

LITERATURE CITED

- Bellman, R., R. E. Kalaba, and J. A. Lockett, Numerical Inversion of the Laplace Transform, American Elsevier, New York (1966).
- Dubner, H., and J. Abate, "Numerical Inversion of Laplace Transforms by Relating them to the Finite Fourier Cosine Transform," *J. Assoc. Comput. Mach.*, **15**, 115 (1968).
- Gautschi, W., "Recursive Computation of the Repeated Integrals of the Error Functions," *Math. Comp.*, **15**, 227 (1961).
- Krylov, V. I., and N. S. Skoblya, Handbook of Numerical Inversions of Laplace Transforms, Israel Program for Scientific Translations, Daniel Davey, Jerusalem (1969).
- Rosen, J. B., *J. Chem. Phys.*, **20**, 387 (1952).
- Salzer, H. E., "Tables for the Numerical Calculation of Inverse Laplace Transform," *J. Math and Phys.*, **37**, 89 (1958).
- , "Additional Formulas and Tables for Orthogonal Polynomials Originating from Inversion Integrals," *ibid.*, **40**, 72 (1961).
- Semerciyan, Mikayel, Ph.D. dissertation, Northwestern Univ., Evanston, Illinois (1972).
- Sy, F., and E. N. Lightfoot, "Transient Creeping Flow Around Fluid Spheres," *AIChE J.*, **17**, 177 (1971).
- Sy, F., J. W. Taunton, and E. N. Lightfoot, "Transient Creeping Flow Around Spheres," *AIChE J.*, **16**, 386 (1970).

Manuscript received December 8, 1971; revision received April 27, 1972; paper accepted April 29, 1972.

Mass Transfer into Dilute Polymeric Solutions

D. T. WASAN, M. A. LYNCH, K. J. CHAD, and N. SRINIVASAN

Department of Chemical Engineering
Illinois Institute of Technology, Chicago, Illinois 60616

Mass transfer into dilute polymeric solutions was studied by using a short wetted-wall column. Oxygen was absorbed into thin films of water and aqueous polymeric solutions. The polymer systems studied included dilute solutions of carboxymethylcellulose, polyethylene oxide, Carbo-pol, and Cyanamer. All of the above systems were moderately non-Newtonian with power law indexes less than unity. Methocel (a Newtonian fluid with a power law index of one) was also studied. The flow of liquid films was well within the laminar flow regime.

The rheological properties of these solutions as well as equilibrium solubility of oxygen in these solutions were determined. In all of the polymer systems studied except Polyox the equilibrium solubility of oxygen decreased with an increase in polymer concentration. In Polyox solutions, however, the equilibrium solubility of oxygen increased with an increase in polymer concentration.

For all of the systems investigated (including Polyox) the mass transfer coefficient for absorption of oxygen at a given flow rate decreased with an increase in polymer concentration. The mass transfer coefficient was highest for water at all flow rates.

The diffusivity of oxygen in all of the systems considered except Polyox was lower than that in water. This was attributed to the increased viscosity of the polymeric solutions. The diffusivity of oxygen in Polyox solutions was higher than it was in water. This was found to be due to the complex chemical reactions which occur in this system. In all of the pseudoplastic systems studied the diffusivity of oxygen increased with increasing wall shear rate (decreasing viscosity).

The diffusive transport rates of low molecular weight solutes such as gases in polymeric or macromolecular solutions and colloidal suspensions are of great interest not only in the chemical industry but also in processes involving biological media. A number of investigators have reported data on the diffusion of low molecular weight solutes in both aqueous and nonaqueous media (2 to 5, 8, 9, 13 to 21, 23, 27, 28, 30, 32, 36, 39). However, there have been only a few determinations of the diffusivity of gases in dilute polymeric non-Newtonian solutions. Furthermore, data on the equilibrium solubility of gases in such systems are scanty. Most recently, Caskey and Barlage (6) presented a review of the existing literature and their new data on the diffusion of carbon dioxide in aqueous solutions of carboxymethylcellulose. The diffusion coeffi-

cient data measured with the liquid laminar jet method were opposite those obtained with a quiescent liquid contactor. These investigators gave no definite reason for this difference in results obtained from the two different experimental techniques. Since different techniques for diffusivity measurements such as laminar jet (2, 10, 27, 39), quiescent liquid contactor (6, 23, 26), rotating disk (13), etc. involve different kinds of fluid mechanical behavior which are not completely understood for non-Newtonian polymeric systems it is apparent that further work is needed before diffusive transport rates in these systems can be accurately discerned from such measurement methods.

In the work presented here, a short wetted-wall column was selected because it is one of the best and simplest pieces of equipment for gas-liquid contacting. The hydrodynamics of such columns have been thoroughly studied and are well understood (29). A second advantage is that the area for mass transfer is constant and known, a feature

M. A. Lynch is with DuPont Co., Louisville, Kentucky. K. J. Chad is with Universal Oil Products, Des Plaines, Illinois. N. Srinivasan is with India Cements Ltd., Madras, India.

not common to most other devices. Furthermore, the flow rates of both the gas and liquid streams can be adjusted to result in well defined streamline flows. These advantages make the mass transfer in these situations amenable to theoretical analysis (7, 11, 19, 27).

THEORETICAL ANALYSIS

Consider the absorption of a slightly soluble gas by the falling liquid film over a short contactor.

Since unsteady state conditions prevail in the liquid, the total amount of gas absorbed per unit area in each time of exposure θ is

$$k_L (c_i - c_1) \theta \quad (1)$$

The penetration theory (15) yields the following equation for the average liquid-side coefficient:

$$k_L = 2 \left(\frac{D}{\pi \theta} \right)^{1/2} \quad (2)$$

where D is the diffusion coefficient.

Knowing the length of the column Z and assuming the interfacial velocity u_s to be constant

$$\theta = Z/u_s \quad (3)$$

Combining Equations (2) and (3) and rearranging results in the following equation:

$$D = \frac{\pi Z k_L^2}{4 u_s} \quad (4)$$

If a rate equation is combined with an overall material balance, the following equation can be derived (4):

$$k_L = \frac{N_a}{(\Delta c)_{lm}} = \frac{q}{A} \ln \frac{c_i - c_1}{c_i - c_2} \quad (5)$$

The velocity profile for non-Newtonian pseudoplastic falling film is developed by considering a momentum balance on the film. The velocity profile is given by the following equation:

$$u_z = \frac{n}{n+1} \left(\frac{\rho g}{m} \right)^{\frac{1}{n}} (\delta)^{\frac{n+1}{n}} \left(1 - \frac{x}{\delta} \right)^{\frac{n+1}{n}} \quad (6)$$

where x is the distance from the free surface of the falling film.

For non-Newtonian films the surface velocity u_s and the average velocity u_0 are given by the following equations:

$$u_s = \frac{n}{n+1} \left(\frac{\rho g}{m} \right)^{\frac{1}{n}} (\delta)^{\frac{n+1}{n}} \quad (7)$$

$$u_0 = \frac{n}{2n+1} \left(\frac{\rho g}{m} \right)^{\frac{1}{n}} (\delta)^{\frac{n+1}{n}} \quad (8)$$

Combining Equations (7) and (8) results in the following equation:

$$u_s = \frac{2n+1}{n+1} u_0 \quad (9)$$

The volumetric flow rate per unit of wetted perimeter Γ is

$$\Gamma = \delta u_0 = \frac{n}{2n+1} \left(\frac{\rho g}{m} \right)^{\frac{1}{n}} (\delta)^{\frac{2n+1}{n}} \quad (10)$$

which yields

$$\delta = \left\{ \frac{\frac{2n+1}{n} \delta}{\left(\frac{\rho g}{m} \right)^{\frac{1}{n}}} \right\}^{\frac{n}{2n+1}} \quad (11)$$

EXPERIMENTAL APPARATUS AND PROCEDURE

Equilibrium Solubility Study

The apparatus was designed to allow accurate measurements of the solubility of oxygen in water and polymer solutions. This was done by using an electric circuit to accurately measure the end point in a Winkler titration.

The apparatus consisted essentially of a 250 ml. Erlenmeyer flask, a burette, and the electric circuit. The circuit used was not the standard amperometric circuit, but the modified amperometric circuit used by Potter and White (25).

Water or polymer solution was mixed while oxygen was bubbled into it from an oxygen cylinder. After bubbling oxygen into the liquid for two hours, a portion was removed and titrated. After bubbling oxygen into the liquid for an additional hour, a second portion was removed and titrated. If the two titrations yielded identical results, the liquid was assumed to be saturated.

The liquid sample withdrawn had to be treated before titration. One ml. of a solution containing 100 g. of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ in 200 ml. of solution was added to the titration sample. One ml. of a solution containing 140 g. of KOH and 30 g. of KI in 200 ml. of solution was also added. After mixing for one minute, 1 ml. of concentrated sulphuric acid was added and the sample was mixed until the precipitate dissolved. At this point three 50-ml. portions were pipetted into Erlenmeyer flasks and each was titrated. These 50 ml. samples were titrated with $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. The end point was reached when the vacuum tube voltmeter registered a voltage drop across the 100 M. OHM resistor. Each ml. of $\text{Na}_2\text{S}_2\text{O}_3$ solution used was equivalent to 200 p.p.m. of dissolved oxygen.

Physical Properties

For the systems studied some physical properties were determined in addition to the solubility of oxygen. The rheological properties are listed in Table 1. In addition, the surface tension was determined with a ring tensiometer. The density was

TABLE 1. CALCULATED RESULTS FROM BROOKFIELD VISCOMETER DATA AT $22.0 \pm 0.5^\circ\text{C}$

Polymer	Conc.	Power Law Index n	Consistency Index m	Apparent viscosity c.p. g/cm (sec)
Polyox	0.001%	0.969	0.0394	5.4
Polyox	0.01%	0.973	0.0650	5.9
Polyox	0.1%	0.967	0.1054	9.7
Polyox	1.0%	0.970	0.4827	45.0
Methocel	0.1%	1.0	0.050	5.0
Methocel	3.93%	1.0	2.00	200.0
CMC	0.06%	0.996	0.050	6.1
CMC	0.10%	0.987	0.061	7.0
CMC	0.5%	0.963	0.101	9.6
CMC	2.0%	0.584	2.41	203.0
Cyanamer*	0.05%	0.952	0.0397	—
Cyanamer	0.5%	—	—	—
Carbopol	0.051%	0.960	0.073	6.8
Carbopol	0.097%	0.951	0.102	9.7
De-ionized water		1.0	0.01	1.0

* Values of m and n are those reported by Wasan and Fischman (37).

also measured. This was done with a Westphal balance. The physical properties of all the systems studied are given in Table 2.

Absorption Study

The apparatus was designed to provide countercurrent contacting of a laminar gas stream with a liquid solvent so that the effect of polymer concentration upon the liquid-side resistance to absorption could be determined. Because the use of a differential absorber was desired, the principle used to determine the mass transfer rate was the measurement of the concentration of gas in the inlet and the outlet liquid streams.

The absorption section was a short, wetted-wall column of the upward slot design reported by Vivian and Peaceman (35). The diameter of the wetted-wall section d was 2.54 cm., and the height of the falling film Z was 3.28 cm. The flow of liquid films was well within the laminar flow regime (maximum $Re_L = 228$).

The oxygen concentrations were measured polarographically by a Beckman oxygen analyzer. The oxygen analyzer indicated the partial pressure of oxygen to be in equilibrium with the gas dissolved in the liquid; hence, from the solubility data, it was possible to obtain the concentration of oxygen in the liquid at a given temperature. The temperature of the liquid was maintained at $22.0 \pm 0.5^\circ\text{C}$. throughout the entire experimental program. The details of the apparatus and procedure are available elsewhere (7, 19).

CMC, Carbopol, Cyanamer, Polyox, and Methocel are general trade names. Their specific names and the names of their manufacturers are given in Table 3.

RESULTS

Solubility Study

The object of this study was to determine if the addition of small amounts of polymer to de-ionized water would affect the solubility of oxygen in these solutions. The performance of the system was checked by gathering data on the solubility of oxygen in de-ionized water. The experimentally determined value of the solubility of oxygen in de-ionized water was calculated by averaging three different experimental runs. The value was found to be 1.38×10^{-6} g.-moles/cu.cm. This value was determined at 22°C . and one atmosphere pressure. The experimentally determined value compares quite well with the value of 1.37×10^{-6} g.-moles/cu.cm. reported by Perry (22). The results of the runs to determine the solubility of oxygen in water and polymeric solutions are shown in Table 4.

Table 4 shows that the solubility of oxygen in any of the polymer solutions is a function of polymer concentration. Addition of any of the polymers except Polyox lowers

TABLE 3. LIST OF CHEMICALS USED

CMC	Sodium carboxymethyl cellulose, medium viscosity, type 4 MH. Hercules Powder Company, Hopewell, Virginia
Carbopol-934	Carboxy polymethylene. B. F. Goodrich Company
Cyanamer P-250	Polyacrylamide. American Cyanamide Company
Polyox	Polyethylene Oxide, WSR-301, blend A-3254. Union Carbide Chemicals Company
Methocel	"Methocel" MC Premium, lot #MMO61681. Dow Chemical Company

TABLE 4. SOLUBILITY OF OXYGEN IN DE-IONIZED WATER AND POLYMER SOLUTION AT 22°C

Polymer	Conc.	Solubility 10^{-6} g moles/cu cm
Water		1.38
CMC	0.06%	1.36
CMC	0.10%	1.36
CMC	0.50%	1.34
CMC	2.0%	1.30
Polyox	0.001%	1.39
Polyox	0.01%	1.45*
Polyox	0.10%	1.51
Polyox	1.0%	1.57
Carbopol	0.051%	1.36
Carbopol	0.097%	1.35
Cyanamer	0.05%	1.36†
Cyanamer	0.50%	
Methocel	0.10%	1.36
Methocel	3.93%	1.33

* Calculated by interpolation.

† Value reported by Chad (6).

the solubility of oxygen in that solution. The addition of CMC lowers the solubility of oxygen 1.4 to 5.8%. The addition of Methocel lowers the solubility of oxygen 1.4 to 3.6%. Carbopol lowers the solubility of oxygen 1.4 to 2.2%.

Unlike the other polymers, the addition of Polyox (commonly used as a drag reducing agent) raises the solubility of oxygen. Adding 0.001% by weight of Polyox raises the solubility of oxygen by 0.7%. The addition of 0.10% and 1.0% by weight of Polyox raises the solubility of oxygen by 9.4 and 13.8% respectively. The validity of these numbers for the solubility of physically absorbed oxygen is questionable. These values are probably values for a combination of physical and chemical absorption.

Polyox is different from all of the other polymers studied in that oxygen will react with an aqueous solution of Polyox (12). Each molecule of oxygen absorbed by the Polyox solution could convert two, one, or zero ether linkages to peroxide linkages. Each peroxide linkage so formed could break down and result in two atoms of oxygen being measured or it may remain intact in which case no oxygen would be measured. Therefore, each molecule (two atoms) of oxygen may result in four, three, two, one, or zero atoms of oxygen being measured. In addition to these spontaneous decompositions, additional peroxide linkages are broken when an electric potential is applied. Both the Beckman oxygen analyzer and the Winkler titration setup employ an electric potential difference in measuring the oxygen concentration.

TABLE 2. PHYSICAL PROPERTIES OF WATER AND POLYMER SOLUTIONS

Polymer	Conc.	Density g/cu cm	Viscosity g/cm (sec)	Interfacial tension dyne/sq cm
Water		1.00	1.0	72.5
Methocel	0.1%	0.997	5.0	56.3
Methocel	3.93%	0.991	200.0	50.8
Polyox	0.001%	0.993	5.4	63.3
Polyox	0.01%	0.993	5.9	63.6
Polyox	0.10%	0.994	9.7	64.0
Polyox	1.0%	0.995	45.0	64.2
CMC	0.06%	0.994	6.1	72.2
CMC	0.10%	0.994	7.0	72.1
CMC	0.13%	0.994	7.9	71.9
CMC	0.50%	0.997	9.6	71.7
CMC	2.0%	1.003	203.0	71.1
Carbopol	0.051%	0.996	6.8	57.2
Carbopol	0.097%	0.995	9.7	55.0

For the above reasons the measured solubility of physically absorbed oxygen may be as much as twice the actual solubility of physically absorbed oxygen (all physically absorbed oxygen reacting and all peroxide linkages being broken). The actual solubility of physically absorbed oxygen can not be higher than the experimentally determined value. But the combined solubility of physically and chemically absorbed oxygen can be higher than the experimentally determined value (not all of the peroxide linkages having been broken by the applied electric potential). Both the amount of peroxide formed and the amount being broken down and registering may be determined by more sophisticated methods. However, they were not used in the present study.

Absorption Study

In this study oxygen was absorbed by falling liquid films in a short wetted-wall column. The effects of polymer concentration, liquid flow rate, and gas flow rate on the liquid-side mass transfer coefficient were determined.

The accuracy of the apparatus was checked by obtaining data on oxygen transport into falling water film. The results of these runs are detailed elsewhere (19). The calculated value of the diffusion coefficient was obtained by averaging the six water runs. The diffusion coefficient of oxygen in deionized water D_{O_2} was found to be 1.87×10^{-5} sq.cm./sec. at 22°C. This value of D_{O_2} is lower than that reported by Vivian and King (34) (2.41×10^{-5} sq.cm./sec.) but compares favorably with the value reported by Arnold (1) (1.8×10^{-5} sq.cm./sec.). Recently Duda and Vrentas (10) established the best value of D_{O_2} as 2.1×10^{-5} sq.cm./sec. at 25°C. It was found by employing the Newtonian laminar jet technique. On the basis of the Nernst-Einstein equation, Duda and Vrentas' (10) value is 1.94×10^{-5} sq.cm./sec. at 22°C. This close agreement demonstrates the validity of using the present apparatus and procedure for analysis of gas absorption data in short wetted-wall columns.

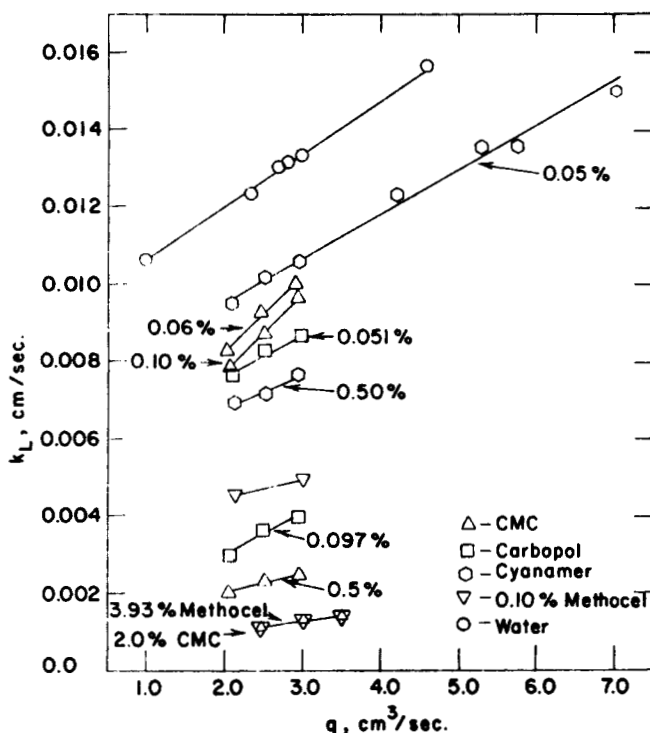


Fig. 1. Liquid-side mass transfer coefficient vs. liquid flow rate for various systems.

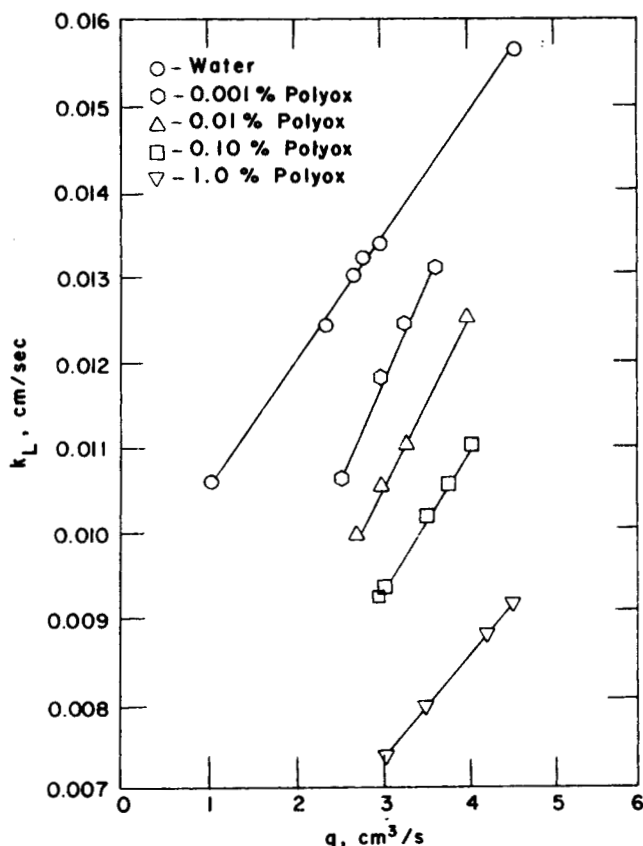


Fig. 2. Liquid-side mass transfer coefficient vs. liquid flow rate for polyox solutions.

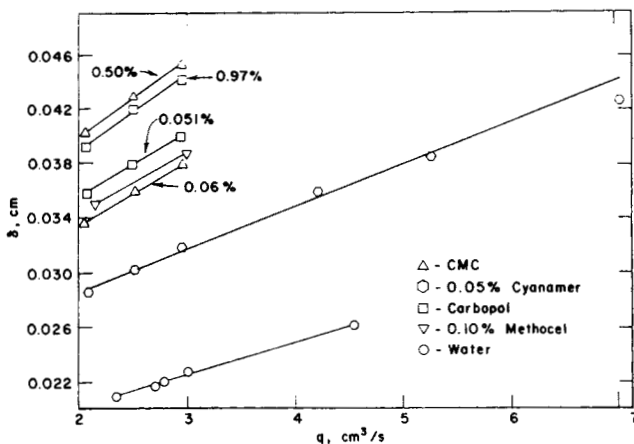


Fig. 3. Film thickness δ as a function of flow rate, q for various systems.

Two water runs were made with spillover of liquid into the gas exit tube to determine the extent to which end effects affect the results in a short wetted-wall column. In the two runs with spillover k_L differed by only 0.8% from the k_L of the runs without spillover. Since the spillover eliminates the end effects (38), this comparison shows that the end effects in this short wetted-wall column are negligible.

The effect of the liquid flow rate q on the liquid-side mass transfer coefficient k_L is shown in Figures 1 and 2. Over the entire flow range the highest liquid-side mass transfer coefficient, at a given volumetric flow rate, was that of water. For all systems studied the liquid-side mass transfer coefficient increased with an increase in liquid flow rate. For any given flow rate k_L decreased with an

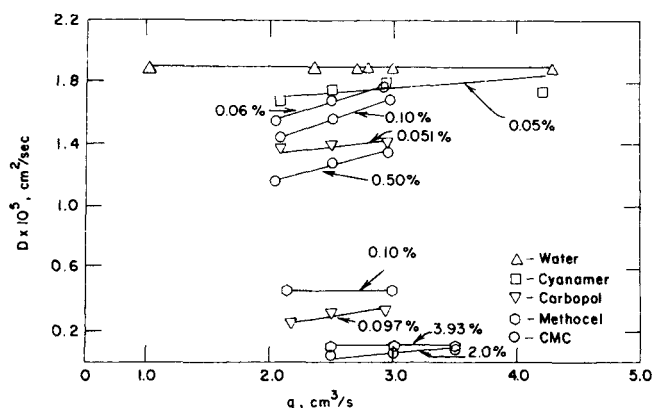


Fig. 4. Diffusivity as a function of flow rate for various systems.

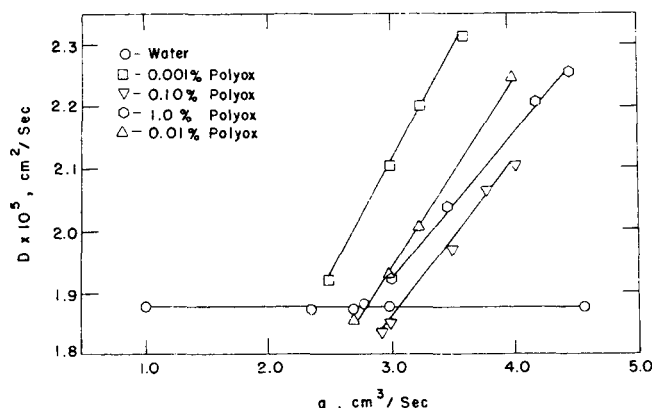


Fig. 5. Diffusivity vs. flow rate for polyox solutions.

increase in polymer concentration; this is most evident in the case of CMC or Polyox.

The hydrodynamic film thickness δ which was computed from Equation (11) increases with increasing flow rate as expected because a greater volume of liquid ($\rho = \text{constant}$) must pass through the column at higher flow rates. Figure 3 which is a plot of δ as a function of flow rate q illustrates this. Figure 3 also shows that, for a given q , δ increases with increasing polymer concentration. This is due to the higher viscosity of the more concentrated solutions. The film thickness varied from 0.0157 to 0.1390 cm, with water having the thinnest film and 3.93% Methocel having the thickest.

Figures 4 and 5 are plots of diffusivity as a function of the flow rate q . For a given flow rate the diffusivity in all polymeric solutions (except Polyox) is less than that in water. Figure 4 also shows that the diffusivity in non-Newtonian fluids (CMC, Carbopol, and Cyanamer) increases as the flow rate increases. The diffusivities for Methocel (a Newtonian fluid for viscosities below 500 c.p.) and water are not functions of flow rate.

Figure 6 is a plot of diffusivity as a function of shear rate at the wall for all of the polymers studied except Polyox. It shows that the diffusivity of oxygen is less in all of the systems than it is in water. It also shows that for non-Newtonian fluids diffusivity is a weak-to-moderate function of shear rate. This is true for Carbopol, Cyanamer, and CMC. But the diffusivities of oxygen in Methocel and water are independent of shear rate. This is because they are both Newtonian fluids. Clough et al. (8) showed that the diffusivity was independent of shear rate for some non-Newtonian systems (among them CMC). In the present study the diffusivity increased with increasing shear rate for all of the non-Newtonian systems (see Fig-

ures 6 and 7) studied (among them CMC). This seems to contradict the findings of Clough et al. (8). However, these investigators conjectured that although the diffusivity in the systems they studied were independent of shear rate, the diffusivity in many non-Newtonian systems should be a function of shear rate.

It should be noted that the power-law model for viscosity applies over the entire range of shear stresses occurring on the wall of the wetted-wall column. The calculation of the shear stress at the wall was based on the relationship for velocity on the wall [Equation (6)] in a power-law liquid. Details of the calculations are presented elsewhere (19).

Table 5 shows the values of the diffusivity of oxygen at zero shear rate as a function of polymer concentration for

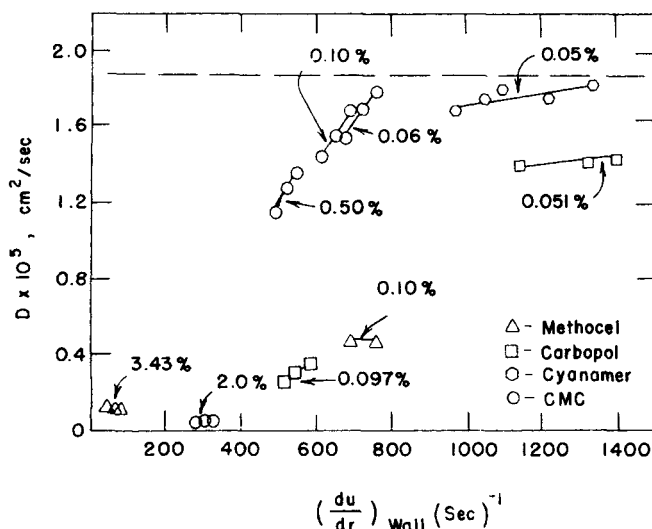


Fig. 6. Diffusivity as a function of shear rate at the wall for various systems.

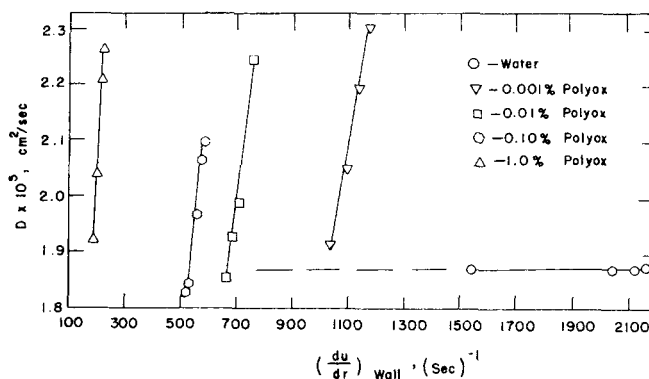


Fig. 7. Diffusivity vs. shear rate at the wall for polyox solutions.

TABLE 5. DIFFUSIVITY AT ZERO SHEAR RATE

Polymer	Conc.	Diffusivity $\times 10^5$ sq cm/sec (at zero shear rate)
Water		1.872
CMC	0.06%	1.180
CMC	0.10%	1.020
CMC	0.50%	0.860
CMC	2.0%	0.020
Polyox	0.001%	1.020
Polyox	0.01%	1.060
Polyox	0.10%	1.105
Polyox	1.0%	1.255

CMC and Polyox. It shows that the diffusivity at zero shear rate decreases as the concentration of polymer increases. Due to the fact that viscosity increases (thereby decreasing mass transfer) as the polymeric concentration increases, these results seem reasonable. Similar results are reported by Quinn and Blair (26) and Caskey and Barlage (6) for the absorption of carbon dioxide in aqueous CMC solution in a quiescent liquid contactor. These results are directly opposite to those reported by Astarita (1965) and interpreted by Metzner (20). Most recently, Caskey and Barlage verified the data reported by Astarita (6). These investigators measured the diffusivity of carbon dioxide in CMC solutions by employing a non-Newtonian laminar jet. They found that the diffusivity increased as the CMC concentration increased. Quinn and Blair (26) pointed out that the high values of diffusivity reported by Astarita (2) may be due to inaccuracies in his experimental technique. However, recent experiments of Caskey and Barlage which virtually substantiate Astarita's data, suggest no such explanation for this system. Previous work in our laboratory (31) was concerned with the measurement of diffusivity of carbon dioxide in aqueous CMC solutions. These measurements, however, lacked the precision of an analytical analysis.

Most recently, Zandi and Turner (39) used the laminar jet technique to measure the molecular diffusivities of oxygen into dilute polymeric solutions. They found that the molecular diffusivity of oxygen in seven different aqueous polymeric solutions including CMC was less than that of water. The only possible exception was one polymer, ET-597 at 1000 mg./l. However, for this case the two batches of polymeric solutions did not yield reproducible results. The results of the present study tabulated in Table 5 (diffusivity decreasing with increasing viscosity due to an increase in polymer concentration) are in agreement with the most recent results obtained by Zandi and Turner (39) for the absorption of oxygen in aqueous polymeric solutions and with the results of many studies on diffusion in solid-liquid (14) and liquid-liquid systems.

Figures 4 and 7 are plots of diffusivity as a function of liquid flow rate and wall shear rate, respectively, for the Polyox solution. These results again show that the diffusivity increases as the flow rate (or the wall shear rate) increases. It also shows that the ratio of diffusivity of oxygen in Polyox to diffusivity of oxygen in water is greater than one. This is due to the chemical reactions which take place in this system (12).

Figure 8 is a plot of diffusivity of oxygen at zero shear

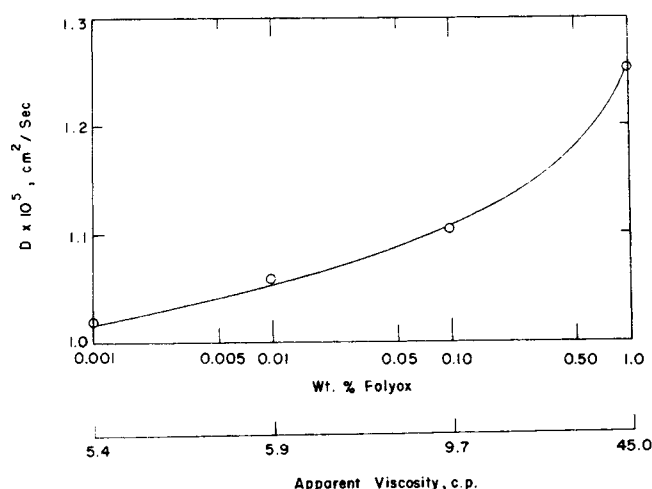


Fig. 8. Diffusivity of oxygen at zero shear rate vs. percent polyox.

rate as a function of Polyox concentration. It shows that the diffusivity of oxygen increases as the concentration of Polyox increases.

In summary, for pseudoplastic fluids such as Cyanamer, CMC, and Carbopol the bulk viscosity increases with decreasing shear rate (liquid flow rate); thus at low shear rates the viscous effects are dominant. Because of this fact and the fact that the shear rates for the polymer solutions were quite low, the ratio of diffusivity of polymeric solution to diffusivity of water was less than one in all of the systems studied except Polyox. The Polyox solutions were also studied at low shear rates, but the ratio of diffusivity of Polyox solution to diffusivity of water was greater than one. Although the higher viscosity of the Polyox solutions tended to impede the mass transfer, this was more than compensated for by the previously mentioned chemical reaction (12). In addition to this peroxide formation a second reaction occurs. In the presence of aqueous Polyox, oxygen will coordinate with any of the transition state elements, cyanide, or a large number of other chemicals which may be present as impurities in the solution (33).

Additionally, 1% Polyox solutions exhibit viscoelasticity (5, 14). Calderbank et al. (15) report data on carbon dioxide dissolution (with no chemical reaction) in 1% Polyox solutions. The mass transfer coefficient of carbon dioxide in Polyox solutions is less than that in water. Their results are consistent with the present observations. Furthermore, as expected, the mass transfer coefficient for carbon dioxide is of the same order of magnitude as for O_2 .

Two runs were made with the addition of acid to Polyox solution. These runs were to determine the effect, if any, of the acid (which was required for clarification of the 1.0% Polyox solution) had on the mass transfer. As indicated elsewhere (19), one of the acid runs was made with $q = 3.50 \text{ cu.cm./sec}$. The flow rate in the other case was 3.0 cu.cm./sec . In both cases the results were identical to runs made without acid.

A series of runs was made with 3.93% Methocel (Newtonian fluid, $n = 1.0$; viscosity = 200 c.p.) and 2.0% CMC (non-Newtonian fluid, $n = 0.54$; apparent viscosity = 203 c.p.) to determine whether mass transfer in a wetted-wall column is affected by the degree of non-Newtonianism of the system. Table 6 compares the data and calculated results for these runs. This table shows that high viscosities impede the mass transfer in CMC and in Methocel to the same extent in each case since the shear rates for the 2% CMC solution were quite low. This is also shown in Figures 1, 2, and 4. Therefore, it seems possible that the mass transfer is affected by the type of polymer and its concentration.

CONCLUSIONS

The conclusions of this study can be summarized as follows:

TABLE 6. COMPARISON OF CALCULATED RESULTS FOR 2.0% CMC AND 3.93% METHOCEL SOLUTIONS

q cu cm/sec	2.0% CMC k_L cm/sec	3.93% Methocel k_L cm/sec	Δk_L
2.50	0.001170	0.001198	2.34%
3.00	0.001289	0.001310	1.60%
3.50	0.001374	0.001418	3.10%

1. For a given liquid flow rate the diffusivity of oxygen in polymeric solutions was lower than that in water in all of the polymeric solutions studied except Polyox.

2. For a given liquid flow rate the diffusivity of oxygen in Polyox solutions was higher than that of water.

3. For all of the non-Newtonian systems studied (including Polyox) the diffusivity of oxygen increased with increasing shear rate (decreasing viscosity). However, additional data are needed at higher shear rates and for highly non-Newtonian polymeric solutions.

4. In all of the polymeric systems studied, except Polyox, the solubility of oxygen decreased with an increase in polymer concentration. However, in Polyox solutions the solubility of oxygen increased with an increase in polymer concentration.

5. The mass transfer rate in Polyox solutions is controlled by the chemical reactions which take place in this system. They prevail over the detrimental effects of viscosity. A kinetic study of the reactions of oxygen with aqueous Polyox solutions needs to be initiated.

6. For a given liquid flow rate the liquid-side mass transfer coefficient k_L decreases with an increase in polymer concentration.

ACKNOWLEDGMENT

This work has been partly supported by the National Science Foundation under Research Grant GK-10756. The authors wish to thank Lalit Gupta for his help.

NOTATION

- A = interfacial area, sq.cm.
 c_i = interfacial concentration, g.-moles/cu.cm.
 c_1 = inlet liquid concentration, g.-moles/cu.cm.
 c_2 = outlet liquid concentration, g.-moles/cu.cm.
 $(\Delta c)_{lm}$ = log-mean concentration, g.-moles/cu.cm.
 D = diffusivity, sq.cm./sec.
 g = acceleration due to gravity, cm./sec.²
 H_L = height of a transfer unit, cm.
 k_L = liquid-side mass transport coefficient, cm./sec.
 m = consistency index, g./cm.(sec.²⁻ⁿ)
 n = power law index (dimensionless)
 N_A = flux, g. moles of gas absorbed per unit of interfacial area per unit time, g.-moles/sq.cm.(sec.)
 q = volumetric flow rate of liquid, cu.cm./sec.
 r = radius of the wetted-wall column, cm.
 Re_L = Reynolds number of liquid phase (dimensionless)*
 t = time, sec.
 u_0 = average velocity of liquid film, cm./sec.
 u_s = interfacial velocity of the film, cm./sec.
 u_z = velocity at any point in the liquid film, cm./sec.
 x = space coordinate in direction normal to the flow
 Z = height of the liquid film, cm.
 z = space coordinate parallel to the direction of flow

Greek Letters

- δ = average thickness of film layer on the wall, cm.
 Γ = volumetric flow rate per unit of wetted perimeter, cu.cm./sec. (cm.)
 μ = viscosity, g./cm. (sec.)

ρ = density, g./cu.cm.

θ = time of contact in penetration theory, sec.

LITERATURE CITED

1. Arnold, J. H., *J. Am. Chem. Soc.*, **52**, 3937 (1930).
2. Astarita, G., *Ind. Eng. Chem. Fundamentals*, **4**, 236 (1965).
3. Barnett, S. M., A. E. Humphrey and M. Litt, *AIChE J.*, **12**, 253 (1966).
4. Berne, E., and M. J. Wei, *Chem. Phys.*, **56**, 103 (1959).
5. Calderbank, P. H., D. S. L. Johnson and J. Loudon, *Chem. Eng. Sci.*, **25**, 235 (1970).
6. Caskey, J. A., and W. B. Barlage, Paper presented at the 72nd National Am. Inst. Chem. Engrs. Mtg., St. Louis, (May, 1972).
7. Chad, K. J., M. S. thesis, Illinois Inst. Technol., Chicago (1968).
8. Clough, S. B., H. E. Read, A. B. Metzner and V. C. Behn, *AIChE J.*, **8**, 346 (1962).
9. Cordier, S., *Pubts. Sci. Tech. Ministere Air (France)*, Note Tech. No. 57 (1956).
10. Duda, J. J., and J. S. Vrentas, *AIChE J.*, **14**, 286 (1968).
11. Emmert, R. E., and R. L. Pigford, *Chem. Eng. Progr.*, **50**, 87 (1954).
12. Goglev, R. S., and M. B. Neiman, *Vysokomolekularnye Soedineniya (Russia)*, **9**, 2083 (1957).
13. Hansford, G. S., and M. Litt, paper presented at Am. Inst. Chem. Engrs. Mtg., New York (1967).
14. Heertjes, P. M., M. H. van Mens, and M. Butaye, *Chem. Eng. Sci.*, **10**, 47 (1959).
15. Higbie, R., *Trans. Am. Inst. Chem. Engrs.*, **31**, 365 (1935).
16. Higdon, W. T., and J. D. Robinson, *J. Chem. Phys.*, **37**, 1161 (1962).
17. Hopper, J. R., M. ChE. thesis, Univ. Delaware, Newark (1964).
18. Li, S. U., and J. L. Gainer, *Ind. Eng. Chem. Fundamentals*, **7**, 435 (1968).
19. Lynch, M. A., M.S. thesis, Illinois Inst. Technol., Chicago (1969).
20. Metzner, A. B., *Nature*, **208**, 267 (1965).
21. Nishijima, Y., and G. Oster, *J. Polymer Sci.*, **19**, 337 (1956).
22. Perry, J. H., *Chemical Engineers' Handbook*, 3rd ed., McGraw-Hill, New York (1950).
23. Plevan, R. E., Ph.D. thesis, Univ. Illinois, Urbana (1965).
24. Ponter, A. B., and G. A. Davies, *Nature*, **210**, 837 (1966).
25. Potter, E. C., and J. F. White, *J. Applied Chem.*, **7**, 309 (1957).
26. Quinn, J. A., and L. M. Blair, *Nature*, **214**, 907 (1967).
27. Scriven, L. E., and R. L. Pigford, *AIChE J.*, **4**, 382 (1958).
28. Secor, R. M., *ibid.*, **11**, 452 (1965).
29. Sherwood, T. K., and R. L. Pigford, *Absorption and Extraction*, McGraw-Hill, New York (1952).
30. Shiotsuka, Tadashi, "Mass Transfer in Non-Newtonian Fluids," Private communication, Dept. of Chem. Eng., Waseda Univ., Japan (1969).
31. Srinivasan, N., M.S. thesis, Illinois Inst. Technol., Chicago (1967).
32. Strobel, G. A., "A Study of Diffusivity into Non-Newtonian Slurries," M.S. thesis, Cornell Univ., Ithaca, N. Y. (1965).
33. Vink, H., "Degradation of Some Polymers in Aqueous Solutions," Supplement, Inst. of Phys. Chem., Univ. of Uppsala, Sweden (1963).
34. Vivian, J. E., and C. J. King, *AIChE J.*, **10**, 220 (1964).
35. Vivian, J. E., and D. W. Peaceman, *ibid.*, **2**, 437 (1956).
36. Wang, J. H., *J. Am. Chem. Soc.*, **73**, 510 (1951).
37. Wasan, D. T., and J. Fischman, "Flow of Non-Newtonian Fluids Through Sudden Expansions and Contractions," in *Proc. of 136th Intern. Congress on Ind. Chem.*, Brussels, Belgium (1966).
38. Wendel, M. M., and R. L. Pigford, *AIChE J.*, **4**, 249 (1958).
39. Zandi, I., and C. D. Turner, *Chem. Eng. Sci.*, **25**, 517 (1970).

* This is based on the hydraulic radius.

$$Re_L = 12 \left(\frac{n}{2n+1} \right)^n \times \left(\frac{\rho u_0^{2-n} \delta^n}{m} \right).$$