Diffusivity Measurements for Gases in Power Law Non-Newtonian Liquids

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The objective of this study was to measure the diffusion coefficient for gases in non-Newtonian liquids. There have been relatively few experimental determinations of diffusivities for gases in non-Newtonian liquids. Astarita (1965) has used the laminar jet technique to measure the diffusivity of carbon dioxide and ethylene in various aqueous non-Newtonian solutions. Zandi and Turner (1970) have also used the laminar jet method to determine diffusivities for oxygen in several aqueous polymer solutions. Wasan et al. (1972) used a short wetted-wall column to study oxygen diffusion coefficients in several aqueous polymer solutions. Greif et al. (1972) used a rotating disk electrode experiment to measure the diffusivity of oxygen in non-Newtonian saline solutions.

In the work described here a relatively long wetted-wall column was used to measure the diffusion coefficient for carbon dioxide in aqueous Carbopol (carboxy polymethylene) solutions. The rheological behavior of these solutions is well characterized by the power law model. Concentrations of Carbopol up to 1.00 wt. % were used resulting in flow behavior indexes as low as 0.594. A surface active agent, Petrowet R, was used to suppress ripples and to give well defined hydrodynamics. The column length used was 20.0 cm which is the approximate length used by Lynn et al. (1955) who demonstrated that for Newtonian liquids in the presence of surface active materials gas absorption rates show close agreement with penetration theory.

THEORY

Pigford (1941) obtained a solution for the differential equation describing gas absorption into a Newtonian liquid flowing in a falling film with a parabolic velocity profile. Emmert and Pigford (1954) show that for short contact times the result of Pigford reduces to the penetration theory prediction of Higbie (1935) which is based on the assumption of a uniform velocity. Thus in the limit of short contact times, the average rate of absorption into a film formed on the outside of a circular tube is given by

$$R_A = 4\pi(r + d)\, l\, (C_s - C)_{lm} \sqrt{\frac{Du_s}{l\pi}} \qquad (1)$$

This should be applicable to both Newtonian and non-Newtonian liquids since it is the surface velocity and not the velocity distribution which appears in Equation (1). A material balance on the film relates the rate of absorption to measured variables.

$$R_A = 2\pi r q (C_2 - C_1) \qquad (2)$$

Equating Equations (1) and (2) gives an expression for the diffusivity.

$$D = \frac{\pi}{4}\, \frac{q^2}{u_s l} \left(\frac{r}{r + d}\right)^2 \left\{ \frac{(C_2 - C_1)}{(C_s - C)_{lm}} \right\}^2 \qquad (3)$$

The rheological behavior of the Carbopol solutions used in this work is well-described by the power law model

$$\tau = K\left(\frac{du}{dy}\right)^n \qquad (4)$$

For fully developed flow in a vertical falling liquid film, the momentum equation may be written as

$$\frac{d\tau}{dy} = \rho g \qquad (5)$$

Substitution of Equation (4) into Equation (5) and integrating for the boundary condition of no shear at the free surface yields the velocity distribution from which relationships for the surface velocity and film thickness may be obtained.

$$u_s = \left(\frac{\rho g}{K}\right)^{1/n} \left(\frac{n}{n + 1}\right) d^{\frac{n+1}{n}} \qquad (6)$$

$$d = \left\{ \left(\frac{2n + 1}{n}\right) q \right\}^{\frac{n}{2n+1}} \left\{ \frac{\rho g}{K} \right\}^{\frac{-1}{2n+1}} \qquad (7)$$

Equation (3) together with Equations (6) and (7) permit a calculation of the diffusion coefficient from measured experimental variables.

EXPERIMENTAL APPARATUS AND PROCEDURE

The experimental wetted-wall column apparatus was that used by Lamourelle and Sandall (1972). The liquid film was formed on a ⅝-in. diameter stainless steel tube enclosed in a 3.0-in. diameter glass pipe. The liquid was distributed on the outside wall of the tube through a distributor cap having an annular width of 0.054 in. The height of the liquid receiver was adjusted to give a film length of 20.0 cm. The liquids used in the wetted-wall column were degassed by recycling them through disk and doughnut baffle tower operated at a vacuum pressure of approximately 45 cm Hg.

Liquid flow rates were measured with a calibrated rotameter. Concentrations of carbon dioxide in solution were determined by precipitating the carbon dioxide as barium carbonate from a solution of barium chloride and sodium hydroxide, and the excess sodium hydroxide was titrated to a phenolphthalein end point with hydrochloric acid.

Liquid samples were withdrawn from the inlet and outlet streams approximately 20 min. after the flow rate had stabilized and a second set of samples were taken 15 min. later as a check on the steady state operation.

The rheological measurements to determine the power law parameters were made using a capillary tube viscometer. Gas solubilities and further details of the experiment may be found in the original thesis, Perez (1973).

RESULTS AND DISCUSSION

The power law parameters at 25°C for the Carbopol solutions used in this work are shown in Table 1.

Figure 1 shows the diffusivity results for the four different solutions used. The diffusivity results show no trend with flow rate and show no effect of surface active agent concentration. The experimental results show that the dif-

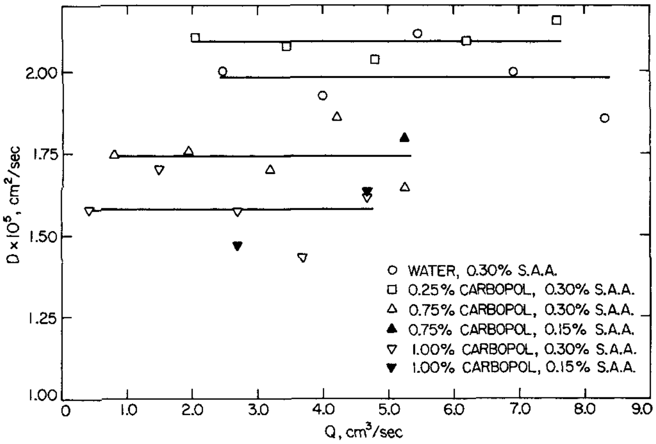

Fig. 1. Diffusion coefficient as a function of liquid flow rate for carbon dioxide in aqueous Carbopol solutions at 25°C.

Table 1. Power Law Parameters for Aqueous Carbopol Solutions at 25°C

Wt. % Carbopol	Flow behavior index, n	Consistency index K, g/cm sec^{2-n}
0.25	0.916	0.0417
0.75	0.773	0.499
1.00	0.594	5.21

Table 2. Diffusion Coefficients for CO_2 in Aqueous Carbopol Solutions at 25°C

Wt. % Carbopol	Diffusion coefficient D, cm^2/sec × 10^5	No. of measurements	Standard deviation, %
0.0	1.98	5	4.8
0.25	2.09	5	2.0
0.75	1.74	5	4.1
1.00	1.58	5	6.0

fusivity at first increases and then decreases with increasing Carbopol concentration. The data shown in Figure 1 are summarized in Table 2.

The experimental results were obtained at temperatures ranging from 22.0° to 26.5°C and were corrected to a uniform temperature of 25.0°C through use of the Stokes-Einstein equation. The temperature correction for water as would be calculated by holding the group $D\mu/T$ constant was assumed to apply also for the non-Newtonian solutions. These temperature corrections averaged 4.6%, the maximum correction being 8.3%.

The diffusion coefficient found for water agrees well with the values found in the literature. Vivian and King (1964) obtained a value of 2.00 × 10^{-5} cm^2/s at 25°C using the diaphragm cell method; Thomas and Adams (1965) reported the diffusivity to be 1.95 × 10^{-5} cm^2/s at 25°C from their laminar jet experiments. These values agree well with the data of this study which give the diffusivity as 1.98 × 10^{-5} cm^2/s.

In the investigation of Emmert and Pigford (1954) evidence was found for the presence of an interfacial resistance to mass transfer due to the surface active agent used to suppress ripples. The surface active agent, Petrowet R, and the concentration, 0.30 wt.%, used by Emmert and Pigford are the same as in this study; however, no interfacial resistance is evident from our data. A possible explanation for this apparent discrepancy may be that a relatively long exposure time is required for there to be a sufficiently high concentration buildup of surface active agent at the surface to result in an interfacial resistance. The column of Emmert and Pigford was 114 cm long compared to a length of 20 cm in this work; thus, for the same flow rate the contact time for the longer column would be approximately six times that of the shorter column. Further evidence supporting this hypothesis is that the data of Emmert and Pigford show closer agreement at high flow rates with penetration theory assuming no interfacial resistance. Lynn, Straatmeier, and Kramers (1955) found good agreement with penetration theory for SO_2 absorption in water using wetted-wall columns of length 12 to 22 cm and for various surface active agent concentrations up to 0.80 wt.%. The three runs in this work which were made using a surface active agent concentration of 0.15 wt.% as shown in Figure 1 are in agreement with the Lynn et al. findings.

There are no data for non-Newtonian fluids in the literature that can be directly compared with this work. Astarita (1965) used the laminar jet method to measure the diffusivity for carbon dioxide in aqueous Carbopol solutions up to concentrations of 0.222 wt.% Carbopol. His results show that the diffusivity increases with increasing polymer concentration. The increase in diffusivity over that for water alone found by Astarita is in agreement with the findings of the present study for 0.25 wt.% Carbopol. Although the data of this work show that the diffusivity for the 0.25% solution is greater than that for water, the 95% confidence limits calculated for these two diffusivities overlap.

Wasan et al. (1972) used a short wetted-wall column, 3.28 cm long, to measure diffusion coefficients for oxygen in various aqueous polymer solutions. The solutions studied could be characterized as power law pseudoplastic or as Newtonian fluids. It was found that the diffusivity decreased with increasing polymer concentration, and it was also observed that the diffusivity increased with increasing flow rate for the non-Newtonian fluids. However, with the exception of the Polyox solutions the diffusivity was only a slight function of flow rate. The diffusion of oxygen in Polyox solutions is complicated by chemical reactions which occur in this system. No effect of flow rate was observed in the present study.

In conclusion, it is felt that the relatively long wetted-wall column used in this work combined with a surfactant to suppress ripples provides a reliable technique for measuring gas diffusivities in non-Newtonian liquids.

NOTATION

C = bulk concentration, g moles/cm^3
C_s = interfacial concentration, g moles/cm^3
d = film thickness, cm
D = diffusion coefficient, cm^2/s
g = acceleration due to gravity, cm/s^2
K = flow consistency index, g/cm s^{2-n}
l = film length, cm
n = flow behavior index
q = flow rate per unit wetted perimeter, cm^3/s cm of wetted perimeter
Q = volumetric flow rate, cm^3/s
r = wetted-wall column radius, cm
R_A = gas absorption rate, g moles/s
u = velocity, cm/s
u_s = interfacial velocity, cm/s
y = distance normal to wall, cm
ρ = fluid density, g/cm^3
τ = shear stress, g/cm s^2

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Use of Tracers in Study of Catalytic Oxidation of Sulfur Dioxide

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This study describes the employment of ^{35}S and ^{18}O to assess the importance of individual steps in the catalytic oxidation of sulfur dioxide over a commercial vanadium oxide based catalyst. It is found that oxygen adsorption is always the slowest step. Desorption of sulfur trioxide also exerts a significant effect on the overall rate, especially close to equilibrium.

The use of tracers for study of this system has been reviewed by Happel (1972). Experimental studies using a vanadium based catalyst were reported by Happel et al. (1971) employing ^{35}S. Preliminary studies using ^{18}O were reported by Happel et al. (1972). This note presents further data using ^{18}O as well as results with simultaneous tracing with ^{18}O and ^{35}S.

The reactor employed is of the recirculating type (Happel et al., 1971). Feed and product streams are analyzed by chromatography. ^{35}S is determined by scintillation counting and ^{18}O is determined by mass spectroscopy.

The catalyst employed is a commercial vanadium pentoxide type (typical analysis V_2O_5—9.1%; K_2O—10.1 wt. %) supplied by American Cyanamid Company. The pellets were crushed and screened to a size range of 0.35 to 0.71 mm. Previous studies (Happel et al., 1971) indicate that diffusional effects due to particle size are not important at the temperatures employed.

RESULTS

The data are interpreted on the basis of a generalized mechanism which allows for slow steps considered by most previous investigators. With the overall reaction written as $2SO_2 + O_2 = 2SO_3$, the following steps are assumed:

$$\begin{array}{ccc} \text{Step no.} & \text{Partial reaction} & \text{Stoichiometric number, } \nu \\ 1 & O_2 + 2l \underset{v_{-1}}{\overset{v_{+1}}{\rightleftharpoons}} 2\,Ol & 1 \\ 2 & SO_2 + l \underset{v_{-2}}{\overset{v_{+2}}{\rightleftharpoons}} SO_2l & 2 \\ 3 & SO_2l + Ol \underset{v_{-3}}{\overset{v_{+3}}{\rightleftharpoons}} SO_3l + l & 2 \\ 4 & SO_3l \underset{v_{-4}}{\overset{v_{+4}}{\rightleftharpoons}} SO_3 + l & 2 \end{array} \qquad (1)$$

The symbol l refers to any site associated with the catalyst that interacts with the chemical species involved to form intermediates. Since the steady state is maintained for the overall reaction being studied by tracing, the amount of each intermediate associated with a given quantity of catalyst remains constant. The velocities $v_{\pm i}$ will also be constant and can be measured by tracers provided that diffusional resistances are not important so that the sites involving intermediates are equally accessible to reacting species. In the case of reactions involving only gases and solids, it is customary to use effectiveness factors to assess the importance of gaseous diffusion and to identify the intermediates as chemisorbed reactants and

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