

Influence of Polymer Additives on the Gas-Liquid Mass Transfer in Stirred Tanks

The influence of polymer additives upon the gas-liquid mass transfer in stirred tanks is examined. While the addition of sodium carboxymethylcellulose brings about a reduction of the overall liquid side mass transport coefficient which is in line with the predictions by earlier works, the reduction of $k_L a$ in polyacrylamide solutions of equal viscosity is much stronger. This is explained by the viscoelasticity of the PAA solutions, and an empirical correlation is proposed.

V. R. RANADE

and

J. J. ULBRECHT

Department of Chemical Engineering
University of Salford
Salford M5 4WT, Greater Manchester, England

SCOPE

Recent research has shown that the addition of small amounts of water soluble polymers can be beneficial in certain biochemical processes. Some of these polymer additives, like polyox and polyacrylamide, which are known to be drag reducing agents, can reduce the power requirement in stirred tanks by about 20% and in gas-liquid contactors by as much as 70%. Lucrative incentives thus exist for the addition of polymers in various processes.

Mixing is, however, rarely carried out for its own sake, and the influence of polymer additives in stirred tanks must be examined with respect of processes like heat and mass transfer. Further, some polymers will not

only influence the viscosity of the aqueous solutions, but they will also make the solution viscoelastic. The manifestations of viscoelasticity can be numerous, ranging from recoil in concentrated solutions to a phenomenon known as drag reduction in very dilute solutions.

In a recent paper, Quaraishi et al. (1977) reported that drag reducing polymers added to stirred aqueous dispersion have no influence upon the performance of the impeller to suspend solid particles and only a limited negative influence upon the liquid phase mixing. The question of the gas-liquid mass transfer was, however, left open in their work. An attempt to find the answer to this question is the scope of this work.

CONCLUSIONS AND SIGNIFICANCE

Polyacrylamide and sodium carboxymethylcellulose polymers were added in small quantities to the gas-liquid dispersion in a stirred tank, and the overall liquid side mass transfer coefficients were measured using a slow chemical reaction technique.

The overall gas-liquid mass transfer coefficient $k_L a$ is reduced in diluted aqueous solutions of polyacrylamide far more than one would expect on the basis of increased viscosity of the solution. Parallel experiments with solutions of sodium carboxymethylcellulose do not show such a drastic reduction. It is argued in this work that this is due to the increased viscoelasticity of the PAA solutions. Following the arguments of Seyer and Metzner (1967), one of the manifestations of the viscoelasticity of diluted

polymer solution is the increase of the elongation viscosity. This, in turn, prevents highly deformed gas bubbles from reaching the final stage when they break up. An indirect support for this model is found in the considerably reduced gas holdup in PAA solutions. The consequence of this is a reduction of the specific interfacial area a .

When selecting polymer additives for any particular process, one has to bear in mind that the addition of a polymer does not control only the viscosity of the system, but that overall rheological behavior can be profoundly altered. While in certain applications the increased viscoelasticity can be beneficial (reduction of power consumption, reduction of small scale turbulence, and thus protection of shear-sensitive materials), in others, such as gas-liquid mass transfer, it can be harmful.

BACKGROUND

An earlier communication by Quaraishi et al. (1977) dealing with the influence of polymer (drag reducing) additives on liquid phase mixing and solids suspension

Correspondence concerning this paper should be sent to J. J. Ulbrecht, Department of Chemical Engineering, State University of New York at Buffalo, Amherst, New York 14260. V. R. Ranade is also at the State University of New York at Buffalo.

0001-1541-78-1609-0796-\$01.05. © The American Institute of Chemical Engineers, 1978.

in stirred tanks hinted at further work on gas-liquid mass transfer being in progress. Results of this work are now reported in this paper.

In a number of industrial processes, water soluble polymers known as thickeners are added to the processed liquid to control its viscosity or its consistency, as the case may be. Examples are found in emulsion and suspension polymerization, in food processing, in hydro-metallurgy, and recently also in biological reactors. Here,

the role of the polymer is to protect the growing micro-organism against excessive shear, and detailed interpretations of this role have been put forward both in the open (Takahara et al., 1965; Moo Young, 1969) and in the patent literature (Dworschack, 1972; Moo-Young, 1976a). Similar claims of the beneficial role of polymers refer to fermentors (Corman, 1959; Moo-Young, 1976b) and to aerobic sewage treatment (Wilson, 1972).

It must be realized, however, that many types of polymer additives will not only affect the viscosity of the aqueous system, but they will also create a new dimension of the rheological behavior, the viscoelasticity. Ranade and Ulbrecht (1977) have shown how the viscoelasticity in a solution of polymers with concentration below 1% will alter the mechanism of gas dispersion and the flow pattern in a stirred tank. Viscoelasticity will, however, manifest itself also in solutions of very low concentrations of certain polymers, say of several hundreds parts per million, where the resistance against vortex stretching interferes with the mechanism of turbulent energy dissipation and thus leads to a reduction of power consumption. This effect is particularly pronounced in aerated tanks, which lead Quraishi et al. (1976, 1977) to suggest that in processes where polymer additives have to be used anyway, one might as well select those which would also reduce the power consumption. Typical examples of these would be polyethylenoxide (PEO) and polyacrylamide (PAA), drag reducing additives. In their second paper, Quraishi et al. (1977) have also shown that at low concentrations (below 250 ppm), these additives have no adverse effect on the suspension of solids and almost no effect on the liquid phase mixing. The question of gas-liquid mass transfer remained, however, open.

Gas-Liquid Mass Transfer

In many industrially important operations involving gas-liquid mass transfer, the resistance on the gas side is negligible, and the rate of mass transfer can be expressed as

$$R'a = k_L a (c^* - c^o) \quad (1)$$

Very little is known about the overall liquid-side mass transfer coefficient $k_L a$ in polymer solution stirred by mechanical agitators. Perez and Sandall (1974) measured $k_L a$ values in aqueous solutions of Carbopol. Although these solutions have shear dependent viscosity, they do not show any appreciable elasticity. The influence of viscoelasticity on the value of $k_L a$ was examined by Yagi and Yoshida (1975) who found $k_L a$ reduced in viscoelastic solutions. The concept of apparent viscosity was used in both these papers to interpret the influence of variable viscosity. Ranade and Ulbrecht (1977) found that the $k_L a$ coefficient in 0.1% PAA solutions was about one quarter of that in a test solution without the polymer, all other conditions being equal. Limited experimental data are available in the literature on gas-liquid mass transfer in dilute polymer solutions (1 000 ppm and less) which are likely to be used in biochemical operations.

Similarly, very little is known about the true liquid side mass transfer coefficient k_L . Some conclusions can be drawn, however, from the studies of Astarita (1965) and of Mashelkar and Soylu (1974) who found that polymer addition leads to a 10 to 20% increase of the diffusion coefficient of gases. On the other hand, however, the true liquid side mass transfer coefficient depends also on the surface renewal rate which is likely to be reduced owing to the suppression of turbulence. Following the arguments of Kolmogoroff, the reduction of k_L will be proportional to the fourth root of the reduction in power consumption due to polymer additives. Since the typical reduction of power observed by Ranade and

Ulbrecht (1977) was about 70%, the k_L is not expected to be reduced by more than about 15% so that the net effect of the polymer addition on the true liquid side mass transfer coefficient will be insignificant. Thus, any change in the value of the $k_L a$ coefficient is likely to be due to the change of the specific interfacial area a .

EXPERIMENTAL

All experiments were carried out in a perspex cylindrical tank (diameter 0.3 m) stirred by standard six-blade, disk mounted turbines with diameters 0.08, 0.1, and 0.14 m, respectively. The vessel was provided with four baffles 0.03 m wide. Height of the liquid in the tank was maintained at 0.3 m. The gas was fed into the vessel through a tube (0.004 m internal diameter), the opening of which was about 0.05 m under the centre of the turbine. The gas flow rate was varied between 20 and 85 l/min. The so-called slow chemical reaction technique suggested by Mehta and Sharma (1971) was employed to measure the overall mass transfer coefficient. This technique uses the absorption of carbon dioxide from carbon dioxide + air mixture into a buffer solution of sodium carbonate and bicarbonate. In order to satisfy the condition of a slow reaction, the total ionic strength of the liquid was kept around 1.8 g ions/l, and the ratio of CO_3^{2-} to HCO_3^{-} was kept between 2 to 5. Further details of this method and a critical analysis of its application are given by Ranade (1977).

The polymer additives used in this work were sodium carboxymethylcellulose (CMC) supplied by Hercules Powder Company, Ltd., and polyacrylamide Separan AP-30 (PAA) supplied by Dow Chemicals, Ltd. Initially, a stock solution of about 0.5% was made, and this was used to prepare the working solutions both in water and in the carbonate buffer. (Rheological properties of the solutions were measured using Rheogoniometer R18.) In water solutions, both CMC and PAA were distinctly shear thinning and, additionally, PAA solutions showed measurable primary normal stress difference. On the other hand, however, the same concentration of polymer in a carbonate buffer did not show any variation of viscosity with shear or any measurable normal stress difference. Thus, the viscosities of these solutions were measured using a capillary viscometer. Nevertheless, the PAA solutions still displayed a markedly different flow behaviour as compared with CMC solutions in that they showed spinnability when stretched between fingers, and they resisted the breakup of a liquid film or a liquid filament. Because of this, the dynamic methods of surface tension measurement lead to very incoherent results, so that the static method of capillary rise had to be used in the end to measure the surface tension of solutions.

RESULTS AND THEIR DISCUSSION

Properties of the Liquids Used

Under steady state conditions, two stress functions can be evaluated from the rotational flow of a liquid between a cone and a plate. The torque M can be converted to the shear stress S_{12} by

$$S_{12} = \frac{3M}{2\pi R^3} \quad (2)$$

and the axial thrust T between the cone and the plate can be used to compute the primary normal stress difference N_1

$$N_1 = \frac{2T}{\pi R^2} \quad (3)$$

which is one of the measures of viscoelasticity. Both S_{12} and N_1 are functions of the shear rate $\dot{\gamma}$

$$\dot{\gamma} = \frac{\omega}{\alpha} \quad (4)$$

which is directly proportional to the angular speed ω and inversely proportional to the angle of the conical

TABLE 1. RHEOLOGICAL PROPERTIES OF AQUEOUS SOLUTIONS OF CMC AND PAA

Concentration, ppm		n	$K \times 10^3$	b	$A \times 10^3$
CMC	PAA	—	Ns^nm^{-2}	—	Ns^nm^{-2}
100	—	1.0	1.54	—	—
—	100	0.975	2.33	0.975	70
200	—	1.00	2.85	—	—
—	200	0.80	5.45	0.92	85
1 200	—	0.92	58.0	—	—
—	1 000	0.55	1.27	0.77	750

TABLE 2. PROPERTIES OF THE CMC AND PAA SOLUTIONS IN THE CARBONATE BUFFER

Concentration, ppm		Viscosity, $\mu 10^3$	Density	Surface tension
CMC	PAA	Ns m^{-2}	kg m^{-3}	Nm^{-1}
100	—	1.48	1 050	0.0677
—	100	1.44	1 010	0.0680
200	—	1.57	1 000	0.0673
—	200	1.52	1 001	0.0677
1 200	—	5.27	1 000	0.0676
—	1 000	5.31	1 000	0.0680
0	0	1.10	1 060	0.0681

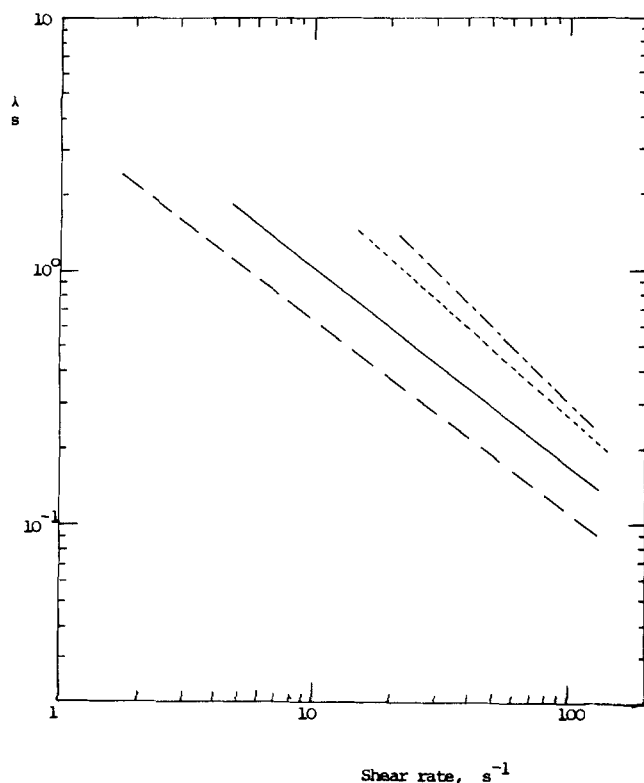


Fig. 1. Characteristic times of aqueous PAA solutions as a function of shear rate $\dot{\gamma}$ and concentration.

— — — — —	100 ppm
- - - - -	200 ppm
— — — — —	1 000 ppm
— — — — —	3 000 ppm

gap α . R is the radius of the cone and plate setup. For the purpose of this exercise, an empirical formula was used to correlate both S_{12} and N_1 with $\dot{\gamma}$. This formula has the advantage of needing only two adjustable parameters and yet is not in breach of the requirements of material invariance. Thus, it will be assumed that

$$S_{12} = K \dot{\gamma}^n \quad (5)$$

and

$$N_1 = A \dot{\gamma}^b \quad (6)$$

where n , K , b , and A are material parameters depending on temperature. The values of these parameters were obtained by interpolation from the experimental data by Devarajan (1975) and Ranade (1977) for the aqueous solutions of CMC and PAA, and they are given in Table 1. These were obtained for the range $1 \text{ s}^{-1} < \dot{\gamma} < 100 \text{ s}^{-1}$ and for temperature of 20°C . It will be noted that only the PAA solutions show any measurable normal stress difference, and therefore they are considered viscoelastic.

On the other hand, the CMC solutions, although very similar in shear behavior, are inelastic. It must be further emphasized that there is a lower limit of both concentration and the shear rate at which a measurable axial thrust can be still picked up. Thus, the values of A or b for the 100 ppm solution are based only on a narrow range of shear rate higher than 100 s^{-1} .

A frequently used measure of viscoelasticity is known as the characteristic time of the liquid λ defined as

$$\lambda = \frac{N_1}{\eta \dot{\gamma}^2} \quad (7)$$

In terms of the parameters K , A , n , and b defined by Equations (5) and (6), the characteristic time can be expressed as

$$\lambda = \frac{A}{K} \dot{\gamma}^{b-n-1} \quad (8)$$

and for the three specific concentrations of PAA this function is also given in Table 1 and in Figure 1.

In aqueous solutions with high concentrations of ions, the degree of hydration of the macromolecules is changed dramatically, and this is reflected both in the reduced viscosity of the polymer solution as well as in the reduction of the normal stress difference. In fact, at all concentrations used in this work, both the CMC and the PAA solutions with carbonates were found to have a constant viscosity and no detectable normal stress difference. The properties of these liquids are summarized in Table 2, from which it can be also seen that the viscosities within each pair of liquids are very close. And yet, as it was pointed out in the experimental part, in certain aspects the flow behavior of the PAA solutions was different from that of a corresponding CMC solution. This is in line with the observations of Chaschin et al. (1975) who found that the characteristic time of aqueous PAA solutions does not change significantly when the pH value is changed from 7 to 12, even though both the shear dependent viscosity and the primary normal stress difference deteriorate rapidly. We shall, therefore, assume that the characteristic times of polymer solutions without ions are valid also for the solutions of the same concentration of polymer in the carbonate buffer of pH 8 to 10.

It is obvious from Equation (8) that the characteristic time λ depends on the shear rate, and thus λ is not a material parameter. It is particularly difficult to determine the value of λ in the turbulent regime where the shear rate is linked to the scale of turbulence. An alternative approach based on the ideas put forward by Astarita et al. (1969) related the characteristic time of the liquid to the characteristic frequency of the turbulent dissipative eddies. This approach was used by Kelkar and Mashelkar (1972) who determined the characteristic time of dilute aqueous solution of PAA from the drag reduction in

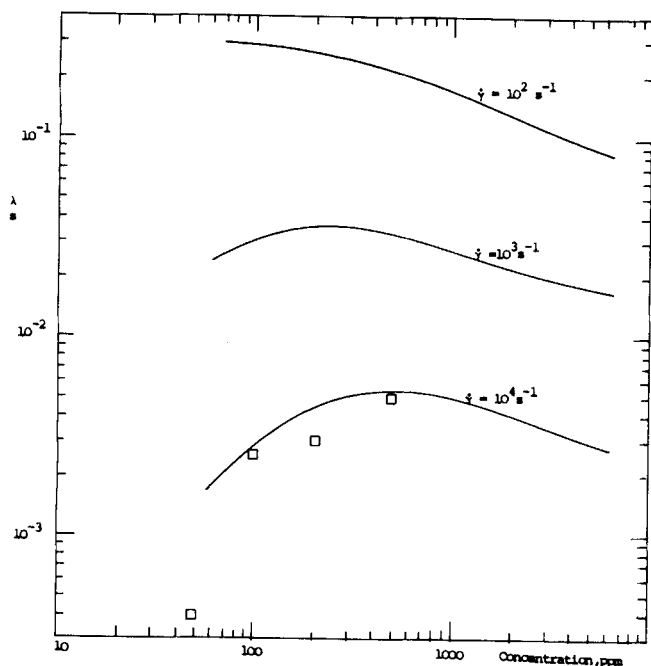


Fig. 2. Characteristic times of aqueous PAA solutions calculated by extrapolation of the lines in Figure 1. □ Data by Kelkar and Mashelkar (1972).

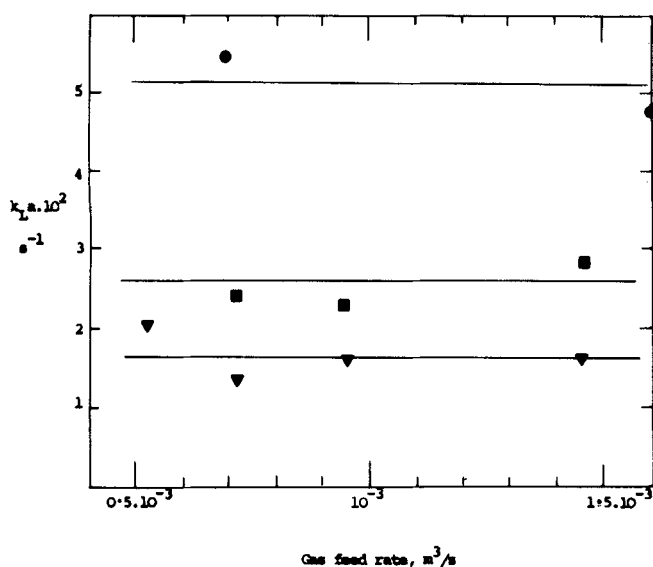


Fig. 3. Overall gas-liquid mass transfer coefficient k_La as a function of the gas feed rate.

- 100 ppm PAA; $N = 13.3 \text{ s}^{-1}$
- 100 ppm PAA; $N = 10 \text{ s}^{-1}$
- ▲ 200 ppm PAA; $N = 10 \text{ s}^{-1}$

straight and coiled tubes. These measurements are shown in Figure 2 together with the extrapolated lines taken from Figure 1. It can be seen that the data points match fairly well the line for $\gamma = 10^4 \text{ s}^{-1}$. This compares favorably with the formula suggested by Mashelkar (1973)

$$f = \Omega \sqrt{Re} \quad (9)$$

which predicts the frequency of the dissipative eddies to be of the order of 10^4 s^{-1} . We shall, therefore, assume that the shear rate throughout the tank is of this order of magnitude, and the values of the characteristic time λ used in the correlation were taken from the plot in Figure 2 for this shear rate.

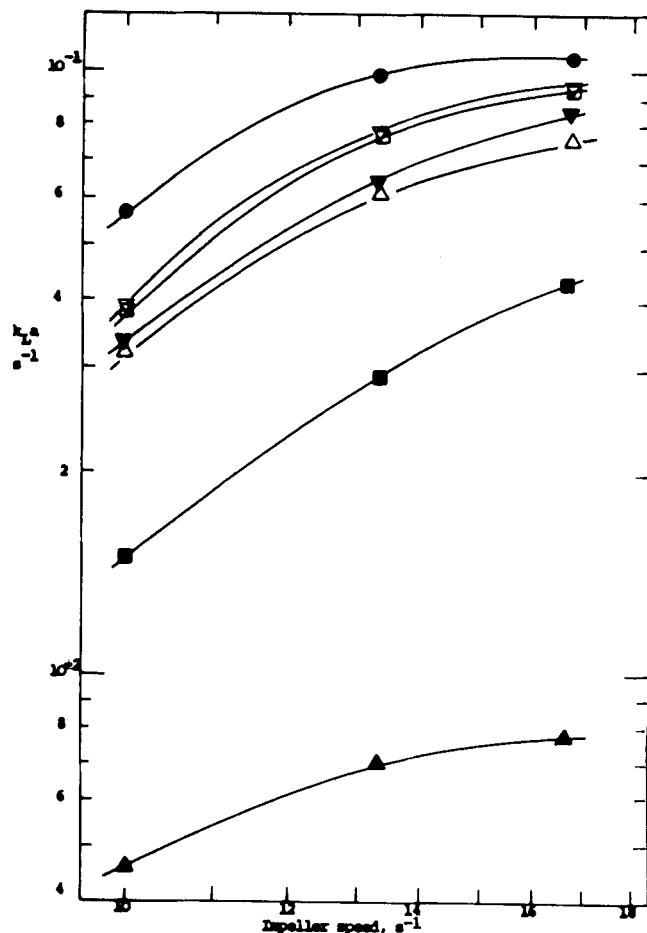


Fig. 4. Overall gas-liquid mass transfer coefficient as a function of polymer concentration and impeller speed. Impeller diameter 0.1 m

Buffer solution	CMC	PAA	Concentration ppm
●	—	—	0
▽	▽	▽	100
□	□	■	200
△	△	▲	1 000/(1 200)

Gas-Liquid Mass Transfer

Great care was taken to ensure that the gas-liquid contacting took place in a regime where the controlling process variable is the impeller speed and not the gas feed rate. Using the criterion suggested by Westerterp et al. (1963), the critical speed was found to be 480 rev/min for the geometry used. This compares well with the findings of Mehta and Sharma (1971). Some data illustrating the independence of the k_La coefficient on the gas flow rate are shown in Figure 3. It should be noted that the specific interfacial area a in this work is related to the volume of the gas-liquid dispersion rather than to the volume of the liquid phase. There is a considerable variance in this respect in the literature, and it may be that the steady increase of the k_La coefficient

TABLE 3. RELATIVE SOLUBILITY AND DIFFUSION COEFFICIENT OF CARBONDIOXIDE IN A SOLUTION OF PAA AP-30 AT 19.5°C GIVEN BY SOYLU (1974)

Concentration of PAA	Relative solubility (C^*/C^* in H_2O)	Relative diffusivity ($D_L/D_{L-\text{H}_2\text{O}}$)
200 ppm	0.999	1.014
500 ppm	0.992	1.093
1 000 ppm	0.985	1.338

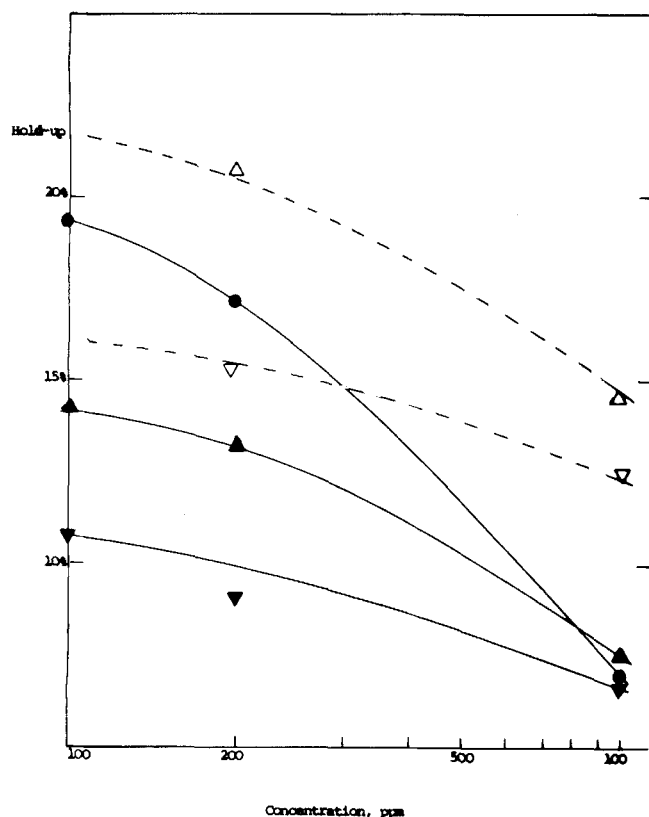


Fig. 5. Gas holdup as a function of PAA concentration, gas feed rate $= 7.5 \times 10^{-4} \text{ m}^3/\text{s}$.

Impeller speed s ⁻¹	Impeller diameter	
	0.1 m	0.147 m
10	▽	▽
13.3	▲	△
16.6	●	

with gas flow rate found in the recent work of Smith et al. (1977) can be explained by a different definition of a . On the other hand, some earlier data published by Yoshida et al. (1960, 1963) indicating dependence of $k_L a$ on gas flow rates were probably obtained in the regime below the critical impeller speed.

The influence of polymer addition upon the overall mass transfer coefficient is shown in Figure 4. It is immediately obvious that even a small concentration of a polymer additive leads to a reduction of the mass transfer coefficient, the PAA showing a more pronounced effect than CMC. In analyzing this phenomenon, the following influences may be considered: diffusivity, solubility, surface tension, and rheological properties of the liquid phase.

The diffusivity and the solubility of carbon dioxide in PAA solutions was reported by Soyulu (1974) and his data are reproduced in Table 3. It can be seen that the diffusion coefficient shows a slight upward trend rather than a reduction. The extent of this enhancement is, however, so small that it is unlikely to have any significant effect on the true gas-liquid mass transfer coefficient k_L , since in the relationship $k_L \propto D_L^m$ the value of the exponent m is usually smaller than one. Similarly, the changes of the saturation solubility are insignificant.

There is a widespread belief that polymers, particularly polyelectrolytes, are strong surface active agents. The surface tension data obtained in this work, however, do not show any surface activity on part of the polymers added (see Table 2). Polyacrylamide was used by Calderbank and Moo-Young (1961) and by Soyulu (1974) in their studies of gas-liquid mass transfer, and none of these

authors report any surface activity due to the polymer presence. The studies of Perez and Sandall (1974) and of Yagi and Yoshida (1975) conclude the same. Soyulu (1974) reports further that whenever surface active agents are present in aqueous solutions together with polyacrylamide, then the polymer has a tendency to suppress the surface activity of the agent. Thus, it may be concluded that the reduction of $k_L a$ is not likely to be attributable to any surface activity due to polymer presence.

There is enough experimental evidence in the literature which shows that an increase in the viscosity of the aqueous phase results in a reduction of the overall mass transfer coefficient. From the work of Yagi and Yoshida (1975), Perez and Sandall (1974), and Calderbank and Moo-Young (1961), it may be concluded that the exponent m_1 in the relationship $k_L a \propto (1/\mu)^{m_1}$ for stirred tanks is between 0.4 and 0.6. Our data for the CMC solutions agree rather well with these earlier reports, but the coefficients for PAA solutions are markedly lower, although the viscosities of the CMC and the PAA solutions do not differ significantly (see Table 2).

In order to gain a further insight into this phenomenon, we have compared the measured holdups in aerated CMC and PAA solutions, and these data are plotted in Figure 5. In the absence of direct measurement of the specific interfacial area a , the gas holdup gives a useful indication about the trends of this variable, since the specific interfacial area decreases as the gas holdup decreases. The data in Figure 5 show that the holdup depends upon the type of polymer added and upon its concentration in the same way as the overall coefficient $k_L a$. This suggests that the influence of the polymer additive is primarily reflected in the reduction of the specific interfacial area a . Broken lines in Figure 5 indicate that the curves are based on only two data points.

The average bubble size in a gas-liquid dispersion is given by the balance of the coalescence and the breakup rates. The higher the breakup rate, the smaller are the bubbles and the higher is the specific interfacial area a . The mechanism of bubble breakup in a turbulent shear field is not yet quite clear, but it is reasonable to assume that the large scale turbulence which it not affected by polymer additives [for this see Quraishi et al. (1977)] takes a part in this process in that it brings about gross deformations of the originally spherical bubble. Whether a deformed bubble breaks or whether it regains its original shape depends upon the extent of liquid stretching in immediate vicinity of the deformed bubble. Astarita et al. (1967, 1970, 1972) and Seyer and Metzner (1967, 1969) have shown that even very dilute solutions of drag reducing polymers show a considerable resistance to stretching, and this phenomenon is considered as an effect of the viscoelasticity under turbulent flow conditions. It is, therefore, conceivable that the different behavior of CMC and PAA solutions in respect to the reduction of the $k_L a$ coefficient is attributable to the elasticity of the liquid phase.

In this context, it is worth noting that Walstra (1974) reported on an influence of drag reducing polymers upon the average droplet size of a liquid-liquid emulsion. He interpreted this by the effect of the additives upon the microscale of turbulence. In our case, however, the bubbles are much larger than the turbulent microscale, and therefore a similar mechanism is not likely.

On the other hand, however, it is conceivable to imagine a process in which the specific interfacial area a is determined by the rate of bubble coalescence. Such a process would be, for example, realized in a contactor with a low shear agitator. In such a process, the bubbles are not subject to any significant breakup, and they grow

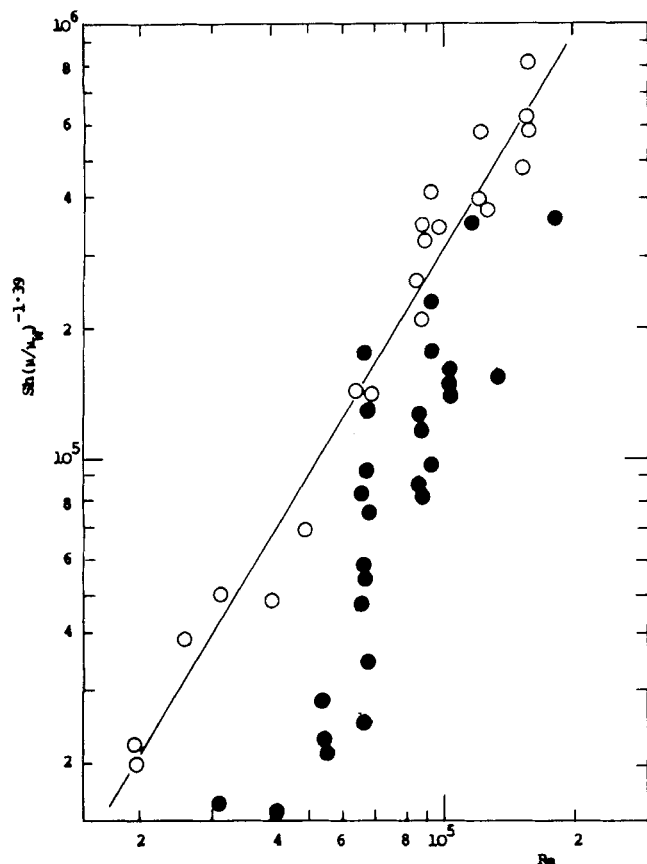


Fig. 6. Dimensionless correlation of the overall gas-liquid mass transfer coefficient.

○ CMC solutions
● PAA solutions

by coalescence. Acharya and Ulbrecht (1977) have recently shown that viscoelasticity leads to a significant reduction of the coalescence rate. One of the reasons for this phenomenon is the resistance of the viscoelastic liquid between the two bubbles to be squeezed out, and thus the coalescence is prevented. In this case, an increase of a with increasing viscoelasticity could be expected.

Empirical Correlation

If more substance is to be given to the suggestion that the considerable reduction of the overall mass transfer coefficient k_{LA} is due to the viscoelasticity of the aqueous solution, then the extent to which the PAA data deviate from those for CMC should correlate with some measure of the solution's elasticity. It has been already said that although the PAA solutions in the carbonate buffer are relatively thin and do not show any measurable normal stress difference, their characteristic time λ is not affected by the presence of ions. The dimensionless numbers which relate the elastic properties with the process parameters are either the Deborah number De or the Weissenberg number Wi . In the Deborah number, the characteristic liquid time is measured against a characteristic process time which, for stirred tanks, is considered to be related in some way to the reciprocal of the impeller speed; thus, $De = N\lambda$. On the other hand, the Weissenberg number was originally conceived to express the ratio of elastic normal stress to the shear stress which, following Equations (5) and (6), are both functions of the shear rate $\dot{\gamma}$ in the vessel. Thus, $Wi = (N_1/S_{12}) = (A/K) \dot{\gamma}^{b-n}$. The choice of an appropriate characteristic shear rate cannot be separated from considerations regarding the scale of the process. For the processes con-

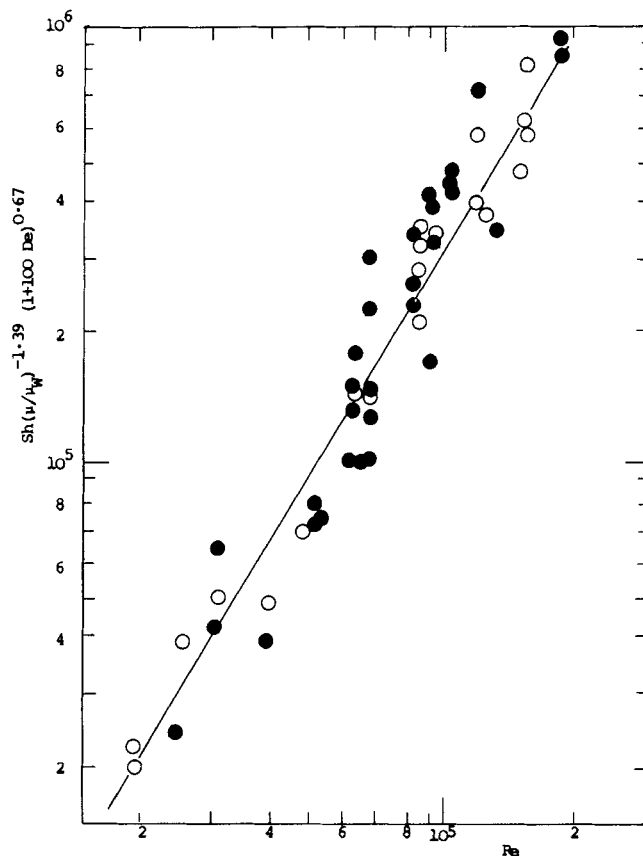


Fig. 7. Dimensionless correlation of the overall gas-liquid mass transfer coefficient incorporating the Deborah number.

○ CMC solutions
● PAA solutions

trolled by the microscale of turbulence, the characteristic shear rate was chosen to be the same as the frequency of the dissipative eddies. The process of bubble breakup and coalescence takes place, however, on a much larger scale, and thus the reciprocal of the impeller speed will be used for characteristic shear rate in correlations involving the specific interfacial area a .

In this context, it should be noted that the Deborah number used by Yagi and Yoshida (1975) is a Deborah number only by name, since the characteristic liquid time used by these authors is based on the flow curve and bears no relationship to the liquid's viscoelasticity [see Kelkar et al. (1972)].

It is customary to express the influence of viscosity upon the mass transfer coefficient in terms of Schmidt number in which the viscosity is related to the diffusion coefficient. It has been already pointed out that the diffusion coefficient of carbon dioxide in polymer solutions does not vary significantly from that for water, and thus the use of a dimensionless Schmidt number is not warranted. Instead, the dimensionless ratio of viscosities (μ/μ_w) was used to correlate the effect of viscosity.

A simple multiple regression exercise shows that the best value of the exponent of the viscosity ratio is 1.39, and the correlation is plotted in Figure 6. The linear dimension in the Sherwood number is represented by the diameter of the turbine impeller. It can be seen that all the data for the viscoelastic PAA solutions deviate considerably from the inelastic (CMC) solutions. The next plot in Figure 7 shows that this deviation can be eliminated by including the Deborah number in the correlation. Using a total of sixty data points for seven different solutions and three different turbine diameters, the multiple regression analysis comes up with a cor-

relation

$$\frac{k_L a \cdot D^2}{D_L} = 2.5 \times 10^{-4} \left(\frac{D^2 N \rho}{\mu} \right)^{1.8} \left(\frac{\mu}{\mu_w} \right)^{1.39} (1 + 100 De)^{-0.67} \quad (10)$$

The coefficient 100 in the last term on the right-hand side is, of course, an arbitrary one chosen to match the order of magnitude of 100 *De* with unity. For inelastic liquids, the last term becomes equal to 1.

When we analyze Equation (10) for the overall effect of viscosity on the mass transfer coefficient, it comes out as $k_L a \propto \mu^{-0.41}$, which compares well with the findings of Perez and Sandall (1974), Yagi and Yoshida (1975), and Ryu and Oldshue (1977).

Implications

Based on the data presented in this work, considerable care must be exercised by the process engineer in selecting polymer additives to control the viscosity of aqueous dispersions. Some of the polymer additives even in very low concentrations might show elastic properties manifested in turbulent regime by a resistance against vortex stretching. This could be advantageous in processes in which the intensity of turbulence is to be reduced, or in processes where energy savings are desirable. On the other hand, however, the viscoelastic additives are likely to reduce to overall gas-liquid mass transfer coefficient by reducing the breakup process of the gas bubbles.

NOTATION

a	= interfacial area per unit volume of dispersion, m^{-1}
A	= material parameter of liquid, $Ns^b m^{-2}$
b	= material parameter of liquid, dimensionless
c^*	= saturation solubility of gas in liquid, kg mole m^{-3}
c^o	= concentration of solute in bulk of the liquid, kg mole m^{-3}
D	= tank diameter, m
De	= modified Deborah number = $N\lambda$
D_L	= molecular diffusion coefficient of gas in the liquid, $m^2 s^{-1}$
f	= frequency of energy dissipating eddies, s^{-1}
k_L	= true liquid side mass transfer coefficient, ms^{-1}
m_1, m	= material parameter of liquid, $Ns^m m^{-2}$
K	= constants, dimensionless
M	= torque experienced by the cone, Nm
n	= material parameter of liquid, dimensionless
N	= impeller speed, s^{-1}
N_1	= normal stress difference, Nm^{-2}
Q	= gas flow rate, $m^3 s^{-1}$
R	= radius of cone, m
R'	= specific rate of absorption, kg mole $s^{-1} m^{-2}$
Re	= Reynolds number = $D^2 N \rho / \mu$
Sh	= modified Sherwood number = $k_L a \cdot D^2 / D_L$
S_{12}	= shear stress Nm^{-2}
T	= normal force between cone and plate, N
Wi	= Weissenberg number = N_1 / S_{12}

Greek Letters

α	= angle of cone, rad
$\dot{\gamma}$	= shear rate, s^{-1}
λ	= characteristic fluid time, s
μ	= viscosity, $Ns m^{-2}$
μ_w	= viscosity of water, $Ns m^{-2}$
η	= viscosity function, $Ns m^{-2}$
ρ	= density, $kg m^{-3}$
ω	= angular velocity of rotating cone, s^{-1}
Ω	= angular velocity of rotating body, s^{-1}

LITERATURE CITED

- Acharya, A., and J. Ulbrecht, "Note on the Influence of Viscoelasticity on the Coalescence Rate of Bubbles and Drops," *AIChE J.*, **24**, 348 (1978).
- Astarita, G., "Diffusivity in Non-Newtonian Liquids," *Ind. Eng. Chem. Fundamentals*, **4**, 236 (1965).
- , "Two Dimensionless Groups Relevant in the Analysis of Steady Flows of Viscoelastic Materials," *ibid.*, **6**, 257 (1967).
- , and L. Nicodemo, "Extensional Flow Behaviour of Polymer Solutions," *Chem. Eng. J.*, **1**, 57 (1970).
- , "Transport Phenomena in Turbulent Flow of Rheologically Complex Fluids," *Progr. Heat Mass Transfer*, **5**, 37 (1972).
- Astarita, G., G. Greco, and L. Nicodemo, "A Phenomenological Interpretation and Correlation of Drag Reduction," *AIChE J.*, **15**, 564 (1969).
- Calderbank, P. H., and M. B. Moo-Young, "The Continuous Phase Heat and Mass-Transfer Properties of Dispersions," *Chem. Eng. Sci.*, **16**, 39 (1961).
- Chaschin, I. P., N. T. Shalavin, and V. A. Saenko, "The Effect of Polymeric Additives on Drag Reduction," *Intern. Chem. Eng.*, **15**, 88 (1975).
- Corman, M. J., *U.S. Patent No. 2,910,410* (1959).
- Devarajan, G. V., "Secondary Flows of Non-Newtonian Fluids," Ph.D. thesis, Univ. Salford, England (1975).
- Dworschack, R. G., and W. R. Lamn, *U.S. Patent N 3666628* (1972).
- Kelkar, J. V., R. A. Mashelkar, and J. Ulbrecht, "On Rotational Flows of Viscoelastic Fluids," *J. Trans. Inst. Chem. Engrs.*, **50**, 343 (1972).
- Kelkar, J. V., and R. A. Mashelkar, "Drag Reduction in Dilute Polymer Solutions," *J. Appl. Polymer Sci.*, **16**, 3047 (1972).
- Mashelkar, R. A., "Drag Reduction in Rotational Flows," *AIChE J.*, **19**, 382 (1973).
- , and M. A. Soylu, "Diffusion in Flow Films of Dilute Polymeric Solutions," *Chem. Eng. Sci.*, **29**, 1089 (1974).
- Mehta, V. D., and M. M. Sharma, "Mass Transfer in Mechanically Agitated Gas-Liquid Contactors," *ibid.*, **26**, 461 (1971).
- Moo-Young, M. B., "The Rheological Effects of Substrate-Additives on Fermentation Yields," *Biotechnol. Bioeng.*, **11**, 725 (1969).
- , *U.S. Patent No. 3,975,236* (1976a).
- , *U.S. Patent No. 3,947,323* (1976b).
- Perez, J. F., and O. C. Sandall, "Gas Absorption by Non-Newtonian Fluids in Agitated Vessels," *AIChE J.*, **20**, 770 (1974).
- Quraishi, A. Q., R. A. Mashelkar, and J. Ulbrecht, "Torque Suppression in Mechanically Stirred Liquids and Multiphase Liquid Systems," *J. Non-Newtonian Fluid Mech.*, **1**, 223 (1976).
- , "Influence of Drag Reducing Additives on Mixing and Dispersing in Agitated Vessels," *AIChE J.*, **23**, 487 (1977).
- Ranade, V. R., "Gas Absorption in and Hydrodynamics of Mechanically Agitated Gas-Liquid Contactors with Polymer Solutions," M.Sc. thesis, Univ. Salford, England (1977).
- , and J. Ulbrecht, "Gas Dispersion in Viscous Inelastic and Viscoelastic Liquids," *Proc. 2nd Euro. Conf. on Mixing (BHRA)* (1977).
- Ryu, D. Y., and J. Y. Oldshue, "A Re-Assessment of Mixing Cost in Fermentation Processes," *Biotechnol. Bioeng.*, **19**, 621 (1977).
- Seyer, F. A., and A. B. Metzner, "Turbulent Flow Properties of Viscoelastic Fluids," *Can. J. Chem. Eng.*, **45**, 121 (1967).
- , "Turbulence Phenomena in Drag Reducing Systems," *AIChE J.*, **15**, 426 (1969).
- Smith, J. M., K. van't Reit, and J. C. Middleton, "Scale Up for Mass-Transfer," *Proc. 2nd Euro. Conf. on Mixing (BHRA)* (1977).
- Soylu, M. A., "Hydrodynamics and Diffusion in Liquid Films of Polymer Solutions," Ph.D. thesis, Univ. Salford, England (1977).
- Takahara, Y., S. Oote, and T. Aikawa, "Aerobic Fermentation," *Hakko Kagaku (J. Fermentation Technol.)*, **43**, 896 (1965).
- Walstra, P., "Turbulence Depression by Polymers and Its Effect on Disruption of Emulsion Droplets," *Chem. Eng. Sci.*, **29**, 882 (1974).

Wilson, G. E., U.S. Patent No. 3763039 (1972).
Westerterp, K. R., van Dierendonck, and A. A. DeKarra, "Interfacial Areas in Gas-Liquid Contactors," *Chem. Eng. Sci.*, **18**, 157 (1963).
Yagi, H., and F. Yoshida, "Gas Absorption by Newtonian and Non-Newtonian Fluids in Sparged Agitated Vessels," *Ind. Eng. Chem. Process Design Develop.*, **14**, 488 (1975).
Yoshida, F., A. Ikeda, and Y. Miura, "Oxygen Absorption Rates

in Gas-Liquid Contactors," *Ind. Eng. Chem.*, **52**, 435 (1960).
Yoshida, F., and Y. Miura, "Gas Absorption in Gas-Liquid Contactors," *Ind. Eng. Chem. Process Design Develop.*, **2**, 263 (1963).

Manuscript received November 2, 1977; revision received April 6, and accepted April 24, 1978.

Hydrodynamic Stability of Thin Liquid Films Flowing Down an Inclined Plane with Accompanying Heat Transfer and Interfacial Shear

SIU-MING YIH

and

RICHARD C. SEAGRAVE

Department of Chemical Engineering
Engineering Research Institute
Iowa State University
Ames, Iowa 50011

An analysis is made on the influence of heat transfer and interfacial shear on the hydrodynamic stability of thin liquid films flowing down an inclined plane. The linear stability of the flow is determined by a successive perturbation solution of the governing Orr-Sommerfeld equation modified to include the effects of temperature on viscosity. Stability criteria are presented which show that a cooled wall is destabilizing, while a heated wall is stabilizing. The surface perturbation stresses of the concurrent gas shear are also shown to be destabilizing factors. Neutral stability curves are presented and compared with the isothermal case.

SCOPE

Falling films are usually employed as a heat or mass exchange medium in industrial equipment such as vertical condensers, film evaporators, and absorption towers. Since surface waves appear at small Reynolds numbers for film flow and enhance the momentum, heat, and mass transfer rates considerably over those predicted for smooth laminar flow, it is often desirable, for process design and prediction purposes, to be able to assess a priori the critical conditions under which waves will appear and to study the stability characteristics of these liquid films under various operating conditions. The hydrodynamic stability

of an isothermal liquid film flowing down an inclined plane was first treated in detail by Benjamin (1957) and Yih (1963). Subsequent workers have followed these two lines with slight modifications, such as incorporating the influence of airflow (Craik, 1966; Smith, 1970), surface contamination (Whitaker, 1964; Smith, 1970), evaporative flux (Bankoff, 1971), and condensation (Marschall and Lee, 1973). Much less, however, is known about the effects of heat transfer and interfacial shear on surface wave instability. The objective of the present study is to establish stability criteria for liquid films that are flowing down an inclined plane and are influenced by heat transfer and interfacial shear. In particular, the effect of variation of viscosity with temperature, the importance of which has