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Short Communication

GAS ABSORPTION INTO FALLING LAMINAR NON-NEWTONIAN FILMS

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Introduction

Mass transfer in non-Newtonian fluid flow is relevant to a number of chemical engineering processes such as polymer production, physiological phenomena, fermentation and biochemical reactor operation, waste disposal, and many other processes.

During the last few years considerable attention has been given to the measurement of the molecular diffusivity (D) of gases in non-Newtonian fluids. A number of classical techniques have been used such as stagnant medium [1–3], laminar jets [4–6] and the wetted-wall laminar film [7–10]. The effects of polymer addition to a solvent, such as water, can increase or decrease the value of D, and according to the careful contribution of Mashelkar and Soylu [10], it can pass through a maximum value as polymer concentration increases from a very dilute solution. It is claimed that flow techniques are better than stagnant ones, since errors in D measurements are smaller when flowing fluids are used.

However the influence of shear stress on D, if any, has not been well established as yet. Most of the experimental conditions were such that this effect could not be detected, since at the gas–liquid interface there was no shear and the penetration depth was small. The results of Wasan et al. [8], regarding the influence of the flow rate on the molecular diffusivity of oxygen in polyox solutions, are rather surprising since a very short wetted-wall column was used in the absorption experimental runs. Perez and Sandall [9] suggested a chemical reaction in the liquid phase between oxygen and polyox.

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On the theoretical side, the problem of mass transfer into a finite laminar film with constant properties was solved by Chavan and Mashelkar [11], following a similar numerical technique to that developed by Olbrich and Wild [12] for the corresponding problem of a Newtonian fluid. This method produces extremely accurate values of local and total rates of absorption, although a rather cumbersome eigenvalue problem must be solved. Moreover it cannot be used when the reciprocal law index of a pseudo-plastic fluid is not an integer, and it is restricted to the asymptotic case of a dilatant fluid with an infinite exponent. To avoid this strong limitation, Mashelkar et al. [13] presented a new contribution in which the same problem was solved with an orthogonal collocation technique previously developed by Villadsen and Stewart [14]. The problem must be solved numerically, for in each particular case a system of eight simultaneous algebraic equations is needed to produce accurate results.

The purpose of this contribution is to present a rather simple matching procedure to solve the problem of estimating the rate of mass transfer into a finite, falling laminar film of non-Newtonian fluid. Thus a simple analytical approximate expression is obtained for estimating the total absorption of a gas into the liquid phase. The results so obtained are compared with previous findings of Chavan and Mashelkar [11], and Mashelkar et al. [13] restricted to the case of power law non-Newtonian fluids. However, the procedure presented here can be used with any kind of non-Newtonian model, provided the velocity profile can be estimated. The case of a sheared interface, considered by Gottifredi et al. [15] and more recently by Yih and Seagrave [16], can also be analyzed with the same simplicity.

Since this powerful and simple method can be used in those cases where D is a spatial function, the effect of the shear rate on D can also be taken into account. From this analysis those experimental conditions needed to detect this effect can be established.

Analysis

Chavan and Mashelkar [13] have shown that the dimensionless mass balance for a species absorbed into a laminar falling thin film, formed over a solid body with certain degrees of symmetry, is given by the following partial differential equation:

$$(1-y^{N+1})\frac{\partial C}{\partial t}=\frac{\partial}{\partial y}\left[D^*\frac{\partial C}{\partial y}\right] \tag{1}$$

where N is the reciprocal power law exponent, y the normal coordinate measured from the interface normalized with respect to the film thickness

(δ), C the dimensionles concentration referred to its surface value and

$$t = \left(z D_0 / V_S \delta^2 \right) \tag{2}$$

the dimensionless contact time, where z is the coordinate parallel to the interface, V_S the surface velocity and D_0 the molecular diffusivity in the absence of any shear stress influence. D^* is the ratio between the molecular diffusivity and D_0.

In writing eqn. (1), it is further assumed that the fluid behaviour is well described by the classical power law model, that the shear stress at the interface is negligible, and that isothermal conditions prevail.

In the present circumstances, even if the effect of shear stress on the molecular diffusivity is taken into account, D^* can be, at the most, a spatial function of y. Thus we intend to investigate the effect of shear stress on molecular diffusivity through the following general model:

$$D^* = 1 + \sigma f(y) \tag{3}$$

in such a way that σ can be any function of $(N-1)$, such that it reduces to zero when $N \to 1$; $f(y)$ can be a general function of y, though in the present case it must reduce to zero when $y = 0$, since shear stress at the interface was assumed negligible. Nevertheless it will become clear that the procedure used here is also useful in those cases where a sheared interface must be considered. If the solid over which the falling film is formed is impermeable to the absorbing species, eqn. (1) must be solved subject to the following initial and boundary conditions:

$$\begin{aligned} C &= 0 \quad z = 0 \quad 0 < y \leqslant 1, \\ C &= 1 \quad z \geqslant 0 \quad y = 0, \\ \frac{\partial C}{\partial y} &= 0 \quad z \geqslant 0 \quad y = 1. \end{aligned} \tag{4a, b, c}$$

Classical analysis would lead to the solution of an eigenvalue problem. Here we will attempt to predict the amount of the species absorbed along the whole interface through a very simple procedure.

By introducing the following transformation:

$$\varphi = S \int_0^{\infty} C \exp(-St) \, \mathrm{d}t, \tag{5}$$

eqn. (1) is reduced to:

$$(1 - y^{N+1}) S\varphi = \frac{\mathrm{d}}{\mathrm{d}y} \left((1 + \sigma f(y)) \frac{\mathrm{d}\varphi}{\mathrm{d}y} \right), \tag{6}$$

subject to:

$$\varphi(o) = 1; \; (\mathrm{d}\varphi / \mathrm{d}y) = 0 \quad y = 1. \tag{7a, b}$$

Since we are only interested in finding an expression for the flux, asymptotic solutions to eqn. (6) for $S \to \infty$ and $S \to 0$ will be sought. By defining

$$\xi = y\sqrt{S}\,, \tag{8}$$

eqn. (6) can be rewritten in the following form:

$$\left\{1 - \left(\frac{1}{\sqrt{S}}\right)^{N+1} \xi^{N+1}\right\}\varphi = \frac{\mathrm{d}}{\mathrm{d}\xi}\left\{\left(1 + \sigma f\left(\frac{\xi}{\sqrt{S}}\right)\right)\frac{\mathrm{d}\varphi}{\mathrm{d}\xi}\right\}. \tag{9}$$

Thus, if it is assumed that $\sqrt{S} \to \infty$, an approximate solution to eqn. (9) is found as:

$$\varphi = F_0(\xi) + \frac{1}{\sqrt{S}} F_1(S) + \dots, \tag{10}$$

which, after being substituted into eqn. (9) and equating terms of like power in S, gives:

$$F_0 = F_0'',$$
$$F_1 = F_1'' + \sigma f'(0)\frac{\mathrm{d}}{\mathrm{d}\xi}(\xi F_0'), \tag{11a,b}$$

since $N > 0$. $f'(0)$ denotes the derivative of f evaluated at the interface. To denote first and second derivatives with respect to ξ, $'$ and $''$ are used. Since it was assumed that $\sqrt{S} \to \infty$, suitable boundary conditions for F_0 and F_1 are:

$$F_0 = 1;\ F_1 = 0 \quad \xi = 0,$$
$$F_0 = F_1 = 0 \quad \xi \to \infty. \tag{12a,b}$$

Solutions to eqns. (11a, b) are straightforward and, since we are only interested in local flux it can be easily shown that:

$$-\left.\frac{\mathrm{d}\varphi}{\mathrm{d}y}\right|_{y=0} = S^{1/2} - \left(\frac{1}{4}\right)\sigma f'(0) + \dots\ . \tag{13}$$

It should be noted that the situation could be varied if a sheared interface is to be considered, not only because $f(0) \neq 0$, but also because the second term in eqn. (13) could have a different value dependent upon $f(0)$. Nevertheless the procedure is exactly the same without any extra effort.

On the other hand when $S \to 0$, eqn. (6) itself suggests the following asymptotic series solution:

$$\varphi = \varphi_0 + S\,\varphi_1(y) + S^2\varphi_2 + \dots\ . \tag{14}$$

$\varphi_0 = 1$ in order to fit boundary conditions (7a, b). φ_1 and φ_2 are the solutions to the following differential equations:

$$(1 - y^{N+1})\,\varphi_{i-1} = \frac{\mathrm{d}}{\mathrm{d}y}\left((1 + \sigma f(y))\frac{\mathrm{d}\varphi_i}{\mathrm{d}y}\right), \tag{15}$$

with $i > 1$, subject to:

$$\varphi_i(0) = 0 \text{ and } \mathrm{d}\,\varphi_i/\mathrm{d}\,y = 0 \text{ at } y = 1. \tag{16a,b}$$

After very simple manipulations, it can be shown that:

$$-\left.\frac{\mathrm{d}\varphi}{\mathrm{d}\,y}\right|_{y=0} = nS + mS^2 + \mathrm{O}(S^3), \tag{17}$$

with:

$$n = 1 - (N+2)^{-1}, \tag{18}$$

$$m = -\int_0^1 \varphi_1(1 - y^{N+1})\mathrm{d}\,y, \tag{19}$$

where:

$$\varphi_1 = \int_0^y \left(y - \frac{1}{(N+2)} y^{N+2}\right)(1 + \sigma f(y))^{-1}\,\mathrm{d}\,y - \int_0^y \frac{n}{(1 + \sigma f(y))}\,\mathrm{d}\,y. \tag{20}$$

In order to match eqns. (13) and (17) over the whole range of S values, the following expression can be used:

$$-\frac{1}{S}\left.\frac{\mathrm{d}\varphi}{\mathrm{d}\,y}\right|_{y=0} = \frac{(\alpha + S)^{1/2}}{(\beta + S)}, \tag{21}$$

which must coincide with eqns. (13) and (17) when $S \to \infty$ and $S \to 0$, respectively. After expanding eqn. (21) for $S \to \infty$ and $S \to 0$, it is shown that α and β must satisfy the following algebraic equations:

$$\alpha^{1/2} \cdot \beta^{-1} = n, \tag{22a,b}$$

$$\tfrac{1}{2}\beta^{-1} \cdot \alpha^{-1/2} - \alpha^{1/2} \cdot \beta^{-2} = m.$$

Thus it is found that:

$$\beta = \frac{n}{2m}\left\{1 \pm \sqrt{1 - \frac{2m}{n^3}}\right\}, \tag{23}$$

$$\alpha = (n\beta)^2. \tag{24}$$

From eqn. (21), the local flux can be found after using Laplace transformation tables:

$$-\left.\frac{\partial C}{\partial y}\right|_{y=0} = (\alpha - \beta)^{1/2} \exp(-\beta t)\,\mathrm{erf}\left((\alpha - \beta)^{1/2} t^{1/2}\right) + \frac{1}{\sqrt{\pi t}} \exp(-\alpha t), \tag{25}$$

and since we need $\alpha > \beta$, the positive root in eqn. (23) must be chosen.

Since most previous results were presented in terms of the mixing cup concentration ($\overline{C}$) at the end of the absorbing element:

$$\overline{C}=\frac{\int_0^1 C(1-y^{N+1})\,\mathrm{d}y}{\int_0^1 (1-y^{N+1})\,\mathrm{d}y}=\frac{1}{n}\int_0^1\left(-\frac{\partial C}{\partial y}\right)_{y=0}\mathrm{d}t, \tag{26}$$

this results in:

$$\overline{C}=\operatorname{erf}\left((\alpha t)^{1/2}\right)-\left(1-\frac{\beta}{\alpha}\right)^{1/2}\mathrm{e}^{-\beta t}\operatorname{erf}\left((\alpha-\beta)^{1/2}t^{1/2}\right). \tag{27}$$

Discussion

Results produced with the approximate expression (27), in conjunction with eqns. (23) and (24), are compared with results obtained by the exact solution of eqn. (1) as performed by Chavan and Mashelkar [11] and Mashelkar et al. [13] for the case in which $\sigma=0$.

In Table 1 values of n, m, α, β and $(1-\beta/\alpha)^{1/2}$ are presented as a function of N for the particular case of $\sigma=0$. While in Table 2 values of $\overline{C}$ obtained by eqn. (27) are compared with previous exact findings (see [11] and [13]) and also with the accurate results of Olbrich and Wild [12] (which are only valid for $N=1$). Approximate values are denoted as $\overline{C}_A$.

It can be seen that not only for engineering design purposes but also for molecular diffusivity experimental measurements, the approximate results can be considered as extremely accurate.

Maximum deviations are well below 2%. Moreover eqn. (27) can be safely used in all the range of t values, while the expression derived by Chavan and Mashelkar [11] is not suitable for small t values where the penetration theory expression must be used. It must be stressed that eqn. (27) is not limited to those cases where N is an integer, as happens with the method of Chavan and Mashelkar [11]. In our case there is no need to solve a system of algebraic equations as suggested by Mashelkar et al. [13] in order to remove the limitation of integer values of N.

Most of the experimental measurements of D_0 have been performed on the basis that penetration theory results can be safely applied. Equation (27) provides a very simple criterion for establishing the maximum value of t under which this procedure is valid. In fact by expanding eqn. (27) when $t\to 0$, it is found that:

$$\overline{C}\simeq\frac{2t^{1/2}}{n\sqrt{\pi}}\{1+(\alpha-\beta)t-\mathrm{O}(t^{3/2})\}, \tag{28}$$

TABLE 1

Parameters for eqns. (25) and (27) as a function of N; $\sigma = 0$

N	0	0.5	1	2	3	4	∞
n	0.5	0.6	0.6667	0.75	0.8333	0.875	1
m	0.05	0.0794	0.1050	0.1444	0.1732	0.1946	0.3333
β	7.2360	5.7269	4.8879	4.0555	3.9297	3.7090	2.3660
α	13.090	11.8071	10.6185	9.2515	10.7231	10.5318	5.5980
$(1-\frac{\beta}{\alpha})^{1/2}$	0.6688	0.7176	0.7346	0.7494	0.7960	0.8049	0.7598

TABLE 2

Approximate and actual values of $\overline{C}$

N	0		1		2		3		4		∞	
t	$\overline{C}$	$\overline{C}_A$	$\overline{C}$	$\overline{C}_A$	$\overline{C}$	$\overline{C}_A$	$\overline{C}$	$\overline{C}_A$	$\overline{C}$	$\overline{C}_A$	$\overline{C}$	$\overline{C}_A$
0.05	0.4761	0.4889	0.3751	0.3802	0.3358	0.3402	0.3152	0.3136	0.3027	0.3000	0.2524	0.2441
0.1	0.6500	0.6610	0.5250	0.5310	0.4730	0.4805	0.4450	0.4506	0.4278	0.4325	0.3568	0.3644
0.2	0.8403	0.8395	0.7164	0.7202	0.6563	0.6623	0.6220	0.6349	0.6000	0.6143	0.5046	0.4893
0.4	0.9667	0.9641	0.8982	0.8956	0.8523	0.8516	0.8224	0.8347	0.8017	0.8171	0.6979	0.7008
0.81	0.9987	0.9981	0.9875	0.9860	0.9738	0.9721	0.9622	0.9670	0.9529	0.9601	0.8901	0.8850
1	0.9996	0.9995	0.9953	0.9945	0.9883	0.9870	0.9815	0.9843	0.9758	0.9803	0.9313	0.9380

TABLE 3

Results of eqn. (25) compared with those of [12]

$-\left.\frac{\partial C}{\partial y}\right\|_{y=0}$	t						
	0.05	0.1	0.2	0.4	0.6	0.8	1.0
Eqn. (25)	2.515	1.670	0.935	0.342	0.127	0.048	0.0181
Olbrich and Wild [12]	2.454	1.664	0.968	0.348	0.125	0.045	0.0161

so that with a 5% maximum error:

$$t_C \leqslant 0.05\ (\alpha - \beta)^{-1} \simeq 7.0 \times 10^{-3}, \tag{29}$$

since $(\alpha - \beta)$ ranges between 3 and 7. It should be stressed that most experiments with falling liquid films have not been performed under these conditions. Values of t in the range of 0.01 can be found in the works of Perez and Sandall [9], and Mashelkar and Soylu [10]. It can be concluded that when $\overline{C} > 0.15$ (approximately) some care should be taken to analyze experimental results in the light of the penetration theory model.

Comparison between approximate and exact values in terms of local flux can also be performed. For the case of Newtonian fluids ($N = 1$), our expression (25) produces results as good as those presented by the very accurate procedure of Olbrich and Wild [12]. This can be seen in Table 3 where a comparison is presented. When $t = 1$ the value of $\overline{C}$ is already 0.995, so there is no need to make comparison above $t = 1$ where, of course, approximate and exact values of the local flux can differ significantly.

The effect of $\sigma\, f(y)$ is only seen in the value of m which, in turn, will modify both the values of α and β. We have performed very simple calculations in order to investigate the effect of this term on $\overline{C}$ as a function of time for two limiting cases $N = 0.5$ and $N = 2$. It was concluded that within the experimental range of contact times previously investigated, it is impossible to detect, if any, the effect of shear stress on D.

Conclusions

A very simple and straightforward procedure is presented to predict, with accuracy, the total amount of gas absorbed in a falling laminar non-Newtonian film. Maximum deviation between approximate and exact results is below 2%. Under these conditions the procedure can be used for engineering design purposes as well as for the analysis of experimental results aimed at measuring molecular diffusivity of gases in non-Newtonian fluids.

A great advantage of the resulting expression is its ability to produce a continuous function of the dimensionless contact time (t). In previous works, the mixing cup concentration ($\overline{C}$) must be calculated with the penetration theory expression below a certain value of t and with a series expression above that value of t. The limitation of the sole use of integer values of N has been removed, and it must be stressed that other kinds of non-Newtonian fluid models can be considered with the same simplicity as the case of a shear-dependent diffusivity model.

Notation

$\overline{C}_A$	approximate dimensionless mixing-cup concentration (eqn. (27))
$\overline{C}$	dimensionless mixing-cup concentration
C	dimensionless concentration of the gas in the liquid
D	diffusion coefficient of gas in the liquid
D_0	diffusivity coefficient in the absence of shear stress influences
D^*	ratio between D and D_0
$F_0, F_1, \ldots$	auxiliary functions
m	parameter defined by eqn. 22(a)
N	reciprocal of the power law exponent
n	parameter defined by eqn. 22(b)
S	Laplace transform variable
t	dimensionless contact time define by eqn. (2)
V_s	surface velocity
y	dimensionless distance normal to the interface
z	coordinate parallel to the interface

Greek letters

α	parameter defined by eqn. (21)
β	parameter defined by eqn. (21)
σ	parameter (see eqn. (3))
δ	film thickness
ζ	parameter defined by eqn. (8)
φ	function defined by eqn. (5)
$\varphi_1, \varphi_1, \varphi_2, \ldots$	auxiliary expansion functions

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