Part III. Experiments in Horizontal Tubes Including Observations on Natural Convection Effects

N. S. REEJHSINGHANI, WILLIAM N. GILL, and ALLEN J. BARDUHN

Syracuse University, Syracuse, New York

Experimental data on the axial dispersion of a solute in laminar flow in capillaries are presented for a range of Peclet numbers from 12 to 50,000 and of dimensionless time from 0.01 to 60. They show good agreement with the mathematical solutions over all ranges of variables as long as natural convection is unimportant. For slow flows it was observed that natural convection can both enhance and depress the dispersion significantly and that extremely small density differences ($\Delta\ \rho/\rho = 10^{-4}$) are adequate to cause these phenomena. A qualitative explanation for the apparently anomalous effects of natural convection is proposed.

The problem of dispersion of soluble matter in a solvent flowing through a tube of circular cross section was first treated by Taylor (*13* to *15*) and was subsequently extended significantly by Aris (*2*). This and later work by other investigators (*3, 4, 16*) have been described in Part I (*1*) of this series. For the case of laminar flow, the diffusion equation for this problem, which describes the transient transport of material by the combined mechanisms of convection with radial and axial diffusion, has been solved numerically by Ananthakrishnan et al., also in Part I. In Part II the numerical work was extended to include the effects of system capacitance and different inlet boundary conditions (*1a*).

Available experimental data (*3, 4, 13*) for laminar dispersion in capillaries at high Peclet numbers are mainly in the τ range greater than 0.5. The region which has not been investigated thoroughly is that for $\tau < 0.5$, where Taylor's solution does not adequately describe the dispersion process. However, even in the region of large τ, there are some discrepancies between the experimental results which have been reported.

Aris (*2*) showed the general form of the effective dispersion coefficient K to be equal to the sum of the molecular diffusion coefficient and Taylor's dispersion coefficient such that

$$K = D\left[1 + \frac{N^2_{Pe}}{192}\right] = D + \frac{a^2U^2}{48D}$$

At high Peclet numbers the solute transported by axial diffusion is negligible compared with that transported by convection and radial diffusion, so the effective dispersion coefficient is just $a^2U^2/48D$ which was found originally by Taylor. However, at low Peclet numbers, the relative effect of axial diffusion increases, and in the limiting case, when N_{Pe} goes to zero, the effective dispersion coefficient is simply the molecular diffusion coefficient D, and solute is transported by pure diffusion only. Experimental results of Bournia et al. (*4*) on the dispersion of finite gas slugs at low Peclet numbers led to the suggestion that a dispersion coefficient of the form proposed by Aris does not satisfactorily account for the additional mechanism of axial diffusion. However, the numerical solution developed in Part I shows that the Aris modification should in fact describe the dispersion for high values of τ, which is a requirement of the Taylor-Aris theory in general.

Differences in density between the displacing and the displaced fluids would be expected to have measurable effects in some instances under laminar flow conditions with the heavier fluid tending to flow underneath the lighter. It was shown by Bournia et al. that when the slug of heavier gas was used in conjunction with lighter carrier gas in a vertical tube, the concentration-time plot showed tailing at the leading edge, while the same effect was observed on the trailing edge on using lighter gas as the slug in the heavier carrier gas. Also, it is to be expected that for the same fluids under identical flow conditions, small density differences will be more pronounced in larger diameter tubes.

Dispersion of dye in tubes per se may not seem very important until one fully appreciates the far reaching implications of the Taylor-Aris theory of this phenomenon. As pointed out by Taylor, it is remarkable that this phe-

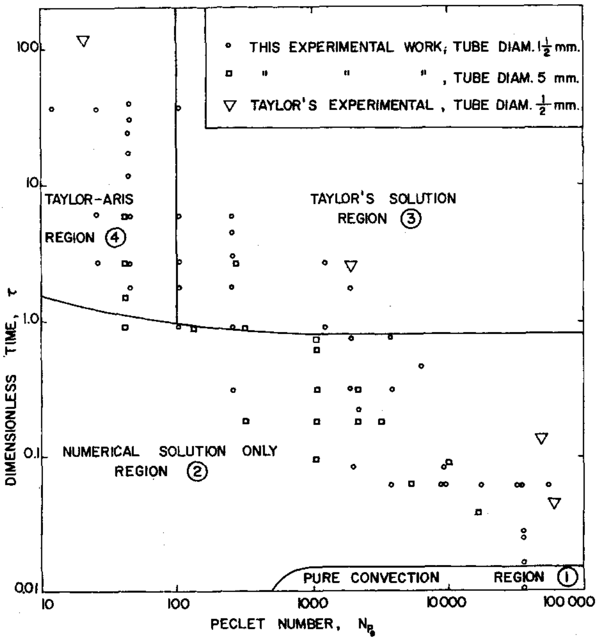

Fig. 1. Summary of all operating conditions, τ vs. N_{Pe}.

William N. Gill is with Clarkson College of Technology, Potsdam, New York.

nomenon is diffusive in nature because the velocity field is highly unsymmetrical with respect to longitudinal dispersion. Thus, if this process can be described by a diffusion model, then one can expect that much more complicated processes can also be described in a similar fashion. Indeed, Aris has shown that the dispersion model applies under much more general conditions than Taylor specified originally. The ultimate objective of the present experimental work is to understand dispersion in porous media, but the immediate objectives of the work reported here involve tubes and are to

1. Obtain data, particularly at low values of τ, for both high and low Peclet numbers in order to check the numerical solution of Part I.
2. Check the application of the Aris modification of Taylor's solution, particularly at low Peclet numbers and at high values of τ.
3. Examine the effects, if any, of small density differences on the dispersion process in tubes of different diameter, under identical flow conditions.

Figure 1 shows the range of independent variables (N_{Pe} and τ) used in the experiments of this investigation and of Taylor for laminar dispersion in capillaries.

DESCRIPTION OF EQUIPMENT

Dispersion experiments for this investigation were carried out with duPont's Pontamine 6 BX, sky blue dye in distilled water which displaced pure water in capillary tubes. The concentration of the diffusing solute along the entire tube length was determined optically.

A sketch of the apparatus is available (*10*) which shows the optical system used in the experimental work. A light beam from a concentrated source is focused at the center of the capillary tube by means of a double convex lens fitted in a rack and pinion focusing mount, and the transmitted light is collected by a second convex lens and sent to the photomultiplier tube to measure its intensity. To obtain the maximum working range of percent transmittance of light, use was made of filters corresponding to the wavelength of maximum absorption of light by the dye solution.

Axial distances on the tube were measured to the nearest 0.5 mm. Focusing of the lenses at the center of the capillary tube was accomplished by inserting a thin metallic wire in the capillary bore and by judging the maximum brightness of the wire surface at the focal point. This lens setting was unaltered throughout the span of work for the same size of capillary tube.

The injection system, which forced the dye solution through the capillary, comprised a synchronous induction motor, gear train, screw motion slide assembly, and glass syringes. A piece of capillary tube about 4 cm. long, with the same inside and outside diameters as those used in the displacement experiments, was attached to the syringe tip to avoid jet effects at the tube entrance.

The capillary tubes held in angle sections were aligned with each other as well as with the syringe. When more than one capillary tube was used, they were butted together with the ends ground flat and joined end to end with a thin coating of wax used as a gasket, while care was taken to prevent penetration of wax into the capillary bore. It was thus possible to get a uniform bore and avoid entrapment of air at mechanical joints. A maximum of three tubes was used in series, depending upon the displacement velocity and the time of flow; when more than one tube was used, they were joined first before being connected to the syringe.

EXPERIMENTAL PROCEDURE

Displacement experiments were carried out in precision bore capillary tubes of 1.5- and 5-mm. I.D., and the length of each tube was about 85 cm. To check the uniformity of the bore, the length of a few centimeters of mercury thread at various positions along the capillary tube was measured. The variation in inside tube diameter was found to be less than 0.2% and hence was insignificant. The precise diameters of these tubes are 1.502 and 4.995 mm.

For calibration, plots of $(A - A_o)$ vs. concentration of dye solution, where A is absorbance of dye solution and A_o is absorbance of distilled water, were prepared for each tube size. The concentration of dye solution used with the 1.5-mm. tube, was 0.2 g./liter, since below this value the curvature of the calibration plot was acceptable and also the change in absorbance was found to be smaller at higher concentrations of the dye. Similarly, for the 5-mm. tube, the optimum dye concentration was found to be 0.1 g./liter. Hence these two concentrations are referred to subsequently as 100% for the two tube sizes. Solutions of various concentrations were prepared by diluting the given volumes of 100% solutions. In the calibration procedure a given tube was filled with a known concentration of dye solution and, after sealing the ends, was placed in the cradle on the horizontal channel of the optical system. The light absorption at various points along the length of the tube was observed, and the readings at different points varied at most by ± 2% probably because of slight nonuniformities of the outside diameter of the capillary tube. An average reading for the whole length of the tube was then made. Calibration plots were thus prepared for each capillary tube. Recalibrations were made whenever changes in the light source were made.

Preparation for an individual run included filling the tube with distilled water and adjusting the variable gear ratio to get a selected velocity of flow. Fluid displacement velocities were measured separately for the particular gear ratio, tube, and syringe and checked with calculated values. The filled tube was plugged at one end and placed in alignment with the syringe containing dye solution. The open end of the tube was next joined with the capillary of the syringe to form the interface of water and dye solutions. This joint was sealed with a coating of wax. Experiments were initiated by removing the plug and starting the motor. Flow was terminated in the capillary tube after a length of time was measured with a stop watch.

After the motor was stopped, the discharge end of the tube was sealed, the joint between the tube and syringe broken, and after the entrance was sealed, concentrations were measured along the whole length of tube. No irregularities were observed in the concentration-distance plots at the points corresponding to tube junctions.

The duration of time which may elapse between stopping the flow and the determination of concentration must be greater than the time for radial concentration gradients to disappear but less than the time for the axial diffusion to be significant. For the 1.5-mm. tube it was found that the transient effects of radial diffusion disappeared in a few minutes which was well within the actual elapsed time between stopping the flow and measuring the concentration. The axial concentration profile remained constant for many hours. For the 5-mm. tube, however, it took about 30 to 45 min. for the concentration to become uniform over the cross section. The measured and reported concentrations are thus average and not bulk values.

All of the experiments were conducted at atmospheric pressure and room temperatures of 25 ± 2°C.

EXPERIMENTAL RESULTS

Results of the individual displacement experiments were plotted as concentration vs. $X/\tau\ [= x/(2Ut)]$, where x is the distance from the inlet of the tube. These plots were made on probability paper, except for very short times of flow in which case linear scales were used. The average value of the molecular diffusion coefficient D, which gave the best agreement between the experimental data and the numerical solution for 1.5-mm. tube, was found to be 3.1×10^{-6} sq.cm./sec. This value of D was checked by comparing the experimental results with Taylor's solution at high values of both N_{Pe} and τ when the concentration vs. X/τ plots were straight lines on probability paper, and they also met the symmetry criterion of having concentration equal 0.5 at the point $X/\tau = 0.5$. The value of D was calculated from the relation $k = a^2U^2/(48D) = L'^2/13.1t$, where L' corresponds to the length of the mixing zone contained between average concentrations of 10 and 90% (*13*). When one uses this value of D, the Schmidt number for this system is 2,900 at 25°C. for all experiments reported here.

The value of D reported by Volko (*17*) for a purified sample of dye at a concentration of 0.5 g./liter is 7×10^{-6} sq.cm./sec. However, a slight impurity of any inorganic salt in commercial grade dye will decrease the measured value of D markedly. For example, Ferrel et al. (*7*) take D equal to 5×10^{-6} sq.cm./sec.

The experimental data for the 1.5-mm. tube were obtained in the N_{Pe} range of 12 to 50,000 for a very wide range of dimensionless times τ. For the 5-mm. tube, N_{Pe} values ranged between 45 and 17,000. The data are restricted by the physical limitations of the apparatus to the region indicated in Figure 1. However, the data were taken systematically so that a range of τ was covered for several, essentially fixed, N_{Pe}; a range of N_{Pe} for fixed τ was studied; adequate data were taken in each of the four regions numbered on Figure 1; and data for the 5- and 1-mm. tubes overlap significantly to assess the effect of natural convection, at essentially fixed τ and N_{Pe}, by varying tube diameter. Some of the data are plotted in Figures 2 to 7 and are discussed in the next section.*

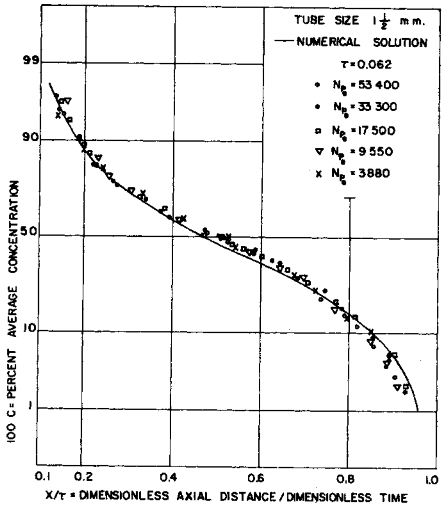

Fig. 3. Concentration vs. X/τ plots for various values of Peclet numbers at $\tau = 0.062$.

DISCUSSION OF RESULTS

The data taken in the 1.5-mm. tube show good agreement between the experimental results and the numerical solution over the entire time range tested as long as natural convection was negligible. Some small deviations were observed at the tail end of the graphs, particularly when τ was in the range 0.3 to 0.5. The deviations at the tail end where τ is very small (< 0.1) are probably due to the fact that in the experimental dispersion process, the initial condition at $\tau = 0$, $C = 1$ at $x = 0$ is not strictly met for a very small period of time, because in the entrance region of the tube initially for at most a few millimeters distance, there is a mixed zone in which C is less than unity. This occurs because of the finite time required to initiate flow after the dye-water interface is created. Axial diffusion will be entirely negligible for this short period (few minutes), but because of the density gradients which exist at the time of creation of this interface, a small amount of solute is transported into the tube by natural convection, and the effect of this diffuse region is probably propagated through the entire length of the tube. However, for higher times and/or for higher flow rates, this effect is very small and essentially negligible. The density difference between the dye solutions at 0.2 g./liter and the pure water was determined to be only 1.2×10^{-4} g./ml. The best test of the approach to a true step change in concentration at $\tau = 0$ is the dispersion results at very short times. Figure 2 shows that results for τ as short as 0.007 agree well with numerical results for a mathematical step change at $\tau = 0$.

In Figure 2, plots on a linear scale of C_{avg} vs. X/τ for small values of τ are almost straight lines, indicating that the dispersion takes place essentially by pure convection and both axial and radial diffusion are negligibly small. This is in agreement with the pure convection solution [Equation (33) of Part I]. As τ increases, the effect of radial diffusion becomes more important and the curves become symmetrical with respect to the pure convection solution.

Figure 3, on probability coordinates, shows the effect of increasing N_{Pe} on the concentration distribution for a

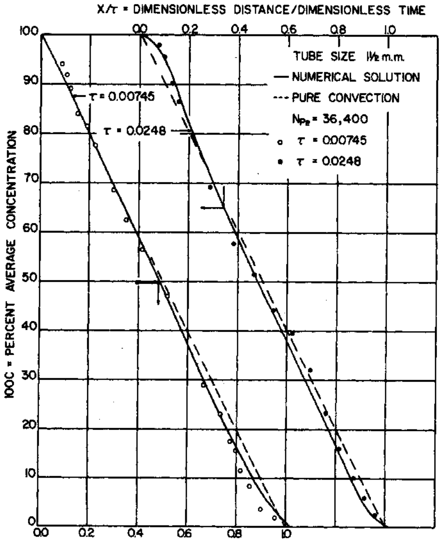

Fig. 2. Concentration vs. X/τ plots for τ = 0.00745 and 0.0248 at N_{Pe} = 36,400.

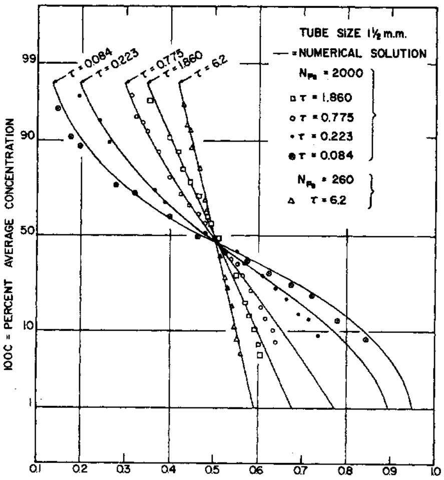

Fig. 4. Concentration vs. X/τ plots for various values of τ at N_{Pe} = 2,000 and 260.

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* Complete tabulations of data for the 1½-mm. and 5-mm. tubes have been deposited as document 8996 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $3.75 for photoprints or $2.00 for 35-mm. microfilm.

fixed dimensionless time of flow, $\tau = 0.062$. From the plots it is to be noted that the concentration distribution change is insignificant for the range of N_{Pe} values indicated. This is to be expected because, in the diffusion equation [Equation (3) of Part I], the axial diffusion term will be negligible at the high values of N_{Pe} shown as is indicated by the single solid line which represents the numerical solution for all cases and is in good agreement with the experimental data.

In Figure 4, for high values of N_{Pe}, curves of C_{avg} vs. X/τ, given on a probability plot, indicate the gradual transition to linearity as τ increases. At high τ values, the curves become error functions which follow Taylor's approximate analytical solution [Equations (34) and (35) of Part I (*1*)].

The experimental results are in good agreement with Taylor's solution for $\tau > 1$ and for high values of N_{Pe}. Taylor's conditions, $t >> a^2/(14.5D)$ or $\tau >> 0.069$, for the radial variations in concentration to be sufficiently small are thus satisfied. If a factor of 10 is used, then the required condition for the application of Taylor's equation becomes $\tau > 0.69$, which is in agreement with the result of this investigation. The corresponding restriction that $4L'/a >> 6.9$, where L' is the mixing length for 10 to 90% concentration change, is not a necessary requirement as was shown in Part I (*1*) and is verified here experimentally as is evidenced by the results given in Figure 4. In Figure 1 it is noted that only one of Taylor's runs was in region (3), where his theory applies.

The Aris modification

$$K = D + \frac{a^2U^2}{48D}$$

gave reasonably good agreement with the experimental data for high values of τ. The main difficulty in testing the Aris expression experimentally is that it differs from Taylor's significantly only for slow flow systems which are most susceptible to natural convection effects. A comparison at $N_{Pe} = 45$ which shows rather good agreement between theory and experiment is given in Figure 5. The results for $N_{Pe} = 12.5$, $\tau = 37$ (not shown) give a 50% greater dispersion coefficient than predicted from the Taylor-Aris theory, and this is probably due to natural convection.

The data from experiments in the 5-mm. tube indicate marked differences between the experimental results and the numerical solution. It was thus found that the effect of natural convection (due to concentration gradients) on the dispersion was very significant, while in the numerical solution this effect was not considered.

The data in Figure 6 for $N_{Pe} = 43.5$, show a much greater dispersion effect than is predicted on the basis of neglecting natural convection. At $N_{Pe} = 326$, Figure 7 indicates much better agreement between theory and experiment. However, instead of having the agreement improve still further at higher flow rates, Figure 7 also shows that as the Peclet number is increased to 1,090 and then on to 3,250, the extent of dispersion is markedly reduced below that predicted mathematically. Thus, if natural convection is the mechanism causing deviations from the theory, then, depending on the Peclet number range, natural convection can both depress and increase dispersion coefficients very significantly. These results strongly indicate the need for a very careful examination of the natural convection phenomena that might be occurring in the system. Such an examination was carried out. Consequently, it is now possible to explain, qualitatively at least, the behavior exhibited in Figures 6 and 7.

To develop a better notion of the nature of the effects involved, the observed dispersion coefficients were determined (for 90 to 10% concentration change) and compared with that of the numerical result. The ratio $k_{\text{obs}}/k_{\text{num}}$ is equal to the square of the ratio of the corresponding lengths over which the 90 to 10% concentration change takes place. When the concentration vs. X/τ plot is not a straight line on the probability graph, this is merely a number useful mainly for comparison. Figure 8 indicates how the ratio $k(\text{obs})/k(\text{num})$ varies with N_{Pe} for several values of τ. Seven of the nineteen points observed are not plotted, since no two of them were at the same value of τ. Specifically, the ratio is greater than one at $N_{Pe} = 45$, drops to unity at $N_{Pe} = 150$ to 250, drops further to a minimum of 0.2 at $N_{Pe} \cong 3{,}000$, and then increases for higher flow rates probably approaching unity asymptotically. In the N_{Pe} range around 200, the interesting phenomenon is occurring in which natural convection is undoubtedly important, but its effect on dispersion is not noticeable. A qualitative explanation of all these natural convection phenomena is possible.

The value of the Grashof number (for mass transfer) for the 5-mm. tube was calculated to be 92 by using the maximum value of $\Delta\rho/\rho$ (dye solution and distilled water)

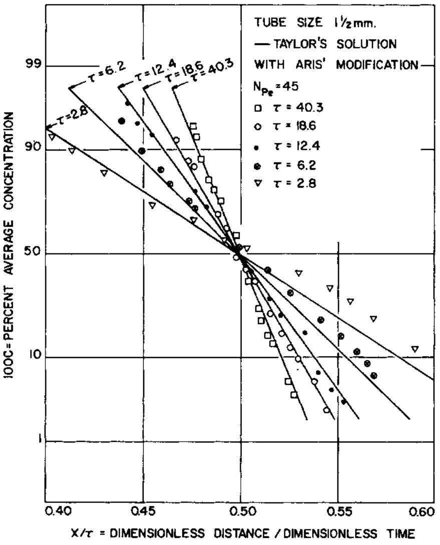

Fig. 5. Concentration vs. X/τ plots for various values of τ at $N_{Pe} = 45$.

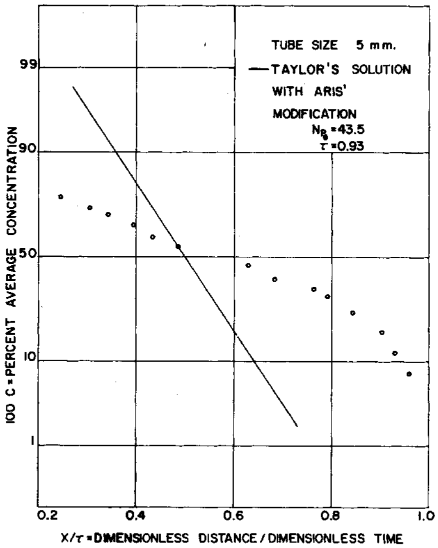

Fig. 6. Concentration vs. X/τ plot for $N_{Pe} = 43.5$ and $\tau = 0.93$ (5-mm. tube) showing excessive dispersion due to natural convection.

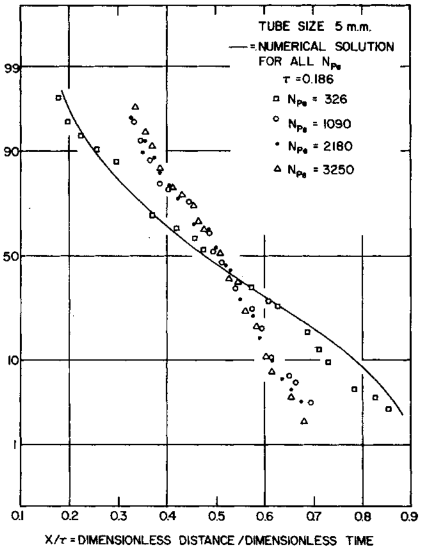

Fig. 7. Concentration vs. X/τ plots for various values of Peclet numbers at $\tau = 0.186$ (5-mm. tube) showing normal and depressed dispersion due to natural convection.

of 0.6×10^{-4} which occurred at the inlet of the tube initially. The corresponding value for 1.5-mm. tube is 5.0 for $\Delta\rho/\rho$ of 1.2×10^{-4}. Thus, the effect of natural convection should be more pronounced in the larger tube as was observed to be the case.

A description of the phenomenon of natural convection, in terms of one of its effects on the dispersion, is indicated in the sketches given on Figure 9. At short values of time, there is a tendency for pure convection to prevail, and this creates a paraboloid finger of dye which grows out into the tube so that the maximum dye concentration is at the axis. As radial molecular diffusion comes into play, at any cross section this will appear as a colored core surrounded by a more or less diffuse ring of distilled water-dye solution. The action of gravity tends to make material in the core sink to the bottom of the tube, thereby causing circulation of the displaced fluid layers. The concentration then tends to uniformity over the cross section by both radial diffusion and convective cross circulation. In this sense natural convection increases radial mixing and depresses the dispersion coefficient as demonstrated in Figure 7. Note that increased radial molecular diffusion decreases axial dispersion in Taylor's expression for k.

The phenomenon of natural convection in heat transfer produces similar effects. For steady state heat transfer in a laminar forced flow in a uniformly heated horizontal pipe, Morton (9) found from his mathematical analysis that the effect of buoyancy forces caused by fluid temperature variations produced a circulatory motion of the fluid in the direction normal to the pipe axis, and this is the so-called *secondary flow.*

Del Casal and Gill (5) carried out a more complete theoretical investigation of the natural convection effects which occur with heat transfer in a horizontal tube by considering the variation of the axial pressure gradient due to axial density variation. They obtained an expression for the friction factor for the combined effect of laminar forced and natural convection as

$$f = \frac{8}{N_{Re}} \left[1 + \left(\frac{34.8\, N_{Re} N_{Pe} + 0.21\, N^2_{Re} N^2_{Pe}}{(2{,}304)^2} \right) \left(\frac{N_{Gr}}{N_{Re}} \right)^2 \right]$$

where the dimensionless quantities N_{Re}, N_{Pe}, and N_{Gr} are based on the tube radius. The Grashof number is defined in terms of the axial temperature gradient, which in the present case would be the axial concentration gradient.

The contribution of each term in the above equation provides strong clues to the mechanisms causing the observed effects of natural convection. In the absence of natural convection the relation $f = 8/N_{Re}$ is well known for laminar flows and corresponds to the case where the numerical solution is valid. The term ($34.8\, N_{Re}N_{Pe}$) is due to axial density gradients which create the axial pressure gradient and thus axial movement. The term ($0.21\, N^2_{Re}N^2_{Pe}$) is due to radial density gradients causing secondary flow across the tube diameter. In general, these two effects of natural convection, respectively, cause more axial mixing and cause more radial mixing. The relative effects of these two terms can be gauged by taking their ratio, which for a fixed N_{Sc} is a function of only the Peclet number.

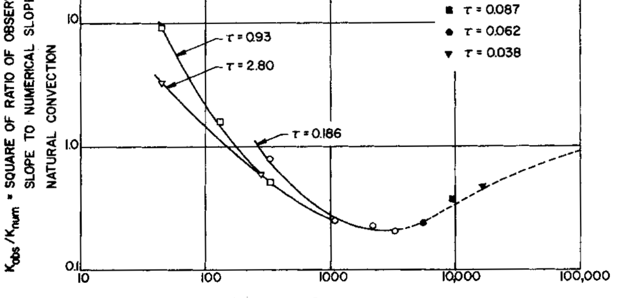

Fig. 8. Plot of k_{obs}/k_{num} vs. N_{Pe} for various τ values (5-mm. tube).

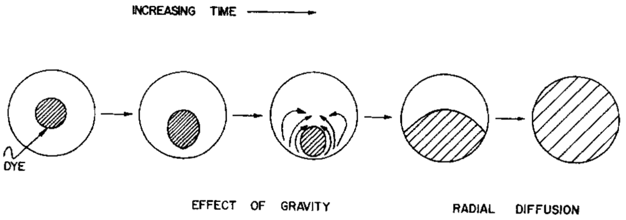

Fig. 9. Mechanism of natural convection effect on dispersion in horizontal tubes.

An increase of radial mixing depresses axial dispersion and this effect thus should be most pronounced at high values of N_{Pe}. More axial mixing by natural convection should enhance axial dispersion, and this should occur at low N_{Pe}. The curves on Figure 8 show that this is precisely what occurs. The occurrence of $(k_{obs}/k_{num}) = 1$ in the N_{Pe} range of 150 to 250 is likely due to the two effects of natural convection cancelling each other. Also, as N_{Pe} becomes very large, $N_{Gr}/N_{Re} \rightarrow 0$, and hence the effect of natural convection becomes negligible.

It would be desirable to find an upper bound on the value of Grashof number below which the natural convection effects become unimportant. The correlations of McAdams (8), Oliver (*11*), and Eckert (*6*) for steady state heat transfer in horizontal tubes indicate (when one ignores the effect of l/d ratio and time) that the ratio $N_{Gr}{}^{3/4}/N_{Re}$ is a criterion for the relative effects of natural vs. forced convection. This criterion does not, however, appear to give consistent results, probably because of the more complicated effects in time-dependent phenomena, and it is used below only tentatively.

In the small tube (1.5 mm.) natural convection effects are negligible for $N_{Gr}{}^{3/4}/N_{Re} < 93$ and at 93 are noticeable only for short times ($\tau < 1$). Other things being equal, clearly one would expect natural convection to be most important at small values of τ, since concentration gradients are largest then and these gradients attenuate with time as the dispersion process continues. At $N_{Gr}{}^{3/4}/N_{Re} = 750$ the excess dispersion is marked even for $\tau = 6$ but becomes slight at $\tau = 37$. As $N_{Gr}{}^{3/4}/N_{Re}$ increases from 93 to 750, the natural convection effects appear at progressively later τ, but enough data on this phenomenon are not available and our understanding is yet inadequate to describe the situation fully or even to know whether the proper criteria are being used. The use of $N_{Gr}{}^{3/4}/N_{Re}$ and τ to compare the natural convection experiments in the 5-mm. tube to those in the 1.5-mm. tube gives inconsistent results. For example in the large tube (5 mm.) natural convection effects were marked under all conditions observed, and this includes values of $N_{Gr}{}^{3/4}/N_{Re}$ as small as 5, although only short time runs could be made at this value ($\tau = 0.04$).

Resolution of these problems awaits a detailed mathematical description of combined natural and forced laminar flow, and work is now in progress to accomplish this for vertical systems.

Bournia et al. (4) have reported results on the dispersion of gases in laminar flow through a 21.7-mm. tube.

Experiments were performed with gases having the same molecular weight in order to eliminate natural convection effects. For velocities less than 2 cm./sec., their results show much larger dispersion coefficients than those predicted by Taylor's equation with Aris' modification. For example, for a velocity of 0.225 cm./sec. in Bournia's experiments (which correspond to $N_{Pe} = 12.5$ and $\tau = 37$), the various dispersion coefficients are k (Bournia) = 0.6 sq.cm./sec., k (Taylor) = 0.0318 sq.cm./sec., K (Aris) = 0.0708 sq.cm./sec. Hence the ratio k (Bournia)/K (Aris) = 8.5.

In contrast, for the same values of N_{Pe} and τ experimental results in the 1.5-mm. tube of the present investigation gave $k_{\text{obs}}/K_{\text{Aris}} = 1.51$. It was thus presumed that there must have been a considerable effect of natural convection in Bournia's experiments at low velocities (and also some in ours).

Even though the gases used by them, that is, butadiene and 1-butyne, are of the same molecular weight, their densities are not equal. The difference in the densities of the two gases at the conditions of their experiments (740 mm. and 300°K.) may be estimated from the critical properties of the gases by using van der Waals' equation, since the pressures are low and the compressibility factors Z are on the order of 0.975. The critical constants were taken from reference *12*.

At low pressures the van der Waals b factor is unimportant, and under these conditions it may be shown that the fractional density difference between the two gases is given by

$$-\Delta\rho/\rho \cong \Delta v/V \cong \Delta Z \cong \frac{27}{64}\,\frac{P}{T^2}\,\Delta\left(\frac{T_c^2}{P_c}\right) = 0.0018$$

Estimated compressibility factors of these two gases at 60°F. and 1 atm. are also available (*12*), which indicate that ΔZ may be more than ten times this value.

Evaluating the Grashof number for mass transfer under the conditions of Bournia et al. by using the density difference between the two pure gases, with $\Delta Z = 0.002$, one finds it to be $N_{Gr} = 14{,}000$, and the value of $N_{Gr}^{3/4}/N_{Re} = 103$. Thus, the effect of natural convection may be very significant in the Bournia experiments.

CONCLUSIONS

1. Experimental data have been obtained for laminar dispersion in capillaries for a wide range of N_{Pe} and τ values. Results were in good agreement with the numerical solution of Parts I and II for a capillary of small diameter.
2. The Aris modification of the dispersion coefficient gives reasonably good agreement with the experimental data at low N_{Pe} and high τ values as long as natural convection is negligible.
3. Very small density differences between the displacing and displaced fluids have measurable effects under laminar flow conditions. The criterion $N_{Gr}^{3/4}/N_{Re}$ is important in determining when natural convection effects are appreciable, but it is insufficient since tube diameter and time also appear to play a role. The large values of the observed dispersion coefficients by Bournia et al. have been explained tentatively on this basis.
4. It was found that natural convection can both depress and accentuate the observed dispersion coefficient substantially as compared with that predicted by laminar flow theory which neglects natural convection effects. Circulation improves radial mixing and depresses the dispersion coefficient. The axial pressure gradient effect, due to axial density gradients, enhances longitudinal mixing and can increase dispersion by an order of magnitude. The fact that natural convection can affect dispersion in these ways does not appear to have been reported previously.

ACKNOWLEDGMENT

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NOTATION

a = radius of the tube
A = absorbance of the solution
C_m = average concentration across the tube section = C_{avg}
d = diameter of the tube = $2a$
D = molecular diffusion coefficient
g = gravitational component perpendicular to earth's surface
k = dispersion coefficient of Taylor = $a^2U^2/48D$
K = dispersion coefficient of Aris = $D + k$
l = length of the tube
L = dimensionless mixing zone length = $DL'/(2a^2U)$
L' = mixing length = Δx between $C_{\text{avg}} = 0.1$ to 0.9
N_{Pe} = Peclet number = dU/D
N_{Re} = Reynolds number = dU/ν
N_{Sc} = Schmidt number = ν/D
N_{Gr} = Grashof number for mass transfer =

$$\frac{d^3 g\beta(C - C_m)}{\nu^2} = \frac{d^3 g(\Delta\rho/\rho)}{\nu^2}$$

t = time of flow
U = average velocity
x = axial distance along the tube
X = dimensionless axial distance = $Dx/(2a^2U)$

Greek Letters

β = $(1/\rho)\,(d\rho/dc_m)$
Δ = incremental value of any variable
ν = kinematic viscosity of the solution at the entrance of the tube section
ρ = density of the solution
τ = dimensionless time = tD/a^2

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