Elution Curves with Double Peaks in Mixed Convection Horizontal Flows

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Axial convection and Taylor-type diffusion interact to create curves with double peaks, the structure of which changes continuously with residence time. Radial convection caused by natural convection in horizontal capillaries with Grashof numbers greater than about 100 eliminates double peaks in elution curves by reducing radial concentration gradients and thereby increasing the relative importance of Taylor-type diffusion over axial convection. Radial convection also significantly decreases the dispersion coefficient.

INTRODUCTION

The theoretical work of Gill and Ananthakirshnan (1967), Golay and Atwood (1979, 1981) and Mayock et al. (1980), in which double peaks were calculated, assumed the fully developed parabolic velocity profile of Poiseuille flow which is independent of the existence of density gradients created by the solute distribution. The experimental work of Reejsinghani et al. (1966) showed clearly that natural convection may have an important effect on dispersion in horizontal tubes and this was followed by confirming theoretical calculations by Erdogan and Chatwin (1967) and by Nunge et al. (1972). Caro's (1966) data seem to suggest the existence of double peaks but he used curved tubes which may generate secondary flows and he did not seem to be aware that natural convection would influence his results which therefore are hard to interpret.

It seems that previous workers have not connected the presence of double peaks in chromatograms with the existence of secondary flows caused by natural convection. Therefore nothing is known about the parametric dependence of the occurrence of double peaks on the Grashof number as a result of density differences between the sample and carrier fluid. Since double peaks exist at small values of the dimensionless contact time, τ, and since axial and radial density differences in the flow are greatest immediately following solute injection, it is our hypothesis that coupling between the velocity and concentration fields profoundly effects the existence of double peaks as well as the residence times at which they will be seen and the shapes that are observed.

The purpose of the work reported here on this interesting phenomenon is to carry out a systematic experimental study which includes three tube radii, two different solutes and a wide range of flow velocities and density differences between samples and carrier fluids for flow in horizontal tubes to determine the range of parameters in which double peaks occur. Carbon tetrachloride and benzene were used as solutes; methanol was used as the solvent. Flow velocities ranged from 0.5 to 12.0 cm/s. The range of Peclet number is about 4,000 to 40,000 and Grashof numbers range from about 2.6 to 3,100. Elution curves for small amounts of injected sample were studied here in contrast to the step change experiments of Reejhsinghani et al. (1966), which seem to be the only other data on the effect of mixed convection in horizontal flows on Taylor diffusion.

THEORY

When a nonbuoyant sample is injected into a fluid which is in laminar fully-developed flow through a straight horizontal tube, diffusion and convection effect the dispersion of the sample with time. Taylor (1953) was the first to treat this phenomenon analytically. He reasoned that, to an observer moving along with the sample at the average fluid velocity, u, the sample would appear to be diffusing longitudinally with a dispersion coefficient, k, given by

$$k = \frac{u^2R^2}{48\,D} \tag{1}$$

where R is the tube radius and D is the molecular diffusion coefficient. Aris (1956) showed that axial diffusion adds D on to the righthand side of Eq. 1.

Taylor (1953) also presented an expression for the area average solute concentration, C, as a function of time and position,

$$\frac{C}{X_SC_0} = \frac{1}{2}\,\frac{\exp\left[\dfrac{(1 - t/\bar{t})\,24X}{t/\bar{t}}\right]}{[(\pi/96)X(t/\bar{t})]^{1/2}} \tag{2}$$

From this result it can be concluded that the reduced dimensionless concentration, C/C_0X_S, is a function of reduced time, $t/\bar{t}$, and dimensionless distance, X. It will be shown that this is a convenient way to correlate the experimental chromatograms over much wider ranges of residence times and Grashof numbers than those for which Eq. 2 is valid quantitatively.

EXPERIMENTAL PROCEDURE

A detailed description of the apparatus, which includes a Waters model 6000A solvent delivery system and U6K universal liquid chromatograph injector, and the procedure employed to measure binary diffusion coefficients and determine elution curves is given elsewhere (Benson, 1983) as are additional experimental data. The diffusion coefficients for C_6H_6 and CCl_4 in methanol were found to be 2.66×10^{-5} cm²/s and 2.24×10^{-5} cm²/s respectively, and values of $\tau \geq 18$ were used to allow for deviations from an ideally distributed input pulse as suggested by Anderson and Berglin (1981). Evans et al. (1977), used the Taylor dispersion technique to measure the diffusivity of carbon tetrachloride and methanol at 25°C. They obtained a value of 2.25×10^{-5} cm²/s which is consistent with the present results.

The effects of tube radius, and length, on dispersion at short times were studied by using four different tubes of various radii and lengths. The dimensions of the tubes used were: 0.0311 cm internal radius by 52 cm long, 0.0563 cm internal radius by 44.6 cm long, and 0.0408 cm internal radius with lengths of 91.6 cm and 51.4 cm.

Measurements of the concentration were made dynamically with an absorbance detector which included a linearizing bridge to obtain elution curves. Ideally one would measure area average concentration. However, in all real systems some mixing occurs when the sample flows through the detector. Flowrates were generally varied between 0.15 and 2.05 mL/min, as suggested by previous numerical studies, which indicated that double peaks occur in the range of dimensionless residence times, τ, between 0.05 and 0.4.

For a specified flowrate, three to five injections of sample were made. The volume of sample injected was typically 5×10^{-3} mL. The concentration of solute in the sample was between 0.5 and 20.0% by volume. Grashof numbers, Gr, are based on the difference between solvent and initial sample densities where the density of the injected sample is calculated as the volume fraction of solute times the solute density plus the volume fraction of solvent times the solvent density.

RESULTS AND DISCUSSION

Benzene was selected as the non-buoyant solute because its density (0.879 g/cm^3 is close to the density of the methanol solvent (0.791 g/cm^3) and Grashof numbers, Gr, of 2.6 to 55 were obtained with these solutions. Carbon tetrachloride (1.594 cm/cm^3) in methanol was used as the buoyant system with Gr between 93 and 3,100.

It was found that secondary flows produced by natural convection have a significant effect on the physical phenomena which give rise to double peaks in breakthrough curves. In the benzene-methanol system double peaks were observed over a range of residence times for all Gr studied. However, with CCl_4–methanol clear evidence of double peaks was observed *only* after systematically lowering Gr to 93 by dilution in which case they evolved with residence time in a similar way to those observed with benzene samples. Weak evidence of double peaks was observed at $Gr = 112$; no evidence was found at $Gr = 139$ or 184 or higher.

Figures 1 and 2 show the development of breakthrough curves with double peaks up to dimensionless distance, X, of about 0.32 One sees that a major peak first appears at residence times smaller than the average, $\bar{t}$, and then as the second peak, which appears at about $t = \bar{t}$, becomes more pronounced it gradually dominates and the peak which appeared first vanishes. The second peak, ultimately becomes that associated with the Gaussian curve of Taylor diffusion.

Figures 3 and 4 illustrate two interesting phenomena. First, by comparing the experimental curves in Figure 3 with the pure convection solution ($C_m/C_0X_S = 1/2(t/\bar{t})\bar{X}$, $t/\bar{t} \geq 1/2$) one sees that the early development of the curve clearly is convection-dominated although the tail of the curve already deviates from the convection solution. Second, to good approximation, that at a fixed X the reduced dimensionless concentration C/C_0X_S is a function only of $t/\bar{t}$ (as suggested by Taylor's solution, for $\tau \geq 0.5$, and by the very short time pure convection solution) for three different capillaries, over a 5-fold range of velocity, even for $\tau \sim 0.1$. This type of cor-

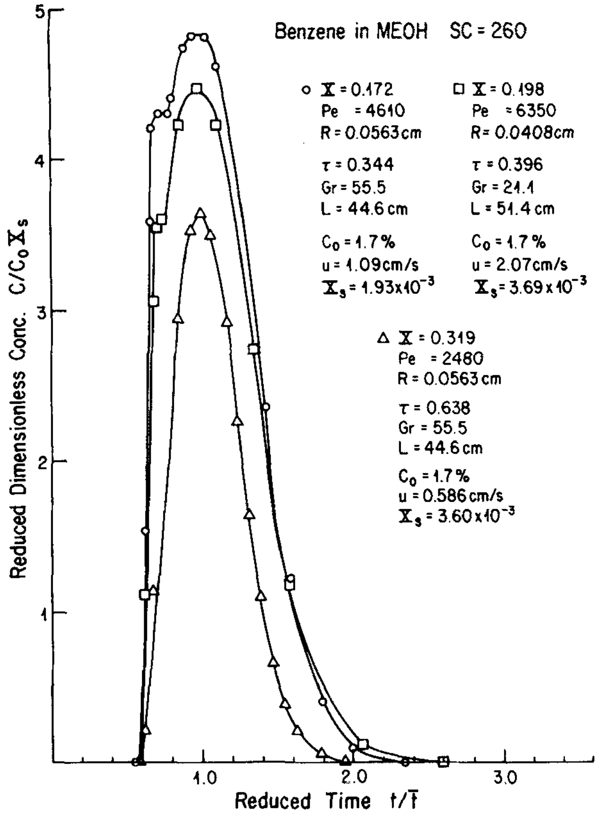

Figure 2. Transition region from double-peak chromatograms to Gaussian distribution.

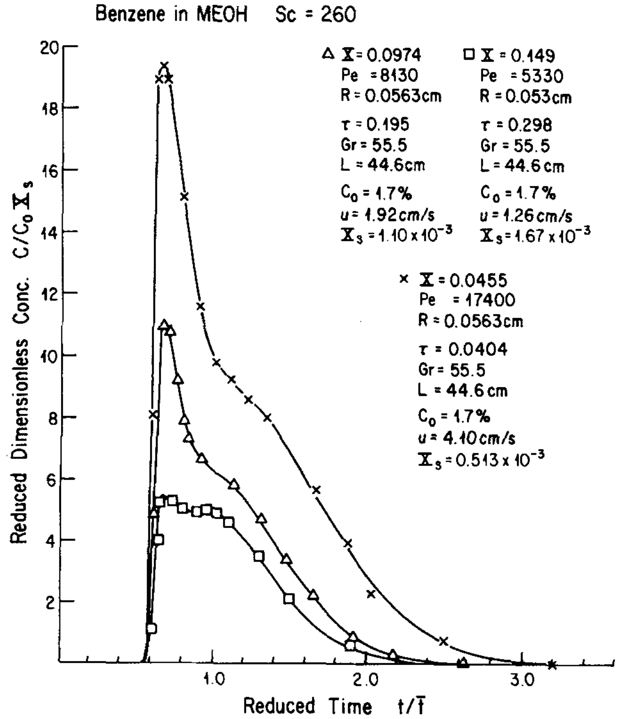

Figure 1. Development of double-peak chromatograms at small residence time.

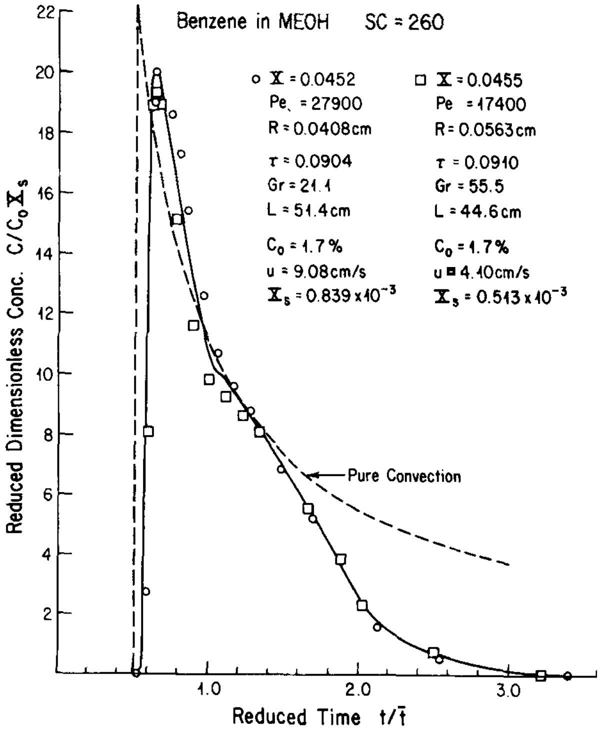

Figure 3. Comparison of pure convection solution with small residence time experimental data.

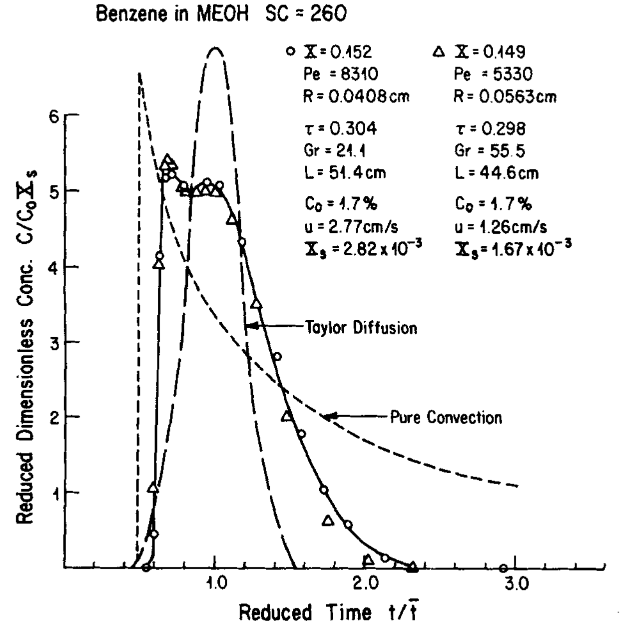

Figure 4. Interaction of pure convection and Taylor-type diffusion to form double-peak chromatogram.

relation ($C/C_0X_S = f(t/\bar{t})$ at fixed X) was found to apply about as well as shown in Figure 4 for all values of τ studied.

Figure 4 also illustrates at $\tau \sim 0.3$ a curve with two peaks and compares it to both the pure convection solution and Taylor solution. Thus one again sees how well the data correlate when plotted this way. Also, it is clear that the front of the curve is still influenced mostly by convection while the latter half now is strongly influenced by Taylor-type diffusion.

Golay and Atwood (1979) also obtained elution curves similar to what we have found. However, it was necessary for them to study very high Peclet number systems, an order of magnitude larger than ours, in order to the observe double peaks. This probably is attributable to the fact that they did not consider the effect of natural convection and had to employ very strong forced flows to render secondary flow effects negligible. Unfortunately they did not report sample concentrations or Grashof numbers.

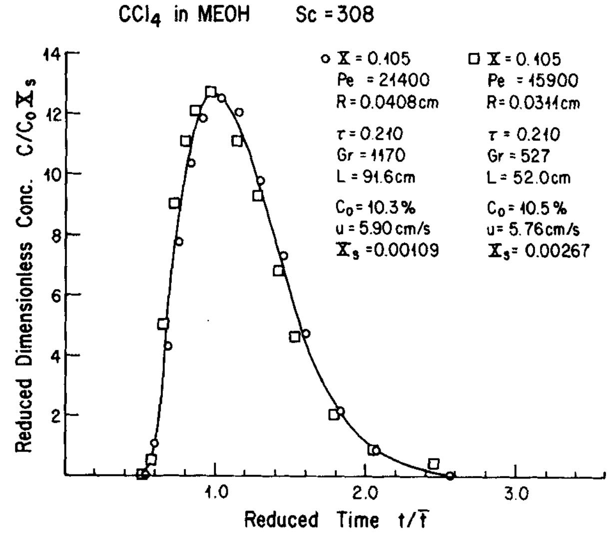

Figure 6. Elution curves at intermediate residence time and large Grashof number.

Figures 5–7 show typical results with CCl_4 samples. One sees that the correlation of data remains good despite having $527 \leq Gr \leq$ 3,100. However, there is no evidence of a double peak or of axial convection domination as was clear at similar values of X for small Grashof numbers. Obviously the radial mixing caused by natural convection eliminates double peaks entirely. Furthermore, on comparing the dispersion coefficients characterizing the curves in Figures 6 and 7, which are in the residence time range of Taylor diffusion, with those predicted by Eq. 1 one finds that the secondary flow caused by natural convection decreases k significantly.

CONCLUSIONS

Double peaks in laminar flow elution curves were observed at dimensionless distances, X, from the sample injection point up to

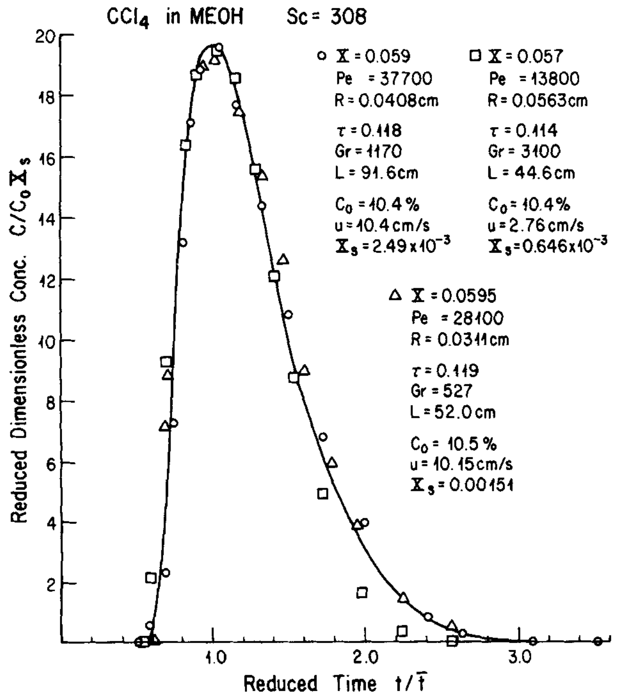

Figure 5. Correlation of elution data for three different capillaries over sixfold change in Grashof number.

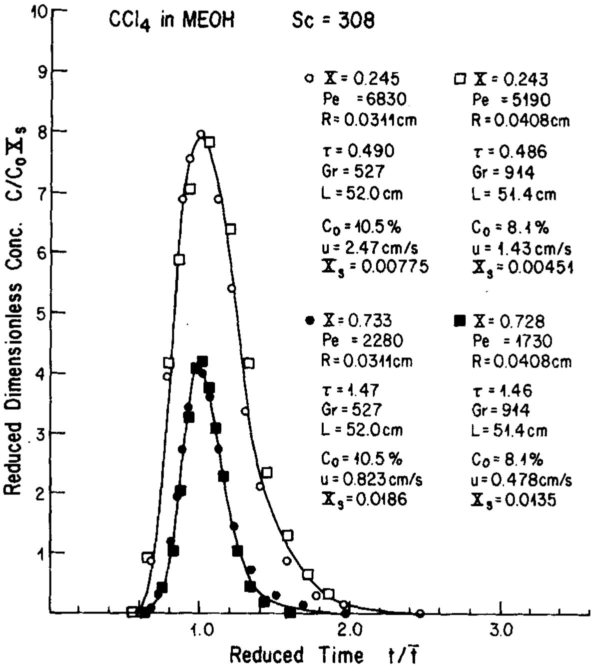

Figure 7. Effect of natural convection on elution curves in Taylor diffusion residence time regime.

0.2. The first peak is dominated by axial convection and the second by Taylor-type diffusion which is a mixture of axial convection and radial diffusoin. The first peak occurs close to $t/\bar{t}$ equal about 0.5 and the second near 1.0

Secondary flows generated by natural convection inhibit the formation of double peaks by reducing radial concentration gradients much more effectively than molecular diffusion can when acting alone; this also reduces the apparent Taylor diffusion coefficient.

Elution curves with double or single peaks observed over the range of conditions studied can be plotted conveniently as reduced dimensionless concentration versus reduced time for a fixed dimensionless distance downstream from the sample injection point. Such plots correlate elution curves whether or not natural convection is significant.

NOTATION

C = solute concentratoin
C_0 = initial solute concentration
D = molecular diffusion coefficient
g = gravitational constant
Gr = Grashof number based on density difference = $8R^3 g\Delta\rho/\rho/\nu^2$
k = Taylor dispersion coefficient
L = tube length from injection point to detector
m = mass of solute in sample = $\pi R^2 x_S C_0$
Pe = Peclet number = $2uR/D$
R = tube radius
Re = Reynolds number = $2uR/\nu$
Sc = Schmidt number = ν/D
t = time
$\bar{t}$ = mean residence time L/u
$t/\bar{t}$ = reduced time
u = average fluid velocity
x = axial distance from sample injection point
x_S = slug length
X = dimensionless distance = x/RN_{Pe}
X_S = dimensionless slug length = x_S/RPe
ρ = solvent density
ρ_S = density of injected sample
$\Delta\rho = \rho_S - \rho$ = difference between sample and solvent density
τ = dimensionless time = tD/R^2
ν = kinematic viscosity

ACKNOWLEDGMENT

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Prediction of the Thermal Conductivity of Gases at High Pressures

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In the past 40 years, a number of investigators have developed several methods to predict the thermal conductivities of gases at high pressure. Comings and Nathan (1947) suggested the use of a plot of thermal conductivity ratio, k/k^* vs. reduced pressure and reduced temperature. Gamson (1949) proposed the first generalized thermal conductivity correlation to make use of the concept of reduced thermal conductivity, k/k_c, where k_c is the critical-thermal conductivity. Unfortunately, the applicability of this correlation is limited to simple fluids where the assumption of the Enskog theory is applicable. Subsequently, Stiel and Thodos (1964), developed a correlation for predicting the thermal conductivity of gases at high pressure completely apart from corresponding states principles. Using a dimensional analysis approach, they related the residual thermal conductivity, $k - k^*$, to the reduced density, ρ_r.

Most recently, Crooks and Daubert (1979) developed a three-