gence might be better than that of Newton's method or of some of its other modifications described in this section. Table 1, however, indicates this to be true only with respect to Newton's method itself when using the same program limits employed for Newton's method. Table 1 also suggests that these other modifications could have smaller regions of convergence.

Lastly, Scherule's (1979) quadratically convergent modification of Newton's method should be mentioned. This scheme avoids solving systems involving the inverse of the Jacobian. It thus requires less computation per iteration than does Newton's method. The author applied Scheurle's scheme to a set of collocation equations arising from a packed column model. Scheurle's modification exhibited a smaller region of convergence than did Newton's method; however, very few starting estimates were tested.

NOTATION

A = tridiagonal matrix in Eq. 1
b = molar rate of production of a component in the bottoms product stream
d = molar rate of production of a component in the distillate product stream
f = vector of feed rates of a single component
g = vector-valued function
I = number of components present
i = component index
j = stage index; reboiler is stage 0, J is top stage
K = equilibrium ratio
L = liquid leaving a stage
n = iteration number
S = correction factor of Boston and Sullivan
u,w = vectors of independent variables
V = vapor arriving at a stage
θ = correction factor of Holland
Υ = vector of vapor flow rates of a single component

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Absorption in Mixed Surfactant-Polymeric Films: A Novel Phenomenon

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The influence of surface-active agents on gas absorption in turbulently falling films has been well known (Levich, 1962; Davies, 1972). The action of soluble surface-active agents presumably occurs by their selective adsorption at the interface. This leads to a gradient of surfactant concentration and therefore to a shear stress which opposes the motion. The effect of an insoluble surface-active agent is normally attributed to the surface convection and surface diffusion leading to a steady-state distribution of the concentration, which generates shear stresses opposing the motion. In either case, the net effect is to dampen the convective motion at the free interface thereby imparting certain rigidity. Such phenomena lead to a reduction in mass transfer rate at the free interface.

Our recent studies (Mashelkar, 1982) have indicated that the addition of soluble drag-reducing polymers (such as polyethylene oxide, polyacrylamide) in minute quantities actually brings in an enhancement in the mass transfer rate at the gas-liquid interface. This is at first sight somewhat surprising in view of the fact that such polymers are known to be mildly surface active (Mohan et al., 1976; Vocel and Ryan, 1971). Mashelkar (1982) explained this phenomenon. It was shown that the drag reduction phenomenon in freely falling films results in the generation of lower shear stresses at the solid-liquid interface. In a gravity-controlled film flow, the response of the fluid is to reduce the film thickness thereby gen-

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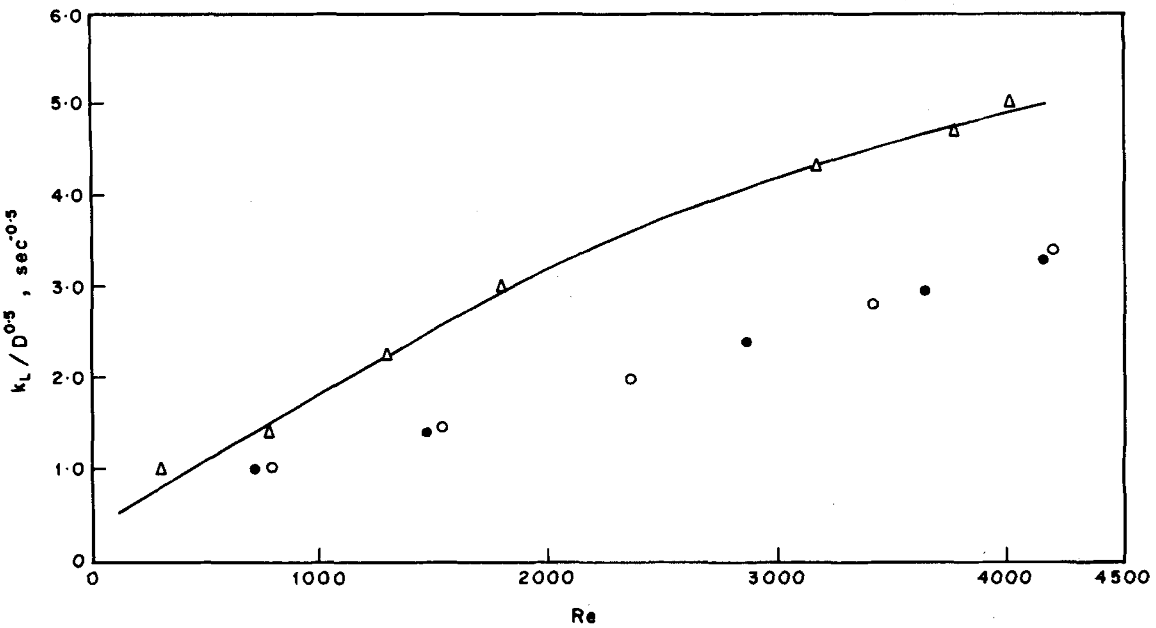

Figure 1. Influence of surfactant addition on gas absorption rate in a wetted column.
△ Water
○ 0.02% Atexal
● 0.05% Atexal

erating larger mean velocities. The resulting enhancement in the convective motion at the free interface was shown to be responsible for the eventually observed enhancement in mass transfer.

The phenomena elucidated in the foregoing imply that the roles of a polymer and a surfactant are exactly opposite in so far as the process of mass transport at the free interface is concerned. The interesting question now arises as to the phenomenon that might be exhibited if a mixed polymer-surfactant system was employed. Apart from the basic scientific curiosity, the resolution of this question might be important in a pragmatic sense. For instance, in the case of gas scrubbing, the presence of surface-active impurities is practically unavoidable. If the benefits of addition of minute quantities of drag-reducing agents for enhancing gas absorption rates were to be exploited, the cumulative influence of

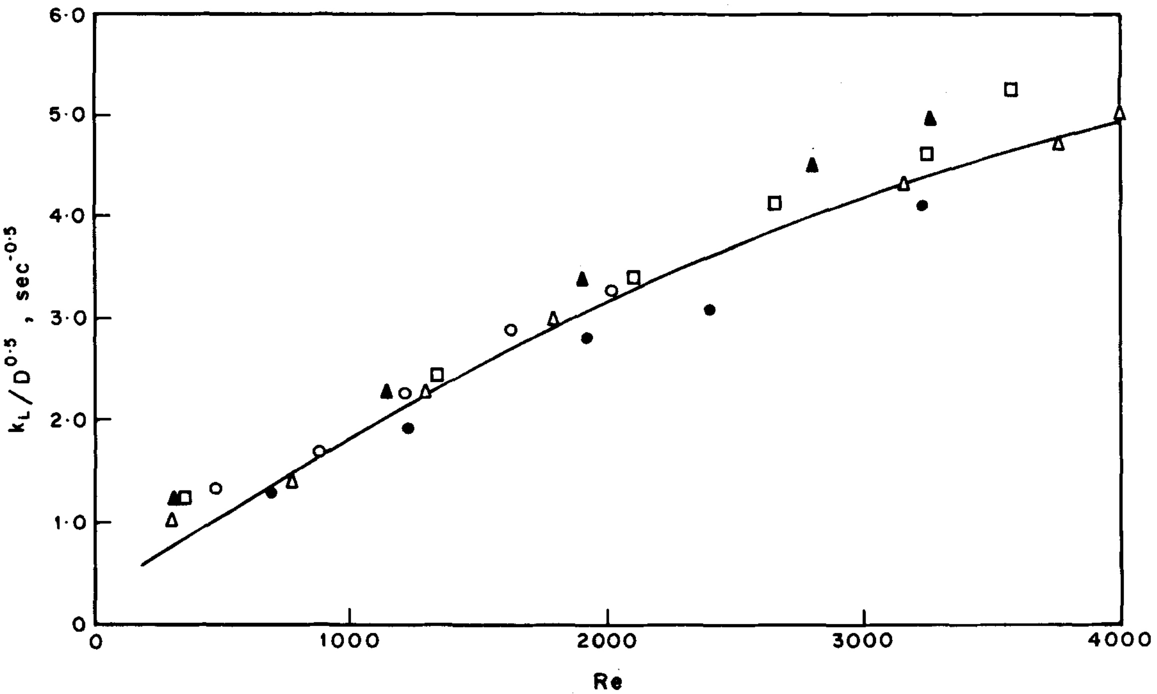

Figure 2. Influence of polymer and mixed polymer–surfactant addition on gas absorption rate in a wetted wall column.
△ Water
□ 0.001% PAA [AP-273]
▲ 0.005% PAA [AP-273]
● 0.001% PAA [AP-273] and
0.02% Atexal
○ 0.005% PAA [AP-273] and
0.01% Atexal

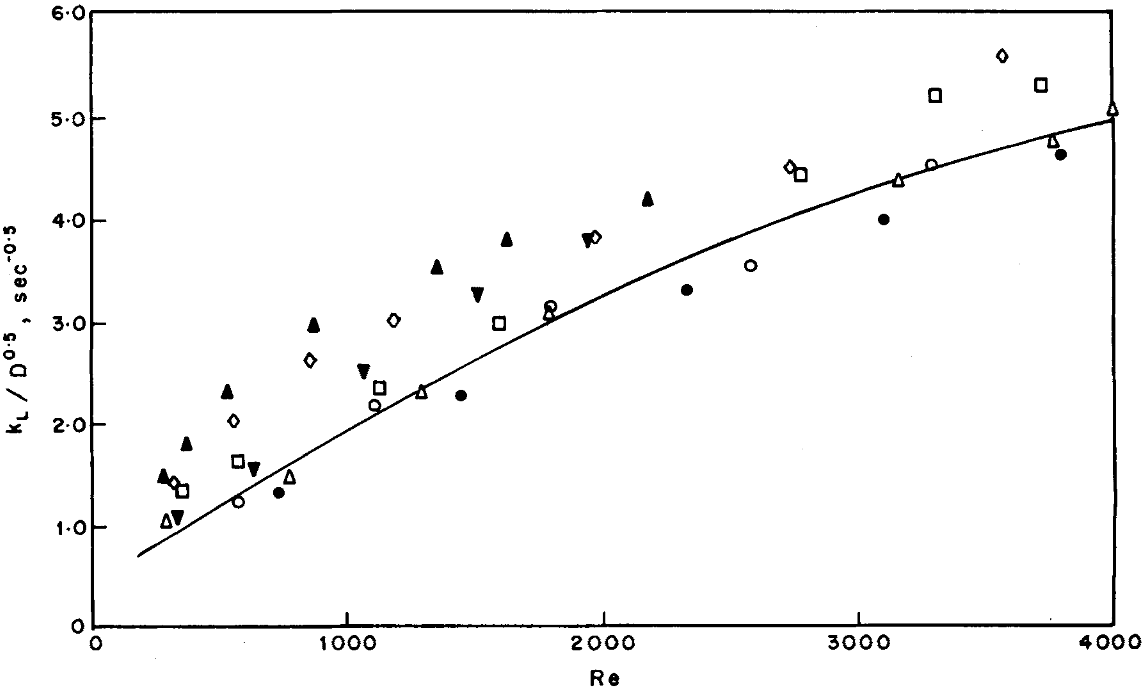

Figure 3. Influence of polymer and mixed polymer-surfactant addition on gas absorption rate in a wetted wall column.

△ Water
□ 0.01% PEO [WSR-301]
◇ 0.02% PEO [WSR-301]
▲ 0.05% PEO [WSR-301]
○ 0.02% PEO [WSR-301] and 0.02% Atexal
● 0.01% PEO [WSR-301] and 0.05% Atexal
▼ 0.05% PEO [WSR-301] and 0.01% Atexal

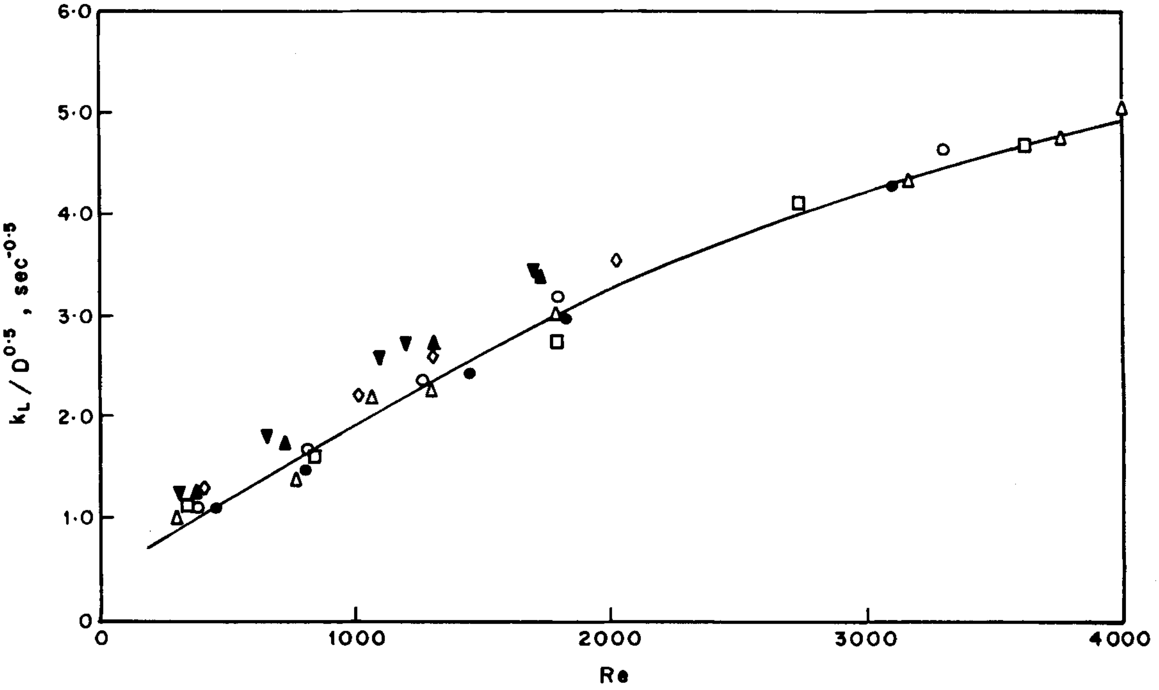

Figure 4. Influence of polymer and mixed polymer-surfactant addition on gas absorption rate in a wetted wall column.

△ Water
□ 0.005/HEC
◇ 0.02% HEC
▼ 0.05% HEC
● 0.005% HEC and 0.02% Atexal
○ 0.02% HEC and 0.02% Atexal
▲ 0.05% HEC and 0.02% Atexal

TABLE 1. SURFACE TENSION MEASUREMENTS OF POLYMER SOLUTIONS, SURFACTANT SOLUTIONS AND THE MIXTURES OF POLYMERS AND SURFACTANTS

Solutions	Conc. wt. %	Temp. °C	Surface Tension dyne/cm (± 0.5 dyne/cm)
Distilled Water	—	23	72.9
	0.05	23	72.2
PAA (AP-39)	0.10	23	72.2
	0.20	23	71.8
	0.05	23	72.0
PEO (WSR-301)	0.10	23	72.1
	0.20	23	71.9
	0.05	23	73.0
PEO (Coagulant)	0.10	23	73.1
	0.20	23	72.5
	0.005	23	34.0
Atexal	0.025	23	30.7
	0.050	23	29.4
PEO (WSR-301)	0.01	21	32.7
Atexal	0.05		
PEO (WSR-301)	0.05	21	49.0
Atexal	0.01		
PAA (AP-273)	0.01	21	31.8
Atexal	0.02		
HEC	0.02	21	32.0
Atexal	0.02		

mixed polymeric-surfactant system has to be fully understood. The present experimental investigation was motivated by these considerations.

EXPERIMENTAL

The experimental work was undertaken in an apparatus and in the manner described by Mashkelkar (1982). The design of this apparatus was exactly the same as used by Emmert and Pigford (1954).

The drag-reducing polymers used were hydroxyethyl cellulose (HEC) supplied by Hercules Co., polyacrylamide (PAA-AP 273) supplied by Dow Chemicals and polyethylene oxide (PEO-WSR 301) supplied by Union Carbide. In the range of concentrations employed in this work, the solutions exhibited a constant Newtonian viscosity. The surfactant used was Atexal supplied by ICI (organic div.) which was a nonionic base product of certain higher alcohols and alkylene oxides. Carbon dioxide was used as the absorbing gas in all the cases.

RESULTS AND DISCUSSION

Figure 1 shows the results on gas absorption in water plotted as $k_L/D^{0.5}$ vs. Re. Here k_L is the liquid-side mass transfer coefficient; D is the molecular diffusivity of the gas in the liquid; and Re is the Reynolds number defined as $Re = 4\Gamma/\nu$. Here Γ the volumetric flow rate per unit width and ν is the kinematic viscosity. As shown by Mashelkar (1982), these data were found to be in good agreement with the correlations proposed by Banerjee et al. (1968) and Lamourelle and Sandall (1972). The surfactant was added in small quantities. The influence of this addition on gas absorption rate is shown in Figure 2. As expected, there is a reduction in the rate of gas absorption. Further, experimental work was carried out with the addition of the polymers HEC, PEO and PAA in small quantities in the drag reduction range. It is readily seen from figures 2–4 that there is an enhancement in gas absorption rate on polymer addition, which can be presumably accounted for by the mechanism outlined in the earlier paper (Mashelkar, 1984). Note that at least a part of the influence of the polymer addition could be due to an end effect. It is not clear as to what is the exact magnitude of such end effect which arises due to polymer addition.

Figures 2–4 also show the influence of the addition of mixed polymer–surfactant system. It is quite surprising to find that the influence of surface-active agents in reducing the gas absorption rates (Figure 1) has been completely overcome when a mixed polymer-surfactant system is used. To our knowledge such an unusual phenomenon has not been reported in the literature heretofore.

For a rational explanation of the phenomenon observed, a detailed knowledge of the surface rheology of the mixed polymeric surfactant system and its influence on the hydrodynamics in the freely falling films is necessary. We carried out some measurements of the surface tension properties of typical fluids and fluid mixtures used in this work by using a du Nuoy tensiometer (Table 1). However, we did not carry out detailed surface pressure concentration measurements. There are some related studies in the literature (Vocel and Ryan, 1971; Mohan et al., 1976) where the interfacial viscoelastic properties of adsorbed surfactant and polymeric films at fluid interfaces have been investigated. It is readily seen from the examination of the data provided by these authors that the presence of a polymer reduces the influence of the surface-active agent considerably. For instance, Mohan et al., while investigating surface rheology of aqueous polyacrylamide solutions with sodium alkyl sulfonate, found that the surface viscosity and surface elasticity barely changed when the surfactant concentration was increased. There is thus a *prima facie* case to believe that in the presence of a polymer the surface rheological properties of mixed systems alter rather dramatically. Of course no generalization of the results obtained by the previous workers could be made to the present system, which is somewhat different. However, it does appear that the polymer helps in reducing the retarding influence of the surfactant on the interfacial convective motion.

The pragmatic implications of the unusual findings reported here are clear. As indicated earlier, the presence of adventition's surface-active impurities is unavoidable in practical situations. The addition of minute quantities of drag-reducing agents for improving the mass transfer characteristics of wetted wall absorbers appears to be exceedingly promising.

NOTATION

D = molecular diffusivity of carbon dioxide in absorbing solutions
k_L = mass transfer coefficient
Re = Reynolds number $\left[= \frac{4\Gamma}{\nu}\right]$
Γ = volumetric flow rate per unit width of wetted wall column
ν = kinematic viscosity

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