

# Steady Viscoelastic Diffusion

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**ABSTRACT:** A viscoelastic constitutive equation is derived for the diffusion flux of an infinitely dilute solute diffusing in a polymeric fluid under steady flow conditions. It is shown that the mass transfer rate of gas into an ideal polymer jet increases with increasing elasticity. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 3256–3263, 2003

**Key words:** diffusion; viscoelastic properties; solution properties

## INTRODUCTION

It is well known<sup>1,2</sup> that viscoelastic effects often play an important role in the flow behavior of polymer solutions and melts. It is thus reasonable to expect that the viscoelastic character of polymeric materials is also important in many mass transfer processes involving the diffusion of penetrants in polymer solutions and melts. Recently,<sup>3</sup> a viscoelastic constitutive equation was developed for the diffusion flux, and it was used to analyze the important problem of one-dimensional diffusion in polymer films. Analytical solutions to the species continuity equation were developed so that sorption curves could be calculated for differential step-change sorption experiments. Although the calculated results in this previous study are strictly applicable to sorption experiments with small concentration changes, the same basic approach could be utilized, with appropriate modifications, to analyze unsteady, one-dimensional mass transfer problems with significant concentration changes. One-dimensional diffusion in polymer films is perhaps the simplest example of unsteady-state viscoelastic diffusion, and solutions to this problem are important in a wide variety of applications.

A second important diffusion problem concerned with elastic effects is the steady-state diffusion of neutral solutes or gases in flow fields involving non-Newtonian fluids. The rate of mass transfer in such systems is governed by the diffusion flux of a small solute species, and, for diffusion in polymer solutions and melts, this diffusion flux will, in general, be described by a viscoelastic constitutive equation. Solute diffusion in non-Newtonian fluids is important in var-

ious polymer processing steps (such as diffusion-controlled polymerization), in fermentation processes, in waste disposal systems, and in physiological processes for various organisms. Not only is the problem of steady viscoelastic diffusion important in a wide range of applications, but it is amenable to a relatively straightforward analysis in the dilute solute limit.

The objectives of this article are to formulate an appropriate version of a previously proposed constitutive equation in the steady limit and to see what effect elasticity has on the steady mass transfer of an infinitely dilute solute dissolved in a flowing non-Newtonian fluid. The basic problem is formulated in the second section of this article, and previous experimental results on diffusion in polymeric solutions are discussed in this section. The proposed steady form of the constitutive equation for the diffusion flux is developed in the third section of this article. The problem of mass transfer of a gas into an ideal polymer jet is formulated in the fourth section of this article, and the uniqueness of solutions of the equation set describing this problem is proved. Solutions to this special mass transfer problem are developed in the fifth section of this article, and the predicted effects of the viscoelasticity of the polymeric solution on the steady mass transfer process are discussed.

## PROBLEM FORMULATION

We consider steady-state flow and diffusion in an effectively binary system of solute (component 1) and polymer (component 2). The polymer is either a molten polymer or a polymer solution which can be treated as a single component. In general, the velocity and concentration fields are three dimensional, and the solute is infinitely dilute so that

$$\omega_1 \rightarrow 0 \quad (1)$$

where  $\omega_1$  is the mass fraction of solute. Consequently, the density of the mixture,  $\rho$ , and the binary mutual

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diffusion coefficient for the system,  $D$ , are essentially constant because pressure effects should be small. The mass average velocity of the system  $\underline{v}$  can be related to  $\underline{v}_1$  and  $\underline{v}_2$ , the velocities of solute and polymer, respectively, by the equation:

$$\underline{v} = \omega_1 \underline{v}_1 + \omega_2 \underline{v}_2 \quad (2)$$

Consequently, because  $\omega_1 \rightarrow 0$  and  $\omega_2 \rightarrow 1$ , the following approximate result is valid:

$$\underline{v} \approx \underline{v}_2 \quad (3)$$

The fact that the velocity of a polymer particle is effectively equal to the mass average velocity at a given point in the flow field makes it possible to use the mass average velocity to determine the particle paths for polymer particles.

For the above problem formulation, the flow and diffusion fields are described by the overall continuity equation

$$\nabla \cdot \underline{v} = 0 \quad (4)$$

the equations of motion

$$\rho \underline{v} \cdot \nabla \underline{v} = \rho \underline{F} - \nabla p + \nabla \cdot \underline{S} \quad (5)$$

and the species continuity equation:

$$\rho \underline{v} \cdot \nabla \omega_1 + \nabla \cdot \underline{j}_1 = 0 \quad (6)$$

Also

$$\rho = \rho_0 = \text{constant} \quad (7)$$

Here,  $\underline{F}$  is the external force per unit mass,  $\underline{S}$  is the extra stress tensor,  $p$  is pressure, and  $\underline{j}_1$  is the mass diffusion flux of component 1 relative to the mass average velocity. If appropriate constitutive equations are formulated for  $\underline{S}$  and  $\underline{j}_1$ , then eqs. (4–6) constitute a set of five equations that can be used to determine the dependence of five unknowns on spatial position  $\underline{x}$ . The five unknowns are  $\omega_1$ ,  $p$ , and the three components of  $\underline{v}$ . Furthermore, it is reasonable to expect that the constitutive equation for  $\underline{S}$  will be negligibly affected by the diffusion process. Consequently, because, in the infinitely dilute solute limit,  $\rho$  and any rheological coefficients will not depend on solute concentration, it is clear that the flow problem is uncoupled from the mass transfer problem. Equations (4) and (5) can be used to determine the velocity and pressure fields regardless of the nature of the concentration field. The fact that all physical properties are

independent of the solute concentration leads to this one-sided coupling between the fluid mechanics of the system and the mass transfer process. There is a significant effect of the fluid mechanics on the diffusion process but the flow behavior does not depend on mass transfer effects in the system.

The above formulation can now be used as a basis for evaluating previous experimental research on diffusion of solutes in viscoelastic liquids. Elastic effects in such systems can be studied either by changing the nature of the solvent or by changing the velocity field. The nature of the solvent can be altered by adding polymer to a solvent or by replacing the solvent by a molten polymer, and the velocity field can be changed, for example, by increasing the flow rate. There are essentially three effects of changing the nature of the fluid and performing experiments at essentially the same flow rate:

1. The rheological constitutive equation for the system can be significantly different so that solution of eqs. (4) and (5) will yield a different velocity field at the same flow rate.
2. The binary mutual diffusion coefficient of the system at infinite solute dilution,  $D_0$ , will in general change because the solute is diffusing in a different solvent.
3. There could be a different constitutive equation for the diffusion flux because an inherently viscoelastic solvent has replaced a purely viscous solvent.

To understand the mass transfer process, it is necessary to study these three effects separately. This can be done in the following way. The mutual diffusion coefficient  $D_0$  should be measured for the new solvent in an experiment conducted by using a stagnant medium. The new fluid should be characterized rheologically, and the mass transfer process should be studied by using a flow experiment for which it is possible to carry out an accurate calculation for the velocity field. This will permit the calculation of the convective effects in the species continuity equation. If  $D_0$  and the flow field are known, a prediction of the mass transfer process for the solute can be made by using a Fickian constitutive equation for the diffusion flux. Differences between experiment and the theoretical prediction can then be attributed to viscoelastic diffusion. In addition, if there are viscoelastic effects, these effects can be further studied by changing the flow rate, possibly further promoting the contribution of viscoelastic diffusion at the higher flow rates. Finally, a viscoelastic constitutive equation for the diffusion flux could be proposed, and a new prediction for the mass transfer rate could be computed and checked with experimental results.

A number of investigators<sup>4–6</sup> have summarized the experimental results for the diffusion of low molecular

weight solutes in non-Newtonian fluids. Most of the reported studies involve polymer solutions, and both flow and stagnant systems have been studied. In many of these investigations, the mass transfer rate in the polymer solution was compared to that for a solvent containing no polymer. Unfortunately, it appears that no definitive conclusions can be reached from the available experiments. For the flow experiments, values of  $D_0$  for the polymer solution are generally not measured. In addition, measurements of the rheological properties of the non-Newtonian fluid and calculation of the velocity field for the experiments have generally not been considered. For stagnant systems, changes in  $D_0$  with the addition of polymer have been attributed to viscoelastic effects, and this, of course, is questionable. In addition, in some stagnant systems, there is a ternary diffusion process because the polymer mass fraction is not effectively uniform in the concentration field. It is thus fair to conclude that there is no definitive experimental evidence for stating whether the viscoelasticity of a solution will enhance a steady mass transfer process or slow it down. In addition, there appear to be no theoretical predictions available. An important objective of this investigation is to provide a theoretical result for this type of diffusion process. In this article, index notation and summation convention are utilized and component results are written in terms of rectangular Cartesian coordinates.

### FORMULATION OF CONSTITUTIVE EQUATION

The following dimensionless form of a constitutive equation for the diffusion flux has been previously proposed<sup>3</sup>

$$j_{1i}(\underline{x}, t) = -\frac{1}{2} \frac{\partial \omega_1}{\partial x_i}(\underline{x}, t) - \frac{1}{2} \int_0^t \frac{\exp\left[-\frac{s}{(\text{De})_2}\right]}{(\text{De})_2} \frac{\partial \omega_1}{\partial \xi_i}(\underline{\xi}, t-s) ds \quad (8)$$

where the following dimensionless variables have been utilized in eq. (8):

$$\underline{x}^* = \frac{\underline{x}}{L} \quad (9)$$

$$\underline{\xi}^* = \frac{\underline{\xi}}{L} \quad (10)$$

$$t^* = \frac{t}{t_c} \quad (11)$$

$$s^* = \frac{s}{t_c} \quad (12)$$

$$j_{1i}^* = \frac{L j_{1i}}{\rho_0 D_0} \quad (13)$$

$$(\text{De})_2 = \frac{\lambda_2}{t_c} \quad (14)$$

Here,  $\underline{x}$  is the present position of a material particle,  $\underline{\xi}$  is its past position,  $t$  is the present time,  $s$  is the backward running time,  $L$  is a characteristic length,  $t_c$  is a characteristic time for the process, and  $\rho_0$  and  $D_0$  are the total density and mutual diffusion coefficient in the infinitely dilute solute limit, respectively. Also, a dimensionless velocity can be defined as

$$\underline{v}^* = \frac{\underline{v}}{U_0} \quad (15)$$

where  $U_0$  is a characteristic velocity. For flow problems, it is convenient to define a characteristic time by using the expression:

$$t_c = \frac{L}{U_0} \quad (16)$$

The asterisks have been dropped for convenience in eq. (8), and they are also deleted in all of the dimensionless equations that follow.

Equation (8) contains a diffusion Deborah number  $(\text{De})_2$  associated with the relaxation time  $\lambda_2$ . The more general form of the constitutive equation<sup>3</sup> contains another relaxation time  $\lambda_1$  and another diffusion Deborah number  $(\text{De})_1$

$$(\text{De})_1 = \frac{\lambda_1}{t_c} \quad (17)$$

with  $\lambda_1 < \lambda_2$ . In flow problems, the viscoelasticity is primarily associated with the transition from rubbery flow to viscous flow behavior with  $(\text{De})_1 \ll 1$  and  $(\text{De})_2 = \mathcal{O}(1)$ . For this case, eq. (8) represents a reduced form of the general constitutive equation for the diffusion flux with the contributions associated with  $(\text{De})_1$  neglected because they are considered to be small for the problems of interest here.

The presence of a memory integral in the constitutive equations for the diffusion flux is not convenient for solving the species continuity equation in a flowing fluid because path lines for the material particles must be calculated. However, eq. (8) provides a useful starting point for the derivation of an asymptotic form of the constitutive equation which should be valid for sufficiently small  $(\text{De})_2$ . At small values of  $(\text{De})_2$ , either the fluid is slightly viscoelastic (small  $\lambda_2$ ), the diffusion process is slow (large  $t_c$ ), or the combination of  $\lambda_2$  and

$t_c$  yields a sufficiently small value of  $(De)_2$ . In such cases, the mass fraction gradients evaluated near  $s = 0$  account for the major part of the contribution of the integral to the diffusion flux because of the presence of  $(De)_2$  in the exponential relaxation term. It is therefore reasonable to expand the mass fraction derivative in a Taylor series about  $s = 0$

$$\frac{\partial \omega_1}{\partial \xi_i}(\xi, t - s) = \left[ \frac{\partial \omega_1}{\partial \xi_i}(\xi, t - s) \right]_{s=0} + \left[ \frac{d}{ds} \left\{ \frac{\partial \omega_1}{\partial \xi_i}(\xi, t - s) \right\} \right]_{s=0} s + \dots \quad (18)$$

and this result can be written as follows

$$\frac{\partial \omega_1}{\partial \xi_i}(\xi, t - s) = \frac{\partial \omega_1}{\partial x_i}(\underline{x}, t) + s B_i(\underline{x}, t) + \dots \quad (19)$$

where

$$B_i(\underline{x}, t) = \left[ \frac{d}{ds} \left\{ \frac{\partial \omega_1}{\partial \xi_i}(\xi, t - s) \right\} \right]_{s=0} \quad (20)$$

A two-term Taylor series will provide an adequate approximation to the contribution of the mass fraction derivative in the integrand to the integral for sufficiently small values of  $(De)_2$ .

For a steady-state process, we need to consider the limit of eq. (8) as  $t \rightarrow \infty$ . Consequently, substitution of eq. (19) into eq. (8) produces the following result at steady state:

$$j_{1i} = -\frac{1}{2} \frac{\partial \omega_1}{\partial x_i}(\underline{x}) \left[ 1 + \frac{\int_0^\infty \exp\left[-\frac{s}{(De)_2}\right] ds}{(De)_2} \right] - \frac{1}{2} B_i(\underline{x}, \infty) \int_0^\infty \frac{s \exp\left[-\frac{s}{(De)_2}\right] ds}{(De)_2} \quad (21)$$

Evaluation of the integrals yields the expression:

$$j_{1i} = -\frac{\partial \omega_1}{\partial x_i}(\underline{x}) - \frac{(De)_2}{2} B_i(\underline{x}, \infty) \quad (22)$$

The vector  $B_i(\underline{x}, \infty)$  can be evaluated by introducing a dimensionless running time

$$\tau = t - s \quad (23)$$

and by considering the following functional dependence of the polymer mass fraction  $\omega_2$ :

$$\omega_2 = \omega_2(\xi, \tau) \quad (24)$$

Here,  $\xi$  refers to the position of the polymer particle at time  $\tau$ . The path lines of the polymer particles are described by an equation of the form

$$\xi = \xi_i(\underline{x}, \tau) \quad (25)$$

where  $\underline{x}$  refers to the position of the polymer particle at time  $t$ . Consequently, eq. (24) can also be written as

$$\omega_2 = \omega_2(\underline{x}, \tau) \quad (26)$$

and application of the chain rule using eqs. (24–26) produces the result:

$$\left[ \frac{\partial}{\partial \tau} \left( \frac{\partial \omega_2}{\partial \xi_i} \right) \right]_{\tau, \xi_k} = \left( \frac{\partial^2 \omega_2}{\partial \xi_j \partial \xi_i} \right)_{\tau} \left( \frac{\partial \xi_j}{\partial \tau} \right)_{x_p} + \left[ \frac{\partial}{\partial \tau} \left( \frac{\partial \omega_2}{\partial \xi_i} \right) \right]_{\tau, \xi_k} \quad (27)$$

In addition,

$$\left( \frac{\partial \xi_j}{\partial \tau} \right)_{x_p} = (v_2)_j \approx v_j(\xi, \tau) \quad (28)$$

where we have utilized eq. (3). Consequently, eq. (27) can be written in the form:

$$\frac{d}{d\tau} \left[ \frac{\partial \omega_2}{\partial \xi_i}(\xi, \tau) \right] = v_j(\xi, \tau) \left( \frac{\partial^2 \omega_2}{\partial \xi_j \partial \xi_i} \right)_{\tau} + \left[ \frac{\partial}{\partial \tau} \left( \frac{\partial \omega_2}{\partial \xi_i} \right) \right]_{\tau, \xi_k} \quad (29)$$

In eq. (29), the polymer mass fraction  $\omega_2$  is now replaced by the solute mass fraction  $\omega_1$  and the running time  $\tau$  is replaced by the backward running time  $s$ . In addition, this equation is evaluated at  $s = 0$  and at the steady-state limit. The final result is the expression:

$$B_i(\underline{x}, \infty) = \left[ \frac{d}{ds} \left( \frac{\partial \omega_1}{\partial \xi_i} \right) \right]_{s=0} = -v_j(\underline{x}) \frac{\partial^2 \omega_1}{\partial x_j \partial x_i} \quad (30)$$

Substitution of eq. (30) into eq. (22) produces the final form of the constitutive equation valid at the steady-state limit:

$$j_{1i} = -\frac{\partial \omega_1}{\partial x_i}(\underline{x}) + \frac{(De)_2}{2} v_j(\underline{x}) \frac{\partial^2 \omega_1}{\partial x_j \partial x_i} \quad (31)$$

In coordinate-free notation, this expression can be rewritten as:

$$\underline{j}_1 = -\nabla\omega_1 + \frac{(\text{De})_2}{2} \underline{v} \cdot \nabla(\nabla\omega_1) \quad (32)$$

The above constitutive equation describes the steady-state diffusion flux for a slightly viscoelastic material (in a diffusion sense) in the infinitely dilute solute limit. It can be shown that the above constitutive equation is frame indifferent.

An equation describing mass transfer in a viscoelastic material can be derived by combining the above constitutive equation for the diffusion flux with the species continuity equation. The dimensionless, steady-state form of the species continuity equation is simply

$$\text{Pe } v_i \frac{\partial\omega_1}{\partial x_i} = -\frac{\partial j_{1i}}{\partial x_i} \quad (33)$$

where the Peclet number is defined as:

$$\text{Pe} = \frac{U_0 L}{D_0} \quad (34)$$

A combination of eqs. (31) and (33) produces the transport equation for the mass transfer process:

$$\text{Pe } v_i \frac{\partial\omega_1}{\partial x_i} = \frac{\partial^2\omega_1}{\partial x_i^2} - \frac{(\text{De})_2}{2} \left[ \frac{\partial v_j}{\partial x_i} \frac{\partial^2\omega_1}{\partial x_j \partial x_i} + v_j \frac{\partial}{\partial x_j} \left( \frac{\partial^2\omega_1}{\partial x_i^2} \right) \right] \quad (35)$$

In coordinate-free notation, this equation takes the form:

$$\text{Pe } \underline{v} \cdot \nabla\omega_1 = \nabla^2\omega_1 - \frac{(\text{De})_2}{2} \{ \underline{v} \cdot \nabla(\nabla^2\omega_1) + \text{tr}[\nabla\underline{v} \cdot \nabla(\nabla\omega_1)] \} \quad (36)$$

These equations provide what is perhaps the simplest characterization of viscoelastic diffusive effects in a steady flow process. Equation (35) can be compared to the following equation which has been derived<sup>7</sup> for the characterization of nonlinear viscous effects on diffusion in a steady diffusion process for a solute in the infinitely dilute limit:

$$v_i \frac{\partial\omega_1}{\partial x_i} = D \frac{\partial^2\omega_1}{\partial x_i^2} + \frac{\psi}{2} \frac{\partial^2 v_j}{\partial x_i \partial x_i} \frac{\partial\omega_1}{\partial x_j} + \psi D_{ij} \frac{\partial^2\omega_1}{\partial x_i \partial x_j} \quad (37)$$

This equation is written in dimensional form. The parameter  $\psi$  is a coefficient that characterizes the flow effect on the diffusion process;  $D$  is again the binary mutual diffusion coefficient, and the  $D_{ij}$  are the components of the rate of strain tensor. Because this equation is a second-order correction to the linear Fickian diffusion result, it provides what is perhaps the sim-

plest description of nonlinear viscous effects on diffusion in a steady flow process. The usual Fickian diffusion limit is recovered from eq. (37) by setting  $\psi = 0$ . There is at least one important difference between eq. (35) and eq. (37). For eq. (35), the diffusion flux depends on a scalar mutual diffusion coefficient, whereas, in eq. (37), the diffusion flux depends on a symmetric diffusion tensor.<sup>7</sup> The development of eq. (37) is based on the fact that the fluid is isotropic, but the presence of the velocity field leads to a situation for which the response of the fluid to a concentration gradient is different in different directions. Both eqs. (35) and (37) are linear equations for the solute mass fraction  $\omega_1$  because the velocity field does not depend on  $\omega_1$ .

### TRANSPORT EQUATION FOR AN IDEAL JET

As an example of viscoelastic diffusive effects, we consider the steady flow of an infinitely dilute solute in a plane jet of polymeric material. The transport domain is two-dimensional, and the jet is a horizontal jet which is negligibly affected by gravity. We further assume that the jet is ideal in the sense that it has a uniform velocity  $U_0$  in the flow direction. Consideration of an ideal jet makes it possible to carry out the mass transfer analysis without having to consider viscoelastic effects on the fluid mechanics of the system. In terms of dimensional variables, the jet extends from  $x = 0$  to  $x = \infty$  in the flow direction and from  $y = -L$  to  $y = L$  in the direction perpendicular to the direction of flow. The jet is surrounded by a pure gas which is absorbed into the polymeric material and is thus the solute for the mass transfer process. The jet has a uniform solute mass fraction  $\omega_{10}$  as it first comes into contact with the gas phase at  $x = 0$ , and the solute equilibrium mass fraction at each gas-liquid interface ( $y = -L$  and  $y = L$ ) is  $\omega_{1E}$ . Far downstream, at  $x = \infty$ , the solute mass fraction achieves a uniform value of  $\omega_{1E}$ . For convenience, we introduce the new concentration variable  $C$ :

$$C = \frac{\omega_1 - \omega_{10}}{\omega_{1E} - \omega_{10}} \quad (38)$$

From eq. (35), it follows that mass transfer in the jet is described by the following third-order partial differential equation:

$$\text{Pe} \frac{\partial C}{\partial x} = \frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} - \frac{(\text{De})_2}{2} \left[ \frac{\partial}{\partial x} \left( \frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} \right) \right] \quad (39)$$

In addition, the following boundary conditions must be imposed:

$$C = 0 \quad x = 0 \quad -1 \leq y \leq 1 \quad (40)$$

$$C = 1 \quad x = \infty \quad -1 \leq y \leq 1 \quad (41)$$

$$C = 1 \quad y = -1 \quad x > 0 \quad (42)$$

$$C = 1 \quad y = 1 \quad x > 0 \quad (43)$$

Although eqs. (40–43) are boundary conditions which are consistent with the physics of the problem, it is not known whether these conditions are sufficient to guarantee that there is a unique solution to the linear problem. We examine uniqueness of a slightly generalized version of the above problem by considering the axial region extending from  $x = 0$  to  $x = H$ . Here,  $H$  is a dimensionless distance which can be infinite as a special case. We thus consider the solution of eq. (39) subject to eqs. (40–43) (for  $0 < x < H$ ) and to the following additional boundary condition:

$$\frac{\partial C}{\partial x} = f(y) \quad x = H \quad -1 \leq y \leq 1 \quad (44)$$

We suppose there are two solutions  $C_1(x, y)$  and  $C_2(x, y)$ , which satisfy the boundary value problem. If we let

$$u = C_2(x, y) - C_1(x, y) \quad (45)$$

then  $u$  satisfies eq. (39) and the following modified boundary conditions:

$$u = 0 \quad x = 0 \quad -1 \leq y \leq 1 \quad (46)$$

$$u = 0 \quad x = H \quad -1 \leq y \leq 1 \quad (47)$$

$$\frac{\partial u}{\partial x} = 0 \quad x = H \quad -1 \leq y \leq 1 \quad (48)$$

$$u = 0 \quad y = -1 \quad x > 0 \quad (49)$$

$$u = 0 \quad y = 1 \quad x > 0 \quad (50)$$

There will exist at most one solution of the boundary value problem for  $C$  if it can be shown that  $u = 0$  is the only solution to the homogeneous problem.

Multiplication of eq. (39) (written in terms of  $u$ ) by  $u$  and integration from  $x = 0$  to  $x = H$  and from  $y = -1$  to  $y = 1$  give the following results for the five individual terms of the integrated differential equation:

$$\int_{-1}^1 \int_0^H u \frac{\partial u}{\partial x} dx dy = 0 \quad (51)$$

$$\int_{-1}^1 \int_0^H u \frac{\partial^2 u}{\partial x^2} dx dy = - \int_{-1}^1 \int_0^H \left( \frac{\partial u}{\partial x} \right)^2 dx dy \quad (52)$$

$$\int_{-1}^1 \int_0^H u \frac{\partial^2 u}{\partial y^2} dx dy = - \int_{-1}^1 \int_0^H \left( \frac{\partial u}{\partial y} \right)^2 dx dy \quad (53)$$

$$\int_{-1}^1 \int_0^H u \frac{\partial^3 u}{\partial x^3} dx dy = \frac{1}{2} \int_{-1}^1 \left( \frac{\partial u}{\partial x} \right)^2_{x=0} dy \quad (54)$$

$$\int_{-1}^1 \int_0^H u \frac{\partial^3 u}{\partial x \partial y^2} dx dy = 0 \quad (55)$$

These results are obtained by repeated integration by parts and by application of the appropriate boundary conditions. Utilization of eqs. (51–55) in the integrated equation for  $u$  yields the result:

$$0 = \int_{-1}^1 \int_0^H \left[ \left( \frac{\partial u}{\partial x} \right)^2 + \left( \frac{\partial u}{\partial y} \right)^2 \right] dx dy + \frac{(\text{De})_2}{4} \int_{-1}^1 \left( \frac{\partial u}{\partial x} \right)^2_{x=0} dy \quad (56)$$

This equation will be satisfied only if

$$\frac{\partial u}{\partial x} = 0 \quad (57)$$

$$\frac{\partial u}{\partial y} = 0 \quad (58)$$

everywhere in the concentration field. Equations (57) and (58) require that

$$u = \text{constant} \quad (59)$$

in the volume containing the concentration field. Because  $u = 0$  on all of the surfaces surrounding this volume, then

$$u = 0 \quad (60)$$

everywhere in the concentration field, and the boundary value problem has a unique solution.

For the problem of interest here, the following special form of eq. (44) must be added to eqs. (40–43) to guarantee that the boundary value problem has a unique solution:

$$\frac{\partial C}{\partial x} = 0 \quad x = \infty \quad -1 \leq y \leq 1 \quad (61)$$

It was anticipated that the third-order equation would require more boundary conditions than a second-order transport equation, and we utilized the requirement that the solution of the linear problem be unique

to formulate a meaningful additional boundary condition.

**SOLUTION OF IDEAL JET PROBLEM**

The concentration field described by eqs. (39–43) and (61) can be obtained by proposing a solution of the form:

$$C(x, y) = 1 - \sum_{n=0}^{\infty} \frac{4(-1)^n}{(2n + 1)\pi} \cos\left[\frac{(2n + 1)\pi y}{2}\right] X_n(x) \tag{62}$$

$$X_n(0) = 1 \tag{63}$$

Substitution of eq. (62) into eq. (39) produces the following equation for  $X_n$  for  $n \geq 0$ :

$$\frac{(De)_2}{2} \frac{d^3 X_n}{dx^3} - \frac{d^2 X_n}{dx^2} + \left[ Pe - \frac{(De)_2}{2} B_n \right] \frac{dX_n}{dx} + X_n B_n = 0 \tag{64}$$

$$B_n = \frac{(2n + 1)^2 \pi^2}{4} \tag{65}$$

This equation must be solved subject to eq. (63), which corresponds to eq. (40), and to the equations

$$X_n(\infty) = 0 \tag{66}$$

$$\frac{dX_n}{dx}(\infty) = 0 \tag{67}$$

which correspond to eqs. (41) and (61), respectively. A solution to the above ordinary differential equation takes the following form for each  $n$

$$X_n(x) = K_{n1} \exp(\lambda_{n1}x) + K_{n2} \exp(\lambda_{n2}x) + K_{n3} \exp(\lambda_{n3}x) \tag{68}$$

where  $\lambda_{n1}$ ,  $\lambda_{n2}$ , and  $\lambda_{n3}$  are the three roots of the following algebraic equation:

$$\frac{(De)_2}{2} \lambda_n^3 - \lambda_n^2 + \left[ Pe - \frac{(De)_2}{2} B_n \right] \lambda_n + B_n = 0 \tag{69}$$

For  $(De)_2 = 0$  (negligible elastic effects), the algebraic equation is a quadratic equation with two real roots, one positive and one negative. For  $Pe = 0$  (negligible convective mass transfer), the cubic equation has three real roots, two positive and one negative. For the general case [ $(De)_2 > 0, Pe > 0$ ], the cubic equation has one negative real root ( $\lambda_{n1}$ ) and either two positive real roots or two complex conjugate roots. If  $\lambda_{n2}$  and  $\lambda_{n3}$  are both positive, then  $K_{n2}$  and  $K_{n3}$  must both be

zero to guarantee that eqs. (66) and (67) are satisfied. If  $\lambda_{n2}$  and  $\lambda_{n3}$  are complex conjugate roots, then the well-known result for the sum of the three roots of a cubic equation can be used to derive the result

$$\text{Re}(\lambda_{n2}) = \frac{1}{(De)_2} - \frac{\lambda_{n1}}{2} \tag{70}$$

where  $\text{Re}(\lambda_{n2})$  refers to the real part of the complex conjugate roots. Because  $\lambda_{n1} < 0$ , it is clear that

$$\text{Re}(\lambda_{n2}) > 0 \tag{71}$$

and again  $K_{n2}$  and  $K_{n3}$  must both be set equal to zero to insure that eqs. (66) and (67) are satisfied. Consequently, from eqs. (63) and (68), it is clear that the solution to eqs. (63), (64), (66), and (67) for  $n \geq 0$  is simply

$$X_n(x) = \exp(\lambda_{n1}x) \tag{72}$$

with  $\lambda_{n1} < 0$ . It appears from the above development that a richer variety of solutions will be available for jets of finite length because the second and third terms will not necessarily be zero. For finite length jets, these two exponential terms will not become unbounded as they do for jets of infinite length.

The mass transfer rate of solute into the jet can effectively be examined by defining a dimensionless average concentration at any position  $x$  along the jet:

$$C(\text{avg}) = \frac{\int_{-1}^1 C \, dy}{2} \tag{73}$$

Substitution of eq. (62) into eq. (73) yields the expression

$$C(\text{avg}) = 1 - \sum_{n=0}^{\infty} \frac{8X_n(x)}{\pi^2(2n + 1)^2} \tag{74}$$

where  $X_n$  is given by eq. (72). At a given value of  $x$ ,  $C(\text{avg})$  depends only on  $(De)_2$  and  $Pe$ . The efficiency of the mass transfer process can be judged by how close  $C(\text{avg})$  is to unity [or, equivalently, how close the second term of eq. (74) is to zero] at a particular value of  $x$ . The decay of the second term of eq. (74) for sufficiently large  $x$  is dominated by the parameter  $\lambda_{01}$  because it is easy to show that

$$\frac{\partial \lambda_{n1}}{\partial B_n} < 0 \tag{75}$$

and, hence, the negative roots increase in magnitude with increasing  $n$ . Consequently, the dependence of the mass transfer rate on  $(De)_2$  and  $Pe$  can be examined by determining how  $\lambda_{01}$  varies with  $(De)_2$  and  $Pe$ .

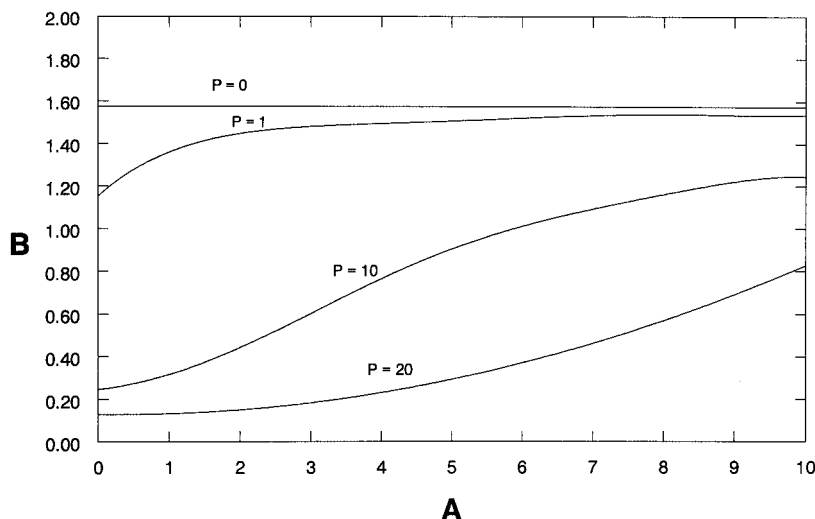


Figure 1 Dependence of  $B = -\lambda_{01}$  on  $A = (De)_2/2$  for four values of the Peclet number.

The elasticity of the material will lead to an enhancement of the mass transfer rate if  $(-\lambda_{01})$  increases with increasing  $(De)_2$  at a fixed value of  $Pe$ .

Values of  $\lambda_{01}$  were determined from eq. (69) for  $Pe$  in the range 0 to 20 and for  $(De)_2$  also varying from 0 to 20. The dependence of  $B = -\lambda_{01}$  on  $A = (De)_2/2$  is illustrated in Figure 1 for four values of the Peclet number. At  $Pe = 0$  (negligible convection), the decay parameter  $B$  is equal to  $(B_0)^{1/2}$  for all values of  $(De)_2$ , the diffusion Deborah number. However, as  $Pe$  increases, there is a significant increase of  $B$  with increasing  $A$ . For example, at  $Pe = 20$ ,  $B$  increases from 0.12 to 0.83 as  $A$  increases from 0 to 10. There is thus a significant mass transfer enhancement with increasing elasticity. The range of validity of the proposed constitutive equation for the diffusion flux is of course not known, but the proposed equation should give reasonable predictions for the Deborah number range considered here.

For the case of an ideal jet, the present results indicate that the presence of elasticity in the fluid enhances the mass transfer rate as the diffusion Deborah number is increased from  $(De)_2 = 0$ , the purely viscous limit. The ideal jet has a very simple velocity field, and not all of the terms in eq. (35) contribute to the diffusive mass transfer. It of course would be of great interest to see what happens to the mass transfer rate when more complicated velocity fields are used. Numerical solutions would very likely be needed for more complex velocity fields because the fluid mechanics of the problem complicates both the convective and the diffusive terms of the species continuity equation. However, eq. (35) is a relatively straightforward equation for studying viscoelastic effects in diffusion, and it should yield realistic predictions for steady diffusion for an infinitely dilute solute and for sufficiently low diffusion Deborah numbers.

Direct comparison of the predicted mass transfer effects with experiments conducted on laminar jets is not possible because the addition of polymer to a solvent can change the fluid mechanics of the system and  $D_0$ , as well as modify the constitutive equation for the diffusion flux. However, if we suppose that changes in the fluid mechanics and  $D_0$  are small, we can see if experimental data are consistent with the predicted mass transfer enhancement. Four laminar jet investigations were reported in three surveys of diffusion data in elastic fluids.<sup>4-6</sup> Three of these studies reported an increase of the mass transfer rate with the addition of polymer, and the fourth study reported both an increase and a decrease of the rate of mass transfer. Hence, the experimental data are generally consistent with the mass transfer enhancement predicted by the theory, but, of course, they do not provide a definitive validation of the theory.

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