

Gas Diffusion in Polymer Solutions: A Double-Cone Flow Technique*

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Synopsis

A new double-cone flow technique for an experimental investigation of gas diffusion in polymer solutions is described. A theoretical development of the pertinent convective diffusion problem for the flow of a non-Newtonian fluid over the double cone is presented. Experimental investigation of diffusion of carbon dioxide in aqueous solutions of certain polymers was carried out. The diffusion coefficient deduced from this work shows a marginal enhancement over its value in pure solvent. Possible mechanistic explanations for this phenomenon are explored.

INTRODUCTION

There are a number of areas of pragmatic importance where the knowledge of diffusion of a small solute through a macromolecular medium assumes importance. Two recent reviews by Astarita and Mashelkar¹ and Mashelkar² indicate a few of these areas. They pertain to polymer processing and production, physiological processes, fermentation processes, and waste disposal systems. Diffusion of small solutes in macromolecular media has attracted a great deal of attention in recent years. Some of the recent articles in this area³⁻⁵ give some indication of the manner in which diffusion of a small solute in macromolecular media is affected.

The diffusion coefficient of a gas in a fluid has been measured by a number of techniques. The technique of adsorption in a falling vertical film⁶ or in a wetted sphere column⁷ has been used in the past. In this study, we report on the development of a new geometry, namely, a wetted double-cone column which can be conveniently used for obtaining the diffusion coefficients of gases in polymeric media. As will be shown later, this geometry offers some advantages in terms of reduced "end effects." This study will substantiate earlier findings on anomalous diffusion in macromolecular media. In addition, the results obtained will be compared with prior studies, and some general comments concerning the present state of this area will be made.

THEORETICAL DEVELOPMENT

We are essentially concerned with flow of a film on a double-wetted cone, as shown in Figure 1. The fluid emerging at the top of the cone flows down. At

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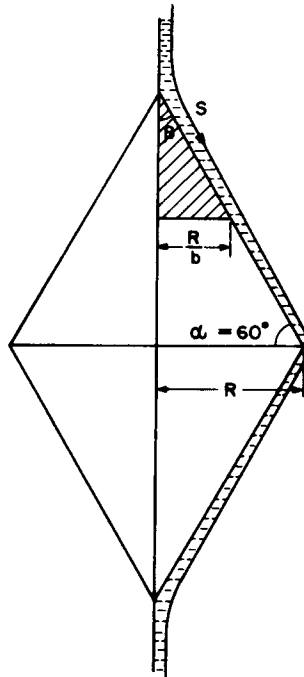


Fig. 1. Schematic diagram of flow on a wetted double cone.

a constant volumetric flow rate, the film thickness on the top of the cone undergoes a reduction, whereas that at the bottom cone undergoes expansion. Therefore, the fluid on the top cone accelerates, whereas that on the bottom cone decelerates. Fluid mechanical investigations of such flows in the case of Newtonian fluids have been published by Lynn et al.⁸ and subsequently verified with more precise analyses by Stepanek and Lee⁹ and Zollars and Krantz.¹⁰ It appears that the lubrication theory approximation developed by Lynn et al.⁸ gives a fairly good prediction of the local film thickness as well as the local velocity. Experimental verification of the validity of the predictions of the measurements of local film thickness as well as of mass transfer rates has appeared in the literature.¹¹ The problem of convective diffusion in such stretching flows was extended by Chavan and Mashelkar¹² and Mashelkar and Chavan¹³ to non-Newtonian power law fluids. The subsequent work of Mashelkar and Soylu⁷ indicated that the approach gives a reasonable base for using a wetted sphere column for diffusion measurements in polymer solutions. The wetted double-cone geometry, however, has not been exploited in the past.

Theoretical Calculation of Gas Absorption from a Falling Conical Film

We now present a brief theoretical analysis of the corresponding diffusion problem for a double-cone geometry. Let us assume that the film under consideration in Figure 1 is a pseudoplastic liquid whose viscosity behavior is given by the traditional Ostwald de-Waele model:

$$\tau = -K[\Delta:\Delta]^{(n-1)/2} \quad (1)$$

By neglecting diffusion in the flow direction and also the curvature of the streamlines, we can write the convective diffusion equation as

$$V_s \frac{\partial C}{\partial S} = D \frac{\partial^2 C}{\partial x^2} \quad (2)$$

The velocity distribution following the arguments of Mashelkar and Chavan,¹³ will be given by

$$V_s = V_i \left[1 - \left(\frac{x}{\delta} \right)^{(n+1)/n} \right] \quad (3)$$

with

$$\delta = \delta_1 \sin \alpha^{-n/(2n+1)} \quad (4)$$

where δ_1 is the film thickness at the base, which is given by

$$\delta_1 = \left[\frac{\left(\frac{2n+1}{n} \right) Q}{2nr \left(\frac{\rho g \cos \alpha}{K} \right)^{1/n}} \right]^{n/(2n+1)} \quad (5)$$

and

$$V_i = V_{\max} S^{-n/(2n+1)} \quad (6)$$

where

$$V_{\max} = \left(\frac{n+1}{n} \right) \left(\frac{\rho g}{K} \right)^{1/n} \delta_1^{(n+1)/n} \quad (7)$$

Let us first consider gas absorption only in the upper cone. In this case, we introduce a new variable such that

$$\frac{d\xi}{dS} = \frac{D}{V_i \delta^2} \quad (8)$$

which implies that

$$\xi = \frac{D}{V_{\max} \delta_1^2} \int_0^{\delta_1} S^{(3n+3)/(2n+1)} ds \quad (9)$$

$$\xi = \frac{5n+4}{2n+1} \frac{D}{V_{\max} \delta_1^2} S_1^{(5n+4)/(2n+1)} \quad (10)$$

Substitution of eq. (3) in eq. (2) with suitable nondimensionalization transforms the convective diffusion equation to

$$(1 - \bar{x}^{(n+1)/n}) \frac{\partial \theta}{\partial \xi} = \frac{\partial^2 \theta}{\partial \bar{x}^2} \quad (11)$$

where $\bar{x} = x/\delta$ and $\theta = 1 - (C/C^*)$. This needs to be solved with suitable boundary conditions. Mashelkar and Soyly⁷ have shown that the penetration theory approximations, which are valid under the conditions where the depth of penetration of the diffusing molecule is very small in comparison to the film thickness, can be used. In that case, the diffusion equation simplifies to

$$\frac{\partial \theta}{\partial \xi} = \frac{\partial^2 \theta}{\partial \bar{x}^2} \quad (12)$$

which needs to be solved with the boundary conditions

$$\theta = 1, \quad \xi = 0, \quad 0 \leq \bar{x} \leq 1$$

$$\begin{aligned} \theta = 0, \quad \bar{x} = 0, \quad 0 \leq \xi \leq \infty \\ \frac{\partial \theta}{\partial \bar{x}} = 0, \quad \bar{x} = 1, \quad 0 \leq \xi \leq \infty \end{aligned} \quad (13)$$

The concentration distribution in the film can be easily obtained as

$$\theta = \operatorname{erfc}\left(\frac{\bar{x}}{2\sqrt{\xi}}\right) \quad (14)$$

Assuming that there is no mixing at the junction of the upper and lower cone, we obtain the dimensionless outlet concentration as

$$\frac{C_0}{C^*} = 2 \left(\frac{2n+1}{n+1}\right) \sqrt{\frac{2\xi}{\pi}} \quad (15)$$

Expressing this equation in terms of normal process and operational variables, we have the following equation for the number of moles absorbed per unit time (N):

$$\begin{aligned} N = \frac{4}{\sqrt{\sin \alpha}} \left(\frac{2n+1}{n+1}\right) \left(\frac{2\pi n}{2n+1}\right)^{n/[2(2n+1)]} \left(\frac{n+1}{5n+2}\right)^{1/2} r^{(5n+2)/[2(2n+1)]} \\ \times \left(\frac{\rho g \cos \alpha}{K}\right)^{1/[2(2n+1)]} C^* D^{1/2} Q^{n+1/[2(2n+1)]} \quad (16) \end{aligned}$$

End Effects in a Double-Wetted Cone Device

It is well known¹¹ that in film-forming devices used for mass transfer studies, accumulation of the surface-active impurity at the top of the column can result in imparting surface rigidity to the film with attendant reduction in mass transfer rate due to reduction in effective surface area. It is therefore important to see the magnitude of the such end effects. We can easily evaluate the error introduced by cutting off a specific top portion of the cone (the shaded area in Fig. 1). It can be easily shown that the fractional reduction due to not taking into account the shaded portion will be given by the following expression:

$$f = 1 - \frac{\int_{r/(b \sin \beta)}^{r/\sin \beta} S^{(3n+1)/(2n+1)} dS}{\int_0^{r/\sin \beta} S^{(3n+1)/(2n+1)} dS} \quad (17)$$

implying

$$f = \left(\frac{1}{b}\right)^{(5n+2)/(2n+1)} \quad (18)$$

This shows that even when $b = 2$, the end effect error that is likely to be introduced is only of the order of 10%; in other words, the end effects in the double-wetted cone column described here are likely to be negligible. Indeed, comparison with a wetted sphere column¹¹ shows that when the same percentage fraction of the top surface area becomes ineffective for mass transfer, the reduction in the case of a wetted double-cone column is less than that in the case of a wetted sphere column.

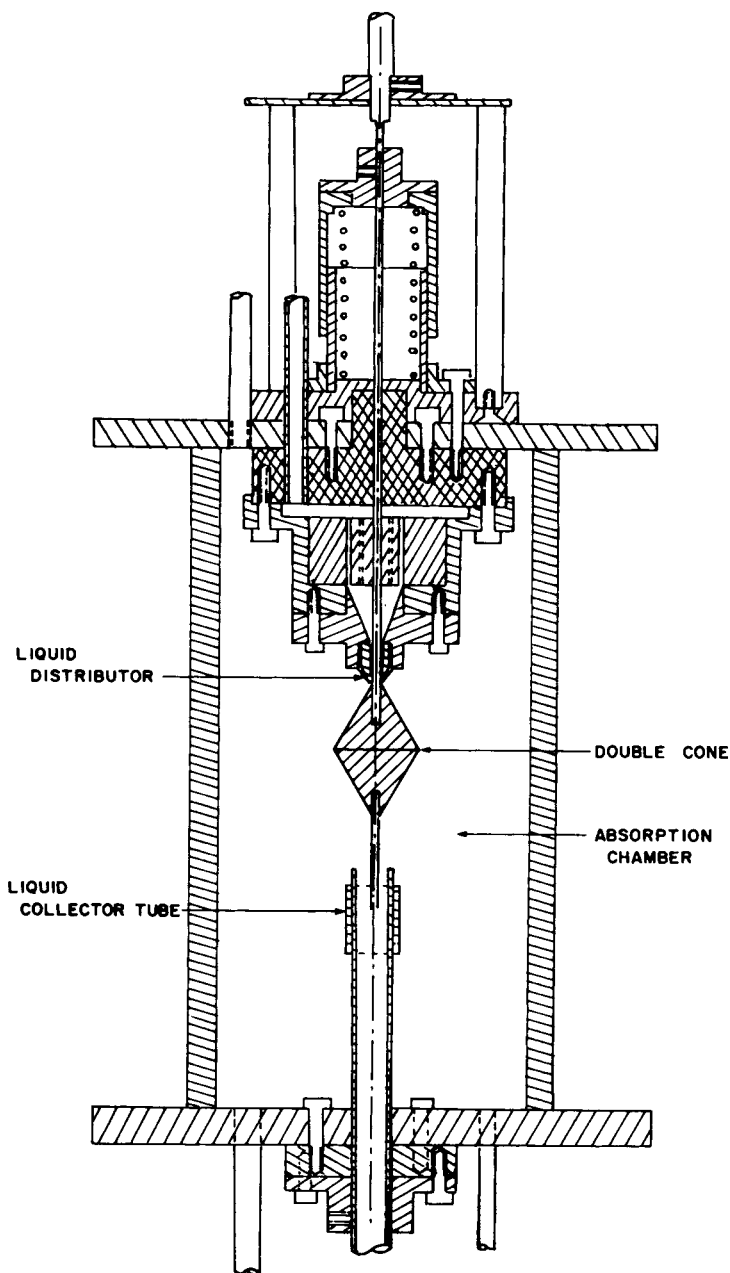


Fig. 2. Mechanical details of absorption assembly for a wetted double cone column.

EXPERIMENTAL

The wetted double cone used in this work had the dimensions as shown in Figure 1. The details of the overall setup are shown in Figure 2. Figure 3 shows the complete experimental setup used in this work.

Polymer solution was metered through a rotameter to the distributor on the top of the double cone. After passing over the double cone, the polymer solution left the column through a constant level device. Purge gas from the cylinder

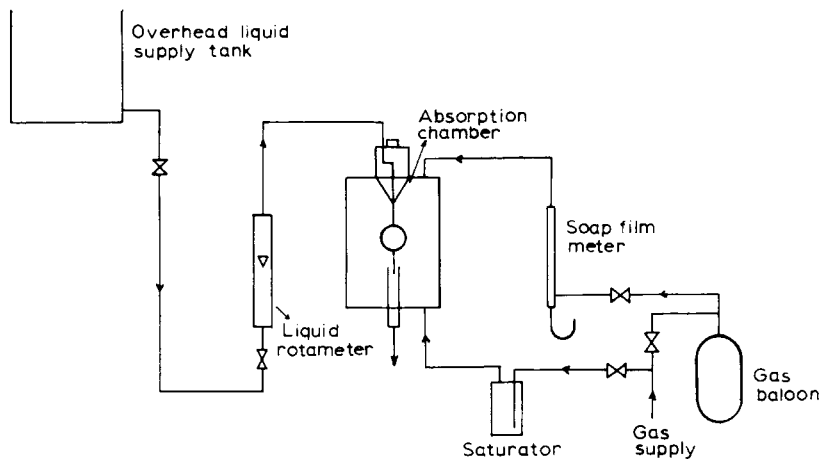


Fig. 3. Experimental setup for absorption in a wetted double cone column.

was saturated with water vapor before entering the column from where it was discharged to the atmosphere. Dry absorption gas was drawn in from an atmospheric balloon and metered through a soap film meter.

Full details of the column are shown in Figure 2. The double cone with a base diameter of 3.81 cm was mounted on a 3-mm SS rod. This rod was accurately centered in the distributor orifice by the alignment block which was sliding fit in the distributor. The polymer solution entering at the top passed through the alignment block via 12 holes which ensured an even flow out of the orifice. After passing over the double cone, the polymer solution ran down the rod in a take-off tube. The polymer solution was maintained at the top of this tube by a constant level device.

The double cone was fixed at 3 mm from the inlet orifice. This distance was crucial, since longer distances produced an uneven distribution and shorter distances produced a spray. The length of the rod between the end of the double cone and the take-off was fixed at 1 cm, since at larger distances the end effects would become appreciable.

Carbon dioxide was used as a diffusing gas throughout this investigation. The values of the saturation solubility of CO_2 in various solutions were determined at the temperature of the experiments by using standard analytical techniques. Table I lists the polymers used, the manufacturers, and the range of concentrations used. The rheological data at lower polymer concentrations were obtained by using an Ubbelohde viscometer; at higher concentrations, a Weissenberg rheogoniometer was used.

TABLE I
Polymers Used in This Work

Polymer	Supplier	Concentration range, wt. %
Polyacrylamide (PAA—AP273)	Dow Chemical	0.0166–0.025
Polyacrylamide (PAA—AP 30)	Dow Chemical	0.02–0.10
Poly(ethylene oxide) (PEO—WSR 301)	Union Carbide	0.01–0.1
Poly(ethylene oxide) (PEO—Coagulant)	Union Carbide	0.02–0.1

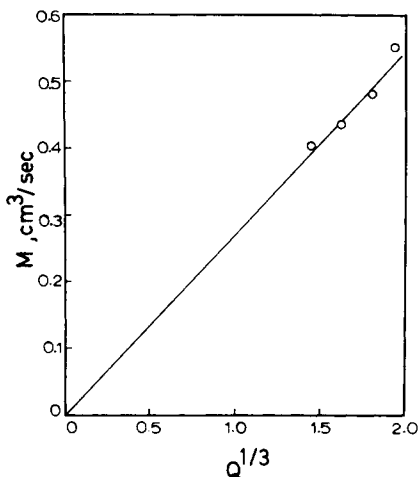


Fig. 4. Rate of absorption of water on a wetted double cone column as a function of volumetric flow rate.

RESULTS AND DISCUSSIONS

Equation (16) shows that a plot of N vs. $Q^{(n+1)/[2(2n+1)]}$ could be a straight line passing through the origin provided the end effects were absent. Figure 4 shows such a plot for data collected for a water film flowing over a cone shown in Figure 1. The diffusion coefficient value calculated at 20°C from the experimental data of Figure 4 was 1.697×10^{-5} cm/s, which compared very favorably with the literature value of 1.713×10^{-5} cm/s (calculated at 20°C).

Figures 5 to 8 show some typical plots of N vs. $Q^{(n+1)/[2(2n+1)]}$ for the polymer systems studied. These are all linear plots which pass through the origin, indicating the absence of end effects.

The diffusion coefficient values in polymer solutions calculated on the basis of the data presented are shown in Table II. For comparison, the corresponding diffusion coefficient values obtained for the same polymers with the same concentration by Mashelkar and Soylu⁷ are also shown. There are two interesting

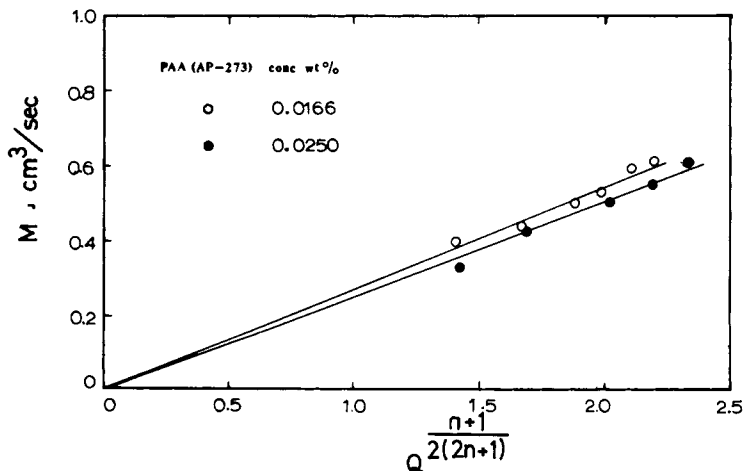


Fig. 5. Rate of absorption in polyacrylamide solutions as a function of volumetric flow rate.

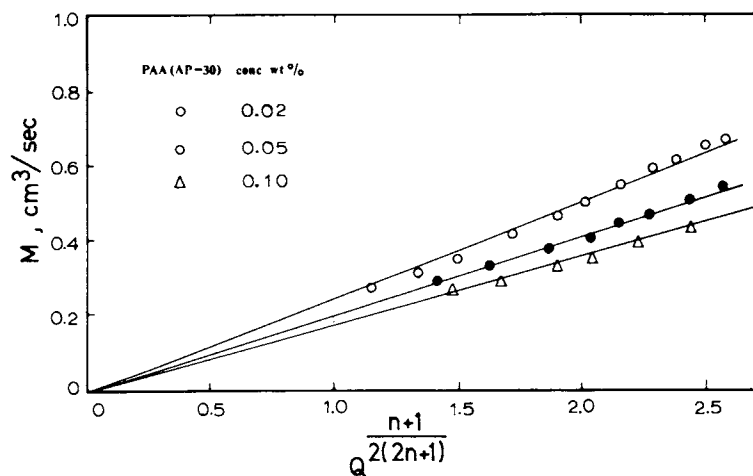


Fig. 6. Rate of absorption in polyacrylamide solutions as a function of flow rate.

observations. The first is that the values of diffusivity obtained by using a double-cone column agree very well with those obtained by using the wetted sphere column. Secondly, the diffusion coefficients appear to undergo a marginal increase with increase in polymer concentration.

It is well recognized by now¹ that the "macroviscosity" of a polymer solution is not an index of the resistance that a diffusing solute encounters in a macromolecular medium. Indeed, the concept that "microviscosity" in polymer solutions represents such a resistance is receiving wide acceptance (see for example, Kulkarni and Mashelkar¹⁴).

The augmentation of the diffusion coefficient on addition of polymer is a rather surprising observation, which has been made by some other workers, too. Table III shows a list of workers who have observed such increases. Interestingly enough, most experimentalists who used stagnant flow techniques have not observed such increases. This has led to a widespread belief that perhaps the fluid mechanical effects are responsible for such an apparent increase. Indeed, some preliminary findings by Dutta and Mashelkar¹⁵ to indicate that wall slip

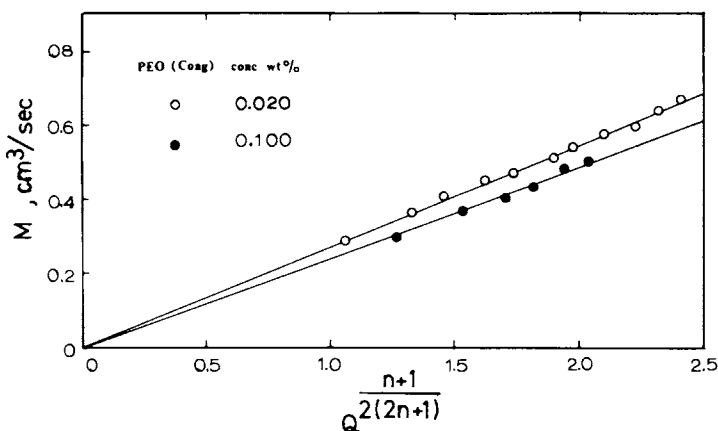


Fig. 7. Rate of absorption as a function of flow rate in polyethylene oxide solutions.

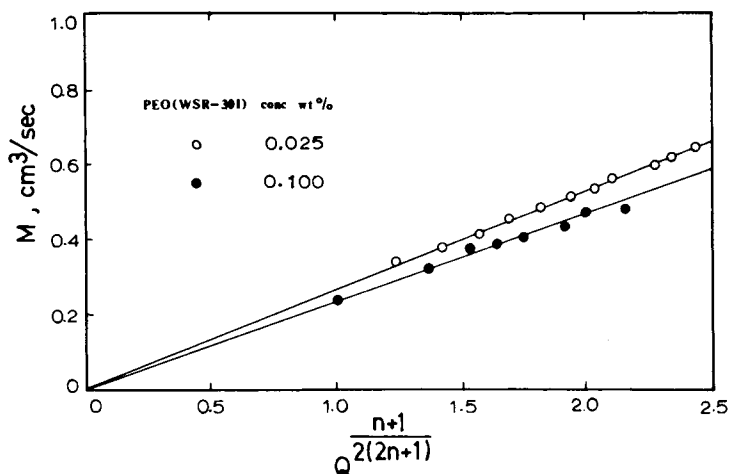


Fig. 8. Rate of absorption as a function of flow rate in polyethylene oxide solutions.

at the solid fluid interface in the case of a falling film of a polymer solution might be responsible for showing such an apparent increase in diffusivity. However, the data presented by Luikov et al.¹⁶ using stagnant flow techniques tend to suggest that perhaps these effects are system specific. It is interesting to note that there is a common link between all the studies who have observed an increase in diffusivity, namely, that the systems used were polyelectrolytes. We shall explore this clue further.

As pointed out by Grisky and Sedahmed,²² solvation of the polymer molecules will occur when a polyelectrolyte is dissolved in a solvent. The influence of this solvation may be to reduce a portion of the solvent molecules and increase the concentration of the diffusing species locally and therefore promote concentration gradients and thus effectively increase the diffusion coefficient. In addition, similar charged segments of the polyelectrolyte molecules might lead to extended polymer molecular configurations due to mutual repulsion. Therefore, the diffusion of solutes will be easier in polyelectrolyte systems.

TABLE II

Polymer	Conc., wt %	Temperature of experiment, °C	<i>D</i> determined by wetted double cone, (cm ² /s) × 10 ⁵	<i>D</i> determined by wetted sphere, ⁷ (cm ² /s) × 10 ⁵
Pure water	0.00	20.0	1.697	1.713
PEO (WSR-301)	0.010	21.0	1.844	1.849
	0.025	21.0	1.794	1.908
	0.050	21.0	1.972	2.230
	0.100	21.0	2.192	2.280
	PEO (coag.)	0.020	20.0	1.910
PEO (coag.)	0.050	20.0	1.960	1.952
	0.100	17.0	1.761	1.630
	PAA (AP-273)	0.0166	19.5	1.930
PAA (AP-273)	0.0250	19.5	2.452	2.411
PAA (AP-30)	0.020	20.0	1.908	1.832
	0.050	20.0	1.921	1.872
	0.100	20.0	2.030	2.291

TABLE III
Previous Studies Reporting Enhancement in Diffusivity on Polymer Addition

Polymer system used ^a	Solute	Polymer concentration range, wt %	Technique used	Reference
CMC	H ₂ O ₂	0-2	static	16
CMC, Carbopol, PAA	CO ₂ C ₂ H ₄	0-3	laminar jet	17
Methocel	CO ₂	0-0.3	laminar jet	13
PAA, CMC, HEC	O ₂	0-0.1	laminar jet	19
Polyox, Methocel, CMC, Carbopol	O ₂	0-4	laminar jet	20
HEC, PAA, Polyox, CMC	CO ₂	0-1	falling film	7
Carbopol	CO ₂	0-1	falling film	20
PAA, PEO, CMC	benzoic acid	0-0.5	falling film	22

^a CMC = carboxymethyl cellulose; Carbopol = carboxy polymethylene; PAA = polyacrylamide; Methocel = methyl cellulose ether; HEC = hydroxyethyl cellulose; Polyox = poly(ethylene oxide).

In the case of diffusing species, which are mildly ionic in nature or neutral, they will not interfere with the conformations of the polymer molecules. On the other hand, in the case of diffusing species that are strongly ionic, there will be an interaction between the diffusing species and the polyelectrolyte molecules, which will possibly bring about a decrease in the repulsion and therefore an increase in the coiling of polyelectrolyte; molecule coiling resulting in decreased diffusivity. This viewpoint is supported by the fact that most of the studies performed by using electrochemical techniques²³⁻²⁵ which use concentrated alkali solutions do show a much stronger decrease in diffusion coefficient than do mildly ionic systems.³ It is thus apparent that for prediction of diffusion coefficient in such polyelectrolyte systems, a model that takes into account the interaction effects will have to be evolved.

It might be worth focussing attention on the existing predictive models concerned with diffusion of a small solute in macromolecular media, which, of course, do not take into account such interactions explicitly. The model by Li and Gainer²⁶ does produce either an increase or decrease in diffusion coefficient with polymer concentration depending upon the sign of the enthalpy of the mixing. The model of Osmer and Metzner²⁷ shows that such an increase or decrease could be predicted depending upon the size of the excess volume of mixing of the polymer-solvent system. The theory of Navari et al.²⁸ has been rather extensively tested with the available experimental data. This theory predicts a continuous decrease of diffusion coefficient with increase in polymer concentration. However, it does appear that the theory takes into account a rather narrow range of unperturbed chain dimensions and calculations for some specific systems not covered by Navari et al.²⁸ such as polyacrylonitrile in dimethylformamide, polyacrylamide in water, carboxymethyl cellulose in water, polyacrylate in water, hydroxyethyl cellulose in water, etc. The theory predicts a continuous increase in diffusivity with increase in polymer concentration. Apparently, there is a need to reconsider some of the assumptions in theory, especially an assumption that implies that RMS end-to-end distance of the polymer chain is independent of the nature of the solvent which amounts to overlooking polymer-solvent and polymer-polymer interactions.

Our final comment concerns the influence of shear rate on the diffusion coefficient. It is obvious that in the experiments reported here, it is not possible to deduce the influence of shear rate on diffusion coefficient, since diffusion takes place in a shear-free field. Although there are studies reported in the literature which do show an increase in diffusivity with shear rate, the in-depth studies on fluorescence polarization by Claesson and Odani²⁹ are rather illuminating in resolving the discrepancy. These authors studied the influence of shear rate on microbrownian motion of a polymer segment by using dilute aqueous hydroxyethyl cellulose solutions and concentrated dextran and polystyrene solutions. Dye molecules were either tagged to the chain end or were kept free. The change in the degree of polarization indicated the extent of microbrownian motion. It was found that there was no change in the degree of polarization when the shear rate was changed from 0 to 10^4 s^{-1} . It is interesting to note that in this range the macroscopic viscosity of the solutions showed remarkable non-Newtonian characteristics. It would thus appear that microbrownian motions which are of relevance to the diffusion of a small solute in a macromolecular media are relatively unaffected, and therefore the diffusion coefficients should remain relatively constant as the shear rate is changed.

Nomenclature

b	dimension in Figure 1
C	local concentration of diffusing solute
C_0	exit average concentration of diffusing solute
C^*	saturation solubility
D	molecular diffusivity in polymer solution
f	fractional reduction in gas absorption
g	gravitational acceleration
K	consistency index
n	power law index
N	rate of gas absorption
Q	volumetric flow rate
r	radius of base in double cone
S	distance in flow direction (see Fig. 1)
S_1	defined in eqs. (9) and (10)
V_i	interface velocity
V_{\max}	velocity defined in eq. (7)
V_s	velocity along streamline
x	distance from free surface
\bar{x}	normalized distance ($= x/\delta$)
<i>Greek</i>	
α	base angle of cone (see Fig. 1)
β	apex angle of cone (see Fig. 1)
δ	film thickness
δ_1	film thickness defined in eq. (5)
θ	dimensionless concentration
ξ	dimensionless axial distance
ρ	density
Δ	rate of deformation tensor
τ	stress tensor

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