ing wave velocity for $\theta = 1$ deg, $Re = 100$, and $We = 0$ are

De Bruin $\alpha = 0.359\,7$ $c = 2.721\,15$

Solesio $\alpha = 0.359\,695\,3$ $c = 2.721\,114\,7$

Nevertheless, for large values of the Reynolds number and for small values of the angle of inclination, the convergence of our method is only secured for small wave number values. For example, for $Re = 5\,000$, $\theta = 1$ deg, and $\zeta = 4\,887$, the convergence is obtained for values of α smaller than 0.15.

CONCLUSIONS

The numerical data obtained by means of the method of quadrature by differentiation are in good agreement with other numerical values and are more accurate for small wave number values than these obtained by Sternling and Towell. Nevertheless, some difficulties still appear with large Re ($\simeq 5\,000$) and small θ ($\theta = 1$ deg).

ACKNOWLEDGMENT

This work was performed within the scope of a doctorate thesis under the auspices of the French Atomic Energy Commission and the guidance of Dr. J. M. Delhaye.

The author is deeply indebted to Dr. W. B. Krantz, University of Colorado, Boulder, and to Dr. S. P. Lin, Clarkson, Potsdam, N.Y., for their constructive comments on a preliminary version of this paper and for their kindness in providing documents.

NOTATION

c = complex velocity
d = mean film thickness
$d_{L,M}$ = matrix element
n = approximation order of the quadrature formula
Re = Reynolds number $\triangleq u_a{}^* d^* / \nu$
u = axial velocity
We = Weber number $\triangleq \sigma / \rho d^* (\overline{u_a}^*)^2$
y = transversal coordinate

Greek Letters

α = wave number
ζ = surface tension group $\triangleq WeRe^{5/3}$
θ = angle of inclination of the plane
ν = kinematic viscosity
ρ = density
σ = surface tension
ϕ = stream function disturbance

Superscripts

$-$ = base flow
$*$ = dimensional quantity
$'$ = differentiation with respect to y
n = approximation order

Subscripts

a = average over the mean thickness of the film

LITERATURE CITED

Anshus, B. D., and S. L. Goren, "A Method of Getting Approximate Solution to the Orr-Sommerfeld Equation for Flow on a Vertical Wall," *AIChE J.*, **12**, 1004 (1966).

Benjamin, T. B., "Wave Formation in Laminar Flow Down an Inclined Plane," *J. Fluid Mech.*, **2**, 554 (1957).

De Bruin, G. J., "Stability of a Layer of Liquid Flowing Down an Inclined Plane," *J. Eng. Math.*, **8**, 259-270 (1974).

Krantz, W. B., and S. L. Goren, "Stability of Thin Liquid Films Flowing Down a Plane," *Ind. Eng. Chem. Fundamentals*, **10**, 91 (1971).

Krantz, W. B., and W. B. Owens, "Spatial Formulation of the Orr-Sommerfeld Equation for Thin Liquid Films Flowing Down a Plane," *AIChE J.*, **19**, No. 6, 1163 (1973).

Lanczos, C., *Applied Analysis*, Prentice Hall, Englewood Cliffs, N.J. (1956).

Lin, S. P., "Instability of a Liquid Film Flowing Down an Inclined Plane," *Phys. Fluids*, **10**, No. 2, 308 (1967).

Shuler, P. J., and W. B. Krantz, "The Equivalence of the Spatial and Temporal Formulations for the Linear Stability of Falling Film Flow," *AIChE J.*, **22**, No. 5, 934 (1976).

Solésio, J. N., "La méthode de quadrature par différentiation appliquée à l'hydrodynamique des films liquides," *CEA-R*, 4888 (1977).

Sternling, C. V., and G. D. Towell, Private communication, Shell Development Co., Houston, Tex. (1965).

Whitaker, S., "Effect of Surface Active Agents on the Stability of Falling Liquid Films," *Ind. Eng. Chem. Fundamentals*, 3, 2, 132-142 (1964).

Yih, C. S., "Stability of Two-Dimensional Parallel Flows for Three-Dimensional Disturbances," *Quart. Appl. Math.*, **12**, 434 (1955).

———, "Stability of Liquid Flow down an Inclined Plane," *Phys. Fluids*, 6, No. 3, 321 (1963).

———, *Fluid Mechanics*, McGraw-Hill, New York (1969).

Manuscript received December 5, 1977; revision received April 6, and accepted April 24, 1978.

The Effects of Plasma Constituents on Diffusivity of Oxygen

JOHN L. GAINER

Department of Chemical Engineering
University of Virginia
Charlottesville, Virginia 22901

There have been several investigations conducted in the past to determine the factors which affect the diffusion of oxygen in blood plasma. The transport of oxygen to and from blood and body tissues is, obviously, necessary for life. Since the oxygen must diffuse through the plasma, it has been thought that the resistance of the plasma layer may be important in determining the rate of oxygen transport, although there is considerable debate over this. For the most part, physiologists have tended to regard diffusion through the plasma as being of minimal importance in the oxygenation and deoxygenation of blood. However, a number of investigators have argued that this may be an important resistance in oxygen transport, perhaps even the controlling one, and more data are needed to determine if this is true or not. This has prompted diffusion studies to determine if oxygen transport is altered by the composition of the plasma.

0001-1541-79-1614-0188-$00.75.

In recent years, chemical engineers have been looking at this problem and conducting mass transfer experiments quite similar to those done previously using nonbiological fluids. There has been, however, disagreement as to what effect the plasma constituents have on oxygen transport, and a recent paper has shown that there are wide variations in the data previously obtained (Goldstick et al., 1976). In actuality, though, such apparent disagreement may not be real but due instead to the methods used in analyzing the previous data.

DISCUSSION

Let us assume that the diffusivity of oxygen in plasma is determined by the chemical composition of the plasma. The composition of an average, normal blood plasma is given in Table 1.

TABLE 1. COMPOSITION OF BLOOD PLASMA

Compound	Concentration, g/dl
Water	91.00
Proteins	
Albumin	3.50
Globulins (α, β, and γ)	2.95
Fibrinogen	0.30
Ionic species	1.86
Lipids	0.22
Carbohydrates	0.10
Amino acids	0.04
Nonprotein nitrogen compounds	0.03

Since it is possible that changing the levels of any of these constituents might affect the diffusion of oxygen through the plasma, one should write

$$D_{O_2-P} = f_1 \text{ (all constituents listed in Table 1)} \quad (1)$$

It would, of course, require a great deal of experimental data to determine the functional form of Equation (1), but it is necessary to do so in order to have a complete knowledge of how the changes in concentration of any of the constituents in plasma will affect the diffusivity of oxygen. This has not been done as of yet, and, instead, a number of simplifications of Equation (1) have been made.

One such simplification is to assume that only the protein levels affect the diffusivity. This is probably not true in reality. For example, there are effects due to some ionic species (Navari, 1970). Of perhaps more importance, there is a rather large effect on diffusivity when plasma glucose concentrations are changed, as well as with changes in the levels of various other compounds (Gainer and Chisolm, 1973). To study such effects systematically, however, would require much experimentation, and thus these effects have been neglected for the most part. Assuming, then, that only proteins affect the diffusivity, another equation can then be written as

$$D_{O_2-P} = f_2 \text{ (plasma protein concentrations)} \quad (2)$$

The choice now becomes whether or not it is necessary to study the effects of each protein individually or, rather, to look only at variations in the total protein concentration.

Several investigators (Dorson et al., 1971; Gertz and Loeschcke, 1954; Goldstick et al., 1976; Hershey and Karban, 1968; Yoslida and Oshima, 1966) have measured diffusion coefficients in plasmas, but only two of these studies (Dorson et al., 1971; Goldstick et al., 1976) have investigated the effects of varying the total protein levels. In other words, they assumed that

$$D_{O_2-P} = f_3(T) \quad (3)$$

Since they were considering variations in the total protein levels, Equation (3) should be written in differential form:

$$\frac{dD_{O_2-P}}{dT} = \frac{df_3}{dT} \quad (4)$$

A change in the total protein level (dT) can occur because of changes in the levels of several different plasma proteins, but the studies do not differentiate as to how the changes occur and concentrate on overall changes in the total protein levels.

A more general way to consider the effect of protein levels is, obviously, to consider the effect of varying the concentrations of each individual protein. This, when stated mathematically, means

$$D_{O_2-P} = f_4(A, \alpha, \beta, \gamma, F) \quad (5)$$

It has been shown (Gainer and Chisolm, 1973; Goldstick et al., 1976) that the level of fibrinogen present in plasma does not affect the diffusivity of oxygen, so

$$D_{O_2-P} = f_5(A, \alpha, \beta, \gamma) \quad (6)$$

If one is interested in the effects on diffusivity of variations of each protein level, then one can write the differential form of Equation (6):

$$\frac{dD_{O_2-P}}{dT} = \left.\frac{\partial f_5}{\partial A}\right)_{\alpha,\beta,\gamma} \frac{dA}{dT} + \left.\frac{\partial f_5}{\partial \alpha}\right)_{A,\beta,\gamma} \frac{d\alpha}{dT} + \left.\frac{\partial f_5}{\partial \beta}\right)_{A,\alpha,\gamma} \frac{d\beta}{dT} + \left.\frac{\partial f_5}{\partial \gamma}\right)_{A,\alpha,\beta} \frac{d\gamma}{dT} \quad (7)$$

All of the partial derivatives of Equation (7) have been determined for average protein concentration levels (Navari, et al., 1971; Bryant and Navari, 1974), and this equation can be used for determining the effect of variations in protein levels on the diffusivity of oxygen no matter how such variations occur. It must be kept in mind, however, that the partial derivatives in Equation (7) may be functions of the parameters being held constant and may not be true constants.

It has been asserted that the dependency of the diffusivity of oxygen with respect to changing total protein levels should be the same whether one considers the variation of each protein level separately [Equation (7)] or whether one considers the variation of the total amount of protein [Equation (4)]. Mathematically, this means the derivative of D_{O_2} with respect to T of Equations (4) and (7) have to be equal. This is not true and can be shown as follows. Since

$$T = A + \alpha + \beta + \gamma$$

Equation (4) can be rewritten as

$$\frac{dD_{O_2-P}}{dT} = \frac{df_3}{dT}\left(\frac{dA}{dT} + \frac{d\alpha}{dT} + \frac{d\beta}{dT} + \frac{d\gamma}{dT}\right) \quad (8)$$

If the diffusivity of oxygen through plasma is independent of how the plasma protein levels vary (individually or as a total), then Equations (7) and (8) should be equal, or

$$\left.\frac{\partial f_5}{\partial A}\right)_{\alpha,\beta,\gamma} = \left.\frac{\partial f_5}{\partial \alpha}\right)_{A,\beta,\gamma} = \left.\frac{\partial f_5}{\partial \beta}\right)_{A,\alpha,\gamma} = \left.\frac{\partial f_5}{\partial \gamma}\right)_{A,\alpha,\beta} = \frac{df_3}{dT} \quad (9)$$

It has been shown previously that the first four of these derivatives are not numerically equal (Navari et al., 1971; Bryant and Navari, 1974), which leads to the conclusion that Equations (7) and (8) are, in turn, not equivalent. A recent paper (Goldstick et al., 1976) compares diffusion data by stating that $\partial f_5/\partial A)_{\alpha,\beta,\gamma}$ should be equal to df_3/dT. There is, clearly, no reason why this should be so. If one wishes to compare data for variations in diffusivity with changing total protein levels, one should account for the effect of each separate protein and its influence on the diffusion of oxygen. Goldstick et al. (1976) state that they found little difference using the total derivative rather than the partial derivatives in accounting for the protein effects on oxygen diffusivity in plasma. However, it is important to realize that each of the partial derivatives in Equation (7) are functions of the concentrations of the other proteins (those held constant during their evaluation). Values of these derivatives have been determined for one range of protein levels (the normal, average values for humans), and much of the data reported by Goldstick et al. (1976) are not for normal, average levels. This makes any comparison of previously obtained data quite difficult, if not impossible. This is compounded further by the fact that blood plasma taken from various hospital patients (Goldstick et al., 1976) is quite likely to contain drugs and medicines which could easily alter the diffusivity values obtained.

SUMMARY

As stated before, the diffusion of oxygen through plasma may prove to be important in physiological systems, and as more chemical engineers work in this area, care should be taken to realize that plasma is a solution containing many components. This makes any study concerning the concentration dependence of the diffusivity a multidimensional one. The assumptions that some variations are not important, or that the problem can be treated as being one dimensional, have not been proven, although many previous studies do not always appear to recognize this. In fact, the effects of drug levels in plasma on oxygen transport may be much more important, physiologically, than the effects of variations of protein levels, where almost all previous interest has centered. In summary, diffusion of oxygen through plasma may be affected by the concentrations of any of the constituents present normally in plasma, as well as those added (drugs), but no study made to date has considered this in detail. This may have also led to some misinterpretation of previous data. However, the experiments performed to date have established a foundation on which to build a future knowledge of this important system.

NOTATION

A = concentration of albumin in plasma
D_{O_2-P} = diffusivity of oxygen in plasma
F = concentration of fibrinogen in plasma
T = total protein level
α = concentration of α-globulin in plasma
β = concentration of β-globulin in plasma
γ = concentration of γ-globulin in plasma

LITERATURE CITED

Bryant, S. C., and R. M. Navari, "Effect of Plasma Proteins on Oxygen Diffusion in the Pulmonary Capillaries," *Microvas. Res.*, 7, 120 (1974).

Dorson, W. J., R. Yee, K. G. Larsen, R. J. Elgas, and M. E. VoorLees, "Oxygen Diffusion in Blood and Plasma," *Proc. 24th ACEMB*, 13, 280 (1971).

Gainer, J. L., and G. M. Chisolm, III, "Altering Diffusion Rates," in *Oxygen Transport to Tissue*, D. Bruley and H. Bicher ed., pp. 729-733, Plenum Press, New York (1973).

Gertz, K. H., and H. H. Loeschcke, "Diffusion in Blood," *Z. Naturforsch.*, 9, 1 (1954).

Goldstick, T. K., V. T. Ciruyla, and L. Zuckerman, "Diffusion of Oxygen in Plasma and Blood," *Adv. in Expt'l. Med. and Biol.*, 75, 183 (1976).

Hershey, D., and T. Karhan, "Diffusion of Oxygen in Whole Blood," *AIChE J.*, 14, 969 (1968).

Navari, R. M., "Mass Transfer in Biological Systems," PhD dissertation, Univ. Va., Charlottesville (1970).

———, J. L. Gainer, and K. R. Hall, "Transport in Human Plasma," *Aerospace Med.*, 42, 1123 (1971).

Yoshida, F., and N. Oshima, "Diffusivity of Oxygen in Blood Serum," *J. Appl. Physiol.*, 21, 915 (1966).

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

Large Schmidt Number Mass Transfer in Turbulent Pipe Flow

ORVILLE C. SANDALL and OWEN T. HANNA

Department of Chemical and Nuclear Engineering
University of California, Santa Barbara, California

Shaw and Hanratty (1977) have recently presented new, large Schmidt number data for fully developed turbulent mass transfer from a pipe wall. The electrochemical method was used, and the data, covering the range 693 $\leq Sc \leq$ 37 200, appear to be of high precision. The authors found that the often assumed large Schmidt number relationship $St \propto Sc^{(1-n)/n}$, corresponding to $\epsilon^+ \propto y^{+n}$ near the wall, did not satisfactorily correlate their data for $n = 3$ or $n = 4$. The modified correlation proposed by Shaw and Hanratty for their data is

$$\frac{St}{\sqrt{f/2}} = 0.0889\, Sc^{-0.704} \tag{1}$$

This expression was determined by fitting a function of the form $St/\sqrt{f/2} = CSc^a$, where C and a are free parameters. They report that a statistical calculation for their model shows that experimental errors could not account for the discrepancy between $a = -0.704$ and either $-2/3$ or $-3/4$. Heretofore, it has generally been accepted that $a = -2/3$ (Notter and Sleicher, 1971; Hanna and Sandall, 1972). The purpose of this note is to show that the large Sc asymptotic expansion of Hanna