AXIAL DISPERSION OF NON-NEWTONIAN
FLUIDS IN POROUS MEDIA

by

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CHAPTER I

INTRODUCTION

The flow of non-Newtonian fluids through porous media is a topic of considerable practical and engineering importance. Non-Newtonian flow through porous media may be encountered in flow through filters, artificial fiber spinnerets, fixed bed chemical reactors, and underground oil reservoirs, when water soluble polymers are added to water which is injected to increase oil recovery.

A theoretical analysis of the flow behavior of a non-Newtonian fluid in a porous medium is laden with difficulties. However, because of the industrial significance of non-Newtonian flow through porous media, a great deal of effort, both theoretical and experimental, has been expended over the years in correlating and predicting the flow behavior which occurs. Even so, the complex geometries involved, the complex rheological behavior of non-Newtonian fluids, and the interaction of these two have given rise to a great many anomalies and differences in results among various researchers. Because of these factors, prediction of flow behavior is generally very uncertain, with the result that experimental data must be heavily relied upon in most situations.

An important phenomenon which occurs when two miscible fluids are flowing sequentially through a porous medium is the mixing or dispersion of the two fluids. It is important to be able to quantify this dispersive behavior since other factors related to the process

under consideration are often influenced significantly by the amount of mixing which occurs. For instance, in a packed bed chemical reactor, dispersion directly affects the conversion of reactants to products which in turn influences the economics of the process. In oil recovery processes, dispersion determines the amount of polymer solution required for a particular reservoir.

Very little work has been done on dispersion of non-Newtonian fluids in porous media, and the objective of this research is to begin a study of this nature. Specifically, the present investigation will consider one of the least complex flow situations which permits the observation of one-dimensional axial dispersion. The simplified conditions selected for this research are one-dimensional flow, equal viscosity for both fluids, uniform isotropic porous media, sufficiently large particle size to minimize surface effects, and sufficiently viscous non-Newtonian fluids to permit convenient measurements of rheological properties.

Since axial dispersion of non-Newtonian fluids in porous media has been studied quite thoroughly, attention will be focused on the non-Newtonian aspects and comparisons between Newtonian and non-Newtonian fluids.

CHAPTER II

LITERATURE REVIEW OF AXIAL DISPERSION IN POROUS MEDIA

Qualitative Aspects

Since Taylor's analysis in the early 1950's (38) on dispersion in a capillary tube, a great deal of research has been completed in the area of dispersion because of its influence on the efficiency of various processes. Dispersion in porous media has been especially appealing for experimental study because a rigorous analysis of the flow inside a porous structure using the equations of continuity and motion is essentially impossible (28).

Detailed treatment of almost every aspect of dispersion in porous media may be found in the literature. Several comprehensive review articles (11, 18, 20, 28, 31) have been published and these provide an excellent overall picture of the subject.

When two miscible liquids are flowing through a porous medium, the fluids tend to mix by molecular diffusion due to the concentration gradients which are present. In general, there is mixing over and above that caused by molecular diffusion. This overall mixing is usually referred to as dispersion and results from uneven fluid flow in the porous medium and the additional concentration gradients that are caused by the uneven fluid flow (31). Some of the mechanisms which may contribute to the convective mixing are summarized (18) into the following categories:

- (1) Eddies in turbulent flow.

- (2) Stream splitting - the tortuous paths in a porous medium cause two fluid elements starting at the same position to become farther apart.
- (3) Hydrodynamic dispersion - in laminar flow the velocity profile within a given channel causes fluid near the center of the channel to move relative to fluid at the wall.
- (4) Heterogeneities - the fact that all flow channels will not be the same size in a porous medium causes fluid in some channels to move relative to fluid in other channels.
- (5) Adsorption - if a component of the fluids is selectively adsorbed by the porous medium, it will be depleted and concentration profiles will be altered.
- (6) Stagnant volume - if a portion of the flow area is stagnant, only molecular diffusion may occur within the stagnant area, and the flow must bypass this area.

In the usual case, overall dispersion is experimentally measured and the individual contribution of each mechanism is not obvious. Since this is the case, it is a wise precaution not to extrapolate data to different flow situations where other mechanisms may be operative.

Dispersion in porous media is frequently divided into two categories, axial and radial. Dispersion in the direction of flow is termed axial (or longitudinal) dispersion, while dispersion perpendicular to the direction of flow is termed radial (or transverse) dispersion. The mechanisms given above contribute to both axial and radial dispersion, but the magnitudes of the contributions are generally not

equal, thus the overall magnitudes of axial and radial dispersion are not usually equal (31). In a flow situation where there are no significant variations in fluid composition over a cross section perpendicular to the main direction of flow in a porous medium, the flow may be considered essentially one dimensional. In one dimensional flow of this type, radial dispersion is unimportant and only axial dispersion need be considered.

The concept of one dimensional axial dispersion may be envisioned by the following discussion. Consider a porous medium initially filled with liquid A. At the inlet to the medium, liquid B is injected uniformly over the entire cross section, which constitutes a step change in the inlet concentration. This arrangement is often referred to as miscible displacement when the two fluids are completely miscible. At the start of this displacement process, the fluids begin to mix by molecular diffusion and by dispersion. If conditions for axial dispersion prevail throughout the medium, the net result of dispersion as the fluids pass through the medium is to establish a mixed zone changing from one pure fluid to the other. As the fluids continue to pass through the medium, this mixed zone will grow in length at a rate determined by the dispersion occurring (31). Obviously, each element of fluid does not follow a one dimensional path through the medium, but the net result of the mixing makes it appear this way. It has been found that flow through porous media often approximates this simplified treatment, thus the axial dispersion approach is frequently used in modeling flow of this nature (28).

Many different types of porous media may be encountered. These are usually divided into two groups, consolidated and unconsolidated. Consolidated media, such as sandstone rocks, are prevalent in underground oil reservoirs. Unconsolidated media, such as fixed bed reactors and sand or glass bead packs may be found in many applications. Generally, the flow channels in either type of media are not uniform in size and the particles or pores often have a distribution of sizes (13, 35). This pore size distribution is one factor in the so called heterogeneities which contribute to dispersion.

Porosity and permeability are two parameters which are often used in characterizing porous media. Porosity is defined as the fraction of total space occupied by voids, while permeability is a measure of the flow resistance used in conjunction with Darcy's law (13). Darcy's law for linear flow in a uniform porous medium may be written as

$$v_0 = - \frac{k}{\mu} \frac{\Delta P}{L}$$

where

v_0 = superficial velocity, cm/sec

k = permeability, cm^2

μ = fluid viscosity, g/cm sec

L = length of the medium, cm

ΔP = pressure differential across medium, dynes/ cm^2 .

Collins (13) and Scheidegger (35) have given the methods for measurement of porosity and permeability.

Techniques for Measuring Dispersion

A variety of experimental techniques have been employed to study axial dispersion in porous media. All of the methods involve the use of tracer injection experiments and subsequent measurement of the response of the system under consideration (3). When combined with the appropriate mathematical model, these residence-time distribution studies lead to quantitative measurements of dispersion.

In most experiments tracers have been injected in sinusoidal, pulse, or step form. The pulse and step function studies are the easiest to accomplish experimentally, and have found more widespread use except in the case of gas dispersion studies where frequency response is very convenient.

The main problem in pulse or step function studies lies in obtaining a perfect pulse of tracer or a perfect step change in tracer concentration. The experimental error incurred due to these end effects at the vessel entrance and exit can be quite serious. Bischoff and Levenspiel (3) have studied this problem in detail for a pulse injection experiment. They point out that the best method for measurement of a systems response to a pulse of tracer is to use two measurement points, both located inside the vessel. In this manner, end effects can essentially be eliminated, and furthermore, a perfect pulse of tracer is not required. The same line of reasoning would apply to a step-function experiment. Liles and Geankoplis (26) studied end effects experimentally in a packed column using a frequency response technique and found that end effects became negligible for length to

column diameter ratios greater than about 16. The data of Miller and King (27) showed no ordered length to diameter effect for a step-function experiment in a packed column.

A number (4, 7, 40) of the experimental studies on axial dispersion in porous media have employed the technique referred to earlier as miscible displacement. Here, one fluid is displaced from the medium by another and the effluent from the medium is analyzed for concentration of one of the fluids. Often the two fluids are identical, except that a tracer is added to the displacing liquid. This method is perhaps the simplest of all for studying dispersion, but all end effects will be present in the data since only one measurement point is used and it is located outside the vessel. The miscible displacement data of Von Rosenberg (40) was analyzed by Crawford and Atkinson (14) and they detected no end effects in his sand packed columns with length to diameter ratios of 8, 16, and 32.

Various experimental porous media, both consolidated and unconsolidated, have been used in dispersion studies. Packs of glass beads or sand have been found to be excellent for experimental porous media because they are easily packed into columns and they provide very realistic flow studies (7).

Somewhat similar to end effects are edge effects caused when particles are packed into a cylinder. This topic has been reviewed by Perkins and Johnston (31). They note that axial dispersion should increase with an increase in packing diameter to column diameter ratio. The region near the container wall will have less flow resistance than

the region near the center of the container because of the packing irregularities. Thus, increased mixing should be observed due to channeling in this wall area. No quantitative values of when edge effects become negligible in axial dispersion are available. Some limited data on radial dispersion, compiled by Perkins and Johnston (31) from several sources, indicate that edge effects are completely negligible below packing diameter to column diameter ratios of 0.01.

Mathematical Model for Axial Dispersion

Several different mathematical models of varying degrees of complexity have been used in dispersion studies. These models, their assumptions, and solutions have been reviewed by Bischoff and Levenspiel (3). The most simple of these models, and the one which has been used most often because of its simplicity, is the axial dispersion model. This single parameter model is often referred to simply as the diffusion model, but is more exactly termed the axial dispersed plug flow model (3) because of the assumptions implicit within its development.

Qualitatively, axial dispersion may be envisioned as a plug flow process with a certain amount of mixing superimposed upon the flow. The objective of the model is then to predict this dispersion quantitatively. Aronofsky and Heller (1) have pointed out that no particular mechanisms need be assumed for the dispersion process, and that the use of the model is justified if the overall dispersion can be described by the model. Modifications by adding additional parameters

to the axial dispersion model have been used at times to improve the fit with experimental data (12, 15).

Development of Equation

The assumptions used to develop the axial dispersion model mathematically have been given (3) as follows:

- (1) Constant density.
- (2) Bulk flow in the axial direction only with radial symmetry.
- (3) Dispersion is characterized by a single constant coefficient which is independent of fluid properties and position.
- (4) Fluid is in plug flow.
- (5) No variation in fluid properties in the radial direction.

The equation may now be developed by performing an unsteady state material balance in a differential element of a porous medium, considering the flow to be composed of a bulk movement term and a mixing term analogous to molecular diffusion.

A material balance on the tracer requires that

$$\text{Input} - \text{Output} + \text{Generation} = \text{Accumulation} \quad .$$

The following quantities are now defined:

$$C = \text{tracer concentration, g/cm}^3$$

$\bar{v}$ = mean interstitial velocity of fluid in the bed, cm/sec

t = time, seconds

D = axial dispersion coefficient which is analogous to a molecular diffusivity, cm^2/sec .

With these definitions, the input, output, and accumulation terms become:

$$\text{Input by bulk flow} = (C\bar{v})_Z$$

$$\text{Input by dispersion} = \left(-D \frac{\partial C}{\partial Z}\right)_Z$$

$$\text{Output by bulk flow} = (C\bar{v})_{Z + \Delta Z}$$

$$\text{Output by dispersion} = \left(-D \frac{\partial C}{\partial Z}\right)_{Z + \Delta Z}$$

$$\text{Accumulation within the element} = \left(\frac{\partial C}{\partial t}\right) \Delta Z$$

Since no generation term is being considered here, the material balance becomes

$$(C\bar{v})_Z - (C\bar{v})_{Z + \Delta Z} - \left(D \frac{\partial C}{\partial Z}\right)_Z + \left(D \frac{\partial C}{\partial Z}\right)_{Z + \Delta Z} = \left(\frac{\partial C}{\partial t}\right) \Delta Z$$

By dividing each term through by ΔZ , recalling that $\bar{v}$ is constant, and applying the definitions of the first and second partial derivatives as ΔZ approaches zero, the following equation is obtained:

$$D \frac{\partial^2 C}{\partial Z^2} - \bar{v} \frac{\partial C}{\partial Z} = \frac{\partial C}{\partial t} \quad (II-1)$$

This partial differential equation is the standard form of the axial dispersion model. The first term is a Fick's second law type expression

(2), and the axial dispersion coefficient D is the parameter upon which most studies are focused.

Actually, the equation is generally easier to use with experimental studies if it is placed in dimensionless form (1). The following dimensionless variables are especially convenient for step function and miscible displacement dispersion studies:

$$X = Z/L = \text{dimensionless distance}$$

$$\bar{C} = C/C_0 = \text{dimensionless concentration}$$

$$T = \bar{v}t/L = \text{dimensionless time}$$

$$Pe = \bar{v}L/D = \text{dimensionless dispersion coefficient.}$$

In the above variable, L is taken to be the length of the porous medium under investigation, and C_0 is the initial or reference concentration in a step-function experiment. Other variables are frequently used (3) with other types of experimental techniques. With the above variables, the equation becomes

$$\frac{1}{Pe} \frac{\partial^2 \bar{C}}{\partial X^2} - \frac{\partial \bar{C}}{\partial X} = \frac{\partial \bar{C}}{\partial T} \quad . \quad (\text{II-2})$$

The term Pe , a parameter related to the dispersion, is called the axial Peclet group in dispersion studies. The Peclet number has been found to be very useful in correlating experimental data on axial dispersion (20).

The dimensionless time T as defined above has a particularly convenient meaning in miscible displacement studies. T may be interpreted as the number of average residence times or the number of pore volumes of displacing liquid that have been injected since the start of displacement (6).

Boundary Conditions and Solution

The boundary conditions for solution of the axial dispersion model should conform as closely as possible to the boundary conditions present in the experimental apparatus under study. Obviously, it is very difficult to know the true nature of the boundary conditions present in flow through a porous medium. As a result, several different sets of boundary conditions have arisen for the axial dispersion model, and a good deal of discussion has been centered on the most appropriate form of these (3, 5, 6, 12, 29).

Three different sets of boundary conditions are frequently employed to solve the axial dispersion model for step-function or miscible displacement experiments. Coats and Smith (12) give these in dimensional form as

Boundary Conditions A:

- (1) $Z = 0, C = C_0$
- (2) $Z \rightarrow \infty, C(Z,t) \rightarrow 0$

Boundary Conditions B:

- (1) $Z = 0, \bar{v}C_0 = \bar{v}C - D \frac{\partial C}{\partial Z}$
- (2) $Z \rightarrow \infty, C(Z,t) \rightarrow 0$

Boundary Conditions C:

- (1) $Z = 0, \bar{v}C_0 = \bar{v}C - D \frac{\partial C}{\partial Z}$
- (2) $Z = L, \frac{\partial C}{\partial Z} = 0$.

A and B above are the so called semi-infinite medium boundary conditions and have been used quite extensively in obtaining solutions to the axial dispersion model. Conditions C were used by Brenner (5) to

effect a finite bed solution. In all the above expressions, planes one and two refer to the inlet and exit of the porous medium. These boundary conditions and their resulting solutions have been discussed and compared in detail by Coats and Smith (12) and Brigham (6). Coats and Smith have noted that the semi-infinite medium solutions are made insensitive to the length of the medium by the second condition of A or B. Scheidegger and Larson (36) studied these asymmetric boundary conditions, and found that, for typical Peclet numbers observed in experiments, the extension of the medium to infinity is perfectly valid for any porous medium greater than approximately 1 mm in length. This does not say that end effects will not be overwhelming in a medium this short, but says that mathematically the semi-infinite solutions cause little if any error in a bed of ordinary length.

Brigham (6) and Coats and Smith (12) have also shown that, when used properly, the solutions for the three boundary conditions generally differ by no more than one to two per cent in a medium of typical length for almost any Peclet number. Brigham concluded that it really does not matter in a practical sense which conditions are more nearly correct, since they all predict about the same results.

An initial condition is also required for solution of the equation. By assigning the initial concentration of fluid in the medium as zero for a miscible displacement experiment, the dimensionless initial condition is

$$\bar{C}(X,0) = 0 \quad .$$

Restated, the problem to be solved with the previous initial condition and boundary conditions A in dimensionless form is

$$\frac{1}{Pe} \frac{\partial^2 \bar{C}}{\partial X^2} - \frac{\partial \bar{C}}{\partial X} = \frac{\partial \bar{C}}{\partial T} \quad (\text{II-2})$$

$$X = 0, \quad \bar{C} = 1$$

$$X \rightarrow \infty, \quad \bar{C} \rightarrow 0$$

$$\bar{C}(X, 0) = 0$$

An appropriate solution to this equation by Laplace transform techniques is shown in the Appendix, and is

$$\bar{C} = \frac{C}{C_0} = \frac{1}{2} \operatorname{erfc}\left(\frac{\sqrt{Pe}}{2} \frac{(1 - T)}{\sqrt{T}}\right) + \frac{\sqrt{T} \exp\left(\frac{-Pe(1 - T)^2}{4T}\right)}{\sqrt{\pi Pe}(1 + T)} \quad (\text{II-3})$$

where erfc = complementary error function (23).

The above equation predicts the fractional concentration of the effluent from the medium as a function of the axial Peclet group and the number of pore volumes injected since the start of the displacement process. It is interesting to note that equation II-3 predicts the effluent concentration when $T = 1$ to be

$$\bar{C}(T = 1) = 0.5 + \frac{1}{2 \sqrt{\pi Pe}} \quad (\text{II-4})$$

In most instances the magnitude of the Peclet number Pe is such that the second term above adds only two or three per cent to the predicted

value of $\bar{C}$ at $T = 1$ (12). For values of T other than 1, the term contributes less than this due to the negative sign on the exponential of equation II-3.

The use of equation II-3 to determine the dimensionless Peclet group from experimental data is discussed in Chapter III.

Important Variables and Their Effects on Axial Dispersion in Laminar Flow

A wide variety of experimental variables have been studied in axial dispersion, and these have all been discussed comprehensively in the several review articles (11, 18, 20, 28, 31). The major variables which affect dispersion in miscible displacement studies have been given by Perkins and Johnston (31) as:

- (1) Molecular diffusion
- (2) Velocity of flow
- (3) Particle size distribution
- (4) Particle shape
- (5) Packing heterogeneities
- (6) Viscosity ratios.

Also, if turbulence or density differences or an immobile phase exists within the medium, dispersion will be altered (28).

Molecular Diffusion

The mixing of two miscible liquids by molecular diffusion due to concentration gradients may be characterized by Fick's first law of diffusion (2). Molecular diffusion can influence axial dispersion in

two ways, by diffusion in the axial direction and by diffusion in the radial direction.

In a miscible displacement, concentration gradients are highest at the inlet to the porous medium at the beginning of the displacement. The effect of axial molecular diffusion on dispersion will be greatest at this time. However, in liquid systems, axial diffusion is generally negligible in relation to the overall dispersion unless the rates of flow become very low since molecular diffusion coefficients for liquids are very low (31). The magnitudes of the molecular diffusion coefficient and the velocity must be considered in assessing when axial diffusion will become important, but in general the effect of diffusion is important if the overall dispersion coefficient is on the order of the molecular diffusion coefficient. Perkins and Johnston (31) also note that the effective molecular diffusion coefficient in a porous medium is generally about two-thirds of the true molecular diffusion coefficient because the fluids must travel a tortuous path from one point to another.

Within the pores and connecting channels of a porous medium, molecular diffusion will also be occurring in the radial direction. The effect of this radial molecular diffusion has an important bearing upon the magnitude of axial dispersion. More radial diffusion within the pores and channels will lessen axial mixing since the fluid is being transported radially which tends to dampen out the axial effects. Thus fluids with higher molecular diffusion coefficients would be expected to show less dispersion if all other factors remain the same (31).

This may be verified by comparing data between gases and liquids at a velocity where axial diffusion is negligible in relation to overall dispersion. Here, axial dispersion in gas systems is much less than for liquids, and the difference can only be attributed to greater radial mixing in gases which inhibits the axial dispersion (20). Miller and King (27), in their work with liquids at low rates of flow, discussed axial dispersion in the absence of radial molecular diffusion. They noted that axial mixing should be greatest for this situation since the molecular diffusion coefficient is zero.

Velocity of Flow

The effect of the liquid velocity on axial dispersion may be seen qualitatively by considering a single capillary tube. At a given average velocity, the fluid at the center of the capillary moves relative to the fluid at the wall and dispersion is observed. If the velocity is doubled, the fluid at the center of the capillary will reach the exit twice as fast as in the previous case (assuming molecular diffusion is negligible). Although the velocity profile is parabolic at both velocities, the case with the higher velocity will exhibit a greater spread of the fluid elements and hence greater axial dispersion. The same type of reasoning applies to a porous medium, but the functional dependence of the dispersion on velocity will be different for a porous medium and a capillary since additional mechanisms of dispersion are present in a porous medium (31).

Particle Size Distribution, Particle Shape, and Packing Heterogeneities

These are three factors which have led to a significant amount of uncertainty in comparing axial dispersion data on different porous media (31). Several authors (18, 21, 28, 31) have discussed these variables in detail. Greenkorn and Kessler (18) refer to these as heterogeneities, while Gunn (21) terms their overall effect the quality of packing. Gunn has shown that these factors can often lead to differences in dispersion when a given porous medium is repacked with the same packing.

The above references all indicate that axial dispersion is increased by greater heterogeneities such as wide or skewed particle size distributions, non-uniform shape of particles, or gross factors such as poor or layered packing.

Various empirical methods and models have been devised in an attempt to correlate the heterogeneities found within real porous media. Several geometric models such as capillary network models (33), random walk models, and statistical models have found some success in incorporating the effects of heterogeneities into a common framework, but the use of these models requires much time and effort. Greenkorn and Kessler (18) have discussed these models and their practical usage. Gunn (21) considered the effects of interstitial velocity variations in a packed bed, and devised a single parameter which is representative of the overall heterogeneity of a given porous medium.

Viscosity Ratio

Dispersion may also be affected if the two fluids in a miscible displacement have different viscosities. The viscosity ratio, or

mobility ratio as it is often called, is the ratio of viscosities of the displaced fluid to the displacing fluid (31). When the displacing fluid is less viscous than the displaced fluid, an unfavorable viscosity ratio exists, and the displacing fluid may "finger" through the displaced fluid (28). Brigham et al. (7) reported some experimental results where a slightly unfavorable viscosity ratio of 1.002 caused a drastic change in the mixing process, even to the extent that the data could not be approximated by the axial dispersion model. They also studied favorable viscosity ratios and found that the mixing behavior was normal and that dispersion decreased towards some limiting value as the viscosity ratio became more favorable. The more recent data of Groboske and Ali (19) did not show the extreme sensitivity of the mixing to unfavorable viscosity ratios that was given by Brigham et al. Groboske and Ali did find that the dispersion was increased at unfavorable viscosity ratios, but only slightly at a ratio of 1.03. Their data for a 1.03 viscosity ratio were well approximated by the axial dispersion model. They observed a slight difference in the shape of their curves at this value which they attributed to small amounts of viscous fingering.

Present Axial Dispersion Correlations for Newtonian Fluids

The variables most useful in correlating the results of dispersion studies have been found to be the dimensionless Peclet, Reynolds,

and Schmidt groups (11, 20). Here the Peclet number is an experimental measure of the dispersion defined previously as

$$Pe = \frac{\bar{v}L}{D} \quad (II-5)$$

where $\bar{v}$ = mean interstitial velocity of the fluid, cm/sec

L = length of the porous medium, cm

D = axial dispersion coefficient, cm²/sec.

The axial Peclet number given above is often changed to a particle Peclet number by multiplication by the ratio of the packing diameter to the length of the medium so that

$$Pe_p = \frac{\bar{v}d_p}{D} = \frac{\bar{v}L}{D} \left(\frac{d_p}{L} \right) \quad (II-6)$$

A particle Reynolds number, also based on some characteristic packing diameter, is often employed such as

$$Re = \frac{d_p \rho \bar{v}}{\mu} \quad (II-7)$$

where ρ = density, g/cm³

μ = viscosity, g/cmsec.

Other definitions of the Reynolds number are often used (3, 11). The Schmidt number is a ratio of transport properties of the fluid, and is defined by (2)

$$Sc = \frac{\mu}{\rho D_0} \quad (II-8)$$

where D_0 = molecular diffusion coefficient, cm²/sec.

Actually, as shown by Gunn (20), the product of the Reynolds and Schmidt groups is the truly important variable in a dispersion study. This can be derived from dimensional analysis considerations (2, 7), and was arrived at from a more qualitative reasoning by Blackwell (4). With the Reynolds and Schmidt groups defined above, their product becomes

$$\text{ReSc} = \frac{\bar{v} d_p \rho}{\mu} \cdot \frac{\mu}{\rho D_0} = \frac{\bar{v} d_p}{D_0} \quad . \quad (\text{II-9})$$

This dimensionless group contains a characteristic length dimension and the ratio of velocity to molecular diffusion. Thus the group is a measure of the ratio of convection to molecular diffusion. The qualitative discussions put forth previously on the effects of velocity and molecular diffusion suggest that this is indeed a worthwhile variable.

Perkins and Johnston (31) have compiled and correlated a large portion of the experimental data on axial dispersion of liquids using the product ReSc. In laminar flow, their result is represented in equation form by

$$\frac{D_L}{D_0} = \frac{D'}{D_0} + 0.5 \frac{\bar{v} \sigma d_p}{D_0} \left(\frac{\bar{v} d_p}{D_0} < 50 \right) \quad . \quad (\text{II-10})$$

where D_L = overall axial dispersion coefficient including molecular diffusion and convection

D' = effective molecular diffusion coefficient in the porous media

σ = a factor to account for heterogeneities in a given medium.

For uniform glass bead packs, they give the value of σ as 3.5. When axial molecular diffusion is negligible in relation to the convective mixing, the first term on the right hand side of the above equation may be neglected, and the equation can be arranged to the form of a particle Peclet number as

$$\frac{\bar{v} d_p}{D_L} = \frac{1}{0.5\sigma} = Pe_p \left(\frac{\bar{v} d_p}{D_0} < 50 \right) \quad . \quad (II-11)$$

This rearrangement shows that, in a region where convection dominates the dispersion, the Peclet number is constant for a given porous medium if $\bar{v} d_p/D_0$ is less than 50. When this is the case, examination of the previous equation shows that the axial dispersion coefficient must be directly proportional to velocity if the Peclet number is to remain unchanged. When $\bar{v} d_p/D_0$ is greater than 50, Perkins and Johnston note that the limited amount of experimental data in this range shows D_L increases with the 1.2 power of velocity, thus the Peclet number shows a slight trend downward. These arguments apply only to laminar flow, since when the transition from laminar to turbulent flow beings, Peclet numbers begin to rise as the velocity profile approaches plug flow where little mixing occurs (27).

Chung and Wen (11) have also correlated a large portion of liquid dispersion data using only the Peclet and Reynolds numbers. Their equation, with a standard deviation of 46 per cent based on 482 data points, is

$$\epsilon Pe_p = 0.20 + (0.011) Re^{0.48} \quad (II-12)$$

where ϵ = fractional porosity of the medium.

Their equation, while applicable from $Re = 10^{-3}$ to $Re = 10^3$, again shows that the Peclet number is essentially constant at low velocities. Their correlation cannot show the trends often noted in individual experiments, and furthermore, it is only valid when molecular diffusion is negligible in the axial direction.

More recently, Gunn (20) has studied dispersion on a theoretical basis and devised the following equation for the limiting case of zero molecular diffusion (infinite Schmidt number)

$$Pe_p = \frac{2P}{1 - P} \quad (II-13)$$

In this expression, P is called the fluid-mechanical probability which Gunn developed from statistical considerations. He notes that P depends upon the flow conditions, and that in a region where convection only is important the value of P will be that due to convective dispersion only. Gunn later (21) modified this approach to include the effects of heterogeneities and variations in the interstitial velocity. This expression, again for infinite Schmidt number, is

$$Pe_p = \frac{2P}{(1 - P) + \sigma_v^2} \quad (II-4)$$

where σ_v^2 = variable to account for the distribution of velocities over a cross-section of a packed bed.

He then calculated values of P from experimental data and found $P = 0.26$ for Reynolds numbers less than one. This result is similar

to the correlation of Perkins and Johnston (31) discussed earlier. Both correlations have one additional parameter to take into account the heterogeneities in a porous medium. Gunn noted that his calculated values of P are not the only values which are capable of correlating the experimental data.

It should be noted that most experimental data for liquid dispersion have been taken with water and generally with salt or dye tracers. The Schmidt number for these situations is typically 10^3 to 10^4 (11). Reynolds numbers have ranged from 10^{-4} to 10^3 . Essentially no data is available outside these ranges, and the correlations available may or may not be valid in these regions.

In summary, all the available experimental data indicate that Peclet numbers are relatively constant in laminar flow, except when $ReSc$ is greater than about 50. As the Schmidt number approaches infinity, the Peclet number should again be constant as predicted by Miller and King (27) and Gunn (20). Thus, Peclet numbers are expected to be constant in laminar flow except in the region where $ReSc$ is between 50 and a value which may be effectively considered as infinite. Also, when velocities become low enough, axial molecular diffusion will become significant and Peclet numbers should decrease and eventually become equal to $ReSc$. A major factor in correlation and comparison of results between different porous media is heterogeneity or quality of the packing.

Previous Research on Non-Newtonian Fluids

A search of the available literature revealed only one study on axial dispersion of non-Newtonian fluids in porous media. This

experimental work, completed recently by Wen and Yim (41), involved measuring axial dispersion of aqueous solutions of a poly (ethylene oxide) (Polyox 301 manufactured by Union Carbide Corporation) polymer in a packed column 3.5 feet in length by two inches in diameter. They studied two different packings, 3/16 and 9/16 inch diameter glass beads, over Reynolds numbers ranging from 7 to 800. The Reynolds numbers used was a modified expression which incorporated the non-Newtonian fluid properties. Their experimental axial dispersion results were obtained by injecting a sharp pulse of fluorescein tracer into the flowing polymer solutions and measuring the resulting response of the system. They concluded, for solutions of 0.1 and 0.35 per cent Polyox, that their non-Newtonian data could be approximated by the correlation equation of Chung and Wen (11) discussed earlier.

Their non-Newtonian solutions were found to follow a power law model (8), although the solutions were not highly non-Newtonian as evidenced by the magnitude of their power law constants n and K . Their values of n were 0.9 and 0.81, and they suggested further work with more highly non-Newtonian fluids to see if differences between non-Newtonian and Newtonian axial dispersion could be observed.

CHAPTER III

APPARATUS AND PROCEDURE

Experimental Apparatus

The equipment used for the axial dispersion measurements is sketched in Figure III-1. The major items are a Plexiglas tube packed with glass beads, a positive displacement pump for metering of solutions, and an automated fraction collector for taking samples of the column effluent at regular intervals. The entire apparatus, except for the pump, was enclosed in a thermostated air bath.

The glass bead pack served as the experimental porous medium for this investigation. The flow cell, a Plexiglas tube 3.81 centimeters in diameter by 60 centimeters in length, was constructed with liquid distributors at both ends to insure that the fluids were well distributed over the entire flow area at the inlet and exit of the bed. The liquid distributors were of a wagon-wheel type design and were integral parts of the end plates of the cell. The fluid enters through the center of a distributor plate and then branches out over the flow area of the cell through the connecting channels in the distributor plate. Correct operation of this type of liquid distributor is dependent upon a high flow resistance in the region immediately beyond the distributor plate within the flow cell. This flow resistance was provided by the glass beads and a fine mesh nylon gauze situated at the top and bottom of the beads.

Glass beads of 470 micron nominal size supplied by the 3M Company (lot number BER-1035-1939) were packed into the flow cell by slowly

Figure III-1 Sketch of Experimental Apparatus

pouring the beads through a funnel located at the top of the cell. Mechanical vibration of the tube was maintained during the packing process. When the cell was full of beads, the top nylon gauze and distributor plate were moved into place. The distributor plate was then tightened via four bolts onto an O-ring seal until the inner face of the distributor plate rested firmly against the nylon gauze and glass beads. No shifting or settling of the beads was observed during this procedure.

The bead pack was initially filled with a solution by evacuating the cell with a vacuum pump and slowly metering the solution into the cell at the bottom. At times, this procedure did not remove all the air, and it was necessary to repeat the evacuation or circulate the fluid at a high rate of flow to remove entrapped air.

To characterize the properties of the bead pack, the porosity, permeability, and effective particle size of the beads were determined.

An attempt was made to determine the porosity of the pack by measuring the amount of fluid required to completely fill the packed cell the first time it was filled. However, some entrapped air could be seen in the cell after filling, so the void volume measured was incorrect. An alternative, and somewhat less appealing, procedure was thus used to determine the porosity. With the pack completely full of an undyed glycerol solution, it is known that one void or pore volume of the liquid is contained in the cell. This liquid was then displaced from the cell by a dyed glycerol solution in the same manner as the axial dispersion studies to be described later on were carried

out. By performing a material balance on the undyed glycerol solution, the pore volume of the pack is easily determined as the total volume of undyed glycerol which is recovered in the displacement. This was determined by weighing the amount of glycerol accumulated in the effluent up until the dyed solution appeared, and then graphically integrating the breakthrough curve to find the amount of undyed glycerol contained in the mixed zone created by dispersion. This procedure gave a pore volume of 248 cm^3 and a resulting porosity of 36.5 per cent. This value is very comparable with the results of others (9, 10, 16) on bead packs of this nature. This value of porosity was felt to be more reliable than obtaining an approximate value in another tube by use of the average particle density and a water displacement method (13, 35).

The permeability of the bead pack was measured by flowing a glycerol solution of known viscosity through the pack and measuring the pressure drop over a length of the cell with a simple manometer system. Permeability was then calculated from the Darcy equation mentioned previously. The average permeability calculated from a combination of three pressure taps was found to be 108 darcies where one darcy is equivalent to $9.87 \times 10^{-9} \text{ cm}^2$. A slight trend towards increasing permeability at the top of the pack was observed by comparing permeabilities calculated from the different combinations of pressure taps. The top two taps gave a permeability of 111 darcies while the bottom two gave 105 darcies. The top and bottom tap combination gave an intermediate value of 107 darcies.

The size of the glass beads was measured with a micrometer. The average bead size for a random sampling of 100 beads was found to be 0.0374 cm. The beads were not completely uniform in size, with some being as small as 0.025 cm and some as large as 0.047 cm. The standard deviation about the mean value was calculated to be 0.0019 cm. An effective bead size based on the previously calculated permeability and porosity was also calculated with the following equation (13, 35) which is often used for estimates of permeability in packs of uniform sized beads:

$$d_p^2 = \frac{150k(1 - \epsilon)^2}{\epsilon^3} \quad (\text{III-1})$$

where d_p = effective particle diameter, cm

k = permeability of bead pack, cm^2

ϵ = fractional porosity of pack.

The effective diameter was calculated to be 0.0355 cm, which is within five per cent of the measured value of 0.0374 cm. A summary of the properties of the experimental bead pack is shown in Table III-1.

Fluids Investigated

Non-Newtonian Fluids

The fluids chosen for this investigation were solutions of Polyox water-soluble resins manufactured by Union Carbide Corporation (39). Because they have many ideal properties and are economical to use, these water-soluble polymers have found widespread usage in industrial applications. For these reasons, and because solutions of these

TABLE III-1

SUMMARY OF BEAD PACK PROPERTIES

Length of Pack	- 59.5 cm
Diameter of Pack	- 3.81 cm
Effective Bead Diameter	- 0.0355 cm (calculated) 0.0374 cm (measured)
Bead Size Distribution	- std. dev. = 0.0019 cm
Permeability	- 108 darcies (average)
Fractional Porosity	- 0.365 (approx.)
Void Volume	- 248 cm ³ (approx.)

polymers are generally non-Newtonian in behavior, Polyox resins have been frequently studied in engineering research.

Polyox resins are nonionic homopolymers of ethylene oxide and are available in molecular weights ranging from several hundred thousand to greater than five million. In the solid state, these resins exist as white granular powders which have a high degree of crystallinity. Hydrogen bonding with the ether linkages accounts for the solubility of Polyox resins in water.

Most solutions of Polyox are non-Newtonian in rheological behavior since the solution viscosity depends upon the shear rate or shear stress which the solution is subjected to. In addition to this, the rheological properties of a Polyox solution are highly dependent upon a number of other factors. Among the most important of these are resin molecular weight, concentration of resin in solution, pH of solution, presence of salt in solution, temperature, and method of preparation of solution. A rigid control must be kept on the above factors if a solution with reasonably reproducible rheological properties is to be studied experimentally.

The non-Newtonian behavior of Polyox solutions is generally considered to be of a shear thinning time-independent variety (39). These solutions are also noted for a high degree of viscoelasticity and pituitousness due to the very flexible structure of the linear, high molecular weight molecule. This elastic or recoil behavior (viscoelasticity) and clinging ability (pituitousness) can be very important factors in non-viscometric flow situations (8, 34).

The two factors which might be mistaken for time-dependent rheological behavior are oxidation and shear degradation. The ether linkages in a Polyox solution can oxidize slowly to peroxides with a subsequent decrease in molecular weight and solution viscosity. However, this oxidation may be stabilized by the addition of an anti-oxidant such as isopropanol to the solution. Concentrations of 0.5 per cent isopropanol are effective for this purpose (39). A situation where high shear exists can cause rupture of the long chains in a solution of Polyox. For this reason, high shear stresses and high energy inputs to these solutions should be avoided if rheological properties are to remain constant. Specialized mixing techniques are often employed in the preparation of polymer solutions such as these in order to avoid shear degradation.

A Polyox WSR-301 water soluble resin (lot No. W-1227-A-01) was the particular type used in this study. The specific properties of this medium-high molecular weight polymer may be seen in Appendix B.

Preparation of Polymer Solutions

Since the polymer solutions are sensitive to pH and the presence of salts, all solutions in this study were mixed in a three per cent solution of sodium chloride prepared from deionized water. This solvent should be a medium which will effectively dampen out the presence of ionic impurities encountered during the experiment, and should aid in mixing polymer solutions of consistent rheological properties.

Solutions of 0.5 and 0.9 per cent Polyox were prepared in four liter quantities in a large glass beaker by use of a magnetic stirrer. First, the appropriate volume of solvent was added to the beaker and

a vortex was created via the magnetic stirrer. Then the weighed amount of resin was dispersed into the vortex in approximately 15-20 seconds so that all the particles were wetted by the solvent. The stirrer speed was then reduced, but kept at a value which maintained motion of the particles. Since the mixing speed was slow and no baffles were used in the container, the particles had a tendency to agglomerate into lumps. It was necessary to maintain slow agitation for 12 or 24 hours (depending upon resin concentration) to completely dissolve all the resin. After this time, stirring was ceased and isopropanol in the amount of approximately one per cent by volume was added to the polymer solution to inhibit oxidative degradation. This preparation method, while slow and inefficient, was found to give satisfactorily reproducible polymer solutions.

After an initial batch of polymer was prepared, a portion of it was mixed with a solution of dye tracer described later. The remaining portion of polymer was then diluted with a quantity of solvent such that the polymer concentration was made equivalent in both the dyed and undyed portions. In this way, no differences in rheological properties between dyed and undyed solutions would be expected unless the tracer material reacted with the polymer in some manner. The tracer material was also prepared in the three per cent sodium chloride solvent.

Newtonian Fluids

For comparative purposes, a Newtonian 90 per cent by weight solution of glycerol in the three per cent sodium chloride solvent was used.

The glycerol solution was then mixed with tracer in the same manner as the polymer solutions were.

Determination of Rheological Properties

Since this study is focused on non-Newtonian aspects of axial dispersion in porous media, it is important to know the rheological behavior of the polymer solutions.

In the mixing of the solutions, it was noted that the polymers tended to climb or swell up on a rotating bob. This Weissenburg climb effect (8, 37) is typical of viscoelastic fluids which can exhibit normal stress differences, thus the previous statement that Polyox solutions are generally viscoelastic is verified for this case. The 0.9 per cent solution appeared to be considerably more viscoelastic than the 0.5 per cent solution. Although no quantitative measurements of viscoelasticity and normal stress differences were possible, viscoelastic effects should be relatively unimportant in this study because the experimental work was confined to a region of low flow rates in the bead pack.

The polymer solutions were checked very carefully throughout the experiment for any time-dependent viscosity behavior. In this regard, a Brookfield rotational viscometer failed to produce a hysteresis loop as rotational speed was varied, and data from a capillary tube viscometer showed no dependence upon length to diameter ratio. Since these are two tests which should show the existence of a time-dependency (8, 37), the Polyox solutions studied here were time-independent. Furthermore, no oxidation of the solutions was observed during the time

a given batch of polymer was on hand, so the isopropanol was effective in stabilizing the solutions from oxidation. This observation was made by measuring Brookfield viscosities of a sample on different days. All the experiments performed here were at low shear rates, so that the problem of shear degradation should not be important. To verify this, a solution was passed through a pump and discharge line at a typical rate used in the experiment. An Ostwald viscometer showed no differences between before and after pumping, so shear degradation is not significant in this range.

The shear stress-shear rate relationship for the Polyox solutions was determined from a capillary tube viscometer, which consisted simply of a solution reservoir to which different small diameter capillaries could be connected. The diameters of these capillaries were accurately determined by weighing the volume of mercury filling a given length of tube, or alternatively, by weighing the capillaries before and after filling with water. The dimensions of these capillaries are given in Appendix B.

All rheological measurements were made in an air bath thermostated at 80°F ($\pm 0.5^\circ\text{F}$). To determine the flow behavior of a given polymer solution, the solution reservoir was filled to a given level and allowed to equilibrate in the temperature bath. The time required for a quantity of solution to flow through a given capillary was then measured along with the weight of the collected sample. It should be noted that the reservoir was of sufficient diameter such that the height of fluid in it changed negligibly during the collection of a sample of size large

enough to be weighed accurately. By varying the height of fluid in the solution reservoir and using different capillaries, the flow behavior of a solution was determined over a range of shear stresses.

The data measured with the capillary viscometer consisted of the difference in heights between the level of fluid in the reservoir and the capillary exit, the magnitude of air pressure (if used) in the reservoir determined from a manometer, and the flow rate over a time interval. This data was then converted into a conventional plot of $r_0 \Delta P / 2L = \tau_w$ versus $4Q / \pi r_0^3$ (8) where

r_0 = capillary radius, cm

ΔP = overall pressure drop across capillary, dynes/cm²

L = capillary length, cm

Q = volumetric flow rate of solution, cm³/sec

τ_w = $r_0 \Delta P / 2L$ = wall shear stress, dynes/cm²

$4Q / \pi r_0^3$ = apparent wall shear rate, sec⁻¹.

Before proceeding beyond this point, it is necessary to correct the capillary data for end effects and slip at the wall (8, 37). The empirical method of Bagley as outlined by Skelland (37) was used to correct for end effects here. First, flow curves as given above were determined for the 0.9 per cent Polyox solution on three capillaries of the same radius but different lengths. At a given value of $4Q / \pi r_0^3$ for each capillary, the length to diameter ratio was plotted versus ΔP for that tube. As can be seen from Figure III-2, the resulting plot was a straight line which essentially passed through a length to diameter ratio of zero when extrapolated to zero ΔP . If significant end

Figure III-2 End Effect Correction for Capillary Viscometer

effects are present, this procedure should give an extrapolated length to diameter ratio of less than zero. The negative of this extrapolated length to diameter ratio is then added to the actual length to diameter ratio to give an effective length to diameter ratio. This graphical procedure gave a zero intercept throughout the entire range of the flow curve investigated, so that end effects were deemed negligible. The capillaries of greater length to diameter ratio were used as much as possible in the determination of flow curves.

To check for possible effective slip at the wall of a capillary, two capillaries of the same length but with different diameters were used (8). The flow curves for these two capillaries could be superimposed upon one another, so wall effects were not present in the capillary measurements.

Most of the capillary measurements were made at low values of shear stress or shear rate. In the lower measurements, evaporation of a sample during the time required to collect it could become important. An approximate evaporation rate was measured experimentally under the conditions of the air bath, and it was found that evaporation losses could be no greater than one to two per cent at the longest sample collection times.

A conventional plot of $r_0 \Delta P / 2L$ versus $4Q / \pi r_0^3$ on log-log coordinates is given in Figure III-3 for the 0.5 and 0.9 per cent Polyox solutions studied here. This capillary shear diagram may now be converted to the true shear diagram by use of the Rabinowitsch-Mooney equation. This method is given in detail by Brodkey (8). At a given value of

Figure III-3 Capillary Shear Diagrams for the Polyox Solutions

$4Q/\pi r_0^3$, the slope n' of the curve is determined where

$$n' = \frac{d \log (r_0 \Delta P / 2L)}{d \log (4Q/\pi r_0^3)} \quad . \quad (\text{III-2})$$

The apparent shear rate $4Q/\pi r_0^3$ is then converted to the true shear rate γ_w by the following equation

$$\gamma_w = \left(\frac{3n' + 1}{4n'} \right) (4Q/\pi r_0^3) \quad . \quad (\text{III-3})$$

This is the true shear rate at the wall of the capillary at the value of $r_0 \Delta P / 2L$ for which the slope was taken. This information gives the true shear stress-shear rate relationship for the solution under viscometric flow conditions. The basic shear diagrams for the 0.5 and 0.9 per cent Polyox solutions may be seen in the results in Chapter IV.

Some data were also taken on the solutions with a Brookfield rotational viscometer to further verify the capillary data. A spindle rotating in a beaker of the polymer solution was used for these measurements. The rotational data were found to be inconsistent with the capillary data in the range where they should coincide. In particular, the rotational data produced different apparent values of n' , and furthermore, these differences were of a different nature in the 0.5 and 0.9 per cent solutions. The rotational calculations were based upon the assumption of a bob in an infinite fluid arrangement. However, the geometry of the spindle and the beaker only approximated this condition and serious end effects were possible, especially for a viscoelastic fluid. In light of this and since the capillary data showed

the same shape of curves for both polymer solutions, the rotational data were disregarded.

No differences in rheological properties of the dyed and undyed Polyox solutions were observed in the capillary or rotational viscometer measurements. Furthermore, an Ostwald viscometer showed the same apparent viscosity for both dyed and undyed solutions, so that the tracer was felt to have no interaction with the viscous properties of the polymer solutions.

Tracer for Dispersion Studies

A Dupont Pontamine Sky Blue 6BX dye was employed as the tracer in this investigation. This dye has been used previously in dispersion studies (9, 16). The molecular diffusion coefficient of this dye in water has been given as 5×10^{-6} cm²/sec (17).

In solution, this dye was found to exhibit an absorbance maximum at a wavelength of 625 microns on a Bausch and Lomb Model 505 recording spectrophotometer.

A base solution of 0.001 grams of dye per milliliter of three per cent sodium chloride solvent was prepared initially. The polymer and glycerol solutions were then prepared from this base dye using a ratio of one part base dye to 35 parts total solution on a volumetric basis.

A calibration of concentration versus absorbance was made for both the glycerol and Polyox solutions by diluting the initial solutions with portions of undyed solutions and measuring the absorbance with the spectrophotometer. The resulting calibrations were found to be linear in

concentration versus absorbance as shown in Figure III-4. This is in accordance with Beer's law (30) for dilute solutions. From these calibration curves, it can be seen that the polymer solutions exhibited less absorbance than the glycerol solutions, although both were prepared to the same initial concentration of dye on a volumetric basis. The polymer possibly shifted the wavelength of maximum absorbance or consumed some of the dye initially. A quantity of dyed Polyox solution was diluted with solvent while another quantity was diluted to the same concentration with undyed polymer. The resulting absorbances of these two solutions were essentially identical, so that any consumption of dye by polymer must have been completed in the initial preparation of the solutions. It is also possible that the Polyox solutions were merely more transparent than the glycerol, thus giving rise to less absorption.

Ebach and White (16) and Carberry and Bretton (9) used this dye for a tracer in their studies of liquid dispersion in packed beds. The data of both indicated that the dye was possibly selectively adsorbed onto the surface of glass beads, although neither felt the problem was particularly serious. Carberry and Bretton noted that their data could not be explained by a single mechanism such as adsorption. Their concentration-time profiles showed considerable "tailing", thus indicating that the tracer was held up in the column due to some cause such as adsorption or stagnant areas or both. This type of behavior is often characteristic of miscible displacement experiments (12).

Figure III-4 Relationship Between Absorbance and Concentration for Tracer in Glycerol and Polyox Solutions

Determination of Breakthrough Curves by

Miscible Displacement

With a given polymer or glycerol solution in the bead pack, the apparatus was thermostated at 80°F ($\pm 0.5^\circ\text{F}$) in preparation for a displacement run. All displacements were carried out in vertical, downward flow. To displace a solution from the pack, either a Beckman Solution Metering Pump (Model No. 746) or an FMI Lab Pump (Model No. RRP2G400) was employed. Displacements were carried out in two ways, the displacement of a dyed solution with a clear solution, and the displacement of a clear solution with a dyed solution. With no fluid flowing through the pack, the discharge line from the pump which was full of the displacing liquid was connected to the top of the cell. The displacement process was then begun by merely turning on the pump. The effluent from the pack was collected in small samples with a Gilson automated fraction collector (Model TMF). The sample size was regulated by setting the rotational speed of the collector prior to the start of a run. Samples of at least 3 cc were required for colorimetric analysis, and sample sizes for most runs were between 3 and 4 cc.

After a displacement run was completed, the flow rate was determined by weighing the amount of solution used from the fluid reservoir over the entire time interval. The pumps produced a uniform rate of flow during displacement as indicated by a constant fluid level in the sample tubes. In most cases, approximately two pore volumes of displacing liquid had to be injected into the cell in order to completely remove all the initial fluid from the pack. The pack was then considered ready for another displacement.

Individual samples of the effluent from a displacement run were analyzed on the Bausch and Lomb Model 505 Spectrophotometer set at a wavelength of 625 microns. The absorbances measured were then converted to concentrations by use of the calibration curves of Figure III-4. The volume of solution injected up to a given time and the concentration of the sample ending at that time give the data required for plotting of breakthrough curves and subsequent calculation of the Peclet number.

Calculation of the Peclet Number

The method used here to calculate the dimensionless Peclet number from the miscible displacement data was developed by Bringham et al. (7). Because of its simplicity and practicality, and the fact that more elaborate procedures do not produce much better results, this method has been used extensively in miscible displacement calculations (6).

The solution to the axial dispersion model was given previously by equation II-3 as

$$\bar{C} = \frac{1}{2} \operatorname{erfc}\left(\frac{\sqrt{Pe}}{2} \left(\frac{1-T}{\sqrt{T}}\right)\right) + \frac{\sqrt{T} \exp\left(\frac{-Pe(1-T)^2}{4T}\right)}{\sqrt{\pi Pe}(1+T)} \quad (\text{II-3})$$

This equation predicts that $\bar{C}$ is linear in the argument $\frac{\sqrt{Pe}}{2} \left(\frac{1-T}{\sqrt{T}}\right)$

when plotted on an arithmetic-probability scale. This is not obvious because of the second term, but the exponential contributes only a small amount and varies in the same manner as the error function does.

Since the Peclet number is a constant in a given miscible displacement,

$\bar{C}$ is also linear in $\frac{(1 - T)}{\sqrt{T}}$ or $\frac{(T - 1)}{\sqrt{T}}$ on a probability scale.

Now the axial dispersion coefficient D is frequently defined by
(38, 33)

$$D = \frac{1}{t} \left(\frac{X_{90} - X_{10}}{3.625} \right)^2 \quad (\text{III-4})$$

where t = time, sec

X_{10} = axial distance from $\bar{C} = 0.5$ to $\bar{C} = 0.1$ at time t

X_{90} = axial distance from $\bar{C} = 0.5$ to $\bar{C} = 0.1$ at time t .

The quantity $X_{90} - X_{10}$ is generally called the zone of transition or mixing length (38). In a miscible displacement experiment the quantity $X_{90} - X_{10}$ is not actually measured since there is a time change between the appearance of the 10 per cent concentration point and the 90 per cent concentration point at the exit of the medium (40). However, Aronofsky and Heller (1) have shown mathematically that, for any Peclet number greater than 50, less than one per cent error is incurred by assuming that the mixing length measured in a miscible displacement is equal to the true mixing length $X_{90} - X_{10}$. Qualitatively, this says that the mixed zone does not change appreciably in length between the time of appearance of the 10 per cent fraction and the time of appearance of the 90 per cent fraction at the bed exit in a miscible displacement.

With the above assumption, Brigham et al. (7) placed equation III-4 in dimensionless form as

$$Pe = \left(\frac{3.625}{U_{90} - U_{10}} \right)^2 \quad (\text{III-5})$$

where $U_{90} = \frac{T - 1}{\sqrt{T}}$ when the effluent from the medium contains 90 per cent displacing fluid

$U_{10} = \frac{T - 1}{\sqrt{T}}$ when the effluent contains 10 per cent displacing fluid.

The quantity U is termed a volume modifying function by Brigham. By now plotting the experimental breakthrough data as $\frac{T - 1}{\sqrt{T}}$ versus per cent displacing fluid on arithmetic-probability paper, the Peclet number can be determined by drawing a straight line through the data points and then reading U_{90} and U_{10} for use in equation III-5.

To demonstrate the validity of this method, numerical values (12) for equation II-3 for a Peclet number of 150 were plotted in the above manner as shown on Figure III-5. The Peclet number was then calculated from this graph by reading values of U_{90} and U_{10} and using equation III-5. As shown on the graph, the calculated Peclet number was 148 which is essentially the number (150) used to prepare the plot.

Figure III-5 Plot of Solution to Axial Dispersion Model for a Peclet Number of 150

CHAPTER IV

INTERPRETATION OF RESULTS

Summary of Variables Investigated

As mentioned previously, 0.5 and 0.9 per cent solutions of Polyox and a 90 per cent solution of glycerol were used in this study. The general properties of these solutions are given in Table IV-1.

The basic shear diagrams constructed from the capillary shear data for the two polymer solutions are given in Figure IV-1. Figure IV-2 is a replot of Figure IV-1, but with apparent viscosity as the dependent variable where the apparent viscosity μ_a is defined (8) from

$$\tau_w = \mu_a (\dot{\gamma}_w) \quad (IV-1)$$

From Figure IV-2, it can be seen that the apparent viscosities of the two solutions tended to approach limiting values as the shear stresses or shear rates became lower. This "zero shear viscosity" behavior is noted to often be a characteristic of viscoelastic polymer solutions such as these (32). This approach to Newtonian behavior can also be observed from the capillary shear diagrams of Figure III-3. There, the log-log plots of shear stress versus shear rate did not have a constant slope n' , and for both solutions n' values approached one at lower shear rates. This type of rheological behavior can often be described by an Ellis model (8, 32). However, the three constants required for the Ellis model were not evaluated for the Polyox solutions since any correlations attempted in terms of the constants could become

TABLE IV-1

SUMMARY OF SOLUTION PROPERTIES

	90% Glycerol Solution	0.5% Polyox Solution	0.9% Polyox Solution
Density	1.22 g/cm ³	1.01 g/cm ³	1.013 g/cm ³
Viscosity	57 cp	see Fig. IV-2	see Fig. IV-2

Figure IV-1 Basic Shear Diagrams for the Polyox Solutions

Figure IV-2 Relationship Between Apparent Viscosity and Shear Rate for the Polyox Solutions

almost meaningless with only two fluids. For this reason, the relationship between n' and shear rate will be relied on to characterize the fluids in the remainder of this work. Figure IV-3 is a plot of n' versus shear rate for both Polyox solutions. It should be noted that the value of n' plotted is as defined by equation III-2 from the capillary shear diagram. Rigorously, this value of n' is not the true slope of a log-log plot of the basic shear diagram since the values of $4Q/\pi r_0^3$ were corrected by different amounts with equation III-3 in converting to true shear rates. However, within the limits of the data and the graphical slope-taking procedure for n' , further refinement of slopes is not actually needed.

In addition to the non-Newtonian and Newtonian fluids investigated, a major variable in the miscible displacement studies was the velocity of flow through the bead pack. Interstitial or frontal velocities ranged from 0.0028 to 0.020 cm/sec for the 0.5 per cent Polyox solution, and from 0.0015 to 0.0168 cm/sec for the 0.9 per cent Polyox solution. Velocities for the glycerol solution were comparable to these, ranging from 0.0035 to 0.029 cm/sec.

Two runs were made to determine the effect of viscosity ratio on the axial dispersion. One run was performed with a favorable viscosity ratio (displacing fluid more viscous) of 0.90, and the other was made with an unfavorable viscosity ratio of 1.05. Both runs were made with the 0.5 per cent Polyox solution at a velocity of 0.006 cm/sec. The unfavorable ratio was created by diluting the displacing fluid very slightly with solvent, while the favorable ratio was created by making up a small batch of slightly more concentrated polymer.

Figure IV-3 Relationship Between n' and Shear Rate for Polyox Solutions

Axial Dispersion Results and Discussion

Typical Breakthrough Curves

A typical breakthrough curve for the glycerol solution is shown on Figure IV-4. In this figure, the fraction of displacing fluid in the effluent from the bead bank is plotted versus dimensionless time T (the number of pore volumes of injected fluid). The curve takes on the familiar S-shape characteristic of residence time studies of this nature (18). Note that no displacing fluid appeared in the effluent until T was approximately 0.8. After this time, the displacement front reached the end of the pack, and the effluent concentration rose rather sharply towards the ultimate value of one. Towards the end of the displacement, the concentration profile began to trail off. In most runs, traces of the initial fluid were observed in the effluent until T was approximately 1.5. This "tailing" of the profile is noted to be common in miscible displacement experiments (12).

The concentration profile does not pass through the 50 per cent point at a value of $T = 1$, but is shifted slightly to the right. This caused some concern, since the solution to the axial dispersion model (equation II-3) predicts that the concentration at $T = 1$ should be slightly greater than 0.5, not less. This has been found to be true in most miscible displacement studies (6, 12). Several factors, or a combination thereof, could lead to this apparent shift in the profile. First, the sample points plotted are not point concentrations, but are average concentrations measured for a sample ending at a given value of T . The sample sizes for this particular run were 0.014 pore volumes,

Figure IV-4 Typical Breakthrough Curve for Glycerol Solution

so this plotting procedure could contribute slightly to the shift. Another obvious possibility is that the measured porosity of the pack was slightly in error. Due to the sharpness of the profile, a two per cent error in the porosity could cause the shift. Other possibilities which could cause a profile shift are channeling or bypassing of some fluid in the pack, and adsorption of the tracer material by the glass beads.

Figure IV-5 is a comparison of breakthrough curves for the previously discussed glycerol run and a run with the 0.5 per cent Polyox solution. The glycerol run was made at a slightly higher velocity. Essentially no difference in the breakthrough points of the polymer and the glycerol solutions can be seen. However, the shape of the polymer curve was considerably flatter in the upper portions which is indicative of greater mixing in the case of the polymer solution. The polymer curve began to deviate from the glycerol curve around a concentration of 0.5.

Figure IV-6 is a similar comparison for the glycerol and 0.9 per cent Polyox solutions. In this case, the polymer solution had a considerably earlier breakthrough than the glycerol solution. The entire profile was flatter for the polymer solution, again indicating a greater amount of mixing than the glycerol solution showed.

By comparing Figures IV-5 and IV-6, a difference between the 0.5 and 0.9 per cent Polyox solutions can also be seen. The 0.9 per cent Polyox exhibited earlier breakthrough, and the shape of the curve was more asymmetrical.

Figure IV-5 Comparison of Breakthrough Curves for Glycerol and 0.5 per cent Polyox Solutions

Figure IV-6 Comparison of Breakthrough Curves for Glycerol and 0.9 per cent Polyox Solutions

In both the polymer runs discussed above, the 50 per cent concentration points occurred at the same value of T as in the glycerol run. This was also observed to be true for almost every run performed in the experiment, and hence, was felt to be an indication that the experimental breakthrough data were reliable.

Typical Error Function Plots

Error function plots for the three runs discussed above are given in Figure IV-7, IV-8, and IV-9. These graphs were constructed by converting the values of T from breakthrough curves to the volume modifying function U discussed in Chapter III. Values of U were then plotted versus per cent concentration of the displacing fluid. Best straight lines were drawn through all points between approximately 5 and 95 per cent in every case. From any of the three figures, it can be seen that a straight line only approximates the data points. In each of the runs, the fluid was initially higher in concentration than predicted by the model as evidenced by the points below the straight line. These points suggest some amount of channeling or bypassing within the pack. The 0.9 per cent Polyox solution (Figure IV-9) showed considerably more of this behavior than did the glycerol or 0.5 per cent Polyox solutions. The three figures also show that the points gradually rose up above the lines in the middle region of the curves. Here, the concentration is less than that predicted by the model. This behavior could be the result of the earlier channeling, or could possibly be due to some adsorption of the dye onto the beads.

The three runs discussed and compared above were considered as typical of all the runs made. The same basic trends were observed in

Figure IV-7 Typical Error Function Plot for Glycerol Solution

Figure IV-8 Typical Error Function Plot for 0.5 per cent Polyox Solution

Figure IV-9 Typical Error Function Plot for 0.9 per cent Polyox Solution

the error function plots for all runs, but the magnitude of the differences observed varied somewhat from run to run.

Effect of Velocity on Breakthrough Profiles

Figure IV-10 shows breakthrough curves for the glycerol solution at two different velocities, 0.0035 cm/sec and 0.023 cm/sec. The two profiles are essentially superimposed upon one another, indicating no differences in dispersion for the two runs.

Figures IV-11 and IV-12 show breakthrough curves at two different velocities for the 0.5 and 0.9 per cent Polyox solutions, respectively. In both cases, the higher velocity run resulted in a flatter profile and greater axial dispersion.

Effect of Viscosity Ratio

The results of three runs performed at comparable velocities and viscosity ratios of 0.90, 1.0, and 1.05 are shown on Figure IV-13. It can be seen that the favorable ratio suppressed the dispersion somewhat, but that the slightly unfavorable ratio was essentially no different than the equal viscosity displacement. These results do not show the extreme sensitivity to viscosity ratio that was found by Brigham et al. (7). Any slight differences in viscosities of displacing and displaced polymer solutions should not be crucial in this experiment.

Correlation of Peclet Numbers

Peclet numbers for all runs were calculated from error function plots by using the method shown in Chapter III. From the best straight lines drawn through the data points, values of U were read from the

Figure IV-10 Effect of Velocity on Breakthrough Profile for Glycerol Solution

Figure IV-11 Effect of Velocity on Breakthrough Profile for 0.5 per cent Polyox Solution

Figure IV-12 Effect of Velocity on Breakthrough Profiles for 0.9 per cent Polyox Solution

Figure IV-13 Effect of Viscosity Ratio on Breakthrough Profile for 0.5 per cent Polyox Solution

lines at concentrations of 10 and 90 per cent, and the Peclet number was calculated from equation III-5. These axial Peclet numbers were then converted to particle Peclet numbers by multiplying by the ratio of particle diameter to column length. The results of these calculations for all runs are shown by Figure IV-14 where Pe_p is plotted against velocity. The data points are quite scattered, but some general trends can be detected. First, the points for glycerol, with the exception of the two at the very lowest velocities, appear to be relatively insensitive to velocity over the range investigated. However, the points for the two Polyox solutions trended downward, with the points for the 0.5 per cent Polyox falling somewhat above those for the 0.9 per cent Polyox. The points for both polymer solutions fell below those of the glycerol solution, but appeared to be approaching the glycerol points at the lower velocities. Since lower Peclet numbers is indicative of greater dispersion, this graph shows essentially the same trends as were shown on the breakthrough curves discussed earlier.

Comparison with Literature Values

Before proceeding to explain these apparent differences between polymer and glycerol runs or attempting any further correlations, it is recalled from the literature review that the Reynolds and Schmidt numbers are important in axial dispersion correlations. These quantities now need to be examined here to determine, if possible, what would have been expected for the glycerol solution and the polymer solutions if there were no differences in dispersion due to non-Newtonian behavior.

Figure IV-14 Particle Peclet Number versus Velocity
for Glycerol and Polyox
Solutions

First, the importance of axial molecular diffusion in relation to overall axial dispersion will be assessed. A typical axial Peclet number observed in the experiment was 250. With a typical velocity of 0.01 cm/sec and a bed length of 60 cm, an axial Peclet number of 250 gives an axial dispersion coefficient of 2.4×10^{-3} cm²/sec. Since the molecular diffusion coefficient of the dye in water was given as 5×10^{-6} cm²/sec, it can be seen that axial molecular diffusion is entirely negligible in relation to overall axial dispersion.

Reynolds numbers based on the particle diameter and interstitial velocity ranged from 3×10^{-4} to 20×10^{-4} for the 57 cp. glycerol solution. The Schmidt number was estimated to be 6×10^6 . This estimate was made by using the known molecular diffusion coefficient of the dye in water, and then assuming that the diffusion coefficient of the dye in glycerol is inversely proportional to the solution viscosity. This is predicted from the theories of diffusion in liquids (2), and has been used by others in estimating Schmidt numbers for liquids. No experimental dispersion data was uncovered with a Schmidt number of this magnitude, so no direct comparisons to literature values are possible. However, the work of Miller and King (27) provides an indication of what should be expected for a high Schmidt number system such as this. They state that Peclet numbers with an infinite Schmidt number should be constant with velocity in the laminar regime, and furthermore, that the magnitude of the Peclet number should be at its lowest value for this case since there is no radial molecular diffusion to dampen out axial convection. This idea has been further corroborated

by Gunn (20). It appears that the glycerol Peclet numbers taken here are in a region where the Schmidt number is effectively infinite. Obviously, if velocities became low enough this would be an oversimplification because molecular diffusion would begin to more effectively dampen out the axial dispersion. The magnitude of the glycerol Peclet numbers taken here seems to further substantiate this idea of an effectively infinite Schmidt number. The average Peclet number neglecting the two high points calculated from the glycerol runs was 0.23. This is considerably lower than a typical value of 0.5 predicted from the correlations of Chung and Wen (11) or Perkins and Johnston (31) mentioned in the literature review. Their correlations were developed mostly from data on water systems where the Schmidt number is typically 10^3 to 10^4 . In light of the discussions above, these correlations are not really applicable to this work. It is difficult to compare magnitudes of Peclet numbers taken on different porous media anyway because of the differences in types and methods of packing, etc. (21, 31), but the values observed here do not seem inconsistent with the ideas discussed above. Thus, the remainder of this work will be based on the premise that the Schmidt number for the glycerol solution is effectively infinite, so that Peclet numbers should be constant (in the absence of other mechanisms).

To determine Reynolds numbers for the non-Newtonian Polyox solutions, it is necessary to have an approximate value of the solution viscosity at a given velocity of flow. Some estimate of the shear stress or shear rate within the bead pack is therefore a must. Obviously, the shear rate in a packed bed is not a constant, but is different

in different flow channels and is also a function of position in a given channel. Since a porous medium is so complex, a geometric model of some type must be used to even approximate a shear rate. Christopher and Middleman (10) have developed an equation useful for estimating an effective shear rate for a power law fluid in a packed bed. They modeled the bed as a bundle of capillary tubes having a mean hydraulic radius and showed the following equation as an estimate of the shear rate at the wall of the "mean" capillary:

$$\gamma_w = \left(\frac{3n' + 1}{4n'} \right) \frac{12v_0}{(150k\epsilon)^{1/2}}$$

where n' = power law rheological parameter

v_0 = superficial velocity in bed, cm/sec

k = bed permeability, cm^2

ϵ = fractional bed porosity.

Although the Polyox solutions studied here did not exhibit power law behavior over a wide range of shear rates, the preceding equation was used in conjunction with the rheological data and the bed pack properties k and ϵ to estimate shear rates and then apparent viscosities. The rheological data of Figure IV-3 give the relationship between n' and shear rate for the two Polyox solutions. With values of n' and γ_w determined from this figure, equation IV-2 was solved for v_0 , thus giving an approximate relation between velocity and n' for the bead pack. This calculated relationship is shown in Figure IV-15 for both solutions. Both polymers become more non-Newtonian as velocity is

Figure IV-15 Approximate Relationship Between n' and Pore Velocity for Polyox Solutions

increased since this was the behavior observed in the experimental rheological data. At a given velocity, viscosities in the bead pack were estimated for the Polyox solutions by obtaining a value of n' from Figure IV-15, then a value of shear rate from equation IV-2, and finally obtaining a value of apparent viscosity from Figure IV-2. Reynolds numbers based on apparent viscosities defined in this way ranged from 0.9×10^{-5} to 28×10^{-5} for the 0.9 per cent Polyox and from 2×10^{-4} to 15×10^{-4} for the 0.5 per cent Polyox. These Reynolds numbers are far from the region where turbulence becomes apparent in a packed bed (2), so turbulence cannot be a factor in these results.

Schmidt numbers for the two Polyox solutions were estimated in the same manner as those for glycerol. These calculations gave approximately 10^9 and 8×10^6 as the Schmidt numbers for the 0.9 and 0.5 per cent solutions, respectively. It is conceivable that the molecular diffusion coefficient varies with shear rate (22) since the viscosity does, but the above Schmidt numbers were based on approximate zero shear viscosities of 750 and 65 cp. for the two solutions. The 0.5 per cent solution thus has a Schmidt number almost identical to that of the glycerol solution while the 0.9 per cent solution has a Schmidt number somewhat higher. The same line of reasoning about effectively infinite Schmidt numbers put forth for the glycerol solution should now apply to the Polyox solutions since the velocity ranges were equivalent for glycerol and polymer runs.

It should be noted that since the Schmidt numbers for the Polyox solutions are equivalent to or greater than that of the glycerol solution, the approximations regarding n' and shear rate discussed above

should not be critical to further analysis of the data. The velocity ranges of both glycerol and polymer were comparable, so the infinite Schmidt number approach predicts Peclet numbers that are insensitive to velocity.

Correlation with Non-Newtonian Fluid Properties

An attempt will now be made to explain the apparent differences in the Peclet numbers for the Polyox and glycerol solutions studied here.

Since the Peclet numbers for the Polyox solutions trended downward over the same approximate range of variables where the glycerol Peclet numbers remained constant, some aspect of the non-Newtonian fluid properties appears to be operative. In considering the rheological properties of the polymers, it is recalled that both solutions tended to become more non-Newtonian as shear rate or velocity in the bead pack increased (see Figure IV-15). This suggests that the variable n' might be a useful tool to explain these differences. Figure IV-16 is a plot of Peclet number versus n' as obtained from Figure IV-15. Now the glycerol points are all grouped at $n' = 1$ since the fluid is Newtonian. The points for the 0.5 and 0.9 per cent Polyox solutions are somewhat grouped, but the general trend is a decrease in Peclet number with decreasing n' . In this plot, the Peclet number is initially quite sensitive to changes in n' , but this effect appears to level out as n' becomes lower.

It is difficult to predict, even in a qualitative sense, what behavior should be occurring without a knowledge of the mechanisms

Figure IV-16 Plot of Peclet Number versus n'

which are in operation in the dispersion process. However, some mechanisms in the overall dispersion process can be theoretically predicted to be different for a non-Newtonian and a Newtonian fluid.

First, the velocity profile is known to be flatter for a shear thinning non-Newtonian fluid than for a Newtonian fluid. This mechanism should contribute to a decrease in axial dispersion in the case of a non-Newtonian fluid flowing in a tube so long as other factors remain essentially unchanged. If a highly non-Newtonian fluid with a very low value of n' were flowing through a tube, the velocity profile would approximate plug flow conditions and very little axial dispersion should be observed. This type of reasoning can partially be extended to non-Newtonian flow through a porous medium, but other mechanisms of dispersion are now operative. Furthermore, the fluid sees constantly expanding and contracting flow channels where velocity profiles would not be expected to remain fully developed.

Secondly, the different sized flow channels in a porous medium might be expected to give rise to greater relative movement in adjacent flow channels for the non-Newtonian case. This can be envisioned by first considering flow of a Newtonian fluid in two channels of the same length but different radii. If the same pressure drop is imposed across both channels, a simple application of Poiseuille's law (2) will show that the ratio of the average velocities is proportional to the square of the radius. If a non-Newtonian, power law fluid is now flowing through the same two channels, an equation analogous to Poiseuille's law may be easily developed. From this expression it can be shown that

the ratio of the average velocities in the two circular channels is proportional to $(n' + 1)/n'$. Thus for a shear thinning fluid with n' less than one, the non-Newtonian case will show greater relative movement than the Newtonian case. This type of relative movement is obviously present in a porous medium which has a distribution of sizes (and lengths) of flow channels. This relative movement, or channeling, is one mechanism which contributes to axial dispersion, and a non-Newtonian shear thinning fluid should increase the contribution of this mechanism. It is possible that this mechanism could become an overriding factor in the mixing in a highly non-uniform, or heterogeneous, porous medium. A poorly packed bed, or a region of higher permeability near the wall of a bed might be expected to manifest the channeling phenomenon for a non-Newtonian fluid. A large amount of such channeling behavior could easily alter concentration profiles in a packed bed, and a poor fit with the axial dispersion model might be obtained.

From the above discussions, it can be seen that non-Newtonian fluid properties should alter some of the mechanisms of dispersion, but the overall contribution of these changes cannot really be rationalized because of the many complexities involved. In part, the quantity n' should reflect these differences, but the functional dependence of axial dispersion on this fluid property cannot be deduced.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The two non-Newtonian Polyox solutions investigated here exhibited greater overall axial dispersion than a Newtonian glycerol solution over a comparable range of variables in an equal viscosity miscible displacement in a single glass bead pack.

As velocity of flow in the bead pack increased, Peclet numbers trended downward for the two Polyox solutions due to their increasing non-Newtonian behavior with increasing shear rate. Increased channeling, and thus greater axial dispersion, became greater at higher velocities due to the increasing non-Newtonian behavior.

Calculated Peclet numbers for the glycerol solution were relatively insensitive to velocity over a Reynolds number range of 3×10^{-4} to 20×10^{-4} . This observation, and the magnitude of the Peclet numbers (0.2-0.3) is consistent with theoretical predictions (2, 9) for a high Schmidt number system such as was investigated here.

Qualitative considerations of non-Newtonian flow in a tube have shown that some differences are to be expected between non-Newtonian and Newtonian axial dispersion. Specifically, channeling should be increased when a shear thinning fluid is flowing through a porous medium, but flatter velocities within individual channels should contribute to less axial dispersion. The channeling mechanism could become a dominant factor in the mixing process in a highly non-uniform medium.

Recommendations

Some data should be taken on the same bead pack with a water solution to further substantiate the magnitude of the Peclet numbers observed in this experiment. Different polymer solutions could also be investigated in this pack to determine the sensitivity of axial dispersion results to fluid properties.

Other bead packs, polymer solutions, and ranges of velocity should be investigated in order to extend the observations made here. Fluids which more nearly approximate power law behavior or a Bingham plastic type material could prove very interesting.

A study on the effects of packing non-uniformities and bead size distribution could be made. Non-Newtonian aspects of axial dispersion should be more prevalent in a situation such as this. Also, a study of this nature could be most valuable even for Newtonian fluids because these factors have been studied little and are the major reason for differences in results between different porous media.

Radial dispersion of non-Newtonian fluids could also be studied to more completely define the true nature of the flow occurring in a porous medium. A new apparatus would have to be designed along with more refined analysis techniques.

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NOMENCLATURE

A	- absorbance of a dyed polymer or glycerol solution, dimensionless
C	- tracer concentration, g/cm^3
C_0	- initial or reference concentration in a step or miscible displacement experiment, g/cm^3
$\bar{C}$	- C/C_0 , dimensionless concentration
D_0	- molecular diffusion coefficient, cm^2/sec
D'	- effective molecular diffusion coefficient in a porous medium, cm^2/sec
D, D_L	- overall axial dispersion coefficient, cm^2/sec
d_p	- particle diameter, cm
K	- power law consistency index, g/cm sec^{1-n}
k	- permeability of bead pack, cm^2
L	- length of porous medium or capillary tube, cm
L/D	- length to diameter ratio of a capillary tube
n	- power law flow behavior index, dimensionless
n'	- slope of log-log plot of $r_0 \Delta P / 2L$ <u>vs.</u> $4Q / \pi r_0^3$
P	- fluid mechanical probability
Pe	- $\bar{v}L/D$, dimensionless axial Peclet number
Pe_p	- $\bar{v}d_p/D$, dimensionless particle Peclet number
Q	- volumetric flow rate, cm^3/sec
Re	- $d_p \rho \bar{v} / \mu$, dimensionless particle Reynolds number
r_0	- radius of capillary tube, cm

Sc	- $\mu/\rho D_0$, dimensionless Schmidt number
T	- $\bar{v}t/L$, dimensionless time or number of pore volumes in a miscible displacement
t	- time, sec
U	- $(1 - T)/\sqrt{T}$, volume modifying function
U_{90}, U_{10}	- value of U when effluent from medium contains 90 per cent or 10 per cent displacing fluid
$\bar{v}$	- interstitial velocity in bead pack, cm/sec
v_0	- superficial velocity in bead pack, cm/sec
X	- Z/L , dimensionless length
X_{90}, X_{10}	- axial distance from $\bar{C} = 0.5$ to $\bar{C} = 0.9$ or $\bar{C} = 0.1$ at time t , cm
Z	- space coordinate in direction of flow, cm
γ_w	- true shear rate at wall of capillary, sec^{-1}
ΔP	- pressure differential across length of porous medium or a capillary tube, dynes/cm^2
ΔZ	- differential element of length in a porous medium, cm
ϵ	- fractional porosity of porous medium, dimensionless
μ	- Newtonian fluid viscosity, g/cm sec
μ_a	- true apparent viscosity of non-Newtonian fluid, g/cm sec
ρ	- fluid density, g/cm^3
σ	- heterogeneity factor for a porous medium, dimensionless
σ_v^2	- a factor to account for non-uniform velocity profiles over a bed cross-section
τ_w	- $r_0 \Delta P / 2L$, shear stress at wall of a capillary, dynes/cm^2

APPENDIX

- A. Miscible Displacement Data
- B. Rheological Data
- C. Solution to Axial Dispersion Model

APPENDIX A: Miscible Displacement Data

Run Number 1 (0.9% Polyox)

Pore Volumes	Absorbance	Tracer Concentration
0.901	0.732	0.079
0.914	0.702	0.116
0.926	0.670	0.155
0.939	0.624	0.211
0.951	0.552	0.299
0.964	0.465	0.405
0.977	0.429	0.449
0.989	0.362	0.530
1.002	0.302	0.604
1.014	0.250	0.667
1.027	0.220	0.704
1.039	0.131	0.813
1.052	0.108	0.840
1.065	0.082	0.872
1.078	0.056	0.904
1.090	0.071	0.885
1.103	0.043	0.919
1.116	0.036	0.928
1.129	0.030	0.935
1.141	0.011	0.959

Flow rate = 0.453 ml/min
Calculated length Peclet number = 306
Pore velocity = 0.00181 cm/sec

Run Number 3 (0.9% Polyox)

Pore Volumes	Absorbance	Tracer Concentration
0.857	0.782	0.982
0.869	0.768	0.965
0.881	0.756	0.950
0.893	0.740	0.931
0.906	0.729	0.917
0.918	0.702	0.884
0.930	0.667	0.842
0.942	0.615	0.778
0.954	0.572	0.726
0.966	0.530	0.675
0.978	0.481	0.615
0.991	0.460	0.589
1.003	0.357	0.463
1.015	0.324	0.423
1.027	0.270	0.357
1.039	0.228	0.306
1.051	0.192	0.262
1.063	0.159	0.222
1.075	0.120	0.174
1.100	0.069	0.112
1.124	0.049	0.088
1.136	0.035	0.071
1.160	0.028	0.062
1.184	0.013	0.044
1.244	0.013	0.044

Flow rate = 0.437 ml/min

Calculated length Peclet number = 309

Pore velocity = 0.00175 cm/sec

Run Number 5 (0.9% Polyox)

Pore Volumes	Absorbance	Tracer Concentration
0.814	0.778	0.977
0.827	0.773	0.971
0.840	0.771	0.969
0.852	0.752	0.945
0.865	0.756	0.950
0.878	0.748	0.941
0.890	0.750	0.943
0.903	0.737	0.927
0.915	0.730	0.919
0.928	0.684	0.862
0.953	0.652	0.823
0.978	0.550	0.699
1.003	0.450	0.577
1.016	0.340	0.443
1.028	0.267	0.354
1.041	0.212	0.287
1.053	0.158	0.221
1.090	0.083	0.129
1.115	0.051	0.090
1.140	0.038	0.074
1.165	0.035	0.071
1.190	0.030	0.065
1.214	0.019	0.051
1.239	0.011	0.041
1.488	0.000	0.028

Flow rate = 0.786 ml/min
 Calculated length Peclet number = 269
 Pore velocity = 0.00314 cm/sec

Run Number 6 (0.9% Polyox)

Pore Volumes	Absorbance	Tracer Concentration
0.786	0.008	0.032
0.847	0.027	0.055
0.872	0.056	0.090
0.896	0.076	0.114
0.921	0.135	0.185
0.946	0.188	0.249
0.970	0.254	0.328
0.994	0.367	0.463
1.019	0.452	0.566
1.043	0.549	0.682
1.067	0.638	0.789
1.092	0.692	0.854
1.116	0.720	0.887
1.140	0.740	0.911
1.164	0.745	0.917
1.211	0.772	0.950
1.331	0.775	0.953
1.390	0.782	0.962

Flow rate = 0.502 ml/min

Calculated length Peclet number = 242

Pore velocity = 0.00201 cm/sec

Run Number 7 (0.9% Pplyox)

Pore Volumes	Absorbance	Tracer Concentration
0.793	0.750	0.923
0.815	0.750	0.923
0.837	0.722	0.890
0.860	0.722	0.890
0.882	0.710	0.875
0.904	0.661	0.817
0.926	0.622	0.770
0.949	0.560	0.695
0.960	0.541	0.672
0.993	0.425	0.533
1.015	0.320	0.407
1.038	0.238	0.309
1.049	0.178	0.237
1.060	0.172	0.229
1.083	0.085	0.125
1.106	0.056	0.090
1.128	0.043	0.074
1.151	0.020	0.047
1.173	0.023	0.050
1.195	0.020	0.047
1.240	0.004	0.028

Flow rate = 0.465 ml/min
 Calculated length Peclet number = 170
 Pore velocity = 0.00186 cm/sec

Run Number 8 (0.9% Polyox)

Pore Volumes	Absorbance	Tracer Concentration
0.804	0.016	0.042
0.821	0.040	0.071
0.838	0.068	0.104
0.855	0.079	0.118
0.872	0.112	0.157
0.888	0.115	0.161
0.905	0.150	0.203
0.922	0.208	0.273
0.939	0.261	0.336
0.956	0.325	0.413
0.973	0.380	0.479
0.990	0.440	0.556
1.007	0.485	0.605
1.024	0.569	0.706
1.041	0.607	0.752
1.057	0.668	0.825
1.074	0.720	0.887
1.091	0.741	0.913
1.108	0.766	0.943
1.125	0.775	0.953
1.142	0.778	0.957
1.159	0.782	0.962
1.334	0.795	0.977

Flow rate = 0.710 ml/min
Calculated length Peclet number = 205
Pore velocity = 0.00284 cm/sec

Run Number 10 (0.9% Polyox)

Pore Volumes	Absorbance	Tracer Concentration
0.825	0.009	0.034
0.850	0.012	0.037
0.876	0.028	0.056
0.901	0.045	0.077
0.927	0.083	0.122
0.992	0.139	0.190
1.017	0.217	0.283
1.030	0.270	0.347
1.043	0.348	0.441
1.055	0.415	0.521
1.068	0.495	0.617
1.081	0.565	0.701
1.093	0.623	0.771
1.106	0.675	0.833
1.158	0.720	0.887
1.171	0.740	0.911
1.183	0.750	0.923
1.209	0.780	0.959
1.234	0.805	0.989
1.259	0.807	0.992
1.284	0.809	0.994
1.347	0.809	0.994

Flow rate = 0.828 ml/min

Calculated length Peclet number = 253

Pore velocity = 0.00331 cm/sec

Run Number 11 (0.9% Polyox)

Pore Volumes	Absorbance	Tracer Concentration
0.824	0.795	0.977
0.838	0.769	0.946
0.866	0.742	0.914
0.894	0.724	0.892
0.921	0.680	0.839
0.949	0.623	0.771
0.977	0.535	0.665
1.006	0.420	0.527
1.020	0.370	0.467
1.034	0.300	0.383
1.049	0.252	0.325
1.063	0.199	0.262
1.077	0.147	0.199
1.092	0.113	0.158
1.106	0.075	0.113
1.121	0.054	0.088
1.136	0.031	0.060
1.151	0.028	0.056
1.165	0.013	0.038
1.255	0.000	0.023

Flow rate = 0.605 ml/min
Calculated length Peclet number = 256
Pore velocity = 0.00242 cm/sec

Run Number 12 (0.9% Polyox)

Pore Volumes	Absorbance	Tracer Concentration
0.796	0.004	0.028
0.810	0.022	0.049
0.824	0.038	0.068
0.838	0.048	0.080
0.851	0.050	0.083
0.865	0.070	0.107
0.879	0.088	0.128
0.893	0.104	0.148
0.907	0.121	0.168
0.921	0.145	0.197
0.935	0.162	0.217
0.949	0.210	0.275
0.963	0.245	0.317
0.976	0.298	0.381
0.990	0.336	0.426
1.005	0.398	0.501
1.019	0.445	0.557
1.033	0.479	0.598
1.047	0.552	0.686
1.061	0.598	0.741
1.076	0.639	0.790
1.090	0.680	0.839
1.104	0.720	0.887
1.118	0.742	0.914
1.132	0.778	0.957
1.162	0.805	0.989

Flow rate = 1.723 ml/min
 Calculated length Peclet number = 231
 Pore velocity = 0.00689 cm/sec

Run Number 13 (0.9% Polyox)

Pore Volumes	Absorbance	Tracer Concentration
0.683	0.778	0.977
0.713	0.782	0.982
0.775	0.750	0.943
0.806	0.772	0.970
0.822	0.750	0.943
0.837	0.745	0.937
0.868	0.745	0.937
0.900	0.700	0.882
0.915	0.700	0.882
0.931	0.670	0.845
0.946	0.648	0.819
0.962	0.613	0.776
0.978	0.567	0.720
0.994	0.520	0.662
1.009	0.448	0.574
1.025	0.373	0.483
1.041	0.278	0.367
1.057	0.281	0.371
1.072	0.220	0.296
1.088	0.176	0.243
1.104	0.122	0.177
1.120	0.095	0.144
1.136	0.073	0.117
1.152	0.047	0.085
1.183	0.029	0.063
1.279	0.021	0.054
1.439	0.014	0.045
1.601	0.005	0.034
1.760	0.000	0.028

Flow rate = 4.015 ml/min
Calculated length Peclet number = 175
Pore velocity = 0.01605 cm/sec

Run Number 14 (0.9% Polyox)

Pore Volumes	Absorbance	Tracer Concentration
0.763	0.042	0.073
0.797	0.050	0.083
0.831	0.088	0.128
0.866	0.118	0.164
0.900	0.159	0.214
0.935	0.200	0.263
0.969	0.271	0.348
0.987	0.312	0.397
1.004	0.375	0.473
1.021	0.411	0.516
1.039	0.461	0.576
1.056	0.500	0.623
1.074	0.553	0.687
1.091	0.600	0.743
1.109	0.640	0.791
1.126	0.670	0.827
1.144	0.715	0.881
1.162	0.748	0.921
1.179	0.768	0.945
1.197	0.771	0.947
1.233	0.780	0.959
1.268	0.780	0.959
1.322	0.808	0.993

Flow rate = 4.208 ml/min
Calculated length Peclet number = 150
Pore velocity = 0.01683 cm/sec

Run Number 15 (0.5% Polyox)

Pore Volumes	Absorbance	Tracer Concentration
0.787	0.743	0.991
0.853	0.724	0.966
0.879	0.695	0.927
0.905	0.673	0.898
0.918	0.668	0.891
0.931	0.649	0.866
0.943	0.645	0.861
0.956	0.571	0.762
0.981	0.525	0.701
0.994	0.501	0.669
1.006	0.414	0.554
1.019	0.404	0.541
1.031	0.355	0.476
1.044	0.322	0.432
1.056	0.266	0.357
1.081	0.211	0.284
1.093	0.181	0.244
1.118	0.135	0.183
1.142	0.101	0.138
1.167	0.060	0.084
1.192	0.034	0.049
1.217	0.022	0.033
1.280	0.011	0.018

Flow rate = 4.008 ml/min

Calculated length Peclet number = 231

Pore velocity = 0.01603 cm/sec

Run Number 16 (0.5% Polyox)

Pore Volumes	Absorbance	Tracer Concentration
0.758	0.011	0.018
0.824	0.034	0.048
0.857	0.059	0.080
0.890	0.098	0.130
0.923	0.140	0.184
0.957	0.208	0.272
0.989	0.278	0.362
1.006	0.318	0.413
1.018	0.368	0.477
1.035	0.421	0.546
1.051	0.473	0.613
1.068	0.522	0.676
1.084	0.568	0.735
1.117	0.643	0.832
1.150	0.709	0.916
1.183	0.736	0.951
1.216	0.755	0.976
1.249	0.754	0.974
1.315	0.774	1.000

Flow rate = 5.111 ml/min
Calculated length Peclet number = 188
Pore velocity = 0.02044 cm/sec

Run Number 17 (0.5% Polyox)

Pore Volumes	Absorbance	Tracer Concentration
0.723	0.773	0.999
0.825	0.745	0.963
0.850	0.728	0.941
0.875	0.700	0.905
0.900	0.692	0.895
0.926	0.660	0.853
0.951	0.621	0.803
0.976	0.563	0.729
0.989	0.528	0.683
1.001	0.494	0.640
1.014	0.449	0.582
1.027	0.391	0.507
1.039	0.359	0.466
1.052	0.311	0.404
1.065	0.262	0.341
1.077	0.221	0.288
1.090	0.185	0.242
1.103	0.151	0.198
1.115	0.118	0.156
1.128	0.093	0.123
1.153	0.070	0.094
1.179	0.040	0.055
1.204	0.023	0.033
1.230	0.040	0.055
1.357	0.020	0.029

Flow rate = 3.859 ml/min
Calculated length Peclet number = 200
Pore velocity = 0.01543 cm/sec

Run Number 18 (0.5% Polyox)

Pore Volumes	Absorbance	Tracer Concentration
0.752	0.009	0.015
0.814	0.034	0.048
0.839	0.049	0.067
0.864	0.079	0.106
0.889	0.104	0.138
0.915	0.151	0.198
0.940	0.189	0.247
0.965	0.257	0.335
0.978	0.315	0.410
0.991	0.343	0.446
1.003	0.391	0.508
1.016	0.434	0.563
1.029	0.473	0.613
1.042	0.528	0.684
1.055	0.569	0.737
1.067	0.602	0.780
1.080	0.644	0.834
1.106	0.708	0.916
1.131	0.745	0.964
1.157	0.753	0.974
1.196	0.755	0.978
1.261	0.772	0.999
1.390	0.764	0.989

Flow rate = 3.925 ml/min
Calculated length Peclet number = 278
Pore velocity = 0.01570 cm/sec

Run Number 19 (0.5% Polyox)

Pore Volumes	Absorbance	Tracer Concentration
0.863	0.754	0.974
0.894	0.725	0.937
0.925	0.683	0.883
0.956	0.637	0.824
0.972	0.589	0.762
0.987	0.532	0.689
1.003	0.473	0.613
1.019	0.415	0.538
1.030	0.351	0.456
1.046	0.288	0.375
1.061	0.244	0.318
1.077	0.194	0.253
1.093	0.144	0.189
1.109	0.103	0.136
1.124	0.092	0.122
1.140	0.077	0.103
1.172	0.045	0.062
1.203	0.038	0.053
1.234	0.023	0.033
1.393	0.021	0.031
1.551	0.016	0.024
1.710	0.009	0.015

Flow rate = 1.255 ml/min
Calculated length Peclet number = 324
Pore velocity = 0.00502 cm/sec

Run Number 20 (0.5% Polyox)

Pore Volumes	Absorbance	Tracer Concentration
0.795	0.022	0.032
0.828	0.035	0.049
0.860	0.069	0.093
0.893	0.104	0.138
0.926	0.151	0.198
0.958	0.205	0.268
0.991	0.288	0.375
1.007	0.332	0.431
1.023	0.383	0.497
1.040	0.435	0.564
1.056	0.484	0.627
1.072	0.533	0.690
1.088	0.589	0.762
1.105	0.638	0.825
1.121	0.683	0.883
1.137	0.709	0.916
1.170	0.744	0.962
1.203	0.753	0.973
1.284	0.763	0.986
1.449	0.765	0.989
1.782	0.773	0.999

Flow rate = 1.339 ml/min
Calculated length Peclet number = 258
Pore velocity = 0.00536 cm/sec

Run Number 21 (0.5% Polyox)

Pore Volumes	Absorbance	Tracer Concentration
0.852	0.746	0.995
0.885	0.719	0.959
0.919	0.683	0.911
0.952	0.622	0.830
0.969	0.571	0.762
0.985	0.533	0.712
1.002	0.465	0.622
1.019	0.400	0.535
1.035	0.330	0.442
1.052	0.267	0.359
1.069	0.208	0.280
1.086	0.154	0.208
1.102	0.109	0.149
1.119	0.091	0.125
1.153	0.060	0.084
1.186	0.032	0.046
1.220	0.028	0.041
1.253	0.025	0.037
1.287	0.020	0.030
1.405	0.016	0.025
1.575	0.014	0.022

Flow rate = 1.376 ml/min
Calculated length Peclet number = 298
Pore velocity = 0.00550 cm/sec

Run Number 22 (0.5% Polyox)

Pore Volumes	Absorbance	Tracer Concentration
0.802	0.01	0.017
0.817	0.02	0.030
0.832	0.03	0.043
0.848	0.045	0.062
0.863	0.060	0.082
0.878	0.075	0.101
0.893	0.095	0.128
0.908	0.095	0.128
0.924	0.126	0.168
0.939	0.158	0.210
0.954	0.193	0.255
0.969	0.212	0.280
0.985	0.253	0.333
1.000	0.300	0.395
1.015	0.360	0.473
1.030	0.388	0.509
1.046	0.436	0.572
1.061	0.484	0.634
1.077	0.545	0.714
1.091	0.595	0.779
1.107	0.638	0.835
1.122	0.673	0.880
1.137	0.708	0.926
1.152	0.727	0.951
1.168	0.738	0.965
1.183	0.752	0.983
1.351	0.762	0.996

Flow rate = 2.490 ml/min
Calculated length Peclet number = 213
Pore velocity = 0.00996 cm/sec

Run Number 23 (0.5% Polyox)

Pore Volumes	Absorbance	Tracer Concentration
0.792	0.742	0.990
0.865	0.721	0.962
0.880	0.685	0.914
0.924	0.655	0.874
0.939	0.615	0.821
0.953	0.582	0.777
0.968	0.540	0.721
0.983	0.530	0.708
0.997	0.450	0.602
1.012	0.415	0.555
1.027	0.368	0.493
1.041	0.330	0.442
1.056	0.286	0.384
1.071	0.228	0.307
1.085	0.188	0.254
1.100	0.148	0.200
1.115	0.121	0.165
1.129	0.090	0.123
1.144	0.078	0.107
1.159	0.062	0.086
1.188	0.032	0.046
1.305	0.020	0.030
1.613	0.012	0.020

Flow rate = 2.581 ml/min
Calculated length Peclet number = 240
Pore velocity = 0.01032 cm/sec

Run Number 24 (0.5% Polyox)

Pore Volumes	Absorbance	Tracer Concentration
0.828	0.028	0.039
0.843	0.040	0.054
0.858	0.060	0.079
0.873	0.068	0.089
0.888	0.085	0.110
0.903	0.095	0.123
0.918	0.125	0.161
0.933	0.143	0.183
0.949	0.186	0.237
0.964	0.222	0.282
0.979	0.270	0.342
0.994	0.305	0.386
1.009	0.365	0.462
1.024	0.418	0.528
1.039	0.470	0.593
1.054	0.535	0.675
1.069	0.585	0.738
1.084	0.615	0.775
1.099	0.650	0.819
1.114	0.710	0.895
1.129	0.740	0.932
1.160	0.752	0.947
1.190	0.775	0.976
1.341	0.785	0.989

Flow rate = 2.630 ml/min
Calculated length Peclet number = 237
Pore velocity = 0.01052 cm/sec

Run Number 25 (0.5% Polyox)

Pore Volumes	Absorbance	Tracer Concentration
0.816	0.772	0.972
0.850	0.752	0.947
0.883	0.708	0.892
0.917	0.681	0.858
0.950	0.629	0.793
0.984	0.556	0.701
1.001	0.488	0.616
1.018	0.430	0.543
1.035	0.375	0.474
1.052	0.300	0.380
1.069	0.246	0.312
1.086	0.198	0.252
1.103	0.152	0.194
1.120	0.110	0.142
1.137	0.082	0.107
1.154	0.065	0.085
1.171	0.040	0.054
1.188	0.035	0.048
1.222	0.020	0.029
1.323	0.015	0.022
1.664	0.010	0.016

Flow rate = 3.765 ml/min
Calculated length Peclet number = 222
Pore velocity = 0.01506 cm/sec

Run Number 26 (0.5% Polyox)

Pore Volumes	Absorbance	Tracer Concentration
0.817	0.027	0.037
0.832	0.030	0.041
0.848	0.040	0.054
0.863	0.055	0.073
0.879	0.077	0.100
0.895	0.090	0.116
0.926	0.135	0.173
0.942	0.154	0.197
0.957	0.192	0.244
0.973	0.250	0.317
0.989	0.300	0.380
1.004	0.345	0.436
1.020	0.378	0.477
1.035	0.437	0.551
1.067	0.558	0.703
1.090	0.610	0.768
1.106	0.647	0.815
1.122	0.692	0.871
1.138	0.725	0.912
1.153	0.747	0.940
1.169	0.765	0.962
1.184	0.774	0.974
1.358	0.785	0.988
1.515	0.795	1.000

Flow rate = 3.515 ml/min
Calculated length Peclet number = 228
Pore velocity = 0.01405 cm/sec

Run Number 27 (0.5% Polyox)

Pore Volumes	Absorbance	Tracer Concentration
0.860	0.748	0.947
0.889	0.720	0.912
0.919	0.692	0.876
0.933	0.670	0.849
0.948	0.652	0.826
0.963	0.618	0.783
0.977	0.595	0.754
0.992	0.558	0.707
1.007	0.508	0.644
1.022	0.456	0.579
1.036	0.398	0.506
1.051	0.335	0.426
1.066	0.280	0.357
1.081	0.233	0.298
1.095	0.180	0.231
1.110	0.152	0.195
1.125	0.125	0.161
1.139	0.082	0.107
1.154	0.060	0.079
1.184	0.045	0.060
1.228	0.025	0.035
1.301	0.018	0.026
1.448	0.012	0.019
1.595	0.005	0.010

Flow rate = 3.601 ml/min
Calculated length Peclet number = 228
Pore velocity = 0.01440 cm/sec

Run Number 28 (0.5% Polyox)

Pore Volumes	Absorbance	Tracer Concentration
0.886	0.728	0.920
0.915	0.676	0.854
0.930	0.655	0.828
0.944	0.635	0.803
0.959	0.595	0.752
0.973	0.558	0.706
0.988	0.515	0.652
1.002	0.468	0.592
1.017	0.418	0.530
1.031	0.350	0.444
1.046	0.268	0.341
1.060	0.230	0.293
1.075	0.172	0.220
1.090	0.120	0.155
1.104	0.110	0.142
1.119	0.080	0.104
1.134	0.062	0.082
1.148	0.052	0.069
1.163	0.050	0.067
1.177	0.040	0.054
1.251	0.020	0.029
1.324	0.012	0.019

Flow rate = 1.201 ml/min
Calculated length Peclet number = 328
Pore velocity = 0.00480 cm/sec

Run Number 29 (0.5% Polyox)

Pore Volumes	Absorbance	Tracer Concentration
0.836	0.018	0.027
0.864	0.035	0.049
0.892	0.057	0.078
0.906	0.062	0.084
0.948	0.131	0.173
0.975	0.212	0.278
0.989	0.247	0.323
1.003	0.296	0.387
1.017	0.333	0.435
1.031	0.385	0.502
1.044	0.430	0.560
1.058	0.492	0.640
1.072	0.522	0.679
1.086	0.563	0.732
1.100	0.613	0.797
1.113	0.650	0.845
1.127	0.680	0.884
1.141	0.720	0.935
1.155	0.730	0.948
1.187	0.748	0.972
1.256	0.752	0.977
1.535	0.763	0.991

Flow rate = 0.687 ml/min
Calculated length Peclet number = 322
Pore velocity = 0.00275 cm/sec

Run Number 30 (0.5% Polyox)

Pore Volumes	Absorbance	Tracer Concentration
0.816	0.750	0.974
0.863	0.742	0.964
0.911	0.692	0.897
0.943	0.638	0.829
0.958	0.600	0.780
0.974	0.552	0.718
0.990	0.512	0.666
1.005	0.450	0.586
1.021	0.440	0.573
1.037	0.332	0.433
1.052	0.282	0.369
1.068	0.228	0.299
1.084	0.183	0.241
1.100	0.150	0.198
1.115	0.100	0.133
1.131	0.080	0.107
1.146	0.067	0.090
1.162	0.050	0.068
1.177	0.032	0.045
1.208	0.028	0.040
1.255	0.016	0.024
1.332	0.015	0.023
1.408	0.005	0.010
1.565	0.000	0.004

Flow rate = 1.549 ml/min
 Calculated length Peclet number = 227
 Unfavorable viscosity ratio = 1.05
 Pore velocity = 0.00620 cm/sec

Run Number 31 (0.5% Polyox)

Pore Volumes	Absorbance	Tracer Concentration
0.823	0.015	0.023
0.899	0.062	0.082
0.914	0.092	0.119
0.929	0.108	0.139
0.944	0.142	0.182
0.960	0.180	0.230
0.975	0.230	0.293
0.990	0.292	0.371
1.005	0.338	0.428
1.020	0.420	0.509
1.035	0.455	0.575
1.050	0.520	0.657
1.066	0.578	0.730
1.081	0.638	0.805
1.096	0.668	0.843
1.111	0.700	0.883
1.126	0.718	0.906
1.141	0.735	0.927
1.156	0.748	0.944
1.171	0.755	0.952
1.187	0.755	0.952
1.277	0.780	0.984
1.353	0.775	0.977
1.504	0.785	0.990

Flow rate = 1.555 ml/min
Calculated length Peclet number = 356
Pore velocity = 0.00622 cm/sec

Run Number 32 (0.5% Polyox)

Pore Volumes	Absorbance	Tracer Concentration
0.853	0.774	0.976
0.882	0.746	0.941
0.912	0.719	0.907
0.941	0.661	0.834
0.956	0.610	0.770
0.970	0.557	0.704
0.985	0.496	0.627
1.000	0.409	0.518
1.015	0.337	0.427
1.029	0.271	0.344
1.044	0.213	0.271
1.059	0.157	0.200
1.073	0.124	0.159
1.088	0.109	0.141
1.118	0.073	0.095
1.147	0.048	0.064
1.177	0.034	0.046
1.206	0.034	0.046
1.250	0.025	0.035
1.323	0.021	0.030
1.471	0.013	0.020
1.617	0.013	0.020

Flow rate = 1.519 ml/min
 Calculated length Peclet number = 466
 Favorable viscosity ratio = 0.90
 Pore velocity = 0.00607 cm/sec

Run Number 4G (Glycerol Solution)

Pore Volumes	Absorbance	Tracer Concentration
0.862	0.849	0.956
0.887	0.816	0.918
0.899	0.794	0.893
0.911	0.786	0.884
0.936	0.749	0.842
0.960	0.668	0.751
0.973	0.622	0.699
0.985	0.582	0.653
0.997	0.528	0.592
1.010	0.469	0.525
1.022	0.418	0.468
1.034	0.356	0.397
1.047	0.308	0.343
1.059	0.245	0.272
1.071	0.204	0.225
1.084	0.159	0.174
1.096	0.128	0.139
1.108	0.099	0.106
1.133	0.053	0.054
1.158	0.032	0.030
1.183	0.027	0.025
1.208	0.014	0.010
1.232	0.017	0.013
1.385	0.010	0.005

Flow rate = 2.341 ml/min

Calculated length Peclet number = 328

Viscosity = 57 cp.

Pore velocity = 0.00936 cm/sec

Run Number 5G (Glycerol Solution)

Pore Volumes	Absorbance	Tracer Concentration
0.830	0.017	0.013
0.853	0.024	0.021
0.876	0.051	0.052
0.899	0.077	0.081
0.922	0.108	0.116
0.945	0.144	0.157
0.967	0.224	0.248
0.979	0.268	0.298
0.990	0.315	0.351
1.002	0.367	0.410
1.013	0.421	0.471
1.024	0.478	0.536
1.036	0.535	0.600
1.047	0.602	0.676
1.058	0.644	0.724
1.070	0.692	0.778
1.081	0.728	0.819
1.092	0.765	0.861
1.104	0.797	0.897
1.115	0.818	0.921
1.126	0.829	0.933
1.149	0.851	0.958
1.206	0.877	0.987
1.263	0.887	0.999

Flow rate = 0.863 ml/min
 Calculated length Peclet number = 388
 Viscosity = 57 cp.
 Pore velocity = 0.00345 cm/sec

Run Number 6G (Glycerol Solution)

Pore Volumes	Absorbance	Tracer Concentration
0.864	0.850	0.957
0.892	0.817	0.920
0.919	0.784	0.882
0.960	0.683	0.768
0.974	0.637	0.716
0.988	0.577	0.648
1.001	0.522	0.585
1.015	0.445	0.498
1.029	0.379	0.423
1.043	0.318	0.354
1.057	0.264	0.293
1.070	0.207	0.229
1.084	0.158	0.173
1.098	0.110	0.119
1.112	0.090	0.096
1.126	0.068	0.071
1.139	0.052	0.053
1.153	0.041	0.040
1.181	0.023	0.020
1.208	0.019	0.016
1.236	0.001	0.000
1.306	0.005	0.000
1.375	0.017	0.013

Flow rate = 5.604 ml/min
Calculated length Peclet number = 357
Viscosity = 57 cp.
Pore velocity = 0.02241 cm/sec

Run Number 7G (Glycerol Solution)

Pore Volumes	Absorbance	Tracer Concentration
0.811	0.010	0.005
0.838	0.019	0.016
0.866	0.028	0.026
0.894	0.068	0.071
0.907	0.075	0.079
0.935	0.130	0.141
0.949	0.175	0.192
0.963	0.227	0.251
0.977	0.284	0.316
0.991	0.329	0.367
1.004	0.409	0.456
1.018	0.479	0.537
1.032	0.544	0.610
1.046	0.603	0.677
1.060	0.661	0.743
1.074	0.718	0.807
1.088	0.754	0.848
1.102	0.795	0.895
1.116	0.817	0.920
1.129	0.828	0.932
1.143	0.850	0.957
1.171	0.862	0.970
1.227	0.863	0.972
1.366	0.874	0.984

Flow rate = 5.674 ml/min
Calculated length Peclet number = 384
Viscosity = 57 cp.
Pore velocity = 0.02269 cm/sec

Run Number 8G (Glycerol Solution)

Pore Volumes	Absorbance	Tracer Concentration
0.865	0.862	0.970
0.893	0.838	0.943
0.921	0.795	0.895
0.950	0.735	0.827
0.964	0.685	0.770
0.978	0.645	0.725
0.993	0.583	0.654
1.007	0.505	0.566
1.021	0.440	0.492
1.035	0.368	0.411
1.049	0.312	0.347
1.064	0.248	0.275
1.078	0.184	0.202
1.092	0.147	0.161
1.106	0.108	0.116
1.121	0.079	0.084
1.135	0.057	0.059
1.149	0.044	0.044
1.178	0.031	0.029
1.206	0.010	0.005
1.291	0.013	0.009
1.433	0.010	0.005

Flow rate = 2.505 ml/min
Calculated length Peclet number = 396
Viscosity = 57 cp.
Pore velocity = 0.0100 cm/sec

Run Number 9G (Glycerol Solution)

Pore Volumes	Absorbance	Tracer Concentration
0.809	0.000	0.000
0.837	0.028	0.032
0.865	0.040	0.045
0.893	0.070	0.079
0.927	0.140	0.158
0.961	0.240	0.270
0.994	0.420	0.472
1.029	0.598	0.672
1.061	0.740	0.832
1.097	0.840	0.944
1.131	0.862	0.969

Flow rate = 6.96 ml/min
Calculated length Peclet number = 414
Viscosity = 77 cp.
Pore velocity = 0.00291 cm/sec

APPENDIX B: Rheological Data

Specific Information on the Polyox Water-Soluble
Resin Used in this Investigation

Type: WSR-301

Molecular Wt.: 4,000,000 (approx.)

Sp. Gr.: 1.21 (approx.)

Lot Number: W-1227-A-01

Dimensions of Capillaries Used for
Rheological Measurements

Capillary Number	Length	Radius
1	38.1 cm	0.0484 cm
2	28.65 cm	0.0485 cm
3	20.3 cm	0.0485 cm
4	26.55 cm	0.0485 cm
5*	26.55 cm	0.03559 cm

*straight glass capillary, all others are stainless steel tubing

Capillary Shear Data for 0.9 per cent
Polyox Solution

Dyed Polymer

$\frac{r_o \Delta P}{2L} \left(\frac{\text{dynes}}{\text{cm}^2} \right)$	$\frac{4Q}{\pi r_o^3} (\text{sec}^{-1})$
4.97	0.688
6.44	0.935
9.34	1.6
9.34	1.69
12.8	2.76
25.5	7.76
33.5	15.05
38.05	18.7
47.1	28.0

Undyed Polymer

10.02	1.65
12.99	2.68
26.85	8.92
26.85	8.95
37.9	19.7
38.7	19.7
49.7	31.1

Data taken with capillaries 1, 2, and 3
Temperature = 80°F

Capillary Shear Data for 0.5 per cent
Polyox Solution

$\frac{r_o}{2} \frac{\Delta P}{L} \left(\frac{\text{dynes}}{\text{cm}^2} \right)$	$\frac{4Q}{\pi r_o^3} \text{ (sec}^{-1}\text{)}$
1.6	2.5
3.6	6.3
5.12	10.44
5.12	10.66
6.45	10.84
6.45	10.48
6.96	15.0
6.96	14.37
8.03	15.32
8.03	14.77
8.79	19.0
8.79	19.07
25.48	79.8
25.56	80.78
25.56	80.31
25.73	84.04

Data taken with capillaries 1 and 2
Temperature = 80°F

APPENDIX C: Solution to Axial Dispersion Model

Solution to Axial Dispersion Model

In dimensionless form, the equation and boundary conditions are:

$$\frac{1}{Pe} \frac{\partial^2 \bar{C}}{\partial X^2} - \frac{\partial \bar{C}}{\partial X} = \frac{\partial \bar{C}}{\partial T}$$

$$X = 0, \bar{C} = 1$$

$$X \rightarrow \infty, \bar{C} \rightarrow 0$$

$$\bar{C}(X, 0) = 0 \quad .$$

By taking the Laplace transform of the equation with respect to T , the following ordinary differential equation may be obtained

$$\frac{1}{Pe} \frac{d^2 C'}{dX^2} - \frac{dC'}{dX} - SC' = 0$$

where C' denotes the transformed $\bar{C}$. The solution for C' is then

$$C' = A_1 \exp(m_1 X) + A_2 \exp(m_2 X)$$

where

$$m_{1,2} = \frac{Pe}{2} \left(1 \pm \sqrt{1 + \frac{4S}{Pe}} \right) \quad .$$

But for the solution to remain bounded as X approaches infinity, the positive root must vanish leaving

$$C' = A_1 \exp \frac{Pe}{2} \left(1 - \sqrt{1 + \frac{4S}{Pe}} \right) X \quad .$$

The constant A_1 is evaluated by noting that at $X = 0$, $\bar{C} = 1$ so that the Laplace of $\bar{C}$ is $C' = 1/S$. Then we have

$$1/S = A_1 \exp(0) = A_1 \quad .$$

Substitution for A_1 gives

$$C' = \frac{1}{S} \exp \frac{\sqrt{Pe}}{2} \left(1 - \sqrt{1 + \frac{4S}{Pe}} \right) X \quad .$$

The above equation must now be inverted to obtain the solution for $\bar{C}$. The inversion may be accomplished by use of the convolution and shifting theorems (23). The resulting expression is

$$\bar{C} = \exp\left(\frac{PeX}{2}\right) \int_0^T \frac{\sqrt{Pe} X}{2\sqrt{\pi T^3}} \exp\left(-\frac{PeX^2}{4T} - \frac{PeT}{4}\right) dT \quad .$$

By making the substitutions $\alpha = Pe X/2$, $\beta^2 = Pe/4$, and performing the manipulations given in equations Viii through Xii on page 299 of reference (23), the preceeding equation may be simplified and rearranged into the following form after changing back into the original variables:

$$\bar{C} = \frac{1}{2} \left(\operatorname{erfc} \frac{\sqrt{Pe}}{2} \left(\frac{X - T}{\sqrt{T}} \right) \right) + \exp(PeX) \operatorname{erfc} \frac{\sqrt{Pe}}{2} \left(\frac{X + T}{\sqrt{T}} \right)$$

where erfc is the complimentary error function (23).

Now we are interested in the concentration $\bar{C}$ at the bed exit where $Z = L$ and $X = L/L = 1$. With this stipulation we then have

$$\bar{C} = \frac{1}{2} \left(\operatorname{erfc}\left(-\frac{\sqrt{Pe}}{2} \frac{(1 - T)}{\sqrt{T}}\right) + \exp(Pe) \operatorname{erfc}\left(-\frac{\sqrt{Pe}}{2} \frac{(1 + T)}{\sqrt{T}}\right) \right) .$$

The second term within the brackets above is very difficult to evaluate accurately due to the generally large values of the exponential term and the vanishingly small values of the erfc term, but the expression may be approximated (12) by the following asymptotic form which is accurate within about 0.5 per cent:

$$\exp(Pe) \operatorname{erfc}\left(-\frac{\sqrt{Pe}}{2} \frac{(1 + T)}{\sqrt{T}}\right) = \frac{\sqrt{T} \exp}{\sqrt{\pi Pe}(1 + T)} \left(\frac{-Pe(1 - T)^2}{4T} \right) .$$

The final form of the solution is then

$$\bar{C} = \frac{1}{2} \operatorname{erfc}\left(-\frac{\sqrt{Pe}}{2} \frac{(1 - T)}{\sqrt{T}}\right) + \frac{\sqrt{T} \exp}{\sqrt{\pi Pe}(1 + T)} \left(\frac{-Pe(1 - T)^2}{4T} \right) .$$