcohol) were measured under flowing conditions, and the influence of shear rate on diffusivity was investigated. The rheological properties of the three polymeric solutions were determined using a Couette-Hatschek viscometer. The absorption experiment was made in a wetted-wall column which was made of a stainless steel tube, and was 16.5mm, 55mm in outside diameter and effective height respectively. The concentration of the physically absorbed oxygen was measured using Winkler titration method. Diffusivity enhancement was observed in the sodium CMC which was the most viscous of solutions experimented with in this study.

INTRODUCTION

Physical absorption of a gas by a liquid has long been studied both theoretically and experimentally, because it has been applied to modern process industries involving heat and mass transfer. Previously many investigators made a study of absorption of a gas into a pure liquid, especially in water[4,5,9,12-14]. However, much attention has been paid to the absorption into polymeric solutions recently. It is mainly because the absorption phenomena in polymeric solutions some of which show non-Newtonian rheological behaviors cannot be often explained by the previous investigations[1,3,8,10,20,24].

Also conflicting results were often reported about the effect of polymer-addition into a liquid which absorbs a gas in the physical absorption; diffusivity reduction or enhancement. In general, the more viscous a liquid is, the lower the diffusion coefficient is.

But it is often reported that though the apparent viscosity of a polymeric solution is much larger than that of the pure liquid, and that though a chemical reaction doesn't exist within the system of the polymeric solution and an absorbed gas, the diffusivity of the former is larger than that of the latter. In addition, the effect of shear rate on the diffusivity in a polymeric solution has been studied, but the experimental results have been inconsistent. Hence, the two main objectives of this study

are to investigate the effect of polymers added into a liquid on the diffusivity and the dependence of the diffusivity on shear rate in several polymeric aqueous solutions.

To achieve such purposes, a wetted wall column was used because its hydrodynamic behaviors are well known.

THEORY

Derivation of the diffusion equation

In a binary system, mass balance on a component, say A, yields;

$$\partial C_A / \partial t = -\nabla \cdot C_A \mathbf{v} + D \nabla^2 C_A + r_A \quad (1)$$

For the steady state physical absorption, it reduces to Eq. (2)

$$\mathbf{v} \cdot \nabla C_A = D \nabla^2 C_A \quad (2)$$

Because a liquid film thickness is much smaller than the outer diameter of a wetted wall column, the curvature of a liquid film can be neglected. As the Peclet number of the system is much smaller than 100, the axial diffusion term can be neglected[19]. The Eq. (2) can then be reduced to

$$v_y \partial C_A / \partial y = D \partial^2 C_A / \partial x^2 \quad (3)$$

And the velocity distribution can be expressed in general

$$v_y = v_1 \left\{ 1 - \left(\frac{x}{\delta} \right)^{\frac{n+1}{n}} \right\} \quad (4)$$

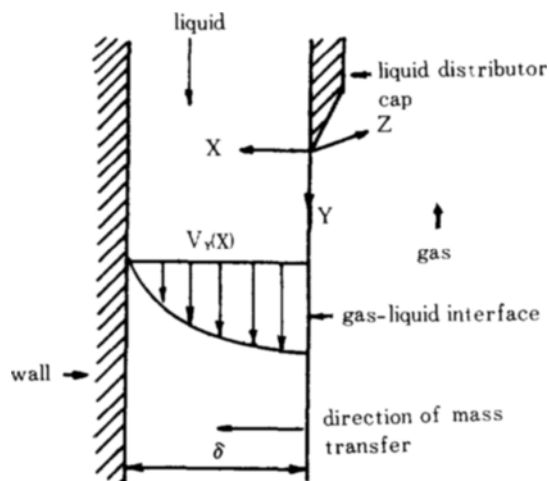


Fig. 1. Physical model and coordinate system

By combining Eqs. (3) and (4) and by introducing dimensionless variables, Eq. (5) may be obtained.

where $\{1 - X^{(n+1)/n}\} \partial \theta / \partial \xi = \partial^2 \theta / \partial X^2$ (5)
 $X = x/\delta$, $\theta = (C - C_{in}) / (C^* - C_{in})$,
 $\xi = Dy/v_i \delta^2$ (6), (7), (8)

The appropriate boundary conditions are as follows.

$$\theta = 1 \text{ at } X = 0, \quad \partial \theta / \partial X = 0 \text{ at } X = 1, \quad \theta = 0 \text{ at } \xi = 0 \quad (9)$$

Mashelkar et al. [15] solved the above equation using orthogonal collocation technique. However, in this study as the degree of saturation is very low, the boundary conditions of "penetration theory" can be sufficiently satisfied.

$$\theta = 1 \text{ at } X = 0, \quad \theta = 0 \text{ at } X = \infty, \quad \theta = 0 \text{ at } \xi = 0, \quad (10), (11), (12)$$

The following solution can be obtained using the method of combination of variables.

$$\theta = \operatorname{erfc}(X/2\sqrt{\xi}) \quad (13)$$

The mass flux at the interface can be calculated as follows.

$$N_{Ax}(y) \big|_{x=0} = -D \partial C_A / \partial x \big|_{x=0} = -(D/\delta) (C^* - C_{in}) \partial \theta / \partial X \big|_{x=0} \quad (14)$$

From Eq. (14), the total absorption rate can be calculated.

$$\dot{M}_A = \int_0^h \int_0^{2\pi} N_{Ax} \big|_{x=0} dz dy = 2\sqrt{\pi} (C^* - C_{in}) d \sqrt{D v_i h} \quad (15)$$

In the meantime, the shear rate at the wall can be obtained from Eq. (4).

$$\dot{\gamma}_{wall} = (n+1)/n \cdot (v_i/\delta) \quad (16)$$

Eq. (16) can be rearranged as Eq. (17)

$$\dot{\gamma}_{wall} = \{(2n+1)/n\}^{(2n+1)^{-1}} (\rho g/K)^{2/(2n+1)} \Gamma v_i^{(2n+1)^{-1}} \quad (17)$$

Determination of rheological properties (K,n)

When an outer cylinder is stationary, and an inner one rotates at ω , the momentum balance reduces to Eq. (18).

$$\partial (r^2 \tau_{r\theta}) / \partial r = 0 \quad \text{or} \quad r^2 \tau_{r\theta} = \text{Const} \quad (18)$$

When a fluid is assumed to follow the power-law model, Eq. (18) becomes Eq. (19).

$$K r^{n+2} \left\{ \frac{\partial}{\partial r} \left(\frac{v_\theta}{r} \right) \right\}^n = \text{Const} \quad (19)$$

From Eq. (19), the velocity profile can be obtained, therefore the shear stress at the inner wall can also be obtained from it [17].

$$\tau_{r\theta} \big|_{r=R_i} = K \left| \beta^{2/n} / (1 - \beta^{2/n}) \right|^n \left(\pi N / 15n \right)^n \quad (20)$$

The following relation of the viscometer used in this study is given by Eq. (21), and so Eq. (22) can be easily obtained

$$F = 637.7 (\phi/100) = 2\pi R_i L \tau_{r\theta} \big|_{r=R_i} \quad (21)$$

$$\log \phi = \log \frac{100 K}{7.4582} \left\{ \frac{\pi \beta^{2/n}}{15n(1 - \beta^{2/n})} \right\}^n + n \log N \quad (22)$$

where ϕ , N represent the dial reading and angular

Table 1. Flow Rates and Hydrodynamic Properties of Polymeric Solutions

Polymer	flow rate ml/sec	n	K × 100	Supplier
0.02% CMC	0.88-3.37	0.97	3.74	Junsei Chemical
0.05% CMC	0.63-3.28	0.97	5.08	Co. (Japan)
0.1% CMC	0.74-3.10	0.96	8.51	Extra Pure
0.1% HEC	0.73-3.23	1.0	1.7	Wako Pure
0.2% HEC	0.64-3.47	1.0	2.3	Chemical Industries
0.3% HEC	0.73-3.12	1.0	3.2	(Japan)
0.03% PVA	0.81-3.15	1.0	1.15	Shinyo Pure Chemicals
0.06% PVA	0.78-3.05	1.0	1.08	Co. (Japan)
distilled water	0.80-3.30	1.0	1.0	Practical Grade

velocity of the inner cylinder respectively.

Eq. (22) shows that the values of K and n can be obtained by plotting $\log \phi$ vs. $\log N$.

EXPERIMENT

The overall schematic diagram of the experimental apparatus in the study is shown in Fig. 2. The main equipment, an absorber, is shown in Fig. 3. A polymer solution was pumped into the inner wetted wall column, and discharged into the outer column wall through 12 small holes in a distributor[18].

While the liquid flowing downwards by gravitation, it came into contact with and absorbed oxygen gas which was flowing upwards slowly and was discharged out of the absorber. The oxygen concentration of the polymer solution was measured by Winkler titration method[2,24].

Table 1 shows the flow rate ranges and hydrodynamic properties of polymeric solutions used in the experiment

RESULTS AND DISCUSSION

To determine D experimentally, it is useful to rearrange Eq. (15) as follows.

$$\dot{M}_A = 2f(n) \sqrt{\pi} (C^* - C_{in}) d \sqrt{hD} (\rho g/K)^{(4n+2)^{-1}} (q/\pi d)^{(n+1)/(4n+2)} \quad (23)$$

where

$$f(n) = \sqrt{(2n+1)/(n+1)} \left(\frac{n}{2n+1} \right)^{n/(4n+2)} \quad (24)$$

\dot{M}_A can be easily measured according to Eq. (25)

$$\dot{M}_A = q(C_{out} - C_{in}) \quad (25)$$

Therefore D can be calculated from Eq. (23), (24) and (25). To check the experimental apparatus and procedure, an experiment on distilled water was made first.

Fig. 5 shows the plot of \dot{M}_A vs. $q^{1/3}$. The saturated concentration of oxygen in water was calculated using Henry's law.

$$C^* = (32/18) p_{O_2} / H, \text{ mg}/10^3 \text{ g} \quad (26)$$

The diffusivity of oxygen in distilled water was measured as $1.39 \times 10^{-5} \text{ cm}^2/\text{sec}$ at 16.5°C .

Davidson et al.[7] suggested the following equation on the dependence of the oxygen diffusivity in water on temperature.

$$D \propto e^{-2.179 \times 10^3 \text{ } ^\circ\text{K}/T} \quad (27)$$

According to Eq. (27), the oxygen diffusivity at reference temperature, 20°C , was found to be $1.58 \times 10^{-5} \text{ cm}^2/\text{sec}$.

The diffusivity measured in the study was reliable compared with oxygen-diffusivities reported in many other investigations[6,22,24].

When polymer is added in water, the saturated concentration of oxygen in the solution decreases according as polymer concentration increase. This effect was suggested by Zandi et al.[25] as

$$C_e' = C^* (1 - S/10^5) \quad (28)$$

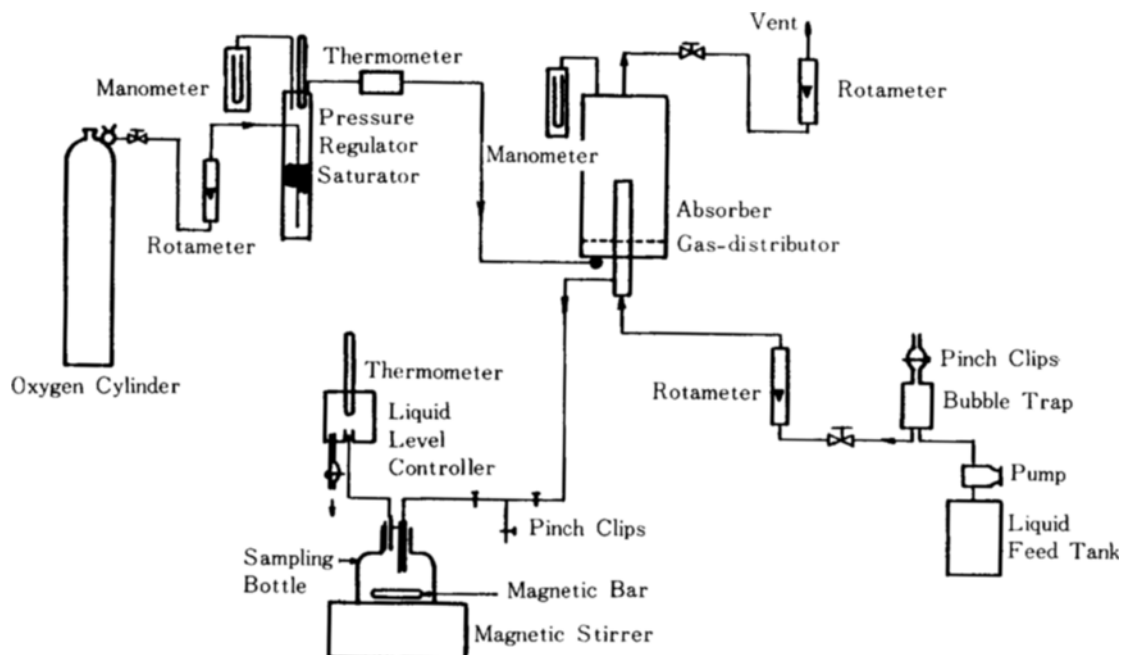


Fig.2. Schematic diagram of experimental apparatus

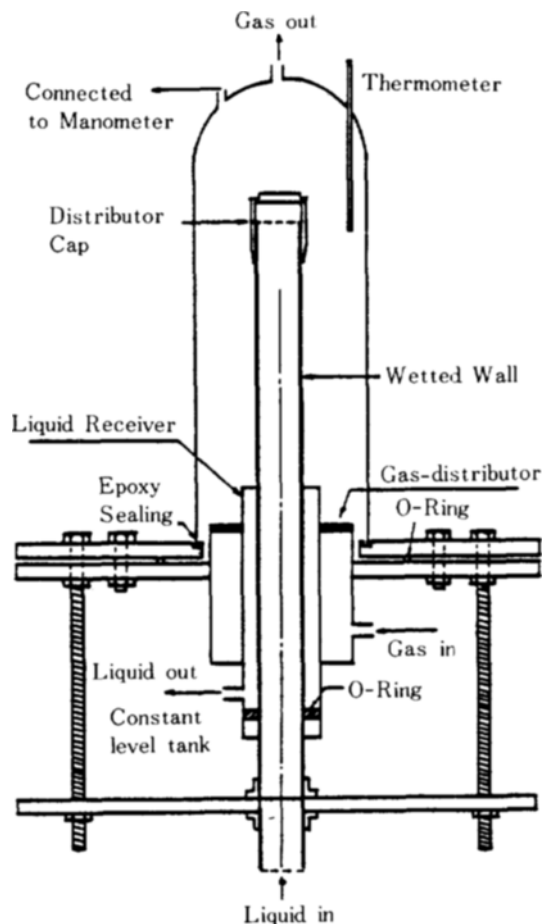


Fig. 3. The absorber

where S is the concentration of dissolved polymer in mg/l. For CMC solutions, the rheological parameters were measured using a Brookfield viscometer.

Fig. 4 shows non-Newtonian behaviors of CMC solutions of three concentrations, 0.02, 0.05, and 0.1 %. And the absorption data measured in the experiment are plotted in Fig. 5.

The results are listed in Table 2.

It was remarkable that the diffusivity in CMC solu-

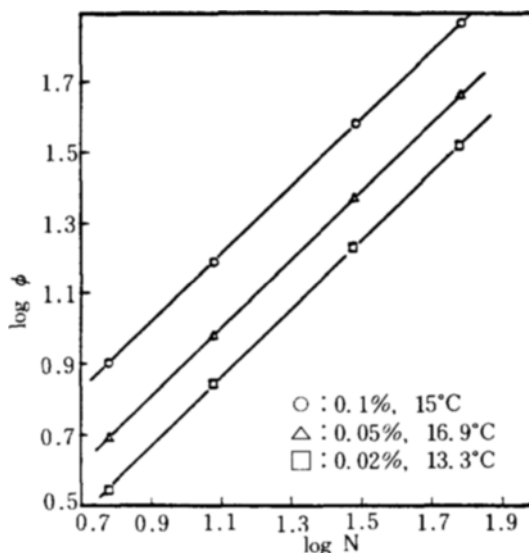


Fig. 4. Rheogram for CMC solution

tions which were more viscous than water was higher than that in water. Mashelkar, et al.[16,21] observed such a diffusivity enhancement in CO_2 -polymeric solution system, too. They suggested that the transport phenomena of diffusion in a macromolecular solution may be different from those in a highly viscous Newtonian solution.

Li, et al.[11] explained the diffusivity enhancement theoretically using the Eq. (29)

$$D_{AS}/D_{AB} = (M_B/M_S)^{1/2} (V_S/V_B)^{1/3} \left(1 - \frac{\Delta H_m}{\Delta H_{v,B}}\right) \quad (29)$$

where subscript "S" means polymer solution, "B" is solvent, and ΔH_m is the enthalpy change in polymer mixing. Eq. (29) shows that if ΔH_m is negative, that is to say mixing process is exothermic, the diffusivity in a dilute polymeric solution may be larger than that in a pure solvent.

HEC solutions were less viscous than CMC solution, showed Newtonian behavior as listed in Table 1.

For HEC solutions, diffusivities decreased according as the concentration of HEC increased as shown in Table 3. It is worth while noticing that though 0.1 %

Table 2. Diffusivities of Oxygen in Sodium CMC Solutions

Solution	Temp. °C of Experiment	Diffusivity $\text{cm}^2/\text{sec} \times 10^5$	Standard Deviation	Diffusivity at 20°C $\text{cm}^2/\text{sec} \times 10^5$	$D/D_{\text{H}_2\text{O}}$ at 20°C	n	$K \times 100$
CMC 0.02%	13.3	1.30	0.043	1.67	1.06	0.97	3.74
CMC 0.05%	15.5	1.41	0.056	1.67	1.06	0.97	5.08
CMC 0.10%	15.0	1.45	0.038	1.76	1.11	0.96	8.51
water	16.5	1.39	0.057	1.58	1.00	1.0	1.0

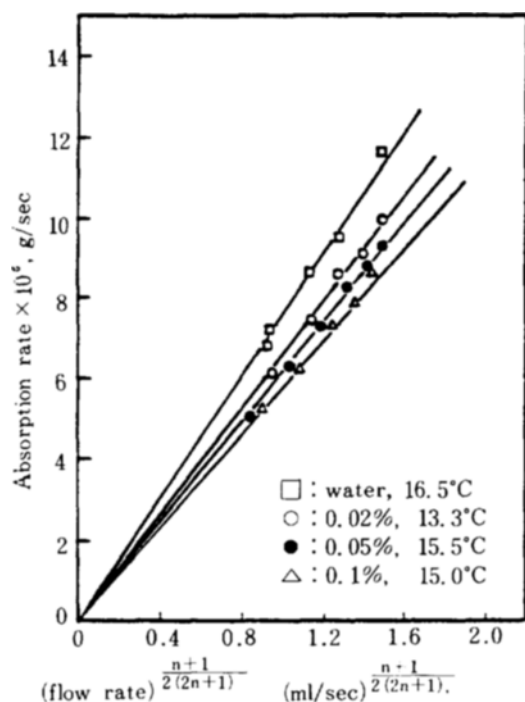


Fig. 5. Absorption rate vs. $(\text{flow rate})^{\frac{n+1}{2(2n+1)}}$ for water and CMC solution

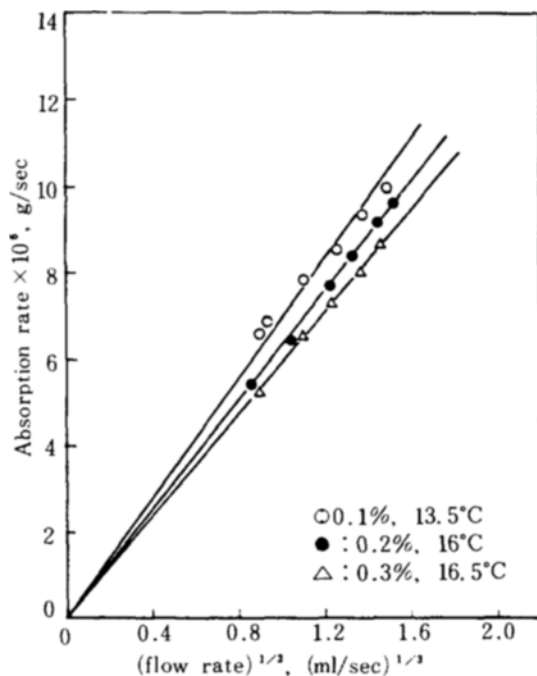


Fig. 6. Absorption rate vs. $(\text{flow rate})^{1/3}$ for HEC solution

Table 3. Diffusivities of Oxygen in HEC Solutions

Polymer, %	D/D_{H_2O} at 20°C	$u \times 100, P$
HEC 01	1.0	1.7
HEC 0.2	0.96	2.3
HEC 0.3	0.87	3.2

Table 4. Diffusivities of Oxygen in PVAS solutions

Polymer, %	D/D_{H_2O} at 20°C	$u \times 100, P$
PVA 0.03	0.87	1.15 (15°C)
PVA 0.06	0.81	1.08 (17°C)

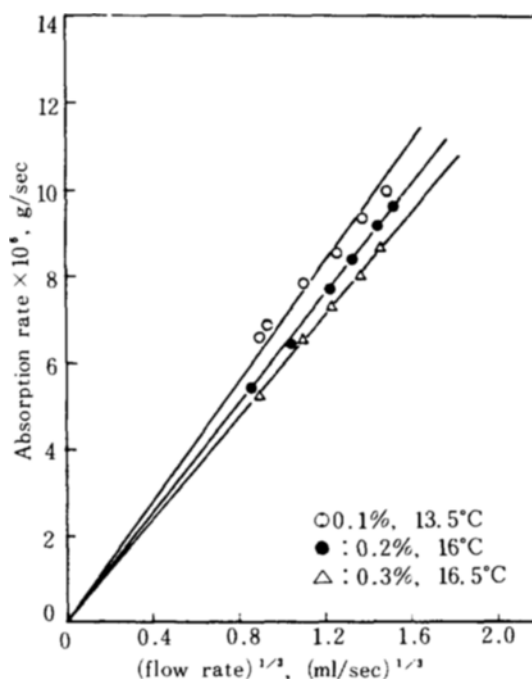


Fig. 7. Gas absorption rate vs. $(\text{flow rate})^{1/3}$ plotted for PVA solution

HEC solution was by 70 % more viscous than water, the diffusivity in that solution was the same as that in water.

PVA solutions showed Newtonian behaviors and were nearly as viscous as water. The diffusivity in PVA solutions decreased as PVA concentration increased, and was lower than that in water.

Fig. 8,9,10 show the effect of shear rate at the wall on diffusivity. Wasan et al.[23] reported that the diffusivity increased with the increase of shear rate, but such a trend was not observed in this study. The diffusivities of oxygen in the polymeric solutions were constant with respect to the change of the shear rate at the wall in the studied range of the flow rate of the solutions.

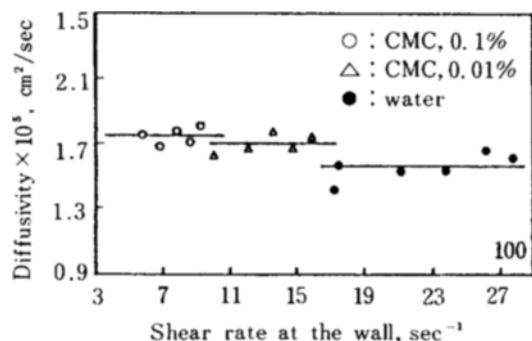


Fig. 8. Diffusivity vs. shear rate at the wall

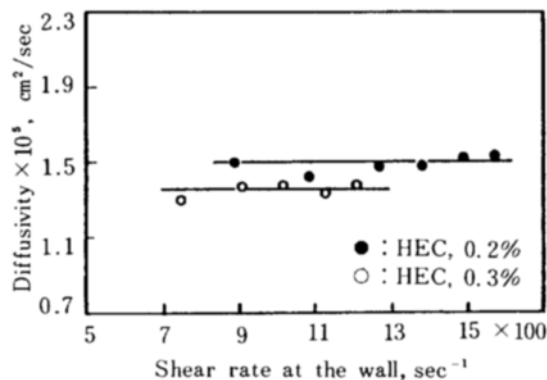


Fig. 9. Diffusivity vs. shear rate at the wall

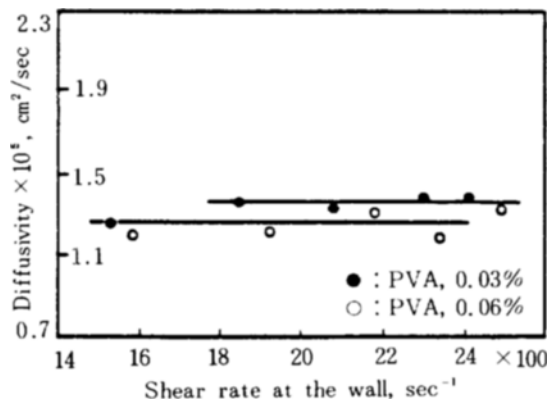


Fig. 10. Diffusivity vs. shear rate at the wall

CONCLUSION

1. The diffusivities of oxygen in distilled water and three dilute polymeric aqueous solutions flowing as thin film were measured, and the following facts were found:
 - a. The diffusivity of oxygen in water at 20°C was $1.58 \times 10^{-5} \text{ cm}^2/\text{sec}$.
 - b. The diffusivity of oxygen in sodium CMC solution

was higher than that in distilled water, and nearly constant in the range of the CMC concentration studied.

- c. The diffusivity of oxygen in HEC solution was the same as or lower than that in distilled water, and decreased as HEC concentration increased.
- d. The diffusivity of oxygen in PVA solution was lower than that in distilled water, and decreased as PVA concentration increased.

2. The diffusivity of oxygen in dilute polymeric aqueous solutions depended mainly on type and concentration of polymer, but the apparent viscosity of the solutions was not a dominant factor to govern the diffusivity.

3. Diffusivity was constant with respect to the change of the shear rate at the wall in the studied range of flow rate of solutions.

NOMENCLATURE

- C^* : interfacial liquid concentration, g/cc
 C_e' : saturated concentration in aqueous solution, g/cc
 C_{in} : inlet liquid concentration, g/cc
 C_{out} : outlet liquid concentration, g/cc
 d : diameter of wetted wall column, cm
 D : molecular diffusion coefficient, cm^2/sec
 $\text{erf}(a)$: complementary error function
 g : gravitational acceleration, cm/sec^2
 h : height of a wetted wall column, cm
 ΔH_m : enthalpy change in polymer mixing, cal/mole
 $\Delta H_{v,g}$: vaporization enthalpy change of solvent, cal/mole
 K : consistency index, $\text{dyne sec}^n/\text{cm}^2$
 L : length of a bob in the Brookfield viscometer, cm
 M : gas absorption rate, g/sec
 M_B : molecular weight of solvent, g/mole
 M_S : molecular weight of polymer solution, g/mole
 n : power law index, dimensionless
 N : round per minute, min^{-1}
 N_A : mass flux, $\text{g}/\text{cm}^2\text{-sec}$
 $N_{A_{x=0}}$: mass flux at the gas-liquid interface, $\text{g}/\text{cm}^2\text{-sec}$
 Pe : Peclet number defined by $4\Gamma/\rho \cdot D$, dimensionless
 q : liquid flow rate, ml/sec
 r_A : chemical reaction rate, g/ml-sec
 Re : Reynolds number defined by $\frac{4\Gamma}{\mu}$, dimensionless
 Ri : radius of a bob, cm
 Ro : radius of a cylinder, cm
 r : radial coordinate, cm
 S : concentration of dissolved polymer, mg/l
 \mathbf{V} : velocity vector, cm
 V_B : molar volume of solvent, cc/mole

v_i : interfacial velocity in y-direction, cm/sec
 V_S : molar volume of polymeric solution, cc/mole
 v_y : y-directional velocity, cm/sec
 x : distance from the interface, cm
 X : dimensionless distance defined by x/δ , dimensionless
 y : coordinate parallel to the direction of flow of liquid, cm
 z : coordinate perpendicular to x and y , cm

Greek Letters

δ : average thickness of film layer on the wall, cm
 I_V : liquid loading in volume, ml/sec·cm
 μ : viscosity, g/cm·sec
 ρ : density, g/ml
 θ : dimensionless concentration defined by $(C-C_{in})/(C^*-C_{in})$
 ζ : dimensionless length defined by $yD/v_i \delta^2$
 ϕ : dial reading in the Brookfield viscometer
 β : ratio defined by R_o/R_i
 τ_{θ} : component of the stress tensor in cylindrical coordinate
 ω : angular velocity of a bob, sec⁻¹
 $\dot{\gamma}$: rate of shear, sec⁻¹

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