Sprow, F. B., and J. M. Prausnitz, "Vapor-liquid equilibria and surface tensions for the nitrogen-argon-methane system at 90.67 K," *Cryogenics*, 6, 338 (1966).
Strobridge, T. R., "The thermodynamic properties of nitrogen from 64 to 300 K between 0.1 and 200 atmospheres," NBS, Tech. Note 129 (Jan. 1962).
Thorpe, P. L., "Liquid-vapor equilibrium of the system nitrogen + argon at pressures up to 10 atm," *Trans. Faraday Soc.*, 64, 2273 (1968).
Wilson, G. M., P. M. Silverberg, and M. G. Zellner, "Argon-oxygen-nitrogen three-component system experimental vapor-liquid equilibrium data," *International Advances in Cryogenic Engineering*, Vol. 10, p. 192, Plenum Press, N. Y. (1965).

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Miscible Displacement with Combined Free and Forced Convection: Laminar Flow in a Vertical Tube

An approximate analysis is given for miscible displacement in vertical tubes when density differences between the displaced and displacing fluids give rise to buoyancy forces which affect the velocity distribution significantly. The results of this analysis agree with the available experimental data fairly uniformly over the range of parameters studied experimentally.

By analogy with studies of heat transfer in vertical tubes it is concluded that both cases studied, when a lighter fluid displaces a heavier fluid in upflow, or when the heavier fluid is below the lighter fluid, are potentially unstable flows because buoyancy forces can create points of inflection in the velocity profile; stagnation at the wall also is predicted for upflow when the lighter fluid is on the bottom initially, and this has been observed to induce a sudden transition to turbulence in heat transfer systems.

Buoyancy forces reduce the extent of dispersion by flattening the velocity profile when the heavier fluid is on the bottom in upflow. The velocity profile is elongated and the dispersion coefficient is increased when the bottom fluid is lighter than the one it displaces in upflow.

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SCOPE

The concept of dispersion as introduced by G. I. Taylor (1953) has been used to model a wide variety of systems of practical interest such as tubular reactors, heat exchangers, chromatographs, displacement of fluids from porous media, distribution of thermal and material pollutants, etc. An objective of the present work is to describe how natural convection can influence the extent of dispersion in laminar flow in vertical tubes. Another objective is to determine whether natural convection effects in such flow can cause the kind of instabilities observed experimentally by Scheele and Hanratty (1962) when heat transfer in vertical flow causes significant density differences across the flow.

Consider two fluids which are at rest in vertical capillary tubes that are separated by a very thin partition. At time zero, the partition is removed and the fluids are instantaneously set in upward motion by a device which creates a constant volumetric flow rate. The bottom fluid may be heavier or lighter than the one it displaces. As the miscible displacement continues in time, a mixing zone develops in which the fluid density varies from point to point in the flow field due to concentration changes. This creates a coupling between the concentration and flow fields which makes a solution for either very difficult because the problem is both time dependent and nonlinear. It will be shown that the dispersion model provides an approximate method of solution for this complex problem of

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simultaneous mass and momentum transport.

The initial condition for this system has some similarities to the classical stability problem of a fluid heated from below. This corresponds to a lighter fluid displacing a heavier one from below.

Most of the previous work on dispersion assumes that the velocity field is a prescribed function of both time and space coordinates but is independent of the concentration field. For the case of flow fields which are only a function of the radial coordinate and time, a dispersion model has been developed by Gill and Sankarasubramanian (1970, 1971) which is an exact solution of the convective diffusion equation. For the more complicated problem of developing velocity fields which vary with distance along the main direction of flow numerical solutions have been given by Gill et al. (1968). Although these methods do not yield exact solutions to the present problem, they do provide the tools with which the approximate solution given here is developed.

The initial treatment of this problem was reported by Reejhsinghani et al. (1968). Their work provides an approximate perturbation theory for unsteady dispersion with combined free and forced convection along with results of experiments carried out under these conditions. However, their results are restricted to relatively weak buoyancy effects and small values of the buoyancy parameter α, where

$$\alpha = \frac{g\beta a^4 c_0}{\nu D}\frac{\partial C_m}{\partial x_1}$$

Our purpose is to present an approximate analysis of miscible displacement in vertical tubes which employs different assumptions from those used by Reejsinghani et al. (1968). By avoiding the need for a perturbation expansion in the buoyancy parameter α, we hope to obtain results which apply equally well to systems with strong buoyancy effects and thus to apply uniformly regardless of the magnitude of α.

CONCLUSIONS AND SIGNIFICANCE

The results of the analysis of Reejhsinghani et al. (1968) were that the velocity profile is given by

$$u = 2U_m(1 - y^2) - \frac{\alpha U_m}{1152}(4 - 18y^2 + 18y^4 - 4y^6)$$

and that the dispersion coefficient is

$$\frac{k}{D} = 1 + \frac{N^2{}_{Pe}}{192}\left(1 - \frac{11}{2880}\alpha + 4.16 \times 10^{-6}\,\alpha^2\right)$$

where N_{Pe} is the Peclet number $\frac{2RU_m}{D}$. Experiments indicated this expression for the dispersion coefficient is a reasonably good approximation only in the range, $-50 < \alpha < 300$; therefore, their analysis is restricted to rather weak buoyancy effects. The experimental results are reported for a rather wide range of parameters for tubes with both 1½ mm and 5 mm diameters, and it was shown that viscosity variations were not important in the range studied.

The present results, which are given by Equations (17) and (33) for u and (32) and (36) for k, differ significantly for large α from those given above because different assumptions have been made in the two studies. Reejhsinghani et al. retained the transient term $\frac{\partial u}{\partial t}$ in the momentum equations and assumed that

$$\frac{\partial u}{\partial t} >> \frac{u\partial u}{\partial x} + \frac{v\partial u}{\partial r}$$

However, if one uses their solution as a first approximation, it can be shown that $\frac{\partial u}{\partial t}$ is the same order of magnitude as $u\frac{\partial u}{\partial x}$ and $v\frac{\partial u}{\partial r}$. Consequently it is also reasonable to employ the quasi steady state assumption and neglect the transient term $\frac{\partial u}{\partial t}$ in the equation of motion; but it should be recognized that the results obtained by neglecting these terms are unlikely to be valid at small values of time or when very large density differences exist. It has been shown here that this quasi steady state assumption with respect to velocity enables one to obtain an approximate solution of the resulting equations which appears to be uniformly valid over a wide range of α as evidenced by the good agreement with the available experimental data on time-averaged dispersion coefficients for upflow in tubes, both when the heavier fluid displaces the lighter and visa versa. Even though the experimental data scatter significantly it is clear that the theory and experimental results show the same major trends.

In contrast to the analysis of Reejhsinghani, the present mathematical results are fundamentally different depending on whether the heavier fluid is initially above or below the lighter one. The analysis of the case with lighter fluid on the bottom in upflow applies only after sufficient time has transpired to ensure that singularities in the velocity distribution and the dispersion coefficient do not occur. Also, for the same absolute value of α the effect of buoyancy on dispersion is predicted to be much larger when the lighter fluid is below the heavier one. The present theoretical results are consistent with the experiments of Reejhsinghani et al. who found that the extent of dispersion is enhanced significantly when lighter fluid is on the bottom and displaces a heavier one. On the other hand, the dispersion coefficient is reduced when the situation is reversed.

Similarities exist between the natural convection effects which occur in miscible displacement with fluids of different density and those in interphase heat or mass transfer processes. If the displacing (bottom) fluid is heavier than the displaced fluid, then the density will be distributed radially such that the highest density is in the central region of the tube; this also is the case when an upflowing fluid is heated by a hotter tube wall. Conversely, if the lighter fluid is on bottom, the density near the wall will be higher than that in the central core; thus, the density distribution is similar to that obtained when the tube wall is colder than the fluid.

The present analysis shows that similarities in the density distributions lead to changes in the velocity distribution which are qualitatively similar for displacement and heat transfer processes. When the heavier fluid is on bottom the velocity distribution is flattened by buoyancy effects, and as α increases the point of maximum velocity moves from the tube axis toward the tube wall. By analogy with the heat transfer system, based on the observations of Scheele and Hanratty (1962), one would expect a transition to an unsteady flow when the point of maximum velocity is displaced from the axis and this is the precursor of a gradual transition to turbulence. For the displacement process, the present results show that the velocity at the axis is never reduced below the mean velocity, whereas constant flux heating of an upflowing fluid can cause back flow in the central core.

When a lighter fluid displaces a heavier one in upflow the velocity in the central core is increased and that near the wall is reduced. Equation (33) shows that this can lead to back flow near the wall which according to the observations of Scheele and Hanratty (1962) on heat transfer systems may lead to an abrupt transition to turbulence.

ANALYSIS

If one neglects the inertia terms and $\frac{\partial u}{\partial t}$, the equations of motion for the present problem are given by

$$0 = \frac{\mu}{\rho_0}\frac{1}{r}\frac{\partial}{\partial r}r\frac{\partial u}{\partial r} - \frac{\rho}{\rho_0}g - \frac{1}{\rho_0}\frac{\partial p}{\partial x} \qquad (1)$$

$$0 = -\frac{\partial p}{\partial r} \qquad (2)$$

and the convective diffusion equation is

$$\frac{\partial C}{\partial t} + u\frac{\partial C}{\partial x} = D\left(\frac{1}{r}\frac{\partial}{\partial r}r\frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial x^2}\right) \qquad (3)$$

where

$$C = c/c_0$$

The equation of state which couples Equations (1) and (3) is

$$\rho/\rho_0 = 1 - \beta(c - c_0) \qquad (4)$$

where

$$\beta = -\frac{1}{\rho}\frac{\partial \rho}{\partial c}\bigg|_{c=c_0}$$

The boundary and initial conditions for Equations (1), (2), and (3) are

$$C(0, x, r) = 0 \quad \text{(initial condition)} \qquad (5a)$$

$$C(t > 0, 0, r) = 1 \quad \text{(step change at inlet)} \qquad (5b)$$

$$C(t, \infty, r) = 0 \qquad (5c)$$

$$\frac{\partial C}{\partial r}(t, x, 0) = 0 \quad \text{(symmetry at center)} \qquad (5d)$$

$$\frac{\partial C}{\partial r}(t, x, a) = 0 \quad \text{(impermeable wall at } r = a\text{)} \qquad (5e)$$

$$u(a) = 0,\ u(0) = \text{finite} \qquad (5f)$$

Rewriting Equation (3) in terms of an axial coordinate x_1 which moves with the mean speed of flow $x_1 = x - \int_0^t U_m\, dt$ gives

$$\frac{\partial C}{\partial t} + (u - U_m)\frac{\partial C}{\partial x_1} = D\left(\frac{1}{r}\frac{\partial}{\partial r}r\frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial x_1^2}\right) \qquad (3a)$$

To find a solution of Equations (1), (2), and (3a) it is convenient to uncouple them. To do this we follow the approach of Taylor (1953) which has been modified by Gill (1967) and let

$$C = C_m + \frac{\partial C_m}{\partial x_1}f(r, t) \qquad (6)$$

where $f(r, t)$ is a concentration distribution function and

$$C_m = \frac{2}{a^2}\int_0^a rC dr.$$

By differentiating the x-direction equation of motion with respect to the radial coordinate to eliminate the pressure gradient term, and substituting Equation (4) in the result, one gets

$$0 = \frac{\partial}{\partial r}\frac{\nu}{r}\frac{\partial}{\partial r}r\frac{\partial u}{\partial r} + g\beta\frac{\partial c}{\partial r} \qquad (7)$$

where the time dependence of the velocity is reflected in the second term on the right of Equation (7).

By using Equation (6), from Equation (7) one gets

$$0 = \frac{\partial}{\partial y}\frac{\nu}{y}\frac{\partial}{\partial y}y\frac{\partial u}{\partial y} + ga^2\beta c_0\frac{\partial f}{\partial y}\frac{\partial C_m}{\partial x_1} \qquad (8)$$

where $y = r/a$. To determine $f(r, t)$ we substitute Equation (6) into (3a), and use the truncated form of the dispersion model developed by Gill and Sankarasubramanian (1970) as

$$\frac{\partial C_m}{\partial t} = k(t)\frac{\partial^2 C_m}{\partial x_1^2} \qquad (9)$$

which yields

$$\frac{\partial C_m}{\partial x_1}\left[\frac{\partial f}{\partial t} + u - U_m - \frac{D}{a^2}\frac{1}{y}\frac{\partial}{\partial y}y\frac{\partial f}{\partial y}\right] + \frac{\partial^2 C_m}{\partial x_1^2}[(u - U_m)f + k - D] + \frac{\partial^3 C_m}{\partial x_1^3}f(k - D) = 0 \qquad (10)$$

If, following Taylor, one neglects the terms involving higher order derivatives of the mean concentration and sets the coefficient of $\frac{\partial C_m}{\partial x_1}$ equal to zero, this gives

$$\frac{\partial f}{\partial t} + u - U_m = \frac{D}{a^2}\frac{1}{y}\frac{\partial}{\partial y}y\frac{\partial f}{\partial y} \qquad (11)$$

The velocity field now must be determined from Equations (8) and (11). The function $f(t, r)$ depends on time because u depends on time; also, $f(t, r)$ exhibits a transient response which dies out at about $t \approx 0.5\frac{a^2}{D}$ if u is independent of time. The calculations are simplified very significantly if it is assumed that the velocity field is a weak function of time. Then one can invoke the quasi steady state assumption and omit the derivative of f with respect to t in Equation (11). This is equivalent to neglecting the transient behavior of f which occurs at small values to time. Thus, if we are concerned only with values of t large enough to neglect $\frac{\partial f}{\partial t}$ compared to the other terms in Equation (11), then we can operate on Equation

(8) with $\left(\frac{1}{y}\frac{d}{dy}y\right)$ and combine the results with

$$u - U_m = \frac{D}{a^2}\frac{1}{y}\frac{d}{dy}y\frac{df}{dy} \qquad (11a)$$

to yield

$$\nabla^4\phi = -\alpha\,\phi \qquad (12)$$

where

$$\phi = u - U_m$$

$$\alpha = \frac{g\beta a^4 c_0}{D\nu}\frac{\partial C_m}{\partial x_1}$$

and

$$\nabla^4 = \frac{1}{y}\frac{d}{dy}y\frac{d}{dy}\frac{1}{y}\frac{d}{dy}y\frac{d}{dy}$$

The neglect of $\frac{\partial f}{\partial t}$ in finding the velocity distribution will be justified a posteriori by showing that the theoretical results based on this assumption compare favorably with the experimental evidence for the values of time considered.

The solution of Equation (12) for the velocity distribution is dependent on the sign of α. For positive values of α the general solution is

$$\phi = c_1 ber\gamma y + c_2 bei\gamma y + c_3\, ker\gamma y + c_4 kei\gamma y, \quad \alpha > 0 \qquad (13)$$

and for negative values

$$\phi = e_1 I_0(\gamma y) + e_2 J_0(\gamma y) + e_3 K_0(\gamma y) + e_4 Y_0(\gamma y), \quad \alpha < 0 \qquad (14)$$

where

$$\gamma = |\alpha|^{1/4}$$

The boundary conditions are

$$\phi(1) = -U_m \qquad (15)$$

$$\phi(0) = \text{finite}$$

and from the definition of U_m

$$\int_0^1 y\phi dy = 0 \qquad (16)$$

The density difference parameter α is physically significant such that the case of $\alpha > 0$ represents the hydrodynamically stable case of the lighter fluid on top in upward flow while $\alpha < 0$ is the potentially unstable case of the heavier fluid on top.

The solution for the case of $\alpha > 0$, using Equations (15) and (16) with Equation (13), is

$$1 - \frac{u}{U_m} = \frac{ber\gamma y + Abei\gamma y}{ber\gamma + Abei\gamma} \qquad (17)$$

where

$$A = bei'\gamma/ber'\gamma,$$

and prime denotes differentiation with respect to y.

Now with the velocity known, we return to Equation (11) to solve for $f(y, t)$ in which $u = u(y, t)$ is given by Equation (17). The time dependence in u occurs in α and we account for this by applying Duhamel's theorem which states that

$$f(y, t) = \frac{\partial}{\partial t}\int_0^t F(t-\lambda, \lambda, y)\,d\lambda \qquad (18)$$

if we define F by

$$\frac{\partial F}{\partial t} - \phi(\lambda, y) = \frac{D}{a^2}\frac{1}{y}\frac{\partial}{\partial y}y\frac{\partial F}{\partial y}, \qquad (19)$$

where λ in Equation (19) replaces t in α and is considered to be a constant in solving for F. To find F, let

$$F = F_0(\lambda, y) - F_t(\lambda, t, y) \qquad (20)$$

such that F_0 and F_t satisfy

$$\phi(\lambda, y) = \frac{D}{a^2}\frac{1}{y}\frac{d}{dy}y\frac{dF_0}{dy}$$

$$\left.\frac{dF_0}{dy}\right|_{y=1} = \left.\frac{dF_0}{dy}\right|_{y=0} = 0 \text{ and } \int_0^1 yF_0dy = 0 \qquad (21)$$

and

$$\frac{\partial F_t}{\partial t} = \frac{D}{a^2}\frac{1}{y}\frac{\partial}{\partial y}y\frac{\partial F_t}{\partial y}$$

$$\left.\frac{\partial F_t}{\partial y}\right|_{y=1} = \left.\frac{\partial F_t}{\partial y}\right|_{y=0} = 0 \text{ and } \int_0^1 yF_tdy = 0 \qquad (22)$$

where

$$F_t(\lambda, 0, y) = F_0(\lambda, y)$$

Direct integration of Equation (21) and use of the boundary and integral conditions results in

$$F_0 = -\frac{a^2U_m}{D\gamma^2}\left[\frac{bei\gamma y - Aber\gamma y + \frac{2}{\gamma}ber'\gamma(1 + A^2)}{ber\gamma + Abei\gamma}\right] \qquad (23)$$

where γ is a function of λ. From Equation (22) it can be shown that

$$F_t = \sum_{n=1}^{\infty} A_n e^{-\frac{\mu_n^2 D t}{a^2}} J_0(\mu_n y) \qquad (24)$$

where the μ_n are defined by $J_1(\mu_n) = 0$. The expansion coefficients A_n are determined by the initial condition of Equation (22)

$$A_n = \frac{\int_0^1 yF_0(\lambda, y)J_0(\mu_n y)\,dy}{\int_0^1 yJ_0^2(\mu_n y)\,dy} \qquad (25)$$

Therefore substituting Equations (23) and (24) in (18) one gets

$$f = \frac{\partial}{\partial t}\int_0^t \left[F_0(\lambda, y) - \sum_{n=1}^{\infty} e^{-\frac{\mu_n^2 D(t-\lambda)}{a^2}} A_n(\lambda)J_0(\mu_n y)\right]d\lambda \qquad (26)$$

By using Leibnitz's rule and integrating by parts, we obtain

$$f = F_0(t, y) + \frac{a^2U_m}{D}\sum_{n=1}^{\infty}\int_0^t \frac{\partial A_n}{\partial \lambda} e^{-\frac{\mu_n^2 D(t-\lambda)}{a^2}} J_0(\mu_n y)\,d\lambda \qquad (27)$$

The term $\frac{\partial A_n}{\partial \lambda}$ can be determined from the approximate relationship between t and α,

$$\alpha = b/\sqrt{t} \tag{28}$$

where b is a constant which depends only on the initial density difference and the Peclet number. Therefore

$$\frac{\partial A_n}{\partial \lambda} = \frac{\partial A_n}{\partial \gamma}\frac{\partial \gamma}{\partial \alpha}\frac{\partial \alpha}{\partial \lambda} = -\frac{\gamma}{8\lambda}\frac{\partial A_n}{\partial \gamma}$$

With both the velocity and concentration field known we can determine the dispersion coefficient by multiplying Equation (3a) by $2y$ and integrating over the interval $y = 0$ to $y = 1$ to yield

$$\frac{\partial C_m}{\partial t} + 2\int_0^1 y(u - U_m)\frac{\partial C}{\partial x_1}dy = D\frac{\partial^2 C_m}{\partial x_1^2} \tag{29}$$

When Equation (6) is substituted into Equation (29) the result is

$$\frac{\partial C_m}{\partial t} = \left[D - 2\int_0^1 y(u - U_m)f\,dy\right]\frac{\partial^2 C_m}{\partial x_1^2} \tag{30}$$

By comparing Equation (30) with Equation (9) it becomes obvious that

$$k = D - 2\int_0^1 y(u - U_m)f dy \tag{31}$$

Note, because of the definition of U_m, that any terms of f which do not depend on y will not contribute to k. Terms which vary weakly with y contribute a relatively small amount to the value of k.

Using Equations (17), (23), and (27) in (31) yields, for $\alpha > 0$,

$$\frac{k}{D} = 1 + \frac{N_{Pe}^2}{2}\;\frac{\left(\frac{1}{2}(1 + A^2)ber'\gamma\right)^2 + \frac{1}{2}(ber\gamma + Abei\gamma)(bei\gamma - Aber\gamma)}{(ber\gamma + Abei\gamma)^2},$$

$$-\frac{N_{Pe}^2}{2}\sum_{n=1}^{\infty}\int_0^t \frac{1}{2}e^{-\left[\frac{\mu_n^2 D(t-\lambda)}{a^2}\right]}C_n\frac{\partial A_n}{\partial \lambda}J_0^2(\mu_n)d\lambda \tag{32}$$

where

$$C_n = \frac{2\mu_n^2\, ber'\gamma(1 + A^2)}{(\gamma^4 + \mu_n^4)(ber\gamma + Abei\gamma)J_0(\mu_n)}$$

The same method of solution for $\alpha < 0$ gives the following results:

$$\frac{u}{U_m} - 1 = \frac{I_1(\gamma)J_0(\gamma y) - I_0(\gamma y)J_1(\gamma)}{I_0(\gamma)J_1(\gamma) - I_1(\gamma)J_0(\gamma)} \tag{33}$$

and

$$f = -\frac{a^2U_m}{D\gamma^2}\left[\frac{\left(I_1(\gamma)J_0(\gamma y) + J_1(\gamma)I_0(\gamma y) + \frac{2}{\gamma}I_1(\gamma)J_1(\gamma)\right)}{F_0(\gamma)J_1(\gamma) - I_1(\gamma)J_0(\gamma)}\right.$$

$$\left. - \sum_{n=1}^{\infty}\int_0^1 \frac{\partial B_n}{\partial \lambda}e^{-\left[\frac{\mu_n^2 D(t-\lambda)}{a^2}\right]}J_0(\mu_n y)d\lambda\right] \tag{34}$$

where

$$B_n = \frac{4\gamma}{(\mu_n^4 - \gamma^4)}\frac{I_1(\gamma)J_1(\gamma)}{J_0(\mu_n)(I_0(\gamma)J_1(\gamma) - I_1(\gamma)J_0(\mu_n))} \tag{35}$$

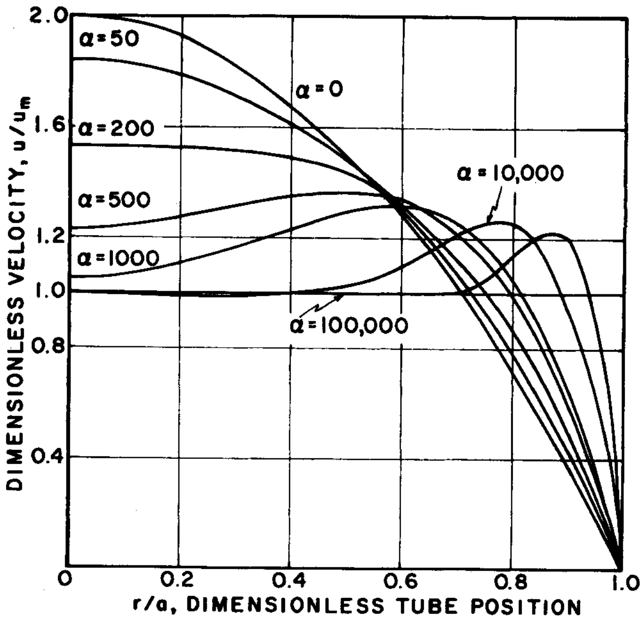

Fig. 1. Reduced velocity vs. radial position for various positive values of α; upflow with heavy fluid on bottom.

and finally the result for the dispersion coefficient is

$$\frac{k}{D} = 1 + \frac{N_{Pe}^2}{2}\left[\frac{I_1^2(\gamma)J_1^2(\gamma) + \frac{1}{2}(I_1^2(\gamma)J_0^2(\gamma) - I_0^2(\gamma)J_1^2(\gamma))}{\gamma^2(I_0(\gamma)J_1(\gamma) - I_1(\gamma)J_0(\gamma))^2}\right]$$

$$-\frac{N_{Pe}^2}{8}\sum_{n=1}^{\infty}\int_0^1 e^{-\left[\frac{\mu_n^2 D(t-\lambda)}{a^2}\right]}B_n\frac{\partial B_n}{\partial \lambda}J_0^2(\mu_n)d\lambda \tag{36}$$

RESULTS AND DISCUSSION

The shapes of the velocity profiles obtained by the present analysis and shown in Figures 1 and 2 for $\alpha > 0$ and $\alpha > -400$ are in agreement qualitatively with predictions which could be made on the basis of physical reasoning. That is, for the case of $\alpha > 0$, the heavier fluid on bottom in upward flow, we would expect that because of the downward buoyant forces exerted on the heavier fluid, the velocity of the more dense fluid layers in the center of the tube is reduced. The results of the analysis show this in Figure 1; as α grows larger the velocity profile continues to flatten out and as $\alpha \rightarrow \infty$ the velocity profile approaches that of plug flow. For values of $\alpha >$

202, a point of inflection exists in the velocity profile and the maximum velocity is no longer at the center of the tube. Scheele and Hanratty (1962) suggest that this inflection in the velocity profile is associated with an instability in the flow which creates a gradual transition to turbulence caused by the slow growth of small disturbances.

For the case of $\alpha < 0$, the results of which are shown in Figure 2, the lighter fluid is on bottom. For $\alpha < -68$ a point of inflection develops at the wall and moves inward radially as α decreases. Also as alpha becomes more negative the slope of the velocity at the wall goes to zero at $\alpha = -216$, and any further decrease in α causes backflow in the region near the wall. The experimental observations of Scheele and Hanratty (1962) for the case of heat transfer in vertical tubes suggest that the transition to turbulence occurs rather abruptly after the condition $\frac{du(1)}{dy} = 0$ is attained. They state "It was found that the stability depends primarily on the velocity profile and only secondarily on the Reynolds number, if at all. For downflow heating the flow instability is associated with separation at the wall. Transition to an unsteady flow is sudden and therefore transition [to turbulence] occurs shortly after an unstable flow occurs." In our case, $\frac{du(1)}{dy}$ is obtained from Equation (33) as

$$\frac{du(1)}{dy} = -U_m \frac{2\gamma I_1(\gamma) J_1(\gamma)}{I_0(\gamma)J_1(\gamma) - I_1(\gamma)J_0(\gamma)} \cdots \quad (37)$$

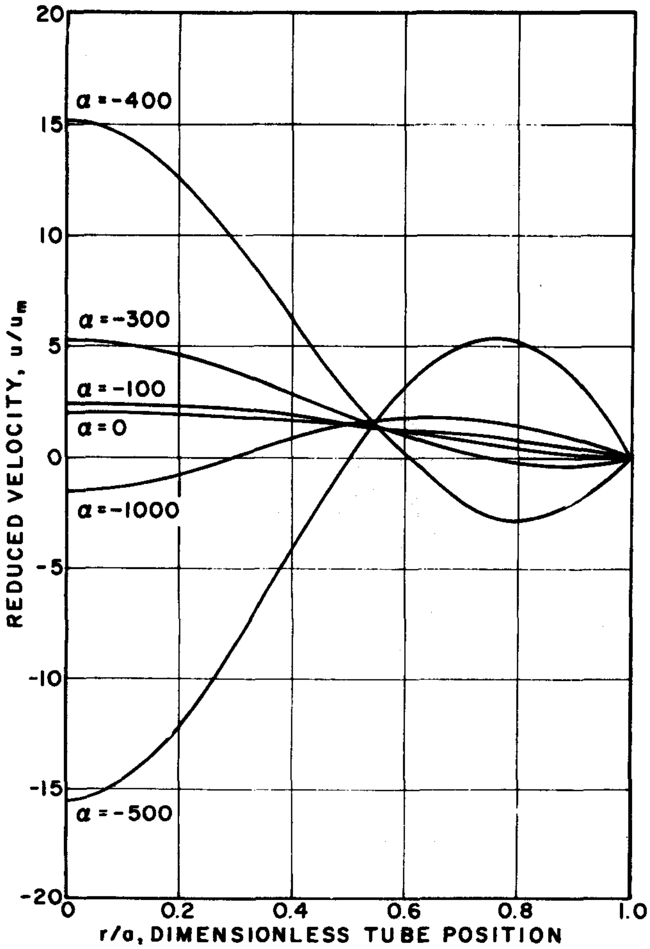

Fig. 2. Reduced velocity vs. radial position for various negative values of α; upflow with light fluid on bottom.

TABLE 1. VALUES FOR k/D AS A FUNCTION OF α

$$\alpha_2 < \alpha \leq \alpha_1 \qquad k/D = 1 + \frac{N_{Pe}^2}{2}(a\alpha^{-b})$$

α_1	α_2	a	b
∞	500	3.483×10^{-1}	0.749
500	150	1.346×10^{-1}	0.595
150	25	1.734×10^{-2}	0.186
25	5	1.102×10^{-2}	0.046

As γ increases from zero, large scale instability would occur either when $\frac{du(1)}{dy}$ goes to zero or when the denominator in Equation (33) goes to zero whichever occurs earlier. It turns out that at $\gamma = 3.832$ or $\alpha \approx -216$, $\frac{du(1)}{dy} = 0$ and the lowest value at which the denominator in equation (33) goes to zero $\alpha \approx -456$. So, according to the observations of Scheele and Hanratty, the flow field probably will become turbulent due to instabilities caused by flow reversal at the wall which occurs at $\alpha \approx -216$.

For $\alpha < 0$ radical changes occur periodically in the predicted flow pattern as alpha varies with time. The smallest negative value at which these changes occur is $\alpha = -456$. For alpha less negative, Equation (33) predicts downflow at the side and upflow at the center. For values of alpha more negative than this the solution predicts upflow at the sides and downflow at the center of the tube as shown in Figure 2.

The neglect of $\frac{\partial u}{\partial t}$ in Equation (1) tends to invalidate the analysis in regions where the velocity changes abruptly with time since $\frac{\partial u}{\partial t}$ would be large. However, both the predicted stagnation at the wall for $\alpha \approx -216$ and the dramatic change in the velocity distribution at $\alpha \approx -456$ suggest that the flow is unstable in this region and that a transition to turbulence occurs after α reaches values more negative than 216. Thus, the velocity profiles shown in Figure 2 for values of α more negative than 216 probably do not exist.

After evaluation of the dispersion coefficients for the case of α greater than, and less than, zero it is found that the last term of Equations (32) and (36) is unimportant for the values of time of interest here. This occurs despite the fact that the last term of Equation (27), which generates the last term of Equations (22) and (36), is significant even for relatively larger values of time. The explanation for this is that the last term of Equation (27) depends only weakly on the radial coordinate; as remarked following Equation (31) such terms do not contribute significantly to the value of k. Table 1 gives approximate relationships for the value of the dispersion coefficient, as evaluated from the first two terms of the right-hand side of Equation (32), over various ranges of values of alpha.

When the mathematical analysis is compared with the experimental data of Reejhsinghani et al. one should realize how they obtained their results. The experimental values were obtained by comparison with the mixing length calculated from the solution

$$C_m = \frac{1}{2}\,\mathrm{erfc}\left(\frac{x_1}{2\sqrt{kt}}\right) \quad (38)$$

The mixing length is defined as the distance over which the dimensionless concentration changes from 90% to 10%. Equation (37) is the solution of the dispersion equation with a time-dependent dispersion coefficient for a semi-infinite slug, where $\overline{k}$ is the time averaged dispersion coefficient

$$\overline{k} = \frac{1}{t} \int^{t} k \, dt \tag{39}$$

Therefore the comparisons in Figures (3), (4), and (5) are for the time averaged dispersion coefficient which is obtained by integrating the approximate values of k, Equation (38), and using the approximate relationship developed by Reejhsinghani et al.

$$\alpha = \frac{N_{Gr} N_{Sc}}{28.96\sqrt{\tau}\left(1 + \frac{N_{Pe}^2}{192}\right)^{1/2}} \tag{40}$$

Equation (39) is likely to be accurate only at sufficiently large values of τ for Equation (37) to apply. As can be seen from Figure 3 the new solution given by Equation (32) shows much better agreement with the data for large Peclet number than the solution given by Reejhsinghani et al. The data for small Peclet number are more scattered, but it is clear from Figure 4 that the present analysis shows better agreement with the experimental data than the previous analysis.

When alpha is less than zero the time averaged dispersion coefficient must be calculated over the time interval from τ_{min} to τ because of the singularities created by the inherent instability of the solution; the minimum value of τ corresponds to the maximum negative value below which no singularity occurs. The instability is manifested in the denominator of the right-hand side of Equations (33) and (34) which is

$$I_0(\gamma)J_1(\gamma) - I_1(\gamma)J_0(\gamma)$$

This relationship shows a periodic occurrence of zeros which causes the dispersion coefficient to take on a series of infinite values, thereby making it necessary to calculate time averages from τ_{min} to τ. A comparison of the dispersion coefficient obtained from the nontransient part, which neglects the last term of Equation (36), and experimental data is given in Figure 5. Below 456, which corresponds to τ_{min} since this is the smallest α below which no singularities occur, the time averaged value of the dispersion coefficient is almost the same as the dispersion coefficient, that is, $k = \overline{k}$. As in the case of alpha greater than zero, much better agreement is obtained between the experimental data and this solution than with the solution of Reejhsinghani, Barduhn, and Gill. However, the analytical results are still somewhat lower than the experimental data in the intermediate range of negative α.

The experimental data presented in Figures 3, 4, and 5 include the results which were obtained for all values of dimensionless time, τ. It should be noted that the approximate dispersion model gives reasonable results which agree with the short time data as well.

The experiments of Reejhsinghani et al. showed that axially the mean concentration profile is asymmetric about the plane moving with the mean speed of the fluid, $x_1 =$

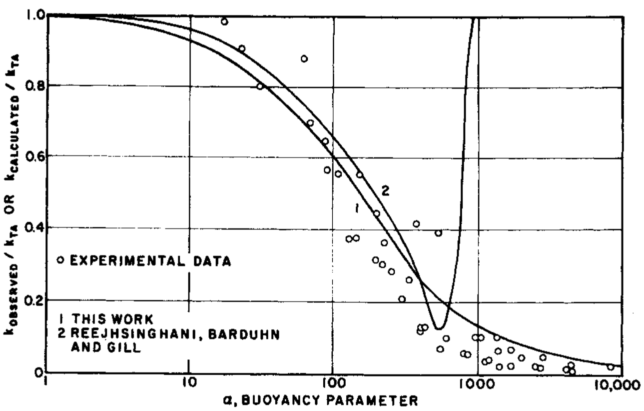

Fig. 3. Comparison of theoretical predictions with the data of Reejhsinghani, Barduhn, and Gill for upflow with heavy fluid on bottom and Peclet number greater than 200.

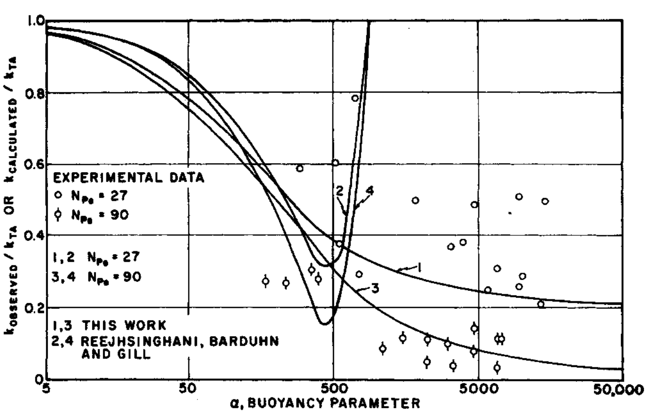

Fig. 4. Comparison of theoretical predictions with the data of Reejhsinghani, Barduhn, and Gill for upflow with heavy fluid on bottom in low Peclet number range.

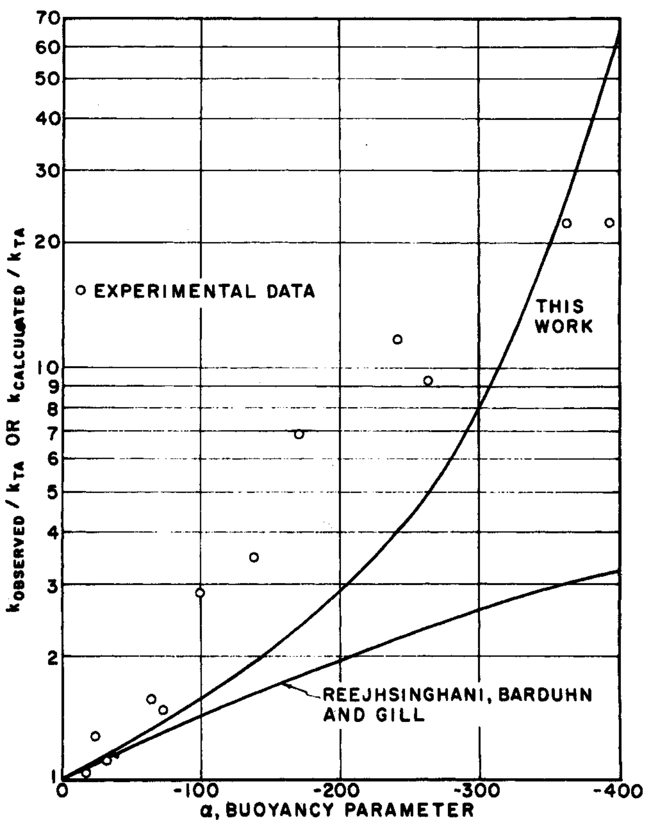

Fig. 5. Comparison of theoretical predictions with the data of Reejhsinghani, Barduhn, and Gill for upflow with light fluid on bottom and Peclet number greater than 90.

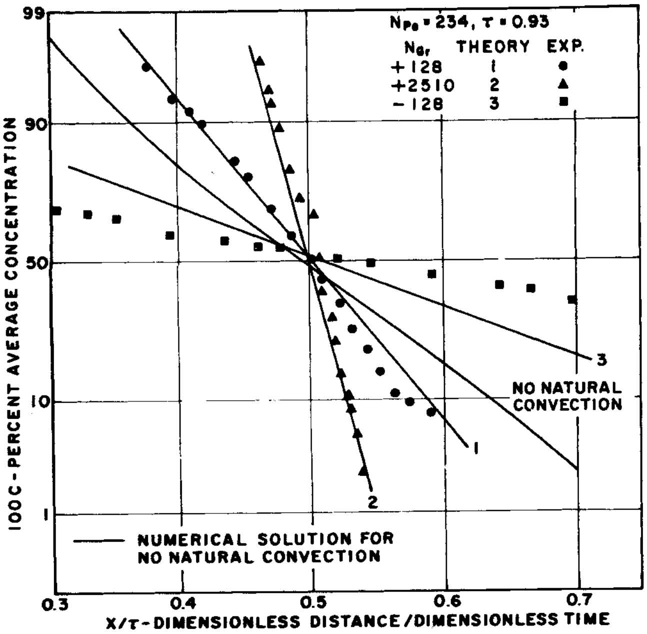

Fig. 6. Comparison of theoretical results for mean concentration distributions with experiments of Reejhsinghani, Barduhn, and Gill.

0. The present results are in rather good agreement with the axial concentration profile as is shown in Figure 6. Clearly, the correspondence between theory and experiment is especially gratifying for the stable case of upflow with the heavier fluid on bottom, $\alpha > 0$. The present theory is in good qualitative agreement with the experimental data for $\alpha < 0$, but it underestimates somewhat the increase in the dispersion coefficient caused by buoyancy forces. This underestimation may have been caused by neglecting the inertia terms in Equation (1).

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NOTATION

a = tube radius
C = dimensionless concentration, c/c_0
c = concentration of solute
D = diffusion coefficient
g = acceleration due to gravity
k = dispersion coefficient
$\bar{k}$ = time averaged dispersion coefficient, $\frac{1}{t}\int_0^t k\,dt$
N_{Gr} = Grashof number, $\frac{8g\beta a^3 c_0 \rho_0^2}{\mu^2}$
N_{Pe} = Peclet number, $2U_m a/D$
N_{Sc} = Schmidt number, ν/D
P = static pressure
r = radial position
t = time
u = axial velocity
U_m = area mean axial velocity, $\frac{2}{a^2}\int_0^a ru\,dr$
v = radial velocity
X = dimensionless distance, x/aN_{Pe}
x = axial position
x_1 = moving axial coordinate, $x - \int_0^t U_m dt$
y = dimensionless radial position, r/a

Greek Letters

α = density difference parameter,
$$\frac{g\beta a^4 c_0}{D\nu}\frac{\partial C_m}{\partial x_1} = \frac{1}{8} N_{Gr} N_{Sc}\, a \frac{\partial C_m}{\partial x}$$
β = density-concentration coefficient,
$$-\frac{1}{\rho_0}\frac{\partial \rho}{\partial c}\bigg|_{c=c_0}$$
γ = density difference parameter, $|\alpha|^{1/4}$
μ = viscosity
ν = kinematic viscosity, μ/ρ_0
ρ = density
τ = dimensionless time, tD/a^2

Mathematical Operators and Functions

A = $bei'\gamma/ber'\gamma$
ber = Kelvin function of the first kind, order zero
bei = Kelvin function of the first kind, order zero
ber' = Kelvin function $-$ $ber'x = \frac{d(ber x)}{dx}$
bei' = Kelvin function $-$ $bei'x = \frac{d(bei x)}{dx}$
$erfc$ = conjugate error function
$f(r,t)$ = concentration distribution function
$F(s)$ = Laplace transform of the residence time distribution
I_0 = Bessel function, modified, of the first kind, order zero
I_1 = Bessel function, modified, of the first kind, order one
J_0 = Bessel function of the first kind, order zero
J_1 = Bessel function of the first kind, order one
Ker = Kelvin function of the second kind, order zero
Kei = Kelvin function of the second kind, order zero
K_0 = Bessel function, modified, of the second kind, order zero
Y_0 = Bessel function of the second kind, order zero
∇^2 = $\frac{1}{y}\frac{\partial}{\partial y} y \frac{\partial}{\partial y}$
∇^4 = $\frac{1}{y}\frac{d}{dy} y \frac{d}{dy}\frac{1}{y}\frac{d}{dy} y \frac{d}{dy}$

Subscripts

0 = inlet condition
m = area mean value

LITERATURE CITED

Gill, W. N., "A Note on the Solution of Transient Dispersion Problems," *Proc. Roy. Soc.*, **A298**, 335 (1967).

Gill, W. N., V. Ananthakrishnan, and R. J. Nunge, "Dispersion in Developing Velocity Fields," *AIChE J.*, **14**, 939 (1968).

Gill, W. N., and R. Sankarasubramanian, "Exact Analysis of Unsteady Convective Diffusion," *Proc. Roy. Soc.*, **A316**, 341 (1970).

———, "Dispersion of a Non-Uniform Slug in Time Dependent Flow," *ibid.*, **A322**, 101 (1971).

Reejhsinghani, N. S., A. J. Barduhn, and W. N. Gill, "Laminar Dispersion in Capillaries, Part V, Experiments on Combined Natural and Forced Convection in Vertical Tubes," *AIChE J.*, **14**, 100 (1968).

Scheele, G. F., and T. J. Hanratty, "Effect of Natural Convection on Stability of Flow in a Vertical Pipe," *J. Fluid Mech.*, **14**, 244 (1962).

Taylor, G. I., "Dispersion of Soluble Matter in Solvent Flowing Slowly Through a Tube," *Proc. Roy. Soc.*, **A219**, 186 (1953).

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