Anomalous Convective Diffusion in Films of Polymeric Solutions

The process of gas absorption in freely falling films of dilute polymer solutions under different kinematic conditions shows some hitherto unreported and dramatic differences. The absorption rates are reduced when films are generated under rapid stretch conditions over axisymmetric bodies of revolution, whereas they are enhanced when films are generated in a long, wetted wall column. Absorption rates are enhanced on polymer addition in freely falling turbulent films. Possible mechanistic explanations have been offered for these phenomena.

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SCOPE

Along with the study of the aspects of momentum transport in dilute polymer solutions, lately the study of heat/mass transport processes appears to be attracting attention. The importance of such a study is threefold. First, whenever heat/mass transport rates are augmented due to polymer addition, one can derive obvious economic advantages by polymer addition. Secondly, the studies are helpful from the viewpoint of enabling us to discern the manner in which dilute polymer solutions may behave in complex flow situations. Finally, if we can accept that the kinematics will be changed in a known way, it is possible to test the validity of the well-known models of heat/mass transfer.

With this view, we have studied here the process of gas absorption in films generated under a variety of flow conditions. These include films rapidly stretched over axisymmetric bodies of revolution and films formed in a long, vertical wetted wall column under laminar wavy and turbulent conditions.

CONCLUSIONS AND SIGNIFICANCE

Rapidly stretched films of dilute polymeric solutions over axisymmetric bodies of revolution show reduced rates of gas absorption, whereas the films formed in a vertical wetted wall column show enhanced rates of gas absorption. A mechanistic explanation for this phenomenon has been offered by focussing attention on the possible kinematic adjustments in rapid accelerating-decelerating flows in elastic fluids. The observations reported place an upper limit on the range of operation of the wetted sphere or double-cone flow technique used for diffusivity measurements in macromolecular solutions. Additionally, a particularly significant point pertains to a caution which must be exercised when applying purely viscous considerations for heat/mass transport processes in external fields where extensional flow elements are dominant.

The rates of gas absorption in a long, vertical wetted wall column are increased in the laminar wavy and turbulent region. This is qualitatively in agreement with a simple eddy diffusivity model. This observation, which is of pragmatic importance by itself, also supports the recent findings that small-scale Kolmogoroff eddies do not control mass transfer processes across free surfaces of falling turbulent films.

INTRODUCTION

The study of mass/heat transport in dilute polymer solutions is attracting increasing attention (Astarita and Mashelkar, 1977; Mashelkar, 1981). There are a number of reasons for a spurt in this activity. Sometimes the anomalous augmentation in mass/heat transport could have a potential advantage in industrial practice. A typical example is the enhancement in nucleate pool boiling rates (e.g., Kotchaphakdee and Williams, 1970).

When polymer addition causes a reduction in transport rates it will be of doubtful utility in industrial practice, but the results could still be useful in discerning certain mechanistic details of the attendant transport phenomenon problem. One may cite the work of Metzner and Astarita (1967), where the reduced heat transfer rates from blunt objects placed in dilute polymer solutions are intuitively related to the abnormally thickened boundary layers (although their arguments lacked in correctness of detail due to the limitation of the so-called "limiting stretch rate hypothesis"); a later kinematic study of an analogous flow situation (Leider and Lilleleht, 1973) did indeed prove the existence of such a kinematic condition. (Unfortunately, the exact explanation of the phenomenon still continues to elude the researchers; see the recent hypothesis of elastic boundary layer by Mashelkar and Marrucci, 1980.)

There is of course a third possible advantage of such studies. If it is possible to accept that the polymer addition can affect the hydrodynamics in a known way, it may indeed be possible to test the validity of the commonly accepted mass/heat transfer models. Of general importance is the observation of the number of ways in which the mass/heat transport processes in dilute polymer solutions may be affected when such solutions are subjected to diverse kinematic fields. The present study on convective diffusion in films of polymer solutions brings out all the three aspects vividly.

PREVIOUS WORK

The interest in transport processes occurring in non-Newtonian films has been rather recent (Mashelkar, 1980), while reviewing the general area of engineering studies in polymer solutions has provided a summary of the previous work on hydrodynamics of non-Newtonian fluid films. The studies by Sylvester et al. (1973), Skelland and Popadic (1974), and Popadic (1975) are particularly relevant.

Some studies on absorption in non-Newtonian flowing films have been published. The efforts by Chavan and Mashelkar (1972), Mohr and Williams (1973), Wasan et al. (1972), Perez and Sandall (1973), and Mashelkar and Soylu (1974) may be mentioned. The primary objective in most of these cases has been to use the falling film techniques for diffusivity measurement in polymer solution. Davies and Shawki (1974) are the only ones who studied heat transport in turbulently flowing films of dilute polymer solutions. No previous studies on mass transport in rapidly stretched films, laminar rippling films, or turbulent films have appeared.

In this paper, we will report on some experimental observations on gas absorption in films of dilute polymeric solutions flowing over axisymmetric bodies of revolution. A wetted sphere, a wetted double cone, and a wetted ellipsoid of revolution have been used for this purpose. Gas absorption studies have then been performed in dilute polymer solution films flowing in a long, wetted wall column under laminar rippling and turbulent conditions.

THEORETICAL CONSIDERATIONS

Gas Absorption in Stretched Films of Purely Viscous Non-Newtonian Fluids

Consider the process of gas absorption in a film flowing over an axisymmetric object such as a sphere or a double cone, Figure 1. The flow of a slowly falling film of a Newtonian fluid can be well described through lubrication theory approximations (e.g., Lynn et al., 1956). Previous published studies (e.g., Hirose et al., 1974; Zollars and Krantz, 1976) demonstrate the validity of these approximations. Gas absorption in falling spherical films was studied by Davidson and Cullen (1957), both theoretically and experimentally, and the excellent accuracy of this work has led many workers to use such techniques for reliable diffusivity measurements.

The flow of a film over an axisymmetric body of revolution involves surface stretching of the film. The technique of calculating the absorption rate under such surface stretch conditions is relatively well established by now for Newtonian fluids, and its extension to purely viscous non-Newtonian fluids poses no difficulties. The "penetration theory" asymptote could easily be calculated in the manner of Chavan and Mashelkar (1972) provided the fluid is assumed to obey an Ostwald-de-Waele power law equation.

$$\tau = -K[\underset{\approx}{\Delta}:\underset{\approx}{\Delta}]\ \frac{n-1}{2}\ \underset{\approx}{\Delta} \tag{1}$$

For a sphere, the rate of gas absorption is calculated as

$$N = \left(\frac{8(2n+1)}{n+1}\right)^{1/2}\left(\frac{2\pi n}{2n+1}\right)^{n/2(2n+1)}\int_0^{\pi}\sin\alpha^{3n+2/2n+1}d\alpha \times R^{5n+2/2n+1)}\left(\frac{\rho g}{K}\right)^{1/2(2n+1)}C^*D^{1/2}Q^{n+1/2(2n+1)} \tag{2}$$

For a double-cone, Figure 1, similar calculations may be repeated to obtain

$$N = \frac{4}{\sqrt{\sin\beta}}\left(\frac{2n+1}{n+1}\right)\left(\frac{2\pi n}{2n+1}\right)^{n/2(2n+1)}\left(\frac{n+1}{5n+2}\right)^{1/2}R^{5n+2/2(2n+1)} \times\left(\frac{\rho g\cos\beta}{K}\right)^{1/2(2n+1)}C^*D^{1/2}Q^{n+1/2(2n+1)} \tag{3}$$

Influence of Slip on Gas Absorption in Falling Films

There is a growing evidence in the literature (Astarita et al., 1964; Carreau et al., 1979) indicating that, at least under laminar flow conditions, flowing films of dilute polymer solutions exhibit a slip effect at the solid-liquid interface. This is probably due to the stress-induced diffusion of macromolecules from the high shear wall region to the low shear region (Metzner et al., 1979). The hydrodynamic consequence of this is that the film thickness at a given volumetric flow rate is reduced and the mean and surface velocities are increased.

Consider a film of a power law fluid flowing over a flat vertical plate of width W and length L. The mass transfer coefficient $[k_L]$ obtained by penetration theory approximation is

$$k_L = 2\sqrt{\frac{Dv}{\pi L}} \tag{4}$$

where v is the velocity at the free surface of the film. The ratio of the mass transfer coefficients with slip $[K_L^*]$ and without slip $[k_L]$ is therefore given by

$$\frac{k_L^*}{k_L} = \left(\frac{v^*}{v}\right)^{1/2} \tag{5}$$

Simple hydrodynamic calculations could be performed for a power-law fluid to calculate v^*/v by assuming a slip condition at the wall (Dutta and Mashelkar, 1981). The results of the calculations show that k_L^*/k_L depends upon the pseudoplasticity index $[n]$ and also a dimensionless parameter p characterizing slip

$$p = \chi\rho g\left(\frac{2n+1}{n}\right)\left(\frac{K}{\rho g\delta}\right)^{1/n} \tag{6}$$

where χ is the slip coefficient relating the slip velocity $[v_s]$ with the wall shear stress $[\tau_w]$

$$v_s = \chi\tau_w \tag{7}$$

and δ is the film thickness under no slip condition

$$\delta = \left[\left(\frac{2n+1}{n}\right)Q\right]^{n/2n+1}\left(\frac{\delta g}{K}\right)^{-1/2n+1} \tag{8}$$

Figure 2 shows a plot of k_L^*/k_L as a function of p and n. As is intuitively obvious, for flow with slip $v^*/v > 1$ and therefore $k_L^*/k_L > 1$.

Gas Absorption in Turbulent Films on Dilute Polymer Solutions

Empirical and semiempirical correlations based on specific models for the mass transfer process have emerged in the past. A simple eddy diffusivity model which uses an eddy diffusion coefficient $[D_t]$ for characterizing the convective mass transfer has gained popularity (e.g., King, 1966). This model assumes an eddy diffusivity form of the following kind:

$$D_t = ay^2 \tag{9}$$

where y is the distance measured from the free interface. An eddy diffusivity model gives k_L as

$$k_L = \frac{2}{\pi}\sqrt{aD} \tag{10}$$

The efforts in the past have focussed on finding out the dependence of a on process variables. It is attractive to use the considerations by King (1966) and relate a to the rate of energy dissipation per unit mass $[\epsilon]$ within the film. ϵ is given by simple positional energy loss consideration

$$\epsilon = gv_m \tag{11}$$

The explicit dependence of a on ϵ (at least in the case of Newtonian fluids) can be found. Henstock and Hanratty (1979) have derived an equation for mass transfer in turbulent falling films

$$Sh \simeq \delta^{+3/2}Sc^{1/2} \tag{12}$$

where Sh is the Sherwood number $[= k_L\delta/D]$, Sc is the Schmidt number $[= \nu/D]$, and δ^+ is the dimensionless film thickness $[= u^*\delta/\nu]$. This can be combined with Brauer's equation (Davies, 1972) for film thickness in turbulently falling films, which gives

$$\frac{\delta^3 g}{\nu^2}\alpha Re^2 \tag{13}$$

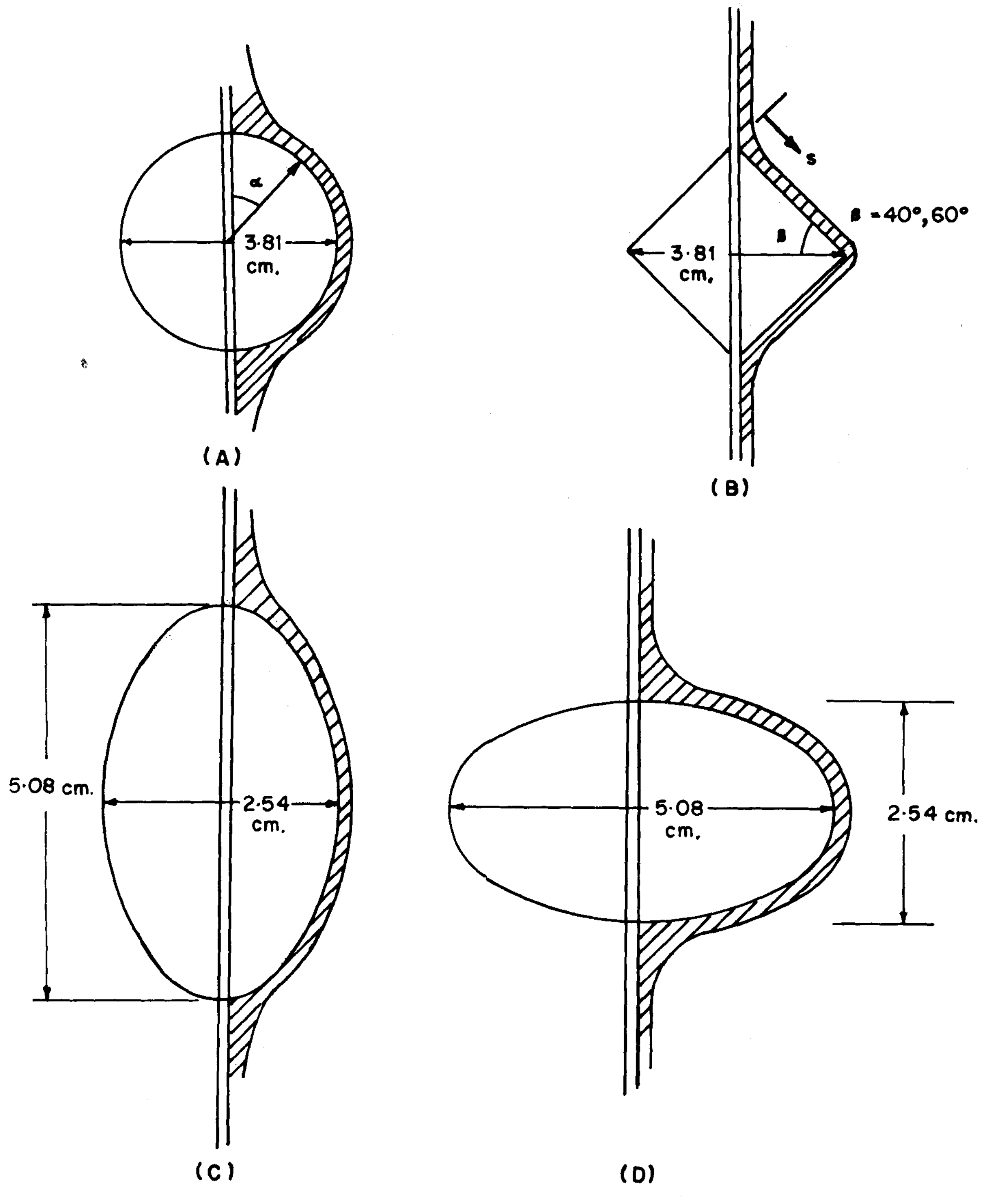

Figure 1. Axisymmetric bodies of revolution for film generation

Combining Eqs. 10, 11, 12 and 13 gives a as

$$a \simeq \frac{\epsilon^5}{g^6 \nu^2} \tag{14}$$

The above result is also obtainable from dimensional considerations alone. Equation 14 can be assumed to be qualitatively valid for absorption in non-Newtonian films also. What needs to be assessed now is the influence of alteration in fluid rheology on ϵ. The possibility of wall slip implies larger v_m at the same Q and therefore larger ϵ (Eq. 11). Simultaneously the manifestation of the drug reduction phenomenon will be to reduce the wall shear stress. Since the stress has to balance the gravity stress exactly, the film thickness δ will have to reduce implying larger mean and surface velocities, and larger k_L values.

It is difficult to estimate quantitatively the exact manner in which these two effects might alter the film hydrodynamics. It is possible that in view of the continuous sweeping of the laminar sublayer due to turbulent eddies (Corino and Brodkey, 1969), there may not be much of an opportunity for stress induced macromolecular diffusion to dominate the process enabling a steady equilibrium concentration difference of the macromolecules between the wall and the bulk region to get established. The major influence could then be that of drag reduction at the solid-liquid interface.

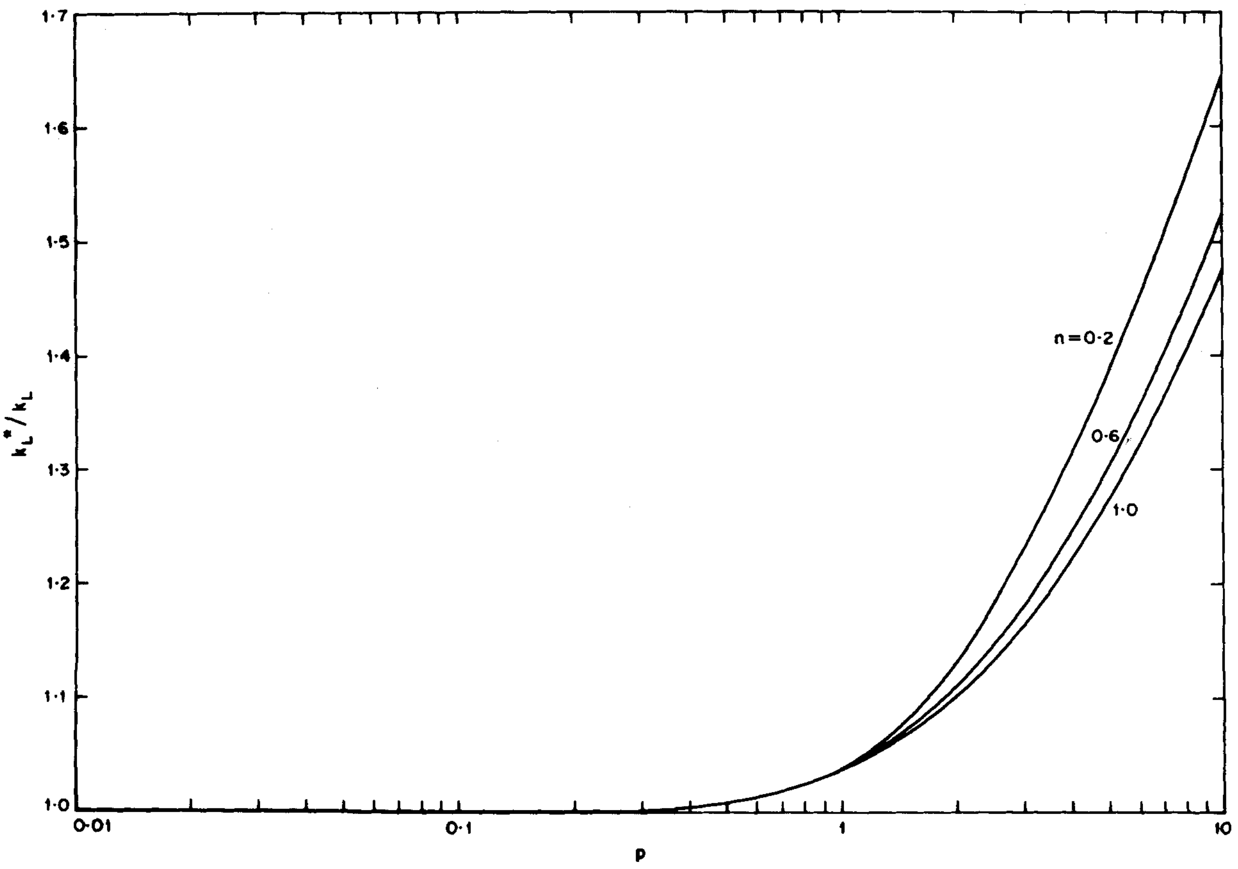

Figure 2. Influence of slip on gas absorption in falling films

An approximate estimation of the possible reduction in film thickness due to the addition of the polymer can be obtained following the procedure of Kosky (1971). The turbulent film thickness can be estimated by knowing $u^+[y^+]$ for any fluid. This function in the case of a Newtonian fluid is

$$u^+ = 8.47\, y^{+1/7} \tag{14}$$

Shenoy and Mashelkar (1981) have derived the corresponding relationship for a drag reducing fluid. In the asymptotic case of very large Deborah numbers the relationship is

$$u^+ = 6.26\, y^{+\,0.379} \tag{15}$$

The expression for film thickness in a Newtonian fluid follows as

$$\delta^+ = 0.0504\, Re^{7/8} \tag{16}$$

and that for fluid flowing under the asymptotic drag reduction conditions can be deduced as

$$\delta^+ = 0.122\, Re^{0.725} \tag{17}$$

A typical calculation with $Re = 5{,}000$ and $\nu = 10^{-2}$ cm^2/s shows that for a dilute polymer solution of the same kinematic viscosity as that of water there is about 25% reduction in film thickness. This implies an increase in v_m leading to increased ϵ (Eq. 11) and increased k_L (Eq. 14). We therefore predict that polymer addition in turbulent films is likely to cause an enhancement in absorption rates.

EXPERIMENTAL

The axisymmetric bodies of revolution used in this work are shown in Figure 2. The absorption column used has been described by Mashelkar and Soylu (1974) and had a design and mode of operation very similar to that used by Davidson and Cullen (1957). Hydroxyethyl cellulose (HEC, Hercules), Polyacrylamide (PAA-AP273, Dow), Polyethylene oxide (PEO-WSR 301 and Coagulant, Union Carbide) were used as water soluble polymers. Pure carbon dioxide was absorbed in films of polymer solutions generated over these surfaces. The extent of fluid stretching could be changed by changing the liquid flow rate, by changing the geometry of the surface over which the film flows (*viz.*, by changing the cone dimensiones), and by changing the orientation of the axisymmetric object w.r.t. flow direction (*viz.*, by using a horizontal vs. vertical ellipsoid of revolution).

The long wetted wall column used had an internal diameter of 2.7 cm, absorption length of 82 cm and a general design similar to that used by Emmert and Pigford (1954).

RESULTS AND DISCUSSION

Gas Absorption in Films Generated on Axisymmetric Bodies of Revolution

The accuracy of the experiments was checked by performing runs at very low water flow rates and using the LPT asymptotes to calculate diffusivity of CO_2 in water. The experiments with the wetted sphere column at 19.5°C gave a value of D of 1.69×10^{-5} cm^2/s which compared extremely well with the literature value of 1.696×10^{-5} cm^2/s. The experiment with the wetted double cone column at 20°C gave a value of D of 1.70×10^{-5} cm^2/s which was in good agreement with the literature value of 1.70×10^{-5} cm^2/s.

We shall now examine the influence of fluid stretching on the gas absorption rate. To accomplish a rational comparison we plot the data as $k_L/D^{0.5}$ vs. the Reynolds number, Re, which was arbitarily defined for the axisymmetric body of revolution as $4Q/W\nu$. Here W is the wetted perimeter based on the largest transverse dimension of the body. Such plots should reflect the true influence of hydrodynamics.

Figures 3 and 4 show the data obtained with a sphere using PEO

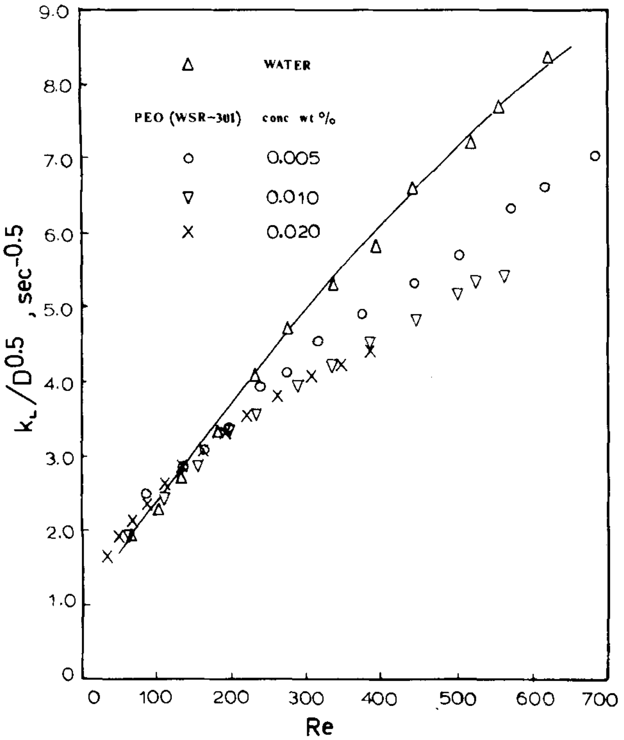

Figure 3. Influence of rapid stretching on absorption in PEO [WSR-301] solutions

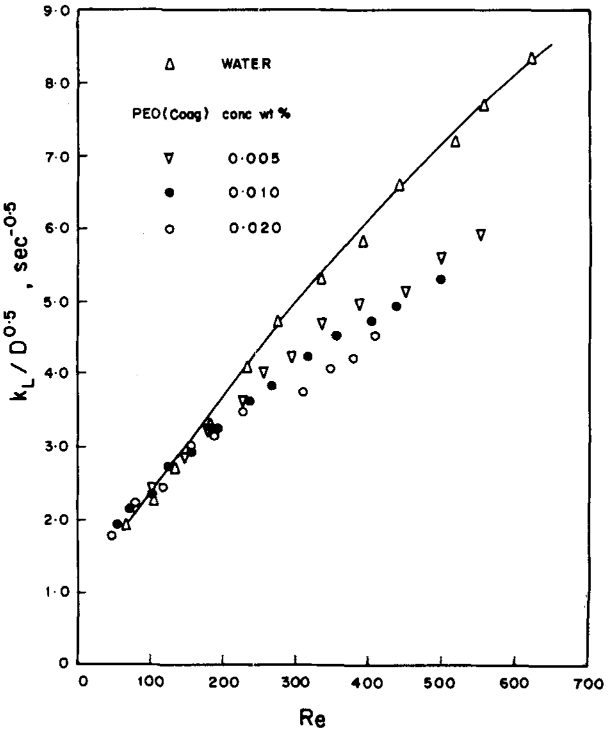

Figure 4. Influence of rapid stretching on absorption PEO [coagulant] solutions

(WSR-301) and PEO (coagulant) solutions. Figure 5 shows data obtained with PEO (coagulant) solutions on a double cone with base angle of 40°. Figure 6 shows the data obtained with PEO (WSR-301) solutions when the ellipsoid of revolution was placed with its major axis vertical (configuration C in Figure 1), and Figure 7 shows the data obtained when the ellipsoid of revolution of the same dimensions was placed with its major axis horizontal (configuration D in Figure 1), the extent of stretching in the latter case is evidently greater due to the more abrupt velocity changes the fluid undergoes.

Figures 3–7 show that the water and polymer solutions data converge together at low *Re*, whereas at higher *Re* the polymer solutions show reduced mass transfer rates.

Possible Mechanistic Explanation for Anomalous Mass Transport in Stretched Films

Bulk Rheology Considerations. The process of convective diffusion in a freely accelerating–decelerating interface is controlled in a region of zero vorticity. We are in fact dealing with an unsteady extensional kinematic field in an elastic fluid which controls the process of convective diffusion. To examine the effects qualitatively, let us consider the problem of development of stresses in a convected Maxwell model which is being stretched at a constant stretch rate (Denn and Marrucci, 1971). The resulting tensile stresses are given as

$$T = \frac{3\mu\Gamma}{(1-2\lambda\Gamma)(1+\lambda\Gamma)} - \frac{2\mu\Gamma}{(1-2\lambda\Gamma)} e^{-(1-2\lambda\Gamma)t/\lambda} - \frac{\mu\Gamma}{1+\lambda\Gamma} e^{-(1+\lambda\Gamma)t/\lambda} \tag{18}$$

where the time t is to be interpreted as the residence time of the material element. μ is the viscosity and λ is the relaxation time. It can be readily shown that if

$$2\lambda\Gamma > 1 \tag{19}$$

and

$$\lambda t > 3 \tag{20}$$

then large internal stresses will be generated in the fluid.

Typical local stretch rates Γ were calculated in the case of a sphere. Near the top pole of the sphere they were as high as 10^{-2} s^{-1}. With typical values of λ for polymer solutions used in this work ranging between $10^{-1} - 10^{-3}$ s, it could be readily seen that the

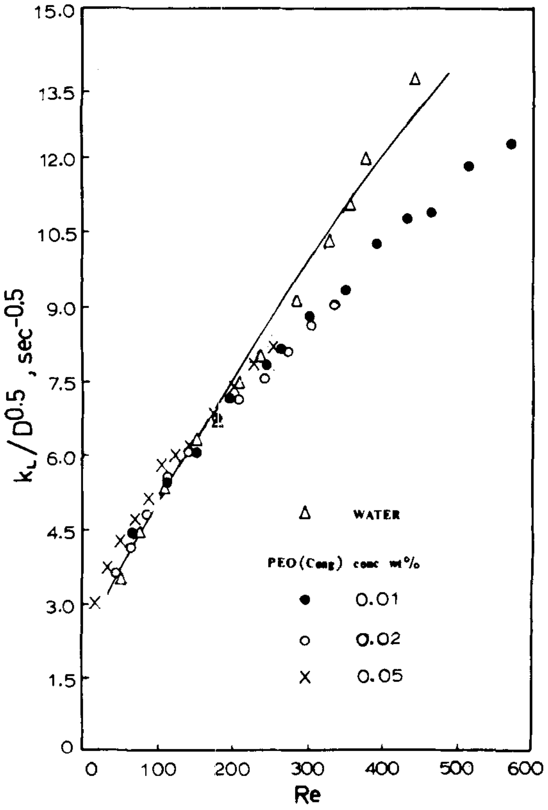

Figure 5. Influence of rapid stretching on absorption in PEO [coagulant] solutions

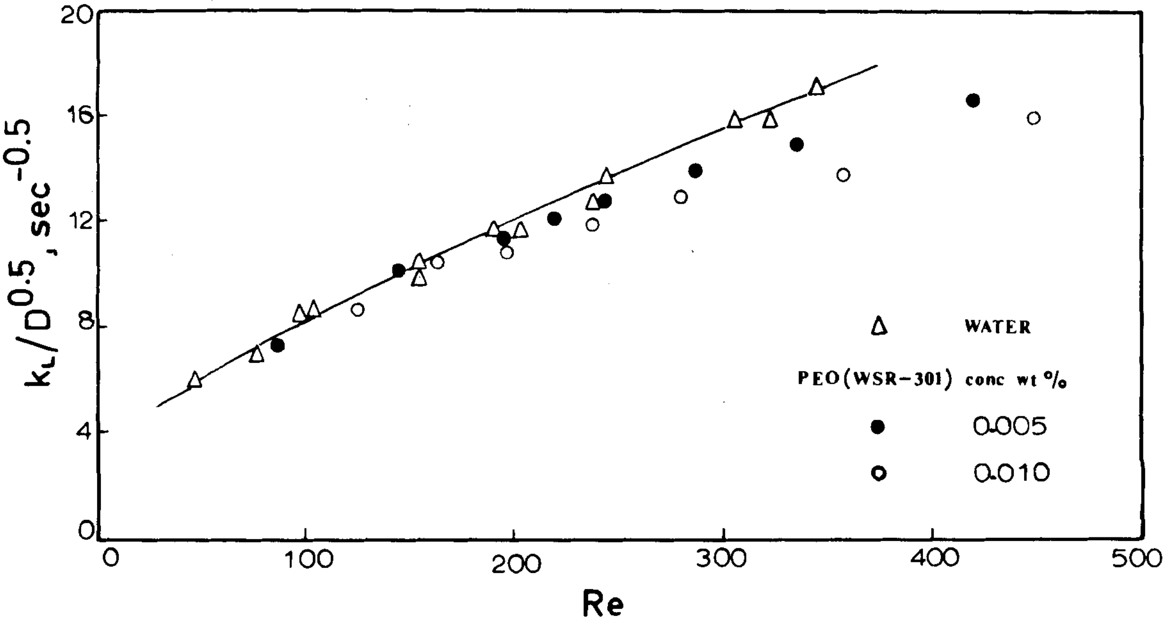

Figure 6. Inflence of rapid stretching on absorption in PEO [WSR-301] solutions

conditions 19–20 were satisfied at least over some portion of the sphere. Therefore, the flowing films might tend to generate large internal stresses during these rapid stretch conditions. In free flows which take place under the action of gravity alone, there is a limit to which the stresses can be built. Therefore, the kinematics in the film will have to adjust itself to reduce the stresses. This can only be done by slowing down the film and therefore reducing the surface velocity. Such a reduction implies large mean contact time, which implies reduced mass transfer rate (Eq. 4). It is evident that more reduction will be obtained by increasing the stretch rate which can be obtained by increasing the flow rate or changing the orientation, Figures 5 and 6, or by increasing the fluid relaxation time by increasing the polymer concentration. The data presented by us are in qualitative support of the expected trends. Note that our experiments involve nonconstant stretch rates. However, the work by Ting and Hunston (1977) shows that the basic considerations in such cases remain the same as above.

Surface Rheology Considerations. Let us now examine an alternative explanation which is based on surface rheological considerations. The polymers used in this work do have some surface activity. Thanawala (1973) provided data pertaining to dynamic surface tension measurements for the kind of polymer solutions used in this work. It is seen that surface pressures of the order of 2 to 10 dyne/cm are exerted in the range of concentrations used in this work. However, the key question is concerned with the speed with which reasonable concentration gradients would be allowed to be established in processes in which such bulky macromolecular surfactant systems participate. Again an order of magnitude of calculation will give some guidance. Davies and Young Hoon (1974) have done such calculations for PEO (coagulant) solutions and shown that the time required for setting up significant surface concentration gradients of the polymer would be of the order of several seconds. A typical calculation for polyethylene oxide (WSR 301) with concentration of 100 ppm (mol wt. = 2.5×10^6) can be done as follows. The diffusivity of polyethylene oxide in water would be of the order of 10^{-7} cm^2/s. Considering typical transport processes at interface, this would imply a mass transfer coefficient of the order of 10^{-4} cm/s. A 100 ppm solution of polyethylene

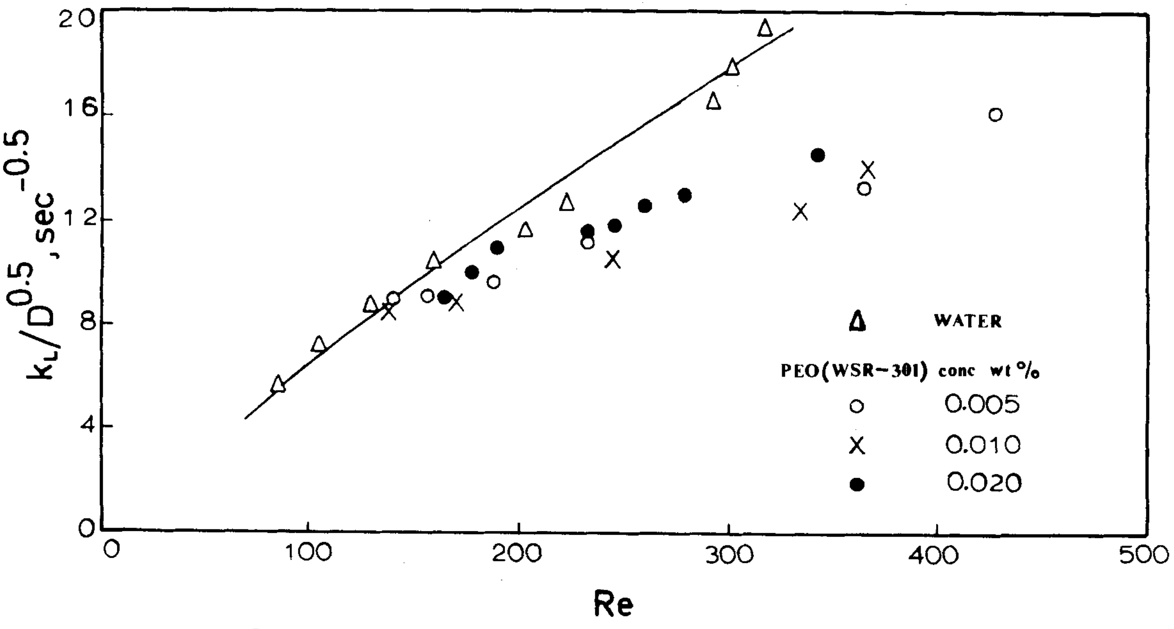

Figure 7. Influence of rapid stretching on absorption in PEO [coagulant] solutions

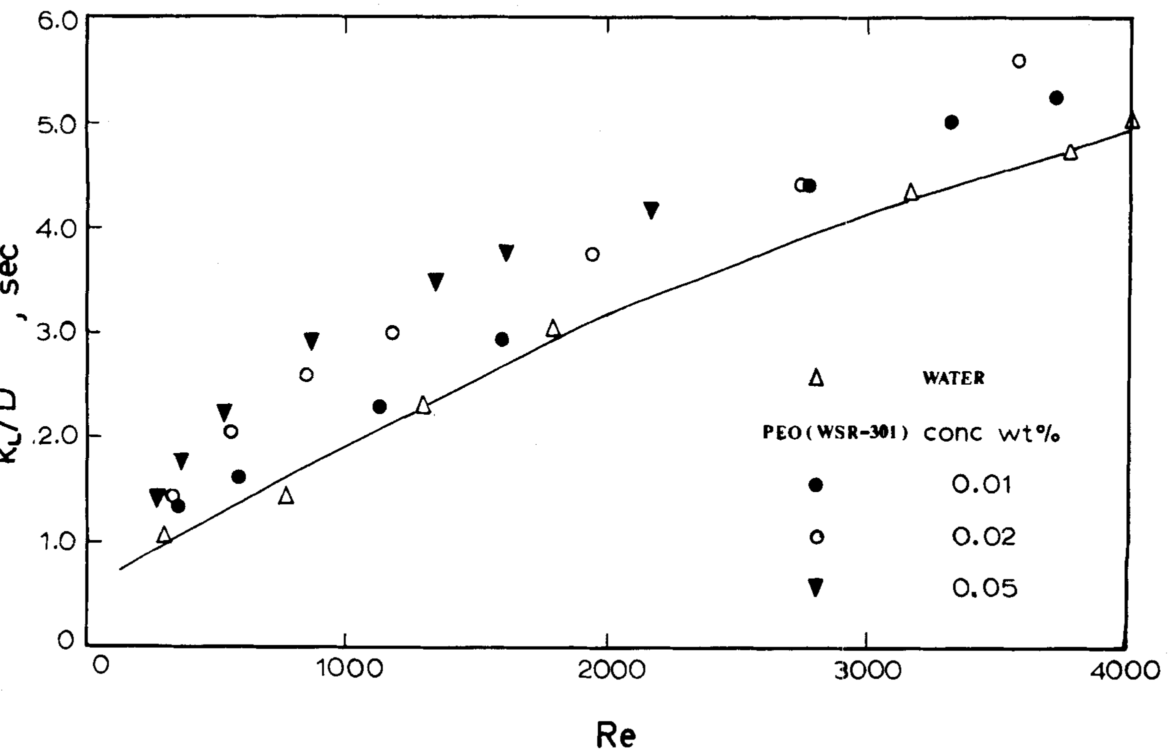

Figure 8. Gas absorption in a long wetted wall column with aqueous solutions of PEO [WSR-301]

oxide would mean a concentration of 4 × 10^{-11} mol/cm^3. If we assume that a significant surface concentration of the order of 10^{-12} mol/cm^2 [C_s/A] will be required to alter the mass transfer rates significantly, we can approximately estimate the time required for setting up such gradient as

$$t \simeq \frac{C_s/A}{k_L C_b} \simeq 250 \text{ s}.$$

On the other hand typical mean contact times in the falling film apparatus of the kind used here will be of the order of $10^{-1} - 1$ s. It is thus seen that such times are much shorter than the minimum times required for significant adsorption to occur so that a surface film could be formed. It is thus obvious that the observed reduction in gas absorption is most unlikely to be a surface effect.

Gas Absorption in Laminar Rippled Films on Vertical Surfaces

Since increasing *Re* caused some rippling to occur on spheres, cones and ellipsoids of revolution, we performed experiments in a long vertical wetted wall column and studied the influence of polymer addition on gas absorption. Figures 8 and 9 show the

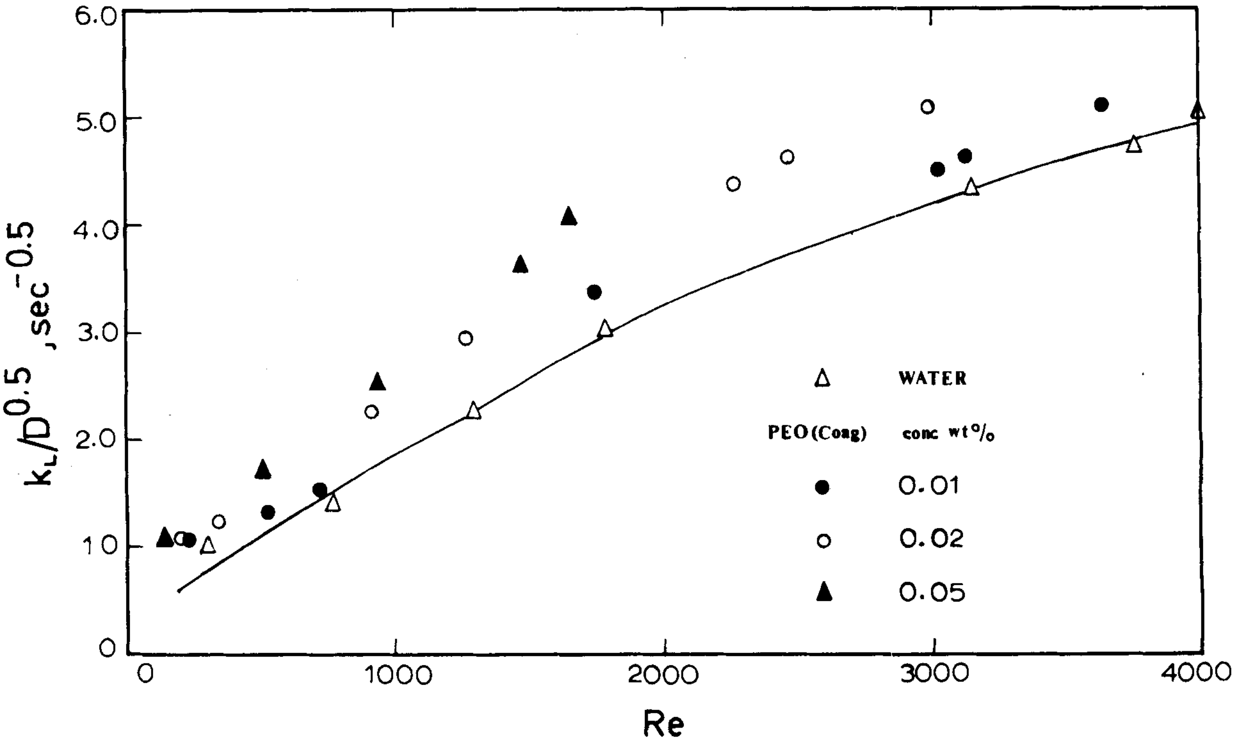

Figure 9. Gas absorption in a long wetted wall column with aqueous solutions of PEO [coagulant]

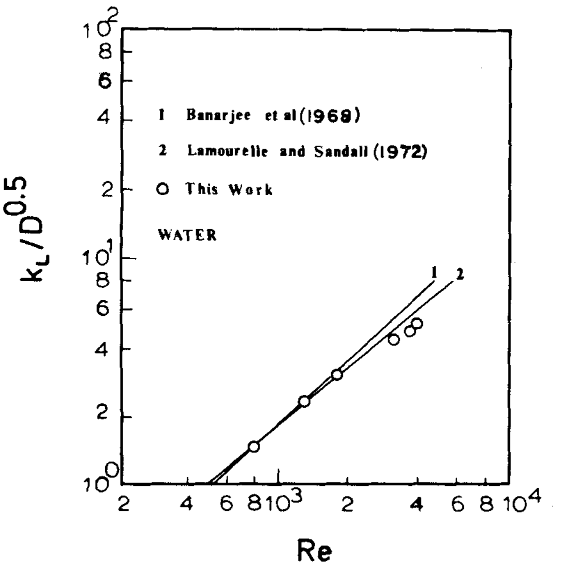

Figure 10. Comparison of mass transfer data (obtained with water) from this work with the correlations in the literature

pertinent data. We shall only examine the data for $200 < Re < 1{,}000$, which are believed to belong to the laminar rippling region. Interestingly enough, we find that the polymer solutions show increased absorption rates in this case.

The observed increase in the unstretched laminar rippling films is most likely to be due to the slip effect. Again in the absence of an exact method of evaluation of the pertinent parameters in the laminar rippling film, it is not possible to make quantitative predictions, but qualitatively the results are in line with the hypothesis postulated earlier, Figure 2.

It is likely that the stress induced diffusion causing macromolecular migration in the vicinity of the solid-liquid interface might play a dominant role in laminar rippling films, since the visual investigations by numerous authors (e.g., Oliver and Atherinos, 1968) do show that the disturbances emanating from the free surface do not penetrate the wall layer in such cases. The apparent "drag reduction" phenomenon for laminar rippled films of polymer solutions reported by Popadic (1975) are in strong support of occurrence of such slip effects.

It is evident that two opposing mechanisms act simultaneously when a gas is absorbed in films flowing under rapid stretch conditions. The slip effects lead to an augmentation in absorption rates, whereas the influence of elasticity on the stretching process at the free interface leads to a reduction in absorption rates. Since the overall effect is seen to be that of reduction it would seem that the latter effects dominate.

Gas Absorption in Turbulent Falling Films

For ordinary Newtonian fluids, the correlation of Banerjee et al. (1968)

$$k_L = 2.93 \times 10^{-3} D^{1/2} Re^{0.938} \tag{21}$$

and that by Lamourelle and Sandall (1972)

$$k_L = 5.65 \times 10^{-3} D^{1/2} Re^{0.839} \tag{22}$$

have been found to give good agreement with the data in the literature. (Note that Eqs. 21 and 22 are dimensional with k_L expressed in cm/s and D expressed in cm^2/s). Figure 10 shows a comparison between our data and the predictions of Eqs. 23 and 24 for water–CO_2 system. The agreement appears to be quite sound. The influence of polymer addition on gas absorption in turbulent films can be seen from Figures 8, 9, 11 and 12, if one examined the data obtained with $Re > 1{,}200$. In all the classes, polymer solutions showed enhanced gas absorption rates, a result which was deduced on the basis of the eddy diffusivity model described earlier. The predictions of the model are thus borne out qualitatively.

The favorable influence of polymer addition on gas-liquid mass transfer in falling films may be contrasted with the related heat/mass transport processes in turbulent flow of drag-reducing fluids in confined flows where the frictional losses as well as wall-fluid heat/mass transfer rates are reduced and the advantages of reduced frictional loss are lost (Mashelker, 1981). The present data are the first to be reported in the literature where polymer addition is shown to augment mass transfer rates.

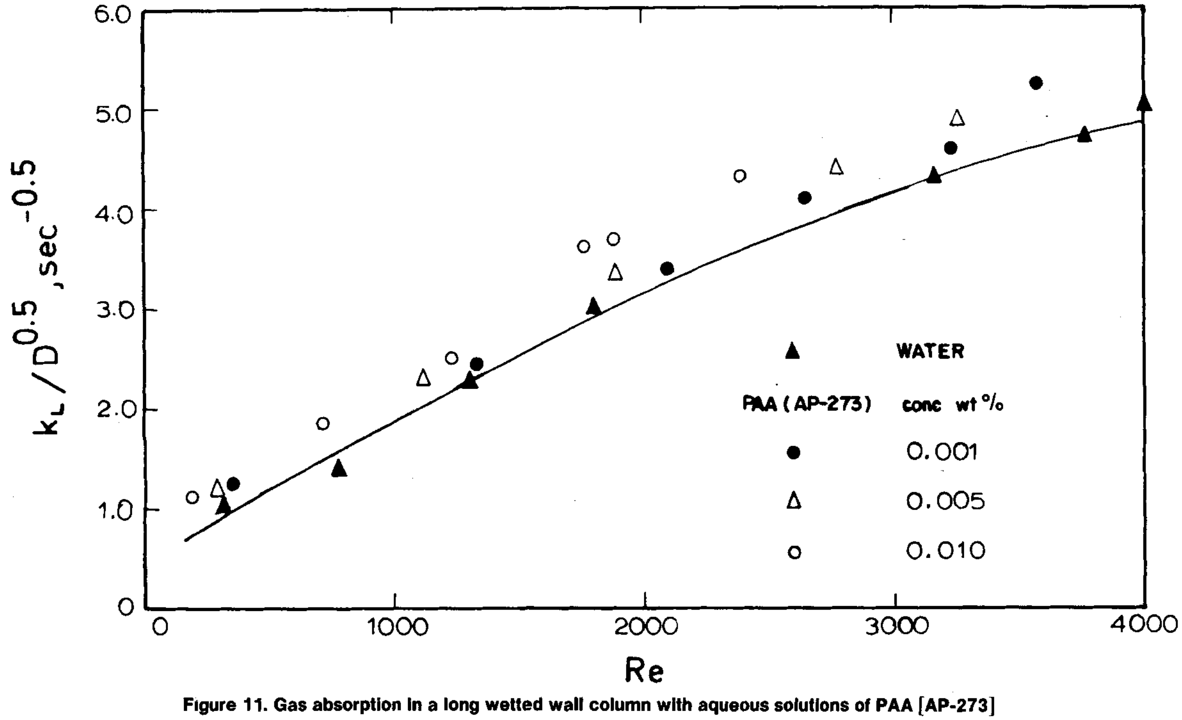

Figure 11. Gas absorption in a long wetted wall column with aqueous solutions of PAA [AP-273]

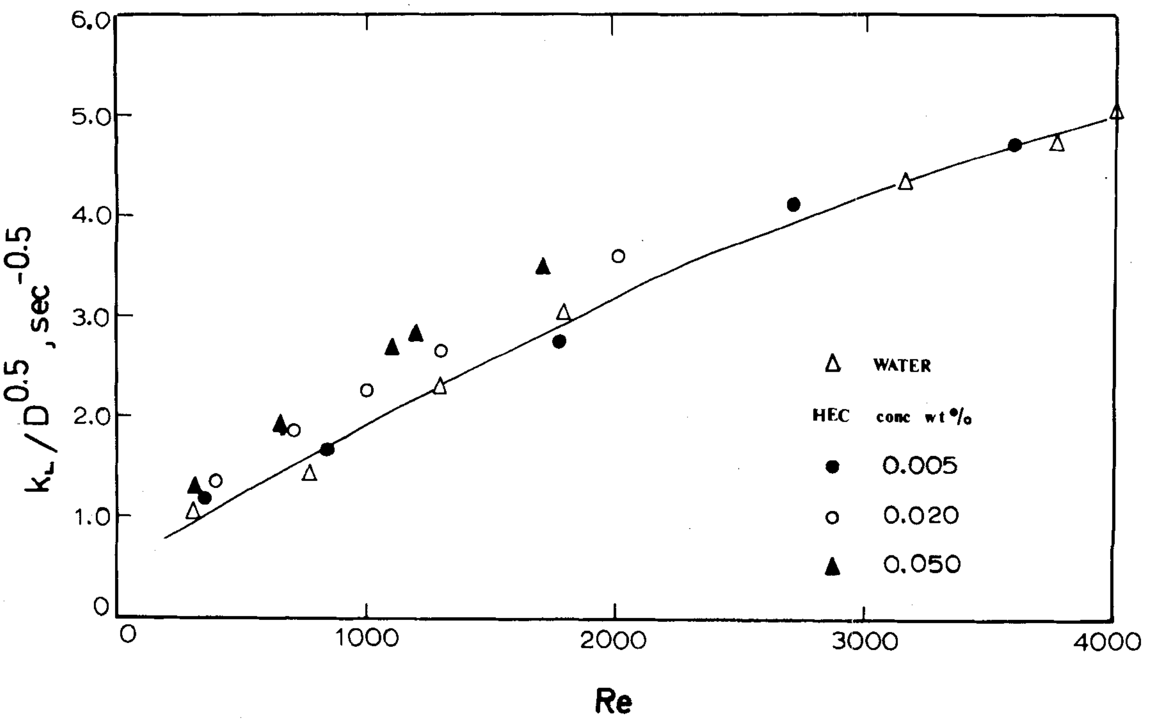

Figure 12. Gas absorption in a long wetted wall column with aqueous solutions of HEC

Theoretical Implications of the Present Work

The question of a reliable estimate of the relevant eddy sizes and frequencies in turbulent mass transfer processes was raised by Fortescue and Pearson (1967) and still continues to be debated. The present work could have an important bearing on this problem.

Two different approaches have been taken to model turbulent mass transfer processes from free interfaces. Some workers such as Fortescue and Pearson (1967) consider that large-scale eddies are responsible for mass transfer. On the other hand, Kolmogoroff-scale dissipative eddies have been assumed to control the process of mass transfer by some workers such as Miyauchi and Kataoka (1970), Lamont and Scott (1970), etc. Calculations show that the reciprocal frequency of such dissipating eddies would be of the order of 10^{-3} s, whereas the relaxation times of dilute polymer solutions would be of the order of 10^{-3} s. It is, therefore, conceivable that these fine-scale eddy motions will be most severely damped in the presence of polymer additives. If the small-scale eddy motion was to be the controlling factor, there would have been a significant reduction in k_L on polymer addition. Since this is not observed, it appears that large-scale motions control the process of mass transfer in falling films. Interestingly, Davies and Lozamo (1979) have determined the distribution of sizes and energies of eddies in free interfaces in thin films of water flowing over smooth and rough plates. They show that it is not the small-scale dissipative eddies but Prandtl-size (and even larger) eddies that are responsible for mass transfer at a free surface. The study by Henstock and Hanratty (1979) supports this strongly in the sense that they have also deduced that the mass transfer process is controlled by eddies whose length and velocities are characterized by bulk turbulence.

Practical Implications

There are many situations in industrial practice where the liquid-side contamination with foreign additives is unimportant. An example is the scrubbing of undesirable impurities from a gas mixture, the liquid absorbent being generally wasteful. Under such conditions, polymer addition may be conveniently used with a significant economic advantage provided wetted wall columns are used. However, use of drag-reducing agents in packed columns where curved surfaces are encountered is likely to lead to an adverse effect on mass transfer. The significant advantages to be obtained in gas-liquid flows of drag-reducing additives have been already noted (Greskovich and Shrier, 1971; Rosehart et al., 1972). In view of the findings of this work, it is important to examine the influence in such situations.

It is interesting to note that drag-reducing additives are being currently added for increasing sewer capacity (Selling, 1978). Purification of the sewage by using the so-called trickling filter devices uses the film mode for operation, and in that case the results of this investigation will be of direct relevance.

NOTATION

a = constant in the eddy diffusivity expression (Eq. 9)
C = concentration
C^* = saturation concentration
D = molecular diffusivity
D_t = eddy diffusivity
g = gravitational acceleration
K = consistency index
k_L = liquid-side mass transfer coefficient without slip
k_L^* = liquid-side mass transfer coefficient with slip
L = length of the flat plate
n = power-law index
N = rate of gas absorption (moles per unit time)
p = slip parameter (Eq. 6)
Q = volumetric flow rate
R = radius of sphere, base radius of cone
Re = Reynolds number $\left(= \frac{4Q}{W\nu}\right)$
Sc = Schmidt number ($= \nu/D$)
Sh = Sherwood number $\left(= \frac{k_L\delta}{D}\right)$
T = tensile stress in a stretching flow
t = time
t_E = time of exposure
u = local axial velocity
u^* = friction velocity ($= \sqrt{g\delta}$)
u^+ = dimensionless axial velocity $\left(= \frac{u}{u^*}\right)$

v = surface velocity
v_m = mean velocity
v_s = slip velocity
v^* = surface velocity in the presence of slip
W = wetted perimeter
y = distance from free interface
y^+ = dimensionless distance $\left(= \frac{u^* z}{\nu}\right)$

Greek Letters

α = angle defined in Eq. 1
β = base angle of the cone (defined in Figure 1)
Γ = stretch rate
ν = kinematic viscosity
δ = film thickness
δ^+ = normalized film thickness $\left(= \frac{\delta u^*}{\nu}\right)$
λ = relaxation time
ϵ = rate of energy dissipation per unit mass
μ = viscosity
ρ = density
χ = slip coefficient
τ = stress tensor
τ_w = wall shear stress
$\underset{\approx}{\Delta}$ = rate of deformation tensor

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