Dispersion in Laminar Flow of Non-Newtonian Fluids

Subhash N. Shah

Follow this and additional works at: https://digitalrepository.unm.edu/cbe_etds

Part of the Chemical Engineering Commons
THE UNIVERSITY OF NEW MEXICO
ALBUQUERQUE, NEW MEXICO 87106

POLICY ON USE OF THESIS AND DISSERTATIONS

Unpublished theses and dissertations accepted for master's and doctor's
degrees and deposited in the University of New Mexico Library are open to
the public for inspection and reference work. They are to be used only with
due regard to the rights of the authors. The work of other authors should
always be given full credit. Avoid quoting in amounts, over and beyond
scholarly needs, such as might impair or destroy the property rights and
financial benefits of another author.

To afford reasonable safeguards to authors, and consistent with the above
principles, anyone quoting from theses and dissertations must observe the
following conditions:

1. Direct quotations during the first two years after completion may be
   made only with the written permission of the author.

2. After a lapse of two years, theses and dissertations may be quoted
   without specific prior permission in works of original scholarship
   provided appropriate credit is given in the case of each quotation.

3. Quotations that are complete units in themselves (e.g., complete
   chapters or sections) in whatever form they may be reproduced and
   quotations of whatever length presented as primary material for their
   own sake (as in anthologies or books of readings) ALWAYS require
   consent of the authors.

4. The quoting author is responsible for determining "fair use" of mate-
   rial he uses.

This thesis/dissertation by Subhash N. Shah has been
used by the following persons whose signatures attest their acceptance of
the above conditions. (A library which borrows this thesis/dissertation for
use by its patrons is expected to secure the signature of each user.)

NAME AND ADDRESS

__________________________________________

__________________________________________

__________________________________________

__________________________________________

8/1/72–500
This dissertation, directed and approved by the candidate's committee, has been accepted by the Graduate Committee of The University of New Mexico in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

Dispersion in Laminar Flow of

Title Non-Newtonian Fluids

Subhash N. Shah

Candidate

Chemical Engineering

Department

Dean

Date

Committee

Chairman
DISPERSION IN LAMINAR FLOW OF NON-NEWTONIAN FLUIDS

BY

SUBHASH N. SHAH

B.S., M.S. University of Baroda, 1968
M.S., University of New Mexico, 1971

DISSERTATION

Submitted in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in Chemical Engineering in the Graduate School of The University of New Mexico Albuquerque, New Mexico

August, 1974
ACKNOWLEDGMENTS

The author wishes to express his sincere gratitude to Dr. Kenneth E. Cox, Chemical and Nuclear Engineering Department, the University of New Mexico, who as the academic advisor and the Chairman of the Dissertation Committee, has given guidance and encouragement throughout the period of this research.

Thanks are extended to Dr. R. C. Allen of the Mathematics Department and Dr. G. F. Cochrane and Dr. F. C. Wessling of the Mechanical Engineering Department for serving on the Dissertation Committee and their valuable suggestions and useful comments. Thanks are also due to Dr. G. H. Quentin, who greatly contributed to the author's academic training.

The guidance and help of Dr. E. A. Walters of the Chemistry Department with the experimental phase of this work is greatly appreciated. Special thanks are due to Dr. G. H. Daub, Chairman, the Department of Chemistry, for permitting the author to use the Model 14 Cary spectrophotometer.

The financial support provided by the Chemical and Nuclear Engineering Department, the University of New Mexico, through Graduate and Teaching Assistantships is also acknowledged.

The encouragement from the author's parents which brought him to the present stage is gratefully acknowledged.

Last, but not least, the author would like to express deep appreciation to his wife, Jaya Shah, for her constant support, understanding and patience during this research.
DISPERSION IN LAMINAR FLOW OF NON-NEWTONIAN FLUIDS

BY

SUBHASH N. SHAH

ABSTRACT OF DISSERTATION

Submitted in Partial Fulfillment of the Requirements for the Degree of

Doctor of Philosophy in Chemical Engineering
in the Graduate School of
The University of New Mexico
Albuquerque, New Mexico

August, 1974
ABSTRACT

In the present investigation, Taylor's analysis of the dispersion of solutes in laminar flow of a Newtonian fluid through a circular tube was extended to the case of a non-Newtonian Eyring model fluid. A new approach was taken to solve the convective diffusion equation for the Eyring model fluid. This approach incorporates the use of the dimensionless longitudinal pressure gradient and the mean velocity to obtain the dimensionless concentration. Using an approach similar to that of Taylor, a solution of the diffusion equation was obtained for quantities such as the dimensionless concentration, mean concentration, and effective dispersion coefficient as a function of a dimensionless parameter describing the fluid.

Experiments were conducted with fluids possessing non-Newtonian characteristics to obtain rheological and dispersion data. Two aqueous solutions, 0.1% and 1.0% Polyox (polyethylene oxide) were tested for rheological properties. These solutions were found to exhibit time-independent non-Newtonian pseudoplastic fluid characteristics and fit the Ostwald-de Waele (Power Law) model quite well over the wide range of shear rate investigated.

Dispersion measurements were first made with Newtonian (KMnO$_4$ - H$_2$O) system in a 1 mm tube. The value of diffusion coefficient found was 2.0 x 10$^{-5}$ cm$^2$/sec which is in good agreement with previously reported results. Displacement experiments were then performed with a non-Newtonian (Dye - 1.0% Polyox) system. The dispersion measurements
were made in two different size tubes, viz. 1 mm and 2 mm, with no apparent effect of tube size noted on the dispersion phenomena. The range of the dimensionless time and Peclet number studied were 0.001 to 4.0 and 200 to $4.75 \times 10^5$ respectively.

The results from experimental measurements showed good agreement with the numerical and Taylor-Fan approximate solutions of the diffusion equation. The value of diffusion coefficient for Dye - 1.0% Polyox system was $3.07 \times 10^{-7}$ cm$^2$/sec over the concentration range of $0 \leq C \leq 0.2$ gm/lit., and $5.09 \times 10^{-7}$ cm$^2$/sec for the range, $0 \leq C \leq 0.1$ gm/lit. The value of diffusion coefficient is thus concentration dependent as expected and it decreases with increasing concentration.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II. LITERATURE REVIEW</td>
<td>3</td>
</tr>
<tr>
<td>2.1 Newtonian Fluids</td>
<td>3</td>
</tr>
<tr>
<td>2.2 Non-Newtonian Fluids</td>
<td>7</td>
</tr>
<tr>
<td>III. NON-NEWTONIAN FLUIDS</td>
<td>10</td>
</tr>
<tr>
<td>3.1 Classification and Characteristics</td>
<td>11</td>
</tr>
<tr>
<td>3.1.1 Time-independent Non-Newtonian Fluids</td>
<td>11</td>
</tr>
<tr>
<td>3.1.2 Time-dependent Non-Newtonian Fluids</td>
<td>15</td>
</tr>
<tr>
<td>3.1.3 Viscoelastic Fluids</td>
<td>16</td>
</tr>
<tr>
<td>3.2 Velocity Distribution of Non-Newtonian Fluids in Laminar Flow</td>
<td>17</td>
</tr>
<tr>
<td>3.3 Determination of Rheological Properties</td>
<td>22</td>
</tr>
<tr>
<td>IV. DISPERSION MODELS AND ANALYSIS FOR NON-NEWTONIAN FLUIDS</td>
<td>25</td>
</tr>
<tr>
<td>4.1 Laminar Convection without Diffusion</td>
<td>26</td>
</tr>
<tr>
<td>4.2 Laminar Convection with Radial Diffusion</td>
<td>30</td>
</tr>
<tr>
<td>4.3 Laminar Convection with Axial and Radial Diffusion</td>
<td>44</td>
</tr>
<tr>
<td>V. EXPERIMENTAL INVESTIGATION</td>
<td>49</td>
</tr>
<tr>
<td>5.1 Selection of Experimental System</td>
<td>49</td>
</tr>
<tr>
<td>5.1.1 System for Rheological Experiment</td>
<td>49</td>
</tr>
<tr>
<td>5.1.2 System for Dispersion Experiment</td>
<td>50</td>
</tr>
<tr>
<td>Chapter</td>
<td>Page</td>
</tr>
<tr>
<td>----------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>5.2 Description of Equipment</td>
<td>51</td>
</tr>
<tr>
<td>5.2.1 Flow Measurement Equipment</td>
<td>52</td>
</tr>
<tr>
<td>5.2.2 Concentration Measurement Equipment</td>
<td>54</td>
</tr>
<tr>
<td>5.3 Experimental Procedures</td>
<td>56</td>
</tr>
<tr>
<td>5.3.1 Preparation of Aqueous Polymer Solutions</td>
<td>56</td>
</tr>
<tr>
<td>5.3.2 Measurement of Tube Diameter</td>
<td>56</td>
</tr>
<tr>
<td>5.3.3 Calibration of Syringe Pump</td>
<td>57</td>
</tr>
<tr>
<td>5.3.4 Rheological Measurements</td>
<td>57</td>
</tr>
<tr>
<td>5.3.5 Calibration of Spectrophotometer</td>
<td>58</td>
</tr>
<tr>
<td>5.3.6 Dispersion Measurements</td>
<td>63</td>
</tr>
<tr>
<td>5.4 Analysis of Data</td>
<td>66</td>
</tr>
<tr>
<td>VI. RESULTS AND DISCUSSION</td>
<td>68</td>
</tr>
<tr>
<td>6.1 Results of Rheological Measurements</td>
<td>68</td>
</tr>
<tr>
<td>6.2 Results of Dispersion Measurements</td>
<td>69</td>
</tr>
<tr>
<td>6.2.1 Newtonian (KMnO4 - H2O) system</td>
<td>69</td>
</tr>
<tr>
<td>6.2.2 Non-Newtonian (Dye - 1.0% Polyox)</td>
<td>77</td>
</tr>
<tr>
<td>System</td>
<td></td>
</tr>
<tr>
<td>A. Conditions for Taylor - Fan Approximate Solution</td>
<td>81</td>
</tr>
<tr>
<td>B. Applicability of Various Equations</td>
<td>84</td>
</tr>
<tr>
<td>C. High Peclet Number Results</td>
<td>87</td>
</tr>
<tr>
<td>D. Diffusion Coefficient and Concentration Dependency</td>
<td>98</td>
</tr>
<tr>
<td>E. Effect of Tube size</td>
<td>99</td>
</tr>
<tr>
<td>F. Effect of Entrance Length of Tube</td>
<td>99</td>
</tr>
</tbody>
</table>

viii
<table>
<thead>
<tr>
<th>Chapter</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>G. Effect of Measurement of Average</td>
<td>100</td>
</tr>
<tr>
<td>Concentration</td>
<td></td>
</tr>
<tr>
<td>VII. CONCLUSIONS</td>
<td>102</td>
</tr>
<tr>
<td>SUGGESTIONS FOR FURTHER STUDY</td>
<td>104</td>
</tr>
<tr>
<td>APPENDICES</td>
<td>106</td>
</tr>
<tr>
<td>Appendix A</td>
<td>106</td>
</tr>
<tr>
<td>Appendix B</td>
<td>114</td>
</tr>
<tr>
<td>Appendix C</td>
<td>130</td>
</tr>
<tr>
<td>Appendix D</td>
<td>134</td>
</tr>
<tr>
<td>Appendix E</td>
<td>144</td>
</tr>
<tr>
<td>BIBLIOGRAPHY</td>
<td>148</td>
</tr>
<tr>
<td>CURRICULUM VITAE</td>
<td>151</td>
</tr>
</tbody>
</table>
# List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Flow curves for various time-independent fluids</td>
<td>13</td>
</tr>
<tr>
<td>2.</td>
<td>Dimensionless velocity profile - Power Law model fluid</td>
<td>19</td>
</tr>
<tr>
<td>3.</td>
<td>Dimensionless velocity profile - Eyring model fluid</td>
<td>21</td>
</tr>
<tr>
<td>4.</td>
<td>Average concentration distribution of tracer in Eyring model fluid - pulse input with no diffusion</td>
<td>29</td>
</tr>
<tr>
<td>5.</td>
<td>Average concentration distribution of tracer in Eyring model fluid - step input with no diffusion</td>
<td>31</td>
</tr>
<tr>
<td>6.</td>
<td>Dimensionless concentration profile - Eyring model fluid</td>
<td>38</td>
</tr>
<tr>
<td>7.</td>
<td>Variation of $K'$, dimensionless effective dispersion coefficient with $b$, Eyring model fluid parameter</td>
<td>41</td>
</tr>
<tr>
<td>8.</td>
<td>Average concentration distribution of tracer in Eyring model fluid - step input with radial diffusion</td>
<td>43</td>
</tr>
<tr>
<td>9.</td>
<td>Average concentration distribution of tracer in Eyring model fluid - step input with radial diffusion</td>
<td>45</td>
</tr>
<tr>
<td>10.</td>
<td>Bulk concentration distribution of tracer in Eyring model fluid - step input with radial diffusion</td>
<td>46</td>
</tr>
<tr>
<td>11.</td>
<td>Experimental setup of flow measurement equipment</td>
<td>53</td>
</tr>
<tr>
<td>12.</td>
<td>Concentration measurement apparatus</td>
<td>55</td>
</tr>
<tr>
<td>13.</td>
<td>Pressure drop of 1.0% Polyox solution from startup (1 mm tube)</td>
<td>59</td>
</tr>
<tr>
<td>Figure</td>
<td>Page</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>14. Pressure drop of 1.0% Polyox solution from startup (2 mm tube)</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>15. Calibration plot of absorbance versus concentration for Dye - Polyox system (1 mm tube)</td>
<td>61</td>
<td></td>
</tr>
<tr>
<td>16. Calibration plot of absorbance versus concentration for Dye - Polyox system (2 mm tube)</td>
<td>62</td>
<td></td>
</tr>
<tr>
<td>17. Calibration plot of absorbance versus concentration for KMnO₄ - H₂O system</td>
<td>64</td>
<td></td>
</tr>
<tr>
<td>18. Schematic diagram of dispersion experiment</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td>19. Plot of shear stress versus shear rate for various polymers</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>20. Plot of dispersion coefficient at fixed velocities for different flow times (KMnO₄ - H₂O) system</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td>21. Plot of dimensionless mixing zone length versus dimensionless time for KMnO₄ - H₂O system</td>
<td>76</td>
<td></td>
</tr>
<tr>
<td>22. Plot of dispersion coefficients at fixed velocities for different flow times (Dye - Polyox) system</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>23. Plot of dimensionless mixing zone length versus dimensionless time for Dye - Polyox system</td>
<td>82</td>
<td></td>
</tr>
<tr>
<td>24. Summary of the regions of application of various solutions</td>
<td>86</td>
<td></td>
</tr>
<tr>
<td>25. Concentration distribution along the length of tube</td>
<td>88</td>
<td></td>
</tr>
<tr>
<td>26a. Plot of concentration versus $X'/\tau$ for various values of $\tau$ at $N_{pe} = 1018$</td>
<td>89</td>
<td></td>
</tr>
</tbody>
</table>
Greek Symbols

\( \alpha \) = Ellis model fluid parameter
\( \dot{\gamma} \) = apparent wall shear rate
\( \dot{\gamma}' \) = actual wall shear rate
\( \zeta \) = dimensionless radial coordinate, \( \zeta = r/R \)
\( \eta \) = dimensionless axial coordinate, \( \eta = x/L \)
\( \eta_0 \) = \( \eta - \theta \)
\( \eta^+ \) = defined by Eq. 4.3-7
\( \theta \) = dimensionless time, \( \theta = t/\Gamma \)
\( \mu \) = viscosity
\( \mu_a \) = apparent viscosity
\( \mu_0 \) = viscosity at zero shear rate
\( \mu_\infty \) = viscosity at infinite shear rate
\( \tau \) = dimensionless time, \( Dt/R^2 \)
\( \tau_o \) = initial yield stress of a Bingham plastic
\( \tau_{rx} \) = shear stress in x-direction on surface normal to r
\( \tau_s \) = Reiner-Philippoff model fluid parameter
\( \tau_w \) = shear stress at the wall
\( \phi_0, \phi_1 \) = Ellis model fluid parameters
CHAPTER I

INTRODUCTION

The general problem of longitudinal dispersion of soluble matter in the study of fluids in flow through a circular tube is, apart from its theoretical interest, of considerable practical importance in a variety of fields. Knowledge of dispersion is very useful in many areas such as: the dispersion of soluble material in blood vessels, the dispersion of solutes in water-conducting organs of plants (biological systems), in describing chromatographic columns, and in the application of processes such as packed bed reactors, distillation and gas absorption towers, and liquid-liquid extraction columns. Dispersion is also very important in the transportation of various petroleum products where a single pipeline is used to convey several liquids over great distances, introducing them consecutively into the pipeline. It is not economical to clean the pipeline and hence it is desirable to know the extent of mixing and the amount of product contaminated.

For a number of years, various research groups have investigated dispersion processes in Newtonian flow systems. Considerable progress has been achieved in predicting the longitudinal dispersion of solutes. In recent years, there has been more attention given to transport processes in non-Newtonian systems. In many non-Newtonian systems of industrial importance, mass transfer is of great concern. The study of such systems together and other biological non-Newtonian fluids is
also of considerable interest. During the past years significant progress has been made in the analysis and understanding of longitudinal mixing in non-Newtonian fluids.

In the steady laminar flow of a Newtonian fluid through a tube of circular cross-section, dispersion is due mainly to the combined action of convection in a direction parallel to the tube axis and molecular diffusion in the radial direction. Numerous workers have studied the above problem numerically as well as experimentally. Little work has been performed in the area of dispersion during the flow of non-Newtonian fluids. Many dilute aqueous polymeric solutions conform closely to the Ostwald-de Waele or Power Law non-Newtonian fluid model. The analysis of dispersion for this case has already been done. Few experimental studies are available to validate the dispersion results predicted from the analysis of this or any other non-Newtonian model fluid in laminar flow.

The purpose of the present investigation is twofold: (1) To extend the analysis of dispersion of a solute in the flow of a non-Newtonian fluid through a circular tube to the case for the flow of an Eyring model non-Newtonian fluid in a similar geometry. (2) To validate experimentally the analysis of dispersion obtained for the Power Law non-Newtonian fluid. The first part of the experiment is to find the rheological properties of the polymeric solutions under study. A second experiment involves dispersion of dye tracer in these fluids and measuring concentration as a function of flow time. Tube size is also investigated as an experimental variable. Values of the dispersion and diffusion coefficient are calculated from the above measurements.
CHAPTER II
LITERATURE REVIEW

2.1 NEWTONIAN FLUIDS

The dispersion of a solute in a fluid flowing through a tube of circular cross-section was first described by G. I. Taylor in 1953 \[45\]. In this study, he considered two limiting conditions: (1) dispersion of a tracer material due to convection only, and (2) dispersion due to the combined effects of convection and radial diffusion. Under the second condition, Taylor concluded that for laminar flow, an effective dispersion coefficient is given by

\[ k = \frac{R^2V_x^2}{48D} \]

In a second paper Taylor \[46\] obtained the conditions,

\[ \frac{4L}{R} \gg \frac{RV_x}{D} \gg 6.9 \]

for which an approximate solution of the equation for diffusion in a moving fluid are valid. Taylor \[47\] later extended the analysis of the dispersion of matter to the case of turbulent flow through a pipe.

Bosworth \[8\] presented a theoretical study of residence time distribution functions for laminar flow by neglecting the effect of radial diffusion. Taylor confirmed this criterion and in Taylor's analysis this is equivalent to the requirement that the time for convective transport is long compared with the time of decay of radial concentration gradients.
Aris [2,3] extended Taylor's work by using a method of moments and showed that the rate of growth of the variance of the distribution of solute is proportional to the sum of the molecular diffusion coefficient and the Taylor diffusion coefficient and the restrictions imposed by Taylor could be removed. His study extended Taylor's analysis to include flow through noncircular pipes and the effect of axial molecular diffusion.

Bournia et al. [9] applied Taylor's analysis to study displacement experiments with gases flowing through a circular tube. Their results showed excellent agreement with Taylor's approximate solution, however they did not agree with those predicted by Aris' analysis in the low flow velocity range.

The solution for the displacement problem, valid for slow radial diffusion was obtained by van Deemter et al. [50] and their theoretical results were compared with Taylor's experimental data.

Evans and Kenney [14] studied experimentally the gaseous dispersion in laminar flow through a circular tube and obtained good agreement with the analytical solutions given by Taylor and Aris. Philip [36, 37] studied the periodic dispersal problem by using the method of eigenfunction expansion and extended the results of Aris [4] for low-frequency oscillating flow with dispersion to high frequency oscillating flow.

Bailey and Gogarty [5] employed a finite difference technique to solve the convective diffusion equation numerically. In this analysis the diffusion and convection effects separated and the axial molecular
diffusion is ignored. Their analysis limits the solution to large Peclet numbers. From the numerical results they indicated that the exponent of the time term should be modified in the solution of the convective diffusion equation as derived by Taylor and confirmed by Aris. They also presented experimental results and found that Taylor's restrictions on the applicability of his solution were too severe.

A series of papers were presented by Gill and his coworkers considering various aspects of laminar dispersion in capillaries. In Part I [1] of their work, a complete numerical solution of the equation describing laminar flow in tubes with both axial and radial molecular diffusion has been obtained for widely varying values of the Peclet number. Their results show no justification for Bailey and Gogarty's empirical modification of the exponent of the time term in the solution of convective diffusion equation. It is also shown that the Taylor-Aris theory is valid for large values of time.

Part II [24] extended the previous results to include the effects of various inlet boundary conditions and of system capacitance.

Part III [39] dealt with the experiments in horizontal tubes including the effect of natural convection. It was found that natural convection can both depress and enhance the dispersion significantly and that extremely small density differences are adequate to cause these phenomena.

In Part IV [25] an exact analysis of the local behavior of finite slugs which are dispersed in three dimensional velocity fields was developed.
Part V [38] presented an approximate theory for transient dispersion with combined free and forced convection in vertical tubes and tested this phenomena experimentally.

Gill [22] has developed a series solution for the problem of transient mass dispersion in fully developed laminar flow in a tube. This method can be extended to more general geometries, and by superposition to include more general boundary conditions. The transient solution of the diffusion convective equation was also developed by Tseng and Besant [48] by the linear combination of the eigenvalues and eigenvectors of the matrix form of the diffusion equation.

Gill et al. [26] also analyzed dispersion in flows which start from rest and in the velocity entrance of tubes. It was found that the extent of dispersion is less in developing velocity fields than in those which are fully developed.

Bischoff [7] and Turner [49] considered the effects of a time-dependent velocity on solutions to the one-dimensional dispersion equation. However, they did not make any attempt to determine the conditions under which this form of dispersion equation is valid. Later, Gill [23] developed a method for finding the solution of the convective diffusion equation when both velocity and dispersion coefficient are time-dependent.

The exact analysis of unsteady convective diffusion equation was obtained by Gill and Sankarasubramanian [27] by using the series expansion originally proposed by Gill. In their second paper [28] they extended this method to include non-uniform initial distributions.
Recently, Gill and Sankarasubramanian [29] have developed a method to handle time-dependent, non-uniform introduction of matter into unsteady flows. In this case the source density was specified but in general the concentration can be specified over the cross-section of the flow. In a later paper [30] the analysis of this type of behavior was presented. They also extended the theory of miscible dispersion to interphase transport systems. Specifically, dispersion of a non-uniform initial distribution in time-variable isothermal laminar flow in a tube with a first-order rate process at the tube wall was analyzed in [31].

2.2 NON-NEWTONIAN FLUIDS

As previously mentioned, extensive work has been done on various aspects of dispersion phenomena in Newtonian fluids. By way of contrast, little has been done on dispersion phenomena in non-Newtonian fields.

In 1965, Fan and Hwang [16] extended Taylor's analysis of dispersion for Newtonian fluids to include the non-Newtonian Ostwald-de Waele model fluid. Later, Fan and Wang [17] presented similar analyses for the case of Bingham plastic and Ellis model fluids. They also indicated that Aris' modification of Taylor's analysis could be applied.

Taylor's analysis of the dispersion of a soluble matter in Newtonian flow through a circular tube was extended by Ghoshal et al. [19, 20, 21] to the cases of the Eyring and Reiner-Philipoff model fluids. In this analysis, the expressions for the effective dispersion coefficient of the Eyring and Reiner-Philipoff models were incorrect
and the correct expressions were derived by Cox and Shah [11]. Also in Ghoshal's analysis some integrals were left unevaluated and further, he did not make an attempt to calculate any results. A new approach was taken in a recent study by Shah and Cox [43] to solve the convective diffusion equation for the Eyring model which incorporates the use of the dimensionless longitudinal pressure gradient and the mean velocity to obtain the dimensionless concentration. Following Taylor's approach, quantities such as the dimensionless concentration, mean concentration, and effective dispersion coefficient were obtained as a function of a dimensionless parameter.

Erdogan [13] obtained an expression for the Taylor diffusion coefficient representing longitudinal dispersion accompanying laminar flow in a tube, for a non-Newtonian fluid which obeys the Casson shear stress - shear rate relationship. He found that the virtual diffusion coefficient depends on the ratio of the fluids yield stress to the wall stress and reaches a maximum value at a certain value of this ratio.

An approximate theoretical solution of the unsteady-state momentum equation for the start-up flow of the Power Law fluid in circular tubes have been presented by Sestak and Charles [42]. The effect of the flow-behavior index and the imposed pressure gradient on the start up time was discussed. Values of the longitudinal dispersion coefficient have been obtained by Kenney and Thwaites [32] for a dilute aqueous polymer system displaying drag reducing properties. Mass transfer into dilute polymeric solutions was studied by using a short wetted-wall column by Wasan et al. [51]. In their study, oxygen was
absorbed into thin films of water and aqueous polymeric solutions.

Recently, Payne and Parker [35] have studied the axial dispersion of non-Newtonian fluids in porous media.

French [18] has presented the numerical solution of the complete diffusion equation considering both axial and radial molecular diffusion for the cases of the Power Law and Bingham plastic fluids. He also conducted dispersion experiments using a radioisotope as a tracer. It was concluded that due to the non-linearity of the model this type of data was unsuitable for evaluating the diffusion coefficient and the Power Law parameter $n$.

Velocity profiles for unsteady laminar flows of non-Newtonian Power Law fluids in pipes have been derived by Edwards et al. [12] using an explicit finite-difference technique. Recently, Mashelkar [33] has discussed the applicability of axial dispersion model for non-Newtonian (Power Law model) laminar flow in tubular reactors in which a first-order homogeneous chemical reaction is taking place.
CHAPTER III
NON-NEWTONIAN FLUIDS

The fluids that exhibit a linear relationship between shear stress and shear rate are known as Newtonian fluids and those do not show a direct proportionality between shear stress and shear rate are defined as non-Newtonian fluids. For a Newtonian fluids thus,

$$\tau_{rx} = -\mu \left( \frac{dV_x}{dr} \right)$$

(3-1)

This equation is known as Newton's law of viscosity and $\mu$ is called the coefficient of viscosity.

It is common in practice to find fluids that do not obey the simple relationship between shear rate and shear stress as given by Eq. 3-1. There are many common fluids that exhibit non-Newtonian characteristics. Examples are: solutions of various high polymers, food products, suspensions of various solids in liquids, paints, emulsions of water in oil, muds used in well drilling, biological fluids and many others. The field of non-Newtonian fluids has not been explored in great detail not because of lack of application of non-Newtonian fluids but because of the complexity involved in explaining the phenomena. So far, elegant and precise analyses have been done mainly for Newtonian fluids, however the flow of non-Newtonian fluids do possess interesting, useful, and even exciting characteristics.

We begin section 3.1 by presenting the classification of various non-Newtonian fluids; even though this classification is by no means
distinctly defined. Section 3.2 deals with the derivation of velocity
distribution for the Power Law and Eyring fluid models under conditions
of steady, isothermal laminar flow in a circular tube. Finally, sec-
tion 3.3 describes briefly the various methods for the determination
of rheological properties of non-Newtonian fluids.

3.1 CLASSIFICATION AND CHARACTERISTICS

Non-Newtonian fluids are commonly divided into the following
three general categories according to Skelland [44]. (1) Time-
independent non-Newtonian fluids. These are the simplest in which
that the shear rate at a given point is unique but not a linear
function of shear stress. (2) Time-dependent fluids have more com-
plex relationship between shear stress and shear rate. In these
fluids, the shear rate is a function of both the magnitude and the
duration of shear. (3) In viscoelastic fluids, distortion of the
fluid may be recovered partially upon the removal of a deforming shear
stress because these materials possess elastic properties.

3.1.1 TIME-INDEPENDENT NON-NEWTONIAN FLUIDS

For the time-independent non-Newtonian fluids, shear rate \( \frac{dV_x}{dr} \)
is a function of shear stress \( \tau_{rx} \) thus

\[
\frac{dV_x}{dr} = f(\tau_{rx}) \quad (3.1-1)
\]

A Newtonian fluid is simply a special case of this where the
function \( f(\tau_{rx}) \) is linear and hence these fluids are also referred to
as viscous non-Newtonian fluids. Many non-Newtonian fluids that
we encounter fall into this class. Some of these exhibit a yield stress and some do not. The flow curves for various types of time-independent non-Newtonian fluids are shown in Figure 1.

(A) **FLUIDS WITH A YIELD STRESS**

Bingham Plastic:

This model exhibits a yield stress at zero shear rate, but flows somewhat like a Newtonian fluid when the shear stress exceeds the yield stress $\tau_o$. The equation for this model is given by Bird et al. [6].

\[
\tau_{rx} = -\mu_o \frac{dV_x}{dr} \pm \tau_o \quad |\tau_{rx}| \geq \tau_o \quad (3.1-2a)
\]

\[
\frac{dV_x}{dr} = 0 \quad |\tau_{rx}| < \tau_o \quad (3.1-2b)
\]

The positive sign is used in Eq. 3.1-2a when $\tau_{rx}$ is positive, and the negative sign is used when $\tau_{rx}$ is negative. This model has been found to closely approximate the behavior of many real fluids such as slurries, fine suspensions, plastics, and pastes. This model is very convenient for analysis because it has a linear relationship between the shear rate and shear stress. Other examples of fluids with a yield stress are given by Skelland [44].

(B) **FLUIDS WITHOUT A YIELD STRESS**

Pseudoplastic and Dilatant Fluids:

Pseudoplastic and dilatant fluids do not have a yield stress. The flow curves are sketched in Figure 1. Pseudoplastic fluids are
Fig. 1. Flow curves for various time-independent fluids.
characterized by a progressively decreasing slope of shear stress versus shear rate and the slope is defined as apparent viscosity thus

\[ \mu_a = -\frac{\tau_{rx}}{\left(\frac{dV_x}{dr}\right)} \]  (3.1-3)

At very high and very low shear rates the relationship between shear rate and shear stress becomes linear. The apparent viscosity at very high shear rate is called viscosity at infinite shear and denoted by \( \mu_\infty \). Similarly, at very low shear rate, it is a viscosity at zero shear rate \( \mu_0 \).

In dilatant fluids the apparent viscosity increases with increasing shear rate. The explanation of this behavior in the case of suspensions was given by Reynolds [40]. These materials are far less common than pseudoplastic fluids.

Many empirical relations or models have been developed but the simplest of these is a Ostwald-de Waele model. It is given by Bird et al. [6] as

\[ \tau_{rx} = -m \left| \frac{dV_x}{dr} \right|^{n-1} \frac{dV_x}{dr} \]  (3.1-4)

where \( m \) is the "consistency index" and \( n \) is the "flow-behavior index." This two parameter model reduces to Newtonian case for \( n = 1 \) with \( m = \mu \). For \( n < 1 \), the behavior is pseudoplastic and for \( n > 1 \), the behavior is dilatant. This model is adequate to analyze flow in pipes and channels because of its inherent simplicity. Many other empirical models have been proposed and given by Skelland [44], but
the most common examples are as follows:

**The Ellis Model**

\[- \frac{dV_x}{dr} = \left( \phi_0 + \phi_1 \right) \left| \tau_{rx} \right|^{\alpha - 1} \tau_{rx} \]

(3.1-5)

**The Eyring Model**

\[ \tau_{rx} = A \operatorname{arc sinh} \left( - \frac{1}{B} \frac{dV_x}{dr} \right) \]

(3.1-6)

**The Reiner-Philipoff Model**

\[- \frac{dV_x}{dr} = \left( \frac{1}{\mu_\infty + \frac{\mu_0 - \mu_\infty}{1 + \left( \frac{\tau_{rx}}{\tau_s} \right)^2}} \right) \tau_{rx} \]

(3.1-7)

Examples of pseudoplastic and dilatant fluids include rubber solutions, polymer solutions, soap, paper pulp, biological fluids, starch, gum arabic in water, and aqueous suspensions of titanium dioxide.

### 3.1.2 TIME-DEPENDENT NON-NEWTONIAN FLUIDS

Time-dependent fluids do not depend only on the shear rate but also depend on the time the shear has been applied. These fluids have two general classes. (A) thixotropic fluids, and (B) rheopetic fluids.

(A) **THIXOTROPIC FLUIDS**

These fluids show decrease in shear stress with time at a constant shear rate and fixed temperature. If a thixotropic fluid is sheared at a constantly increasing rate, then at a constantly decreasing rate, a curve similar to a hysteresis loop is generated. It should be remembered that the location of this loop would be different for a different
time history. As the fluid is sheared from a state of rest, it breaks
down on a molecular scale, but then the structural reformation will
increase with time. After equilibrium has been reached if it is
allowed to rest, the fluid builds up slowly and eventually regains its
original consistency. Hence thixotropy is a reversible process. A
few examples of thixotropic fluids are: printing inks, margarine and
shortening, paints, greases, etc.

(B) **RHEOPECTIC FLUIDS**

Rheoplectic fluids are often known as antithixotropic because their
behavior is opposite to that of thixotropic fluids. Again this is a
reversible process in which shear stress increases with time at a con-
stant shear rate and fixed temperature. These fluids are very rare in
occurrence. A few examples as given by Skelland [44] are: vanadium
pentoxide suspensions, bentonite clay suspensions, gypsum suspensions,
and suspensions of ammonium oleate. Many materials lose their
rheoplectic property at extremely high shear rates and may even be-
have as thixotropic fluids.

3.1.3 **VISCOELASTIC FLUIDS**

The fluids which exhibit both elastic and viscous properties are
called viscoelastic fluids. When these fluids are subjected to stress
they flow and part of their deformation is recovered upon removal of
the stress. Oldroyd [34] has studied the viscoelastic characteristics
of the dispersion of one Newtonian fluid in another which may lead to
emulsions. In the extrusion of synthetic fibers e.g. nylon, viscoelastic
effects occur. Examples of viscoelastic fluids are bitumens, flour dough, Napalm and similar jellies, and polymer melts. Rather complex models of viscoelastic materials have been developed but they will not be discussed further since they are not subject to the present investigation.

3.2 VELOCITY DISTRIBUTION OF NON-NEWTONIAN FLUIDS IN LAMINAR FLOW

This section concerns itself with the derivation of the equations for the velocity profiles of two non-Newtonian fluids, viz. the Power Law and Eyring model fluids, flowing through a circular tube. The following assumptions are made in deriving the theory.

(1) The flow is steady, one-dimensional, and fully developed laminar flow.

(2) The density is constant i.e. flow is incompressible.

(3) There are no end effects.

(4) There is no slip between the fluid and the wall.

(5) The fluid behaves as a continuum.

The steady state equation of motion for fully developed flow is

\[
\frac{1}{r} \frac{d}{dr} \left( r \tau_{rx} \right) = - \left( \frac{dP}{dx} \right) \tag{3.2-1}
\]

which on integration becomes

\[
\tau_{rx} = - \frac{r}{2} \left( \frac{dP}{dx} \right) \tag{3.2-2}
\]

The term \( \frac{dP}{dx} \) may be written as \( \Delta P / L_1 \) where \( \Delta P \) is the pressure drop and \( L_1 \) is the length of the tube and Eq. 3.2-2 can be written as
\[ \tau_{rx} = r \left( \frac{\Delta P}{2L_1} \right) \] (3.2-3)

This equation can be solved by substituting the appropriate equation for \( \tau_{rx} \) for a non-Newtonian fluid and considering the boundary condition

\[ V_x = 0 \quad \text{at} \quad r = R \] (3.2-4)

**POWER LAW MODEL FLUID**

Substituting Eq. 3.1-4 into Eq. 3.2-3 and integrating the resulting equation using the boundary condition of Eq. 3.2-4 gives (see Appendix A.1)

\[ V_x = \frac{n}{n+1} \left( \frac{\Delta P}{2mL_1} \right)^\frac{1}{n} \frac{n+1}{R^n} \left[ 1 - \left( \frac{r}{R} \right)^{n+1} \right] \] (3.2-5)

and the average velocity is given by

\[ \overline{V}_x = \frac{n}{3n+1} \left( \frac{\Delta P}{2mL_1} \right)^\frac{1}{n} \frac{n+1}{R^n} \] (3.2-6)

The local velocity and the mean velocity then are related by the following expression

\[ V_x = \frac{3n+1}{n+1} \left[ 1 - \left( \frac{r}{R} \right)^{n+1} \right] \overline{V}_x \] (3.2-7)

For \( n = 1 \), all the above expressions reduce to the Newtonian case. Figure 2 shows the velocity profiles given by Eq. 3.2-7 for various values of the parameter \( n \). The lower the value of \( n \) the flatter the velocity profile is, until eventually for very low values of \( n \)
Fig. 2. Dimensionless velocity profile - Power law model fluid.
the flow assumes a plug-like form. As \( n \) approaches infinity the flow assumes a cone-like profile.

**EYRING MODEL FLUID**

In this case we need to substitute the relation given by Eq. 3.1-6 into Eq. 3.2-3 and use Eq 3.2-4 as a boundary condition to give (Appendix A.2)

\[
V_x = \frac{BR}{b} \left( \cosh b - \cosh b \xi \right)
\]

(3.2-8)

The expression for the mean velocity is

\[
\bar{V}_x = \frac{BR}{b} \cosh b
\]

(3.2-9)

where

\[
E = \left( 1 - \frac{2 \sinh b}{b \cosh b} + \frac{2}{b^2} - \frac{2}{b^2 \cosh b} \right)
\]

(3.2-10)

From Eqs. 3.2-8 and 3.2-9

\[
V_x = \frac{1}{E} \left( 1 - \frac{\cosh b \xi}{\cosh b} \right) \bar{V}_x
\]

(3.2-11)

Eq. 3.2-11 is plotted in Figure 3 for various values of the dimensionless parameter \( b \). It is obvious from this figure that as the value of the dimensionless parameter increases, the velocity profile becomes more blunt, departing from the parabolic profile obtained for a Newtonian fluid. The Eyring model reduces to the Newtonian case for \( b = 0 \). As \( b \to \infty \), a plug flow results.
Fig. 3. Dimensionless velocity profile - Eyring model fluid.
3.3 DETERMINATION OF RHEOLOGICAL PROPERTIES

There are many types of viscometers available to measure flow properties of the fluids. Each has certain advantages and disadvantages compared to the others. These viscometers determine the relationship between shear stress and shear rate. For engineering and scientific purposes there are four major types of viscometers available to obtain data for the flow of fluids: (1) capillary tube viscometer, (2) concentric cylinder rotary viscometer, (3) the rotary cylinder in an "infinite" medium, and (4) the cone-and-plate type of rotary viscometer. Details of each type of viscometer is treated by Skelland [44]. He also describes the detection of time-dependent characteristics and the determination of viscoelastic flow properties. The present treatment is restricted only to the capillary tube viscometer because in this investigation a capillary tube was used to find the two unknown parameters in the Power Law model fluid. The detailed description of this apparatus can be found in the chapter on experimental investigation.

It is necessary to mathematically develop the theory involved in finding the two parameters of the Power Law model using the capillary tube viscometer. In the derivation of theory, the assumptions made are: (1) the fluid is time-independent, (2) the fluid is in steady, laminar flow, (3) there is no slip between the fluid and the tube wall.

From Eq. 3.2-3, \( \tau_{rx} \) at \( r = R \) i.e. the shear stress at the wall \( \tau_w \) can be written as

\[
( \tau_{rx} )_{r=R} = \tau_w = \frac{R \Delta P}{2L_1}
\]  
(3.3-1)
Combining Eqs. 3.2-3 and 3.3-1 we have

\[ \tau_{rx} = \tau_w \left( \frac{r}{R} \right) \]  
(3.3-2)

This equation says there is a linear distribution of shear stress in the fluid, from zero at the centerline to \( \tau_w \) at the tube wall, regardless of flow regime.

It is necessary to find the equation giving the rate of shear at the wall of the tube under the above assumptions. The resulting equation is known as the Rabinowitsch-Mooney equation and is given in [44] and further derived in Appendix A.3:

\[ \left( - \frac{dV_x}{dr} \right)_w = \frac{3q}{\pi R^3} + \frac{R \Delta P}{2L_1} \frac{d(q/\pi R^3)}{d\left( \frac{R \Delta P}{2L_1} \right)} \]  
(3.3-3)

Rearranging, this becomes

\[ \left( - \frac{dV_x}{dr} \right)_w = \frac{4V_x}{R} \left[ \frac{3}{4} + \frac{1}{4n'} \right] = \left( \frac{3n' + 1}{4n'} \right) \frac{4V_x}{R} \]  
(3.3-4)

where

\[ n' = \frac{d \ln \left( \frac{R \Delta P}{2L_1} \right)}{d \ln \left( \frac{4V_x}{R} \right)} \]  
(3.3-5)

The relationship between \( n \) and \( n' \) is given by
\[
n = \frac{n'}{1 - \frac{1}{3n'+1} \left[ \frac{dn'}{d(\mathcal{L} n \tau_{\tau x})} \right]}
\]  
(3.3-6)

Experimentally, a plot of \( \left( \frac{R \Delta P}{2L_1} \right) \) versus \( \left( \frac{4V_x}{R} \right) \) on log-log coordinates is linear then the derivative of \( n' \) is zero and from Eq. 3.3-6, \( n = n' \) and the fluid in question follows the Power Law. Substituting Eq. 3.3-4 in the Power Law model gives

\[
\tau_w = m \left[ \frac{3n'+1}{4n'} \frac{V_x}{R} \right]^n
\]  
(3.3-7)

Plotting \( \tau_w = \left( \frac{R \Delta P}{2L_1} \right) \) versus \( \frac{dV_x}{dr} = \left( \frac{3n'+1}{4n'} \frac{V_x}{R} \right) \) on logarithmic paper gives a line with a slope equal to the flow behavior index, \( n \), and an intercept on the shear stress axis for \( \left( -\frac{dV_x}{dr} \right) = 1 \) giving the value of the consistency index \( m \).
CHAPTER IV

DISPERSION MODELS AND ANALYSIS FOR NON-NEWTONIAN FLUIDS

For fully developed steady laminar flow in a circular tube, the convective diffusion equation describing the local concentration of solute material C, as a function of the axial distance x, the radial distance from the axis of the tube r, and time t, is expressed by the following partial differential equation

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

(4-1)

where D, the molecular diffusivity, is assumed to be independent of position and concentration. The fluid is assumed to be incompressible. The term $\frac{\partial C}{\partial t}$ describes the change in local concentration with time at a fixed point while the second term on the left hand side is the concentration change in axial direction due to convection. The first term on the right hand side represents the axial molecular diffusion and the other two terms indicate radial molecular diffusion. To find the solution of Eq. 4-1 as it stands is rather difficult; however, it can be solved approximately by neglecting certain terms which may be physically insignificant.

In the treatment of the following sections, some simplifications of the general case given by Eq. 4-1 are made on the basis of physical assumptions. An analysis of the simplified form of Eq. 4-1 is presented and the physical implications are examined in each case. Here we deal with only three important types of dispersion models: (1) laminar
convection without diffusion; (2) laminar convection with radial diffusion; and (3) laminar convection with both axial and radial diffusion.

The analysis of these dispersion models is given in the next three sections for the case of the Eyring model fluid. A similar expression for the Power Law model fluid is also presented in each case but the derivation is not given since it has been already done by French [18].

4.1 Laminar Convection Without Diffusion

For this case of no diffusion, Eq. 4-1 reduces to

$$\frac{\partial C}{\partial t} + V_x(r) \frac{\partial C}{\partial x} = 0$$

(4.1-1)

Two cases will be examined: (A) pulse injection, and (B) step input.

Before we go further, let us define an average concentration of tracer.

The average concentration of solute material at any section perpendicular to the tube is defined as the mass of the solute contained in that section to the volume of the section thus

$$C_m = \frac{2\pi \int_0^R C(r)rdr}{\pi R^2} = \frac{2}{R^2} \delta \int_0^R C(r)rdr$$

(4.1-2)

A. Pulse Injection of Tracer

When a thin section of a tracer bounded by the two planes \(x = 0\) and \(x = X\), \(X/R\) being small, is injected into the flowing fluid, it will be distorted due to the velocity gradient in the tube. The average concentration of the solute material which is injected in Newtonian fluids is presented by Taylor [45] and is given by
\[ C_m = \frac{C'_o X}{tV_m}, \quad 0 < x < tV_m \] 
\[ = 0, \quad x < 0 \text{ and } x > tV_m \] 

where \( C'_o \) is the initial concentration of solute at \( t = 0 \). It can be seen from the Eq. 4.1-3 that the average concentration of tracer is the same at all points and it decreases linearly with time.

Following the procedure as given by Taylor [45] the treatment for non-Newtonian fluid of the Eyring model fluid is given in Appendix B.1 and the expression is

\[ C_m = \frac{2(cosh-b-1)C'_o X}{b^2tV_m} \frac{1}{\sqrt{[cosh-b-\frac{x}{tV_m}(cosh-b-1)]^2-1}} \cosh^{-1}\left[\frac{x}{tV_m}(cosh-b-1)\right] \]
\[ 0 < x < tV_m \] 

\[ C_m = 0 \quad \text{when} \quad x < 0 \quad \text{and} \quad x > tV_m \] 

The similar expression for the Power Law model is given by [16]

\[ C_m = \frac{2n}{n+1} \frac{C'_o X}{tV_m \left(1-\frac{x}{tV_m}\right)^{1-n}} \quad 0 < x < tV_m \]
\[ = 0 \quad \text{when} \quad x < 0 \quad \text{and} \quad x > tV_m \]

In Eq. 4.1-5 and Eq. 4.1-7, the average concentration is not constant between \( x = 0 \) and \( x = tV_m \) as in the case of the Newtonian fluid. This is because the tracer in the fluid is moving at the average velocity of flow \( \bar{V}_x \). The tracer is distributed such that one-half of the tracer
is between $x = 0$ and $x = t\bar{v}_x$, and the other half is between $x = t\bar{v}_x$ and $x = t\bar{v}_m$. For a Newtonian fluid the average velocity is one-half the maximum velocity. Therefore the distance over which the tracer is going to spread is the same, hence the average concentration is constant. This is not true for non-Newtonian fluids of the Eyring and Power Law models type. As the value of dimensionless parameter $b$ for the Eyring model fluid increases, the velocity profile becomes blunter and thus the average value of the velocity is not one-half of the maximum velocity. Hence the concentration distribution would be expected to be low in the region $x = 0$ and $x = t\bar{v}_x$ and higher in the region $x = t\bar{v}_x$ and $x = t\bar{v}_m$. The concentration distribution is shown in Figure 4 for various values of the parameter $b$.

B. **Step Input of Tracer**

In this case a solution of constant solute concentration enters a tube which at time $t = 0$ contains only solvent. Here,

\[
\begin{align*}
C &= C'_0, & x \leq 0 \\
C &= 0, & x > 0 \\
\end{align*}
\at \ t \leq 0 \tag{4.1-9}
\]

The concentration of solute for the system given by Eq. 4.1-1 will be $C'_0$ for $x \leq 0$ for all values of $r$. It moves down the tube at a velocity $V_x(r)$. The tracer moves the fastest at the centerline of the tube and moves slowly closer to the tube wall.

Taylor [45] has given the mean concentration distribution of Newtonian fluid for this case as
Fig. 4. Average concentration distribution of tracer in Eyring model fluid - pulse input with no diffusion.
\[ C_m = C'_o \quad , \quad x < 0 \quad (4.1-10) \]
\[ C_m = C'_o (1 - \frac{x}{t V_m}) \quad , \quad 0 < x < t V_m \quad (4.1-11) \]
\[ C_m = 0 \quad , \quad x > t V_m \quad (4.1-12) \]

For the case of the Eyring model fluid the distribution of mean concentration is
\[ C_m = C'_o \quad , \quad x < 0 \quad (4.1-13) \]
\[ C_m = C'_o \left[ \frac{1}{b} \cosh^{-1} \left( \cosh b - \frac{x}{t V_m} (\cosh b - 1) \right) \right]^2 \quad , \quad 0 < x < t V_m \quad (4.1-14) \]
\[ C_m = 0 \quad , \quad x > t V_m \quad (4.1-15) \]

The derivation of Eq. 4.1-14 is given in the Appendix B.2. The similar expression for the Power Law model fluid is given by
\[ C_m = C'_o \left(1 - \frac{x}{t V_m}\right)^{n+1} \quad (4.1-16) \]

The concentration distribution of Eq. 4.1-14 for the Eyring model fluid is plotted in Figure 5 for various values of \( b \).

### 4.2 Laminar Convection With Radial Diffusion

Here, neglecting longitudinal diffusion, Eq. 4-1 reduces to
\[ \frac{\partial C}{\partial t} + V_x(r) \frac{\partial C}{\partial x} = D \left( \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C}{\partial r} \right) + \frac{\partial^2 C}{\partial r^2} \right) \quad (4.2-1) \]

Again \( D \) is assumed to be independent of position and concentration and the longitudinal diffusion term \( \frac{\partial^2 C}{\partial x^2} \) in Eq. 4.1 is assumed much less
Fig. 5. Average concentration distribution of tracer in Eyring model fluid - step input with no diffusion.
than the radial diffusion terms \( \frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} \).

A. Newtonian Fluid

The velocity distribution for the Newtonian fluid is parabolic and is given by the expression

\[
V_x = V_m \left[ 1 - \left( \frac{r}{R} \right)^2 \right] 
\]

(4.2-2)

Substituting Eq. 4.2-2 into Eq. 4.2-1 and using \( \xi = r/R \), yields

\[
\frac{R^2}{D} \frac{\partial C}{\partial t} + \frac{R^2 V_m}{D} (1 - \xi^2) \frac{\partial C}{\partial x} = \frac{\partial^2 C}{\partial \xi^2} + \frac{1}{\xi} \frac{\partial C}{\partial \xi} 
\]

(4.2-3)

It is difficult to find the complete solution of Eq. 4.2-3, but Taylor [45] has found an approximate solution which is valid under certain limiting conditions. In the analysis, he considered the time necessary for appreciable effects to appear, owing to convective transport, to be long compared with the "time of decay" of radial concentration gradients by molecular diffusion. The longitudinal transfer of concentration of solute is only due to convection since we have neglected molecular diffusion in the longitudinal direction.

For convection across a plane which moves with the mean speed of flow, we can write

\[
x_1 = x - V_x t 
\]

(4.2-4)

Since we have assumed that the radial variation in \( C \) is small compared to the longitudinal variation, \( \frac{\partial C}{\partial x_1} \) is indistinguishable from \( \frac{\partial C_m}{\partial x_1} \).

Taylor has shown that if the following inequalities
\[ \frac{4L}{R} \gg \frac{V_x R}{D} \gg 6.9 \]  

(4.2-5)

are satisfied, a diffusion type of equation is applicable, i.e.

\[ \frac{\partial c_m}{\partial t} = k \frac{\partial^2 c_m}{\partial x^2} \]  

(4.2-6)

where \( k \), the dispersion coefficient for the Newtonian fluid is given by

\[ k = \frac{R^2 V_x^2}{48 D} \]  

(4.2-7)

Eq. 4.2-6 can be readily solved for the cases of an impulse of tracer and step input of tracer. The expressions for these two cases as derived by Taylor are as follows:

\textbf{Pulse injection:} \quad c_m = 0.5 \frac{c^i X}{\sqrt{\pi k t}} \exp \left[ -\frac{(x-V_x t)^2}{4 k t} \right]  

(4.2-8)

\textbf{Step input:} \quad c_m = 0.5 c_o \left[ \text{erfc} \left( \frac{x-V_x t}{\sqrt{4 k t}} \right) \right]  

(4.2-9)

The concentrations given by these equations are symmetrical about \( x = V_x t \).

Aris [2] concluded, for the case in which axial molecular diffusion is significant, Taylor's approximate solution can be modified by replacing \( k \) by \( k' \) thus

\[ k' = \frac{R^2 V_x^2}{48 D} + D \]  

(4.2-10)

Introducing the following dimensionless quantities
\[ x' = \frac{x D}{2 R^2 V_x}, \quad \tau = \frac{D t}{R^2}, \quad N_{pe} = \frac{2 R V}{D} \]  

(4.2-11)

into Eq. 4.2-9 it becomes

\[ C_m = 0.5 \ C_o' \ \text{erfc} \left( \frac{x' - \tau/2}{\sqrt{\tau/48}} \right) \]  

(4.2-12)

Considering Aris' modification Eq. 4.2-10, in terms of the dimensionless quantities, Eq. 4.2-9 becomes

\[ C_m = 0.5 \ C_o' \left[ \text{erfc} \left( \frac{x' - \tau/2}{\sqrt{\tau/48 + 4 \ \tau/\eta_{pe}^2}} \right) \right] \]  

(4.2-13)

The physical significance of the Peclet number, \( N_{pe} \) in above Eq. 4.2-11, is that it provides some measure of the relative magnitude of axial convective transport and diffusive transport of solute in the flow system.

When it is not possible to measure the average concentration, the concept of bulk concentration will be very useful. In a circular tube considering only axial velocity, the bulk concentration is given by

\[ C_b = \frac{\int_{Vx(r)}^{R} C(r) r dr}{\int_{Vx(r)}^{R} r dr} \]  

(4.2-14)

For a Newtonian fluid, this becomes

\[ C_b = \frac{4}{R^2} \int_{0}^{R} \left[ 1 - \left( \frac{r}{R} \right)^2 \right] C r dr \]  

(4.2-15)

The equation for bulk concentration in this case for which Eq. 4.2-9 is valid is given by Ananthakrishnan et al. [1] as
The document contains text that is not legible due to the quality of the image.
\[ C_b = C_o \left[ 0.5 \text{erfc} \left( \frac{x - \overline{V}_x t}{\sqrt{4kt}} \right) + \frac{1}{96} \frac{1}{\sqrt{4kt}} \exp \left\{ - \frac{(x - \overline{V}_x t)^2}{4kt} \right\} \right] \]  

(4.2-16)

B. *Eyring Model Fluid*

Neglecting longitudinal diffusion and introducing the following dimensionless quantities

\[ \theta = \frac{t}{\tau} = \frac{t \overline{V}_x}{L}, \quad \eta = \frac{x}{L}, \quad \zeta = \frac{r}{R} \]  

(4.2-17)

in Eq. 4-1, we have

\[ \frac{\partial C}{\partial \theta} = \frac{D \overline{V}_x}{R^2} \left[ \frac{\partial^2 C}{\partial \eta^2} + \frac{1}{\zeta} \frac{\partial C}{\partial \zeta} \right] - \frac{V_x}{\overline{V}_x} \left( \frac{\partial C}{\partial \eta} \right) \]  

(4.2-18)

with the boundary conditions

\[ \frac{\partial C}{\partial \zeta} = 0 \quad \text{at} \quad \zeta = 1 \quad \text{and} \quad \zeta = 0 \]  

(4.2-19)

Following Taylor, relative to the plane which moves with the mean speed of the flow, the velocity distribution is

\[ V_{x1} = V_x - \overline{V}_x \]  

(4.2-20)

Using Eq. 3.2-11, Eq. 4.2-20 becomes

\[ V_{x1} = \overline{V}_x \left[ \frac{1}{E} \left(1 - \frac{\cosh b \zeta}{\cosh b} \right) \right] \]  

(4.2-21)

Substituting Eq. 4.2-21 into Eq. 4.2-18, it becomes
\[
\frac{\partial C}{\partial \theta} = \frac{D}{r^2} \left[ \frac{\partial^2 C}{\partial \xi^2} + \frac{1}{r} \frac{\partial C}{\partial \xi} \right] - \left[ \frac{1}{E} (1 - \frac{\cosh b \xi}{\cosh b}) - 1 \right] \left( \frac{\partial C_m}{\partial \eta_1} \right) \tag{4.2-22}
\]

where \( \eta_1 = \eta - \theta \) and \( C = C_m \).

Assuming \( \left( \frac{\partial C_m}{\partial \eta_1} \right) \) is independent of \( \xi \), and

\[
S = \frac{R^2}{dt} \left( \frac{\partial C_m}{\partial \eta_1} \right) \quad \text{when} \quad \frac{\partial C}{\partial \theta} = 0, \quad \text{Eq. 4.2-22 becomes}
\]

\[
\left[ \frac{d^2 C}{d\xi^2} + \frac{1}{r} \frac{dC}{d\xi} \right] = S \left\{ \frac{1}{E} (1 - \frac{\cosh b \xi}{\cosh b}) - 1 \right\} \tag{4.2-23}
\]

The analytical solution of Eq. 4.2-23 is given in Appendix B.3; it is

\[
C = C_0 + S \left[ \frac{1}{E} \left( \frac{1}{b^2 \cosh b} + \frac{(1-E)^2}{4} - \frac{\cosh b \xi}{b^2 \cosh b} \right) + \frac{1}{b^2 \cosh b} \left( \ln \xi + \frac{(b \xi)^2}{4} + \frac{(b \xi)^4}{96} + \frac{(b \xi)^6}{4320} \right) + \right. \ln \xi \left( \frac{\tanh b}{b} - \frac{1}{b^2} \frac{(1-E)}{2} \right) \right]\]

\[
C = C_0 \tag{4.2-24}
\]

where \( C_0 \) is the value of concentration at \( \xi = 0 \).

\[
C' = \frac{C - C_0}{S} \tag{4.2-25}
\]

in Eq. 4.2-24, it becomes

\[
C' = \frac{1}{E} \left[ \frac{1}{b^2 \cosh b} + \frac{(1-E)^2}{4} - \frac{\cosh b \xi}{b^2 \cosh b} + \frac{1}{b^2 \cosh b} \left( \ln \xi + \frac{(b \xi)^2}{4} + \frac{(b \xi)^4}{96} + \frac{(b \xi)^6}{4320} \right) + \right. \ln \xi \left( \frac{\tanh b}{b} - \frac{1}{b^2} \frac{(1-E)}{2} \right) \right] \tag{4.2-26}
\]
The effect of the dimensionless parameter $b$, on the dimensionless concentration profiles is shown in Figure 6. It can be seen from this plot that as the value of the dimensionless parameter $b$ increases, the concentration profile becomes flatter; i.e. the difference in concentration between that at the wall and that at the center of the tube becomes less.

The dimensionless mean concentration is given by

$$C'_m = 2 \int_0^1 C'(\xi) \, d\xi \quad (4.2-27)$$

By substituting Eq. 4.2-26 into Eq. 4.2-27, the exact form of Eq. 4.2-27 is

$$C'_m = \frac{2}{E} \left[ \frac{1}{2b^2 \cosh b} + \frac{(1-E)}{16} - \frac{1}{b^3} \left( \tanh b - \frac{1}{b} + \frac{1}{b \cosh b} \right) + \frac{1}{b^2 \cosh b} \left( \frac{b^2}{16} + \frac{b^4}{576} + \frac{b^6}{34560} - \frac{1}{4} \right) + \left( \frac{1}{4b^2} + \frac{(1-E)}{8} \right) \frac{\tanh b}{4b} \right] \quad (4.2-28)$$

Details of the derivation of Eq. 4.2-28 are given in Appendix B.4.

The volumetric flow rate, $Q$, across the plane moving at a velocity $V_{xl}$ is

$$Q = 2\pi R^2 \int_0^1 C(\xi) \, V_{xl}(\xi) \, \xi \, d\xi \quad (4.2-29)$$

Based on the dimensionless concentration

$$Q'' = 2\pi R^2 \int_0^1 C'(\xi) \, V_{xl}(\xi) \, \xi \, d\xi \quad (4.2-30)$$
Fig. 6. Dimensionless concentration profile - Eyring model fluid.
The dimensionless volumetric flow rate is
\[
Q' = \frac{Q'}{2\pi R^2 v_x} \tag{4.2-31}
\]
or,
\[
Q' = \int_0^1 C'(\xi) \frac{V_{x_1}(\xi)}{V_x} \xi d\xi \tag{4.2-32}
\]

Substituting Eqs. 4.2-21 and 4.2-26 into Eq. 4.2-32, we get
\[
Q' = \frac{1}{E^2} \left[ \frac{F}{4b^2 \cosh b} + \frac{F^2}{16} + \frac{F}{16 \cosh b} + \frac{Fb^2}{\cosh b} \left( \frac{b^2 + 60}{34560} \right) - \frac{1}{b^3 \cosh b} \left( \sinh b \right) - \frac{\cosh b}{b} + \frac{1}{b} \right] \left( F + \frac{1}{\cosh b} \right) - \frac{1}{\cosh b} \left( \frac{\tanh b}{b} - \frac{1}{b^2} - \frac{F}{2} \right) \right] + \frac{1}{b^2}
\]
\[
- \frac{3}{b} \left[ \left( \frac{1}{b} + \frac{2}{b^3} \right) \cosh b - \frac{2 \sinh b}{b^2} - \frac{2}{b^3} \right] \right] + \frac{1}{4b^4 \cosh^2 b} \left( b \sinh 2b - \frac{\cosh 2b}{2} - \frac{7}{2} + 4 \cosh b - \frac{b^4}{24} - \frac{b^6}{1080} \right) - \left[ -5bcosh b + 20sinh b - \frac{60}{b} \right] \cosh b + \frac{2 \cosh b}{b^2} - \frac{2 \sinh b}{b} - \frac{2}{b^2} \right] \right] + \frac{1}{4 \cosh 2b} \left( 7 - btanh b \right) \tag{4.2-33}
\]

where \( F = (1-E) \). The complete derivation of this is given in Appendix B.5.

Using \( C = \frac{C'}{R^2} \left( \frac{\partial c_m}{\partial \eta_1} \right) + c_o \) from Eq. 4.2-25, Eq. 4.2-29 becomes
\[ Q = 2\pi R^2 \left[ \frac{R^2}{\Delta t} \left( \frac{\partial C_m}{\partial \eta_1} \right)_o \right] \int_0^1 C'V_{x1} \, \xi \, d\xi + \int_0^1 C_{oV_{x1}} \, \xi \, d\xi \]  
(4.2-34)

Since \( \int_0^1 C_{oV_{x1}} \, \xi \, d\xi = 0 \)

\[ Q = 2\pi R^2 \frac{R^2}{\Delta t} \left( \frac{\partial C_m}{\partial \eta_1} \right)_o \int_0^1 C'V_{x1} \, \xi \, d\xi \]  
(4.2-35)

Substituting Eqs. 4.2-21 and 4.2-26 into Eq. 4.2-35, we have finally that

\[ Q = -\frac{\pi R^2}{\Delta V_x} \left( \frac{\partial C_m}{\partial \eta_1} \right)_o \]  
(4.2-36)

where

\[ k = \frac{2R^2V_x^2}{D} (-Q') \]  
(4.2-37)

The dimensionless effective dispersion coefficient, \( K' \) is defined as

\[ K' = k \frac{D}{2R^2V_x^2} \]  
(4.2-38)

and so \( K' = -Q' \).

Eq. 4.2-38 signifies that the dimensionless volumetric flow rate \( Q' \) is equivalent to the dimensionless effective dispersion coefficient \( K' \).

Figure 7 shows a plot of \( K' \) versus the parameter \( b \). The value of \( K' \) for a Newtonian fluid is greater than that for a non-Newtonian fluid.

The asymptotic case occurs when the value of the dimensionless parameter \( b \) for the Eyring fluid reaches infinity. \( K' \) is then equal to zero for plug flow conditions in the tube.

The fact that no material is lost in the process is expressed by the continuity equation for \( C_m \)

\[ \frac{\partial Q}{\partial x_1} = -\pi R^2 \frac{\partial C_m}{\partial t} \]  
(4.2-39)
Fig. 7. Variation of $K'$, dimensionless effective dispersion coefficient, with $b$, Eyring model fluid parameter.
Hence substituting for \( Q \) from Eq. 4.2-36 gives the governing partial differential equation of axial dispersion:

\[
\frac{\partial c_m}{\partial t} = k \frac{\partial^2 c_m}{\partial x_1^2} ;
\]  
(4.2-40)

\( k \) is defined by Eq. 4.2-37.

Following Taylor, the solutions of Eq. 4.2-40 for a pulse injection and a step input of tracer are given as:

Pulse injection: \( C_m = 0.5 \frac{c'_0 x}{\sqrt{\pi k t}} \exp\left(\frac{-x_1^2}{4kt}\right) \)  
(4.2-41)

Step input: \( C_m = 0.5 c'_0 \text{erfc}\left(\frac{x_1}{\sqrt{4kt}}\right) \)  
(4.2-42)

where \( c'_0 \) is the initial concentration. Using Eqs. 4.2-37 and 4.2-11, Eq. 4.2-42 becomes

\[
C_m = 0.5 c'_0 \text{erfc}\left[\frac{x'_1 - \tau/2}{\sqrt{-2Q'}\tau}\right]
\]  
(4.2-43)

As \( b \to 0 \), \( Q' = -1/96 \) and Eq. 4.2-43 reduces to

\[
C_m = 0.5 c'_0 \text{erfc}\left[\frac{x'_1 - \tau/2}{\sqrt{\tau/48}}\right]
\]  
(4.2-44)

which is the equation for the Newtonian case. Figure 8 shows the response of the average concentration to a step input in tracer of the Eyring model fluid for various values of \( b \) as predicted by Eq. 4.2-43. This is the response at various axial positions \( x' \) at a fixed time \( \tau = 2.0 \). The time response of the average concentration of tracer to a step input at a fixed axial position \( x' = 6 \) for the various values of
Fig. 8. Average concentration distribution of tracer in Eyring model fluid - step input with radial diffusion.
b is given in Figure 9.

The expression for the bulk concentration is derived in Appendix B.6 and is:

$$
\frac{C_b}{C^0} = \frac{1}{E \cosh b} \left( \sinh b - \frac{\cosh b}{b} + \frac{1}{b} \right) - \frac{0.5 C_m}{\sqrt{2 \pi Q^0}} \exp \left( \frac{(X' - \tau/2)^2}{2Q^0} \right) \left( Q' + \frac{C_m}{2} \right)
$$

(4.2-45)

Eq. 4.2-45 is plotted in Figure 10 for various values of the parameter b for the fixed axial position X' = 12 and various values of time $\tau$. The expressions as given by Eqs. 4.2-41 and 4.2-42 can be used for the case of the Power Law model fluid where the dispersion coefficient k as derived by Fan and Hwang [16] can be replaced by

$$
k = \frac{R^2V_x^2}{D} \frac{n^2}{2(3n+1)(5n+1)}
$$

(4.2-46)

Introducing the dimensionless quantities of Eq. 4.2-11 into Eq. 4.2-42 for the case of the Power Law model

$$
C_m = 0.5 C^0 \text{erfc} \left[ \frac{X' - \tau/2}{\sqrt{\frac{n^2}{2(3n+1)(5n+1)} \tau}} \right]
$$

(4.2-47)

4.3 Laminar Convection With Axial and Radial Diffusion

When both the axial and radial diffusion are significant with respect to the convective transport, the problem becomes very complex. In this case, one needs to find the complete solution of Eq. 4-1 using
Fig. 9. Average concentration distribution of tracer in Eyring model fluid - step input with radial diffusion.
Fig. 10. Bulk concentration distribution of tracer in Eyring model fluid - step input with radial diffusion.
the different velocity profiles for the Newtonian and non-Newtonian cases. Thus substituting the expression for velocity profile for a Newtonian fluid into Eq. 4-1

$$D \left( \frac{\partial^2 C}{\partial x^2} + \frac{1}{r} \frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial r^2} \right) = \frac{\partial C}{\partial t} + 2v_x \left( 1 - \left( \frac{r}{R} \right)^2 \right) \frac{\partial C}{\partial x} \quad (4.3-1)$$

The analytical solution of this equation is complex to obtain; a numerical solution using finite-difference techniques was first given by Ananthakrishnan et al. [1].

If the non-Newtonian fluid in question is a Power Law model fluid whose velocity profile is given by Eq. 3.2-7, Eq. 4-1 becomes

$$D \left( \frac{\partial^2 C}{\partial x^2} + \frac{1}{r} \frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial r^2} \right) = \frac{\partial C}{\partial t} + \frac{3n+1}{n+1} \frac{1}{v_x} \left( 1 - \left( \frac{r}{R} \right)^n \right) \frac{\partial C}{\partial x} \quad (4.3-2)$$

Eq. 4.3-2 with the following boundary conditions,

$$\frac{\partial C}{\partial r} = 0 \quad \text{r = 0 and} \quad \text{r = R} \quad (4.3-3)$$
$$C = 0 \quad \text{x > 0} \quad t \leq 0 \quad (4.3-4)$$
$$C = 0 \quad \text{x = \infty} \quad (4.3-5)$$
$$C = C_o' \quad \text{x \leq 0} \quad t \geq 0 \quad (4.3-6)$$

can be transformed into the dimensionless quantities by using Eq. 4.2-11 and introducing the following transformations

$$\zeta = \frac{r}{R} \quad , \quad C^+ = \frac{C}{C_o'} \quad , \quad \eta' = \frac{x'}{\sqrt{t}} \quad (4.3-7)$$

French [18] showed that the diffusion equation, Eq. 4.3-2, becomes
\[
\frac{1}{\tau N_{pe}^2} \frac{\partial^2 C^+}{\partial \eta'^2} + \frac{\partial^2 C^+}{\partial \xi^2} + \frac{1}{\tau} \frac{\partial C^+}{\partial \tau} = \frac{\partial C^+}{\partial \eta'} + \left[ \frac{1}{2} \frac{3n+1}{n+1} \left( \frac{n}{n+1} \right) - \frac{1}{2} \eta' \right] \frac{\partial C^+}{\partial \eta'}
\]

\(\tau \leq \frac{n}{n+1}\) \(\eta' > 0\)  

\(\eta' \geq 0\)

It is clear from Eq. (4.3-8) that the effect of the axial diffusion term will be negligible at the high values of Peclet number \(N_{pe}\). As mentioned earlier, French [18] has used a numerical technique similar to that of Ananthakrishnan et al. [1] to solve Eq. (4.3-8) for the case of the Power Law model fluid.

For the case of the Eyring model fluid, substituting Eq. (3.2-11) for the velocity profile in Eq. (4.1) gives

\[
D \left( \frac{\partial^2 C}{\partial x^2} + \frac{1}{r} \frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial r^2} \right) = \frac{\partial C}{\partial t} + \frac{1}{E} V x \left( 1 - \frac{\cosh \left( \frac{br}{R} \right)}{\cosh b} \right) \frac{\partial C}{\partial x}
\]

Using a numerical approach of French [18], one could solve Eq. (4.3-10) for the Eyring model fluid; however, no attempt was made in this study to solve Eq. (4.3-10) numerically.
CHAPTER V
EXPERIMENTAL INVESTIGATION

The present investigation has been undertaken to collect experimental data from a non-Newtonian flow system and could be analyzed in the following manner.

(1) To find the non-Newtonian fluid which exhibits the properties of a time-independent fluid and fits the Power Law model for a wide range of shear rate.

(2) To validate experimentally the dispersion analysis presented for the Power Law non-Newtonian model fluid for a wide range of dimensionless times and Peclet numbers and discuss the applicability of various theoretical solutions presented earlier.

(3) To examine the influence, if any, of various sizes of tubes on dispersion phenomena.

(4) To determine values of the dispersion coefficient and the diffusion coefficient of the non-Newtonian fluid using a tracer material.

5.1 SELECTION OF EXPERIMENTAL SYSTEM

5.1.1 SYSTEM FOR RHEOLOGICAL EXPERIMENT

The first part of the experiment was to find the two unknown parameters \((m, n)\) of the Power Law model fluid for different non-Newtonian fluids. As seen in Chapter III, to find these parameters one needs to know the relationship between the shear stress and the
shear rate. Pressure drop data for flow through a tube at different volumetric flow rates of fluid were used to determine this relationship. A capillary tube was chosen as a flow conduit and a positive displacement pump was used to pump the fluid through the capillary tube. A syringe pump was chosen since it delivers fluid at a constant flow rate. The flow rate can be measured very accurately, and it can be varied by moving the position of the selector on the pump. This experimental setup is simple to install, inexpensive, and very convenient in a way that the same apparatus can be used for both experiments — rheological and dispersion.

5.1.2 SYSTEM FOR DISPERSION EXPERIMENT

The second experiment was to inject a tracer material or dye into the non-Newtonian fluid for a known period of time and measure the concentration of the tracer along the tube. In the past, various investigators [45, 9, 50, 5, 39, 35] have used a dye as a tracer material for both the Newtonian and non-Newtonian fluids, and their experimental results are comparable to those predicted from the theory. Recently, French [18] used Na$^{24}$ radioactive isotope as a tracer in his studies on dispersion in non-Newtonian laminar flow. His experience shows that the use of a radioactive isotope is not convenient. The use of a dye has many advantages over the use of Na$^{24}$ isotope because:

(1) One has to make the isotope of Na$^{24}$ by bombarding crystalline or aqueous solutions of sodium chloride with a radiation flux while dyes are available commercially.
(2) There is always a danger of exposure to radiation since $^{24}\text{Na}$ isotope is extremely radioactive. There is no such danger involved in using dye.

(3) It is potentially dangerous to handle a radioactive material since there is always a danger of contamination to the researcher, the equipment, and the building.

(4) It has been found from past experience that even a strong isotope is good only for a few experimental runs. Hence, the experimenter has to make a new isotope very often and a long time is necessary to perform the experiment.

In the present experiment, DuPont Pontamine Sky Blue 6BX dye was chosen as a tracer material. The concentration of dye at different positions along the tube was measured by a Cary 14 spectrophotometer. It was found that the absorption of light by different solutions is a linear function of concentration of dye in the concentration range used. It is relatively simple to measure concentrations at different axial positions along the capillary tube without withdrawing samples from the system.

It was decided to choose an aqueous solution of polyethylene oxide or Polyox as a non-Newtonian fluid since it dissolves readily in water. It was also found from previous experimental studies that aqueous solutions of Polyox fit the Power Law model very well over a wide range of shear rate.

5.2 **DESCRIPTION OF EQUIPMENT**

The various pieces of equipment used in the present experiment
can be divided into two classes: (1) flow measurement equipment, and (2) concentration measurement equipment.

5.2.1 FLOW MEASUREMENT EQUIPMENT

Precision-bore Pyrex brand capillary tubes were used for flow-pressure drop data in the tube and also for dispersion measurements in the displacement experiment. The capillary tube was connected to the syringe pump by ball-and-socket joints. A manometer with either carbon tetrachloride or mercury as a manometer fluid was used to measure the pressure drop. The complete experimental setup is shown in Figure 11.

Desired flow rates were obtained by choosing the proper size of the syringe and position of the selector switch on the pump. A Model 341 syringe pump, Sage Instruments, Division of Orion Research Inc., was used. The rate selector switch has eleven positions, and the size of the syringes that can be used varies from 10 µL to 50 ml. The minimum flow rate that can be delivered by the pump is 0.000092 ml/hr, and the maximum is 13.0 ml/min.

Two tubes of 0.1 and 0.2 cm internal diameter and approximately 94 cm in length were used. The capillary tube was supported by level wood blocks and the alignment of the tube was checked with a spirit level. B-D Yale hypodermic syringes were used in the present experiment. To study the rheological properties, aqueous solutions of 0.1 and 1.0% Polyox (a polyethylene oxide water-soluble resin) were used. The Polyox used in the present study was Polyox WSRN - 3000 Lot 1450 manufactured by Union Carbide Corporation.
Fig. 11. Experimental setup of Flow Measurement Equipment.
5.2.2 CONCENTRATION MEASUREMENT EQUIPMENT

The concentration of dye at various axial positions of the capillary tube was determined by a Cary 14 spectrophotometer. A separate assembly similar to the one used by Bailey and Gogarty [5] in their experiment on dispersion in Newtonian fluid was designed and built. This assembly fits inside the sample box of the spectrophotometer and holds the capillary tube perpendicular to the light beam. Details of the assembly are shown in Figure 12.

The centering mechanism of the tube is mounted on the plate A, which is attached to the sample box of the spectrophotometer. The tube holder B is mounted on the movable plate C. This plate can travel perpendicular to the beam of light, and its motion can be controlled by a knob D. The beam of light passes through a hole in the tube holder and then through the capillary tube E which is positioned in the tube holder by means of a V-groove. The tube is held by spring tension clamps and thus can be moved up and down so that the beam of light passes through any desired axial tube position. The position along the tube can be measured by an attached meter stick F.

The beam from the light source of the spectrophotometer passes through a lens, a prism, then through the capillary tube, a biconvex lens, and finally arrives at a detector. The amount of light absorbed by the solution in the capillary tube can be found by knowing the change in intensity of the light between the source and detector.
A. Plate  
B. Tube Holder  
C. Movable Plate  
D. Knob  
E. Capillary Tube  
F. Meter Stick  
G. Lens Holder

Fig. 12. Concentration Measurement Apparatus.
5.3  **EXPERIMENTAL PROCEDURES**

5.3.1  **PREPARATION OF AQUEOUS POLYMER SOLUTIONS**

It can be readily shown by calculation that 10.0735 gm of Polyox powder dissolved in 1000 ml of water makes a 1.0% wt. aqueous Polyox solution. Since the mode of preparation of solution affects the reproducibility of results, it is very important how one mixes polymer powder with water. The powder was added to distilled water in a beaker in small amounts. A magnetic stirrer was used to dissolve the powder in water. The rate of stirring was kept low to minimize mechanical degradation of the polymer molecules. Twenty hours was required for preparation of one batch (1000 ml). During the process of dissolution, the room temperature was maintained at 74 ± 1°C.

After 3 liters of solution was prepared, it was filtered, and the concentration of the solution was checked by gravimetric analysis. The density of the prepared solution was determined using a specific gravity bottle. The 1.0% solution of Polyox was then diluted to the required concentration of 0.1%.

5.3.2  **MEASUREMENT OF TUBE DIAMETER**

The length of the capillary tube was measured with a steel tape to the accuracy of 0.1 cm. To measure the average inside diameter, the tube was filled with mercury, and the mercury was collected in a weighing bottle. Knowing the length of the tube, weight of mercury, and the density of mercury, the average inside diameter was calculated. The precise diameters of the tubes used in the rheological measurements
were 1.0584 and 2.1422 mm and the length of each tube was approximately 93 cm.

5.3.3 CALIBRATION OF SYRINGE PUMP

The pump was first calibrated by choosing different sizes of the syringes and selecting different positions of the selector switch on the pump. The fluid was run through a capillary tube for a known period of time, and the discharge from the tube was collected and weighed. It was found that the measured flow rates for all cases agreed well within ±2% with the tabulated flow rates specified for the pump.

5.3.4 RHEOLOGICAL MEASUREMENTS

The capillary tube and the syringe were filled with the polymer solution to be tested and connected together with a clamp. Tygon tubing was used to connect the manometer as shown in Figure 11. A sufficient length of the tube was provided at either end of the main tube (across which the pressure drop was measured) to lessen the end effects. The pressure difference in the manometer was noted during flow after allowing sufficient time to reach steady state. The pump was then stopped, the syringe was refilled, and the pressure drop was obtained at another flow rate. This procedure was then repeated for different tube sizes. The pressure drop-flow rate data were obtained for both solutions, namely 0.1% and 1.0% Polyox solution, at two different tube sizes.
Figures 13 and 14 are plots of pressure drop versus time. It is seen from these plots that the pressure increases very rapidly for the initial period of time and becomes steady after about 5 mins. Each pressure drop reading was taken after reaching the steady state. These pressure drop-flow rate data can easily be converted to shear stress-shear rate data as outlined in Chapter III.

The time required to reach a steady value of the pressure drop for 1.0% Polyox was due to the time response of the pressure measurement manometer. To verify this, the response time was measured for two Newtonian fluids, water and 65% wt. glycerol (μ = 13 CP). It was found that the time response of the manometer for the Newtonian and non-Newtonian fluids was equivalent.

5.3.5 CALIBRATION OF SPECTROPHOTOMETER

The calibration of the spectrophotometer was based on a reading of zero absorption for 1.0% Polyox solution. This was done by filling the tube with 1.0% Polyox solution and centering it in the beam of light source and adjusting the various electronic controls on the spectrophotometer. The tube was then cleaned, dried, and filled with either 100 or 200 ppm dye solution and the absorbance measured. This value of absorption was considered as equal to a concentration of 100%. Solutions of various concentrations were prepared and the absorption of these solutions was determined. A linear relationship was observed between the absorbance and various concentrations. Calibration plots were thus prepared for each capillary tube. These calibration curves are shown in Figures 15 and 16. All light
Dia. of tube: 1 mm

Flow Rate

- 0.32 ml/min
- 0.65 ml/min

Fig. 13. Pressure drop of 1.0% Polyox solution from startup.
Fig. 14. Pressure drop of 1.0% polyox solution from startup.

Pressure drop, \( \Delta p \) vs \( \Delta \sigma \) (dynes/cm²) x 10^3 (mm Hg)

Dia. of tube: 2 mm
Flow Rate
0.32 ml/min
0.65 ml/min
Fig. 15. Calibration plot of absorbance versus concentration for Dye - Polyox system.
Fig. 16. Calibration plot of absorbance versus concentration for Dye - Polyox solution.
absorption measurements were made at a wavelength of 6370 Å which corresponds to the absorption peak for Pontamine dye.

A similar procedure was followed for a 700 ppm $\text{KMnO}_4$ - water solution and the calibration plot is shown in Figure 17.

5.3.6 **DISPERSION MEASUREMENTS**

The displacement experiment was again carried out in precision bore capillary tubes of 1.0 and 2.0 mm internal diameter, approximately 103 cm in length. The length of each tube was measured and the average inside diameter was determined as mentioned earlier. The precise diameters of these tubes were 1.040 and 2.106 mm. The sketch of the experimental setup is shown in Figure 18.

As mentioned previously, the rheological properties were measured for two non-Newtonian fluids, but only 1.0% Polyox solution was chosen for the dispersion experiment. The concentration of dye solution used with the 1.0 mm tube was 200 ppm, and with the 2.0 tube - 100 ppm.

Dispersion measurements were done first with the Newtonian ($\text{KMnO}_4$ - $\text{H}_2\text{O}$) system in the 1.0 mm tube to check the experimental procedure. The results obtained from this experiment were compared to previous results reported in the literature. Several runs were done at various flow rates and flow times.

To begin an individual run, the tube was filled with a solution containing dye. A certain velocity of flow was selected. The filled tube was plugged at one end and joined with the syringe containing pure water or Polyox solution. The run was started by removing the plug and starting the pump and stop watch simultaneously. The flow
Fig. 17. Calibration plot of absorbance versus concentration for KI vs. H₂O system.
Fig. 18. Schematic Diagram of Dispersion Experiment
was stopped after the preselected time had elapsed. The tube was then disconnected and sealed.

The length of the mixed zone was determined by measuring the concentration of dye as a function of distance. The concentration was measured at 5 cm intervals along the tube. All measurements were done at atmospheric pressure and a temperature of 74 ± 1°F.

5.4 ANALYSIS OF DATA

The theory of the dispersion of solutes in non-Newtonian fluids through a tube of circular cross-section is presented in Chapter IV. In this theoretical development, it was assumed that the capillary tube at time \( t \leq 0 \) contains only a pure solvent, i.e. the dimensionless concentration of solute \( \frac{C^+}{C_0} = 0 \) in the tube. Step input of dissolved material of uniform concentration at \( C^+ = 1 \) is allowed to enter the tube at uniform rate at \( x = 0 \) starting at time \( t = 0 \). In the experimental work the situation was just the opposite. The tube was initially filled with fluid containing tracer material, and pure solvent was introduced at \( t = 0 \). In order to use the present experimental data and the Taylor - Fan model, it is necessary to introduce the dimensionless average concentration \( C_m^{++} \) as

\[
C_m^{++} = 1 - C_m^+ \quad (5.4-1)
\]

Introducing Eq. 5.4-1 into Eq. 4.2-42 where \( k \) is defined by Eq. 4.2-46

\[
C_m^{++} = 1 - 0.5 \left[ 1 - e^\frac{x}{2} (\frac{1}{\sqrt{4kt}}) \right] \quad (5.4-2)
\]
Simplifying

\[ C_{m}^{++} = 0.5 \left[ 1 + \text{erf} \left( \frac{x}{\sqrt{4kt}} \right) \right] \quad (5.4-3) \]

If \( L \) is the length of the mixing zone in which concentration of solute changes from 10% to 90% then from Eq. 5.4-3 it follows that

\[ L = 3.62 \sqrt{kt} \quad (5.4-4) \]

or

\[ k = \frac{L^2}{13.1 t} \quad (5.4-5) \]

From the experimental data of concentration versus axial length of the tube, \( L \) can be determined corresponding to concentrations of 90% and 10%. Knowing the time of flow for each run, the dispersion coefficient, \( k \), can be calculated from Eq. 5.4-5. The diffusion coefficient, \( D \), can be determined from Eq. 4.2-46 thus

\[ D = \frac{\frac{2}{R} V_x^2}{k} \left[ \frac{n^2}{2(3n+1)(5n+1)} \right] \quad (5.4-6) \]

Taking the natural logarithm of Eq. 4.2-46

\[ \ln k = 2\ln V_x + \ln \frac{\frac{R^2 n^2}{n}}{2D(3n+1)(5n+1)} \quad (5.4-7) \]

The log-log plot of \( k \) versus \( V_x \) should have a slope of 2 and an intercept of \( \frac{R^2 n^2}{2D(3n+1)(5n+1)} \). Knowing the value of intercept, the radius of the tube, and the value of the flow behavior index \( n \), one can calculate the value of the diffusion coefficient \( D \).
CHAPTER VI

RESULTS AND DISCUSSION

The results obtained from the analysis of the experimental measurements are included in this chapter, and the range of applicability of various results are discussed. Experimental results are divided into two categories: (1) rheological measurements, and (2) dispersion measurements.

6.1 RESULTS OF RHEOLOGICAL MEASUREMENTS

As mentioned earlier, the polymer solutions were characterized by measuring the pressure drop across a given length of glass capillary tube of known inside diameters for various flow rates. In Chapter III it was shown that the wall shear stress \( \tau_w \) and apparent wall shear rate \( \dot{\gamma}' \) are given by

\[
\tau_w = \frac{R \Delta P}{2L_1}
\]

(6.1-1)

\[
\dot{\gamma}' = \frac{4V_x}{R}
\]

(6.1-2)

From Eq. 3.3-5 it is clear that a log-log plot of \( \tau_w \) versus \( \dot{\gamma}' \) is linear with its slope equal to \( n' \) and that \( n' = n \), the flow behavior index from Eq. 3.3-6. The actual wall shear rate \( \dot{\gamma} \) is then given by

\[
\dot{\gamma} = \left( \frac{3n' + 1}{4n'} \right) \dot{\gamma}'
\]

(6.1-3)
A linear plot of $\tau_w$ versus $\dot{\gamma}$ on log-log coordinates will give a slope equal to the flow behavior index and the intercept on the shear stress axis for $\dot{\gamma} = 1$ gives the value of the consistency index $m$.

The results of the rheological measurements of various polymers are plotted in Figure 19. From this figure it is clear that the plots of shear stress versus shear rate on log-log coordinates are linear. Therefore, the polymers studied obey the Power Law model over the shear rate range considered. The range of shear rate and shear stress investigated was from 4 to 300 sec$^{-1}$ and 0.3 to 50 dynes/cm$^2$ respectively. Since the data obtained from the two different size of tubes lie on the same line, it is evident that these materials exhibit the characteristics of time-independent fluids. The values of the Power Law constants were evaluated from the results and tabulated in Table 1 together with the physical properties of various polymers. The apparent viscosities of the polymer solutions were determined using an Ubbelhode viscometer.

6.2 RESULTS OF DISPERSION MEASUREMENTS

6.2.1 NEWTONIAN (POTASSIUM PERMANGANATE - WATER) SYSTEM

The displacement experiment was first performed with the Newtonian ($\text{KMnO}_4 - \text{H}_2\text{O}$) system as described earlier. No attempt was made to obtain the measurements for a wide range of dimensionless time and Peclet number. However, these results did satisfy the purpose of the experiment.
Fig. 19. Plot of shear stress versus shear rate for various polymers.
### TABLE 1. Power Law constants and physical properties of various solutions at 74 ± 1°F.

<table>
<thead>
<tr>
<th>Test Liquid</th>
<th>Concentration</th>
<th>Flow behavior index, n</th>
<th>Consistency index, m, dynes sec^2/cm^2</th>
<th>Density, gm/cm^3</th>
<th>Apparent Viscosity, C.P.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyox</td>
<td>0.1%</td>
<td>0.938</td>
<td>0.017</td>
<td>0.9977</td>
<td>1.3</td>
</tr>
<tr>
<td>Polyox</td>
<td>1.0%</td>
<td>0.981</td>
<td>0.175</td>
<td>0.9988</td>
<td>14.73</td>
</tr>
<tr>
<td>Water</td>
<td>-</td>
<td>1.000</td>
<td>0.0089</td>
<td>0.9973</td>
<td>1.00</td>
</tr>
</tbody>
</table>
The concentration at various axial positions was measured, and the results were plotted as concentration versus distance from the inlet of the tube. These plots were made on probability paper since both the numerical and Taylor's approximate solutions predict that straight lines should result after sufficiently long flow times. These results are presented in Figure C1-C3 (Appendix C) for various velocities and times of flow.

As predicted from the theory, for the shorter times of flow, the plots of concentration versus tube length on probability paper were non-linear, but straight lines resulted for longer flow times. A straight line was drawn through the experimental data points as shown in these figures. The length of the mixing zone contained between average concentrations of 90 and 10% was determined from these lines. Using the value of the mixing zone length and corresponding flow time, the dispersion coefficient, $k$ was calculated from Eq. 5.4-5 for each run.

The values of diffusion coefficients were evaluated using the relation given by Eq. 5.4-6 and substituting $n = 1$ for water. The results thus obtained for the Newtonian ($\text{KMnO}_4 - \text{H}_2\text{O}$) system are summarized in Table 2.

The range of the dimensionless time considered was 0.1 to 2.0 and the Peclet number from 1300 to 6600. Taylor has shown that the dispersion coefficient should be constant for a fixed flow velocity regardless of time of flow. Also, the log-log plot of the dispersion coefficient versus average velocity should be linear with slope equal
TABLE 2. Experimental Results of Newtonian (KMnO$_4$ - H$_2$O) system.

<table>
<thead>
<tr>
<th>Average velocity $\bar{V_x}$, cm/sec</th>
<th>Time of flow $t$, sec</th>
<th>Mixing zone length $L$, cm</th>
<th>Dispersion coefficient $k$, cm$^2$/sec</th>
<th>Diffusion coefficient $D \times 10^5$, cm$^2$/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.255</td>
<td>100</td>
<td>16.1</td>
<td>0.198</td>
<td>1.844</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>20.5</td>
<td>0.214</td>
<td>1.705</td>
</tr>
<tr>
<td></td>
<td>230</td>
<td>25.9</td>
<td>0.223</td>
<td>1.639</td>
</tr>
<tr>
<td>0.429</td>
<td>80</td>
<td>24.0</td>
<td>0.549</td>
<td>1.886</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>26.5</td>
<td>0.536</td>
<td>1.934</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>28.8</td>
<td>0.528</td>
<td>1.965</td>
</tr>
<tr>
<td>1.270</td>
<td>18</td>
<td>32.5</td>
<td>4.480</td>
<td>2.028</td>
</tr>
<tr>
<td></td>
<td>23.2</td>
<td>33.8</td>
<td>3.760</td>
<td>2.417</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>45.8</td>
<td>4.003</td>
<td>2.270</td>
</tr>
</tbody>
</table>
to two. This plot is shown in Figure 20. From the results of Table 2 it is obvious that the values of the dispersion coefficient are not constant for a fixed velocity and different flow times. It can be inferred that the experimental results do not agree with Taylor's solution over the time range studied. However, the present experimental results are in good agreement with the results obtained by previous investigators [5, 39] in their experimental studies of this nature.

In Figure 20, a line was drawn through the data points with slope of 2, and the diffusion coefficient was found to be $2.0 \times 10^{-5}\text{cm}^2/\text{sec}$ as compared to a value of $2.3 \times 10^{-5}\text{cm}^2/\text{sec}$ found by Bailey and Gogarty [5].

As mentioned in Chapter IV, Taylor [45] found an approximate solution of the convective diffusion equation (Eq. 4-1) with axial molecular diffusion ignored. Later, numerical solution of Eq. 4-1 was offered by Bailey and Gogarty [5], with longitudinal molecular diffusion neglected. The data of this work was converted into the dimensionless quantities to check the validity of previous theoretical developments. For this, the dimensionless mixing zone length is plotted against the dimensionless time in Figure 21. Experimental results are compared with Taylor's approximate solution and the numerical solution of Bailey and Gogarty [5]. Experimental points of their study are also shown in Figure 21 for comparison. From this figure, it can be seen that the results obtained from the present experiment are in close agreement with Taylor's solution near $\tau = 1.0$. 
Fig. 20. Plot of dispersion coefficients at fixed velocities for different flow times.
Fig. 21. Plot of dimensionless mixing zone length versus dimensionless time for KMnO₄ - H₂O system.

\[ \tau = \frac{D \tau}{R^2} \]
The results agree well with the numerical solution over the entire time range studied, suggesting the validity of the theory.

6.2.2 NON-NEWTONIAN (DYE - 1.0% POLYOX) SYSTEM

Dispersion experiments were then carried out with DuPont Pontamine Sky Blue 6BR dye in a non-Newtonian fluid (1.0% Polyox) by displacing it with pure 1.0% Polyox solution in capillary tubes. It was found that the dye did not change the characteristics of the fluid. The values of density and apparent viscosity of dye - 1% Polyox solution were the same as 1% Polyox solution. The concentration of the diffusing solute along the entire tube length was determined spectrophotometrically. The results obtained from the displacement experiments were plotted as concentration versus the length from the inlet of the tube. These plots are presented in Figures D1-D5 (Appendix D) for the 1.0 mm tube and Figures D6-D9 (Appendix D) for the 2.0 mm tube. In each case the velocity of flow and time of flow are indicated. A visual fit of a straight line through the experimental points for each flow time was used. The mixing zone length was determined from these plots as before.

The value of the dispersion coefficient was calculated from Eq. 5.4-5 and the diffusion coefficient from Eq. 5.4-6. These results are summarized in Tables 3 and 4.

The dispersion coefficient was plotted against the average velocity of flow in Figure 22. A "best" straight line was drawn with slope equal to 2.0 through the points for which $\bar{v}_x$ is less than 0.1 cm/sec. The reason why all the experimental points were not
<table>
<thead>
<tr>
<th>Average velocity $V_x$, cm/sec</th>
<th>Time of flow t, sec</th>
<th>Mixing zone length L, cm</th>
<th>Dispersion coefficient $k$, cm$^2$/sec</th>
<th>Diffusion coefficient D x $10^3$, cm$^2$/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00193</td>
<td>28800</td>
<td>15.6</td>
<td>0.000645</td>
<td>0.0322</td>
</tr>
<tr>
<td>0.00301</td>
<td>7200</td>
<td>13.9</td>
<td>0.00205</td>
<td>0.0247</td>
</tr>
<tr>
<td></td>
<td>15360</td>
<td>18.5</td>
<td>0.00170</td>
<td>0.0383</td>
</tr>
<tr>
<td>0.0301</td>
<td>780</td>
<td>36.5</td>
<td>0.130</td>
<td>0.0388</td>
</tr>
<tr>
<td></td>
<td>1200</td>
<td>40.9</td>
<td>0.106</td>
<td>0.0475</td>
</tr>
<tr>
<td>0.180</td>
<td>90</td>
<td>28.5</td>
<td>0.689</td>
<td>0.246</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>63.5</td>
<td>1.710</td>
<td>0.0993</td>
</tr>
<tr>
<td></td>
<td>230</td>
<td>73.1</td>
<td>1.774</td>
<td>0.0957</td>
</tr>
<tr>
<td></td>
<td>230 (2mm tube)</td>
<td>63.5</td>
<td>1.338</td>
<td>0.127</td>
</tr>
<tr>
<td></td>
<td>1440</td>
<td>243.0</td>
<td>3.130</td>
<td>0.0542</td>
</tr>
<tr>
<td>0.429</td>
<td>80</td>
<td>46.0</td>
<td>2.019</td>
<td>0.509</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>79.2</td>
<td>4.788</td>
<td>0.215</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>91.0</td>
<td>5.268</td>
<td>0.195</td>
</tr>
<tr>
<td>1.270</td>
<td>20</td>
<td>45.6</td>
<td>7.937</td>
<td>1.136</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>70.5</td>
<td>12.647</td>
<td>0.713</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>85.6</td>
<td>13.984</td>
<td>0.645</td>
</tr>
</tbody>
</table>
TABLE 4. Experimental Results of Non-Newtonian (Dye - Polyox) system in 2 mm tube.

<table>
<thead>
<tr>
<th>Average velocity $V_x$, cm/sec</th>
<th>Time of flow $t$, sec</th>
<th>Mixing zone length L, cm</th>
<th>Dispersion coefficient $k$, cm$^2$/sec</th>
<th>Diffusion coefficient $D \times 10^5$, cm$^2$/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000471</td>
<td>72000</td>
<td>10.6</td>
<td>0.000119</td>
<td>0.0426</td>
</tr>
<tr>
<td>0.00311</td>
<td>7200</td>
<td>21.7</td>
<td>0.00499</td>
<td>0.0444</td>
</tr>
<tr>
<td></td>
<td>13500</td>
<td>24.6</td>
<td>0.00342</td>
<td>0.0648</td>
</tr>
<tr>
<td>0.0287</td>
<td>780</td>
<td>36.8</td>
<td>0.133</td>
<td>0.143</td>
</tr>
<tr>
<td></td>
<td>1200</td>
<td>50.3</td>
<td>0.161</td>
<td>0.117</td>
</tr>
<tr>
<td>0.158</td>
<td>180</td>
<td>40.2</td>
<td>0.685</td>
<td>0.834</td>
</tr>
<tr>
<td></td>
<td>230</td>
<td>61.4</td>
<td>1.251</td>
<td>0.457</td>
</tr>
<tr>
<td>0.402</td>
<td>120</td>
<td>82.4</td>
<td>4.319</td>
<td>0.857</td>
</tr>
<tr>
<td>1.148</td>
<td>20</td>
<td>38.8</td>
<td>5.746</td>
<td>5.259</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>86.5</td>
<td>14.279</td>
<td>2.116</td>
</tr>
</tbody>
</table>
Fig. 22. Plot of dispersion coefficients at fixed velocities for different flow times.
considered is explained later in this chapter. The average value of diffusion coefficient for the 1 mm tube and the 2 mm tube was found to be $3.0704 \times 10^{-7}\text{cm}^2/\text{sec}$ and $5.0922 \times 10^{-7}\text{cm}^2/\text{sec}$ respectively. For these values of $D$ the best agreement between the experimental data and the numerical solution was obtained. The difference in value of $D$ for the two different sizes of tube is discussed later.

The experimental results of the present study with two tube sizes were compared with those predicted by various theoretical solutions by converting the data into the dimensionless quantities. The dimensionless mixing zone length $L'$ is plotted against the dimensionless time $\tau$ in Figure 23. A complete numerical solution of the convective diffusion equation (Eq. 4-1) was employed by French [18] for the case of the Power Law model for different values of Power Law index $n$ and various values of $N_p$ and $\tau$. The present experimental results were compared with French's numerical solution in Figure 23 together with the Taylor - Fan approximate solution. It may be noted that there is close agreement between the experimental and numerical results. Experimental results agree within ±2% with the Taylor - Fan approximate solution for the $\tau$ range of $0.7 \leq \tau \leq 4$. This was to be expected as the numerical solution predicts that the Taylor - Fan solution is valid for about $\tau \geq 0.7$.

A. CONDITIONS FOR TAYLOR - FAN APPROXIMATE SOLUTION

Following Taylor's approach, it can be seen that the conditions under which Taylor - Fan approximate solution is valid for laminar flow with radial diffusion is
Fig. 23. Plot of dimensionless mixing zone length versus dimensionless time for Dye - Polyox system.

\[ \tau = \frac{D \tau}{R} \]

\[ x_{\Delta z} \left( \frac{1 + u}{1 + u \xi} \right) \frac{d \xi}{d\tau} = \xi \]
\[
2 \left( \frac{1}{n} + 1 \right) \frac{L}{R} \gg \frac{RV}{D} \gg \sqrt{2 \left( \frac{1}{n} + 3 \right) \left( \frac{1}{n} + 5 \right)} \quad (6.2-1)
\]

where, \( L \) is the mixing zone length of the tube in which appreciable change in concentration of solute occurs.

The first inequality of Eq. 6.2-1

\[
\frac{L}{R} \gg \frac{1}{2 \left( \frac{1}{n} + 1 \right)} \frac{RV}{D} \quad (6.2-2)
\]

in terms of \( N_{pe} \) can be written as

\[
N_{pe} < < \frac{4 \left( 1 + \frac{1}{n} \right)}{R} L \quad (6.2-3)
\]

Substituting Eqs. 5.4-4 and 4.2-46 into Eq. 6.2-3, it becomes

\[
\tau \gg 0.03816 \left[ \frac{(3n+1)(5n+1)}{(1+n)^2} \right] \quad (6.2-4)
\]

For the present case where \( n = 0.981 \),

\[
\tau \gg 0.23 \quad (6.2-5)
\]

This establishes the lower limit of \( \tau \) for the validity of the Taylor - Fan solution but the numerical solution indicates the lower limit of \( \tau \) as \( \tau \approx 0.7 \). From the second restriction given by Eq. 6.2-1,

\[
N_{pe} \gg 2 \sqrt{2 \left( \frac{1}{n} + 3 \right) \left( \frac{1}{n} + 5 \right)} \quad ; \quad (6.2-6)
\]

for \( n = 0.981 \)

\[
N_{pe} \gg 13.91 \quad (6.2-7)
\]
The Taylor - Fan analysis also shows that the condition 
\( t \gg 0.0682R^2/D \) or \( \tau > 0.0682 \) is necessary for the radial variations 
in concentration to be sufficiently small for the applicability of the 
solution. Experimental results show that the Taylor - Fan solution is 
valid for \( \tau > 0.7 \) and for high Peclet numbers. Therefore the condition 
of the Taylor - Fan approximate solution that \( \tau > 0.0682 \) is thus satis-
fied. This could be relaxed by an order of magnitude. Then the 
condition becomes \( \tau > 0.682 \) which is in best agreement with the pre-
sent results. The corresponding restriction that 

\[
\frac{4L}{R} \gg \frac{2 \sqrt{2(3n+1)} (5n+1)}{(n+1)}
\]

is not a necessary requirement.

B. APPLICABILITY OF VARIOUS EQUATIONS

The numerical solution indicated that the Taylor - Fan solution is 
applicable only in the region where \( N_{pe} \) is approximately greater 
than 100 and \( \tau \geq 0.7 \). For \( N_{pe} < 100 \), Aris' [2] modification of the 
effective dispersion coefficient should be employed and the dispersion 
coefficient \( \kappa \) could be replaced by \( \kappa' = \kappa + D \) in the Taylor - Fan 
analysis. The range of Peclet number studied in the present work was 
650 to \( 4.3 \times 10^5 \) for the 1 mm tube and 200 to \( 4.75 \times 10^5 \) for the 2 mm 
tube. Hence no significant effect can be derived from the Aris' modifi-
cation in the present study. In other words, the region where Aris - 
Fan solution is valid was not explored.
As noted before, the Taylor - Fan solution is valid for $T \geq 0.7$ and high values of Peclet numbers. Unfortunately, due to the physical limitations of the apparatus, very few data could be gathered for both high $N_{pe}$ and $T$. It is shown in Figure 22 that for a fixed velocity, the dispersion coefficient increases as time increases. The data at higher velocities were discarded because the time of flow was not high enough to meet the necessary criteria of the Taylor - Fan theoretical solution. However, it is seen from Figure 23 that these data are in good agreement with the numerical solution as expressed by French.

Even at higher velocities the dispersion coefficient increases as time increases for a fixed velocity. If sufficient time of flow is allowed at higher flow rate, it should meet the applicability of the Taylor - Fan theory. To allow for longer time of flow and high $N_{pe}$, three tubes of totalling 330 cm in length were connected in series. One experimental run was taken to see whether the results for both high $N_{pe}$ and $T$ do agree with the Taylor - Fan solution. The experimental conditions chosen were $\bar{V}_x = 0.1800$ cm/sec and $t = 1440$ sec. It was observed from the results of this run that the value of dispersion coefficient increases and approaches the plotted straight line in Figure 22 for high values of $T$. Of course even this time allowed was not long enough to meet the necessary condition. One needs to use a tube longer than 330 cm to satisfy the condition imposed by the Taylor - Fan solution.

Figure 24 summarizes the approximate regions of application of the various solutions as given by Reejhsinghani et al. [39] and the range of $N_{pe}$ and $T$ used in the present experimental study.
C. **HIGH PECLET NUMBER RESULTS**

Figure 25 is the plot of the dimensionless concentration against the distance from the inlet of the tube on linear coordinates. It shows the effect of time of flow on the concentration of solute in the tube at high Peclet numbers. For very short time of flow the data points resulted in a straight line while non-linearity was observed at higher time. This is because at short times of flow both axial and radial diffusion are very small compared to the convective effects involved while at longer time the effect of radial diffusion becomes more important.

The experimental measurements using the 1 mm tube are plotted in Figures 26a, 26b, 26c, and 26d as the dimensionless concentration $C_m^+$ versus axial distance $X'/\tau$ for various values of $N_{pe}$ and the dimensionless time $\tau$. All results are for high Peclet number ranges. The experimental results of this study are compared with the numerical solution and/or the Taylor - Fan analytical solution. The following were inferred from these figures.

1. Figures 26a and 26b are the plots at higher values of $\tau$ i.e. $\tau > 0.7$ at which the effect of radial diffusion becomes very important, and the curves become error functions. This is evident from the linearity of the curves on the probability graph paper.

2. The effect of axial and radial diffusion is negligible compared to that of pure convection for shorter time of flow. This is clear from the curvature of the plots in Figures 26c and 26d.
Fig. 25. Concentration distribution along the length of the tube.
Fig. 26a. Plot of concentration versus $X'/\tau$ for various values of $\tau$ at $N_{pe} = 1018$. 

**Tube size:** 1 mm

$N_{pe} = 1018$

$n = 0.981$

$\Delta \; \tau = 0.8175$; This Expt.

$\Box \; \tau = 1.7441$; This Expt.

--- Taylor - Fan

--- Numerical
Fig. 26b. Plot of concentration versus $X'/\tau$ at $N_{pe} = 653$. 

- Taylor - Fan
- Numerical

$\triangle$ This work 1 mm tube
$N_{pe} = 653$
$\tau = 3.2702$
$n = 0.981$
Fig. 26c. Plot of concentration versus $X' / \tau$ at $N_{pe} = 59038$. 

- **** Taylor - Fan
- --- Numerical
- Δ This work 1 mm tube

$N_{pe} = 59038$

$\tau = 0.01021$

$n = 0.981$
Fig. 26d. Plot of concentration versus $X'/\tau$ at $N_{pe} = 430170$. 

- Numerical
- $\triangle$ This work 1 mm tube
- $N_{pe} = 430170$
- $\tau = 0.004542$
- $n = 0.981$
For longer times, as expected, the results from experiment follow the Taylor - Fan analytical solution more closely as can be seen from Figures 26a and 26b.

For short times, the experimental results agree more closely with the numerical solution than with the Taylor - Fan solution. This is again clear from Figures 26c and 26d.

The estimate of error in the experimental measurement for the run plotted in Figure 26c was computed in Appendix E and the estimated precision of measurements are shown in this figure. It was found that the error involved in the analysis was ±5%.

The effect of increasing Peclet number on the concentration distribution of solute for a fixed value of \( \tau = 0.01 \) is shown in Figure 27. It is seen from Eq. 4.3-8 that at high values of \( N_{pe} \) the effect of axial diffusion is not important. This results in a single line for all \( N_{pe} \) in Figure 27. The experimental results show agreement to within ±5% of the numerical solution. It is obvious from Figure 27 that the concentration distribution change is not significant for the \( N_{pe} \) range shown.

Results obtained from the 2 mm tube are also plotted as concentration versus axial distance in Figures 28a, 28b, and 28c. As mentioned earlier, as time increases, for high \( N_{pe} \) the plot of concentration distribution becomes an error function and the plots become straight lines on probability paper. This is shown in Figure 28c for \( \tau = 3.3066 \). For short times, curves result as can be seen in Figures 28a and 28b. The results of the present study are in good agreement with those predicted from theory.
Fig. 27. Plot of concentration versus $X'/\tau$ for various values of $N_{pe}$ at $\tau = 0.01$. 
Fig. 28a. Plot of concentration versus $X'/\tau$ at $N_{pe} = 166215$. 

Numerical

- This work 2 mm tube

$N_{pe} = 166215$

$\tau = 0.005512$

$n = 0.981$
Fig. 28b. Plot of concentration versus $X'/\tau$ at $N_{pe} = 1286$. 

Taylor - Fan
Numerical
This work 2 mm tube

$N_{pe} = 1286$
$\tau = 0.33066$
$n = 0.981$
Fig. 28c. Plot of concentration versus $X'/\tau$ at $N_{pe} = 194$. 

---

- Taylor - Fan
- Numerical
- This work 2 mm tube

$N_{pe} = 194$

$\tau = 3.3066$

$n = 0.981$
Ananthkrishnan et al. [1] concluded that the effect of axial diffusion becomes significant for \( N_{pe} < 500 \). However, this effect is important only for very short times of flow at \( N_{pe} > 100 \). From Figure 28c it may be noted that the experimental results at \( N_{pe} = 194 \) and \( \tau = 3.3066 \) show close agreement with the Taylor - Fan solution. This indicates that the effect of axial diffusion is negligibly small, which is in agreement with the previous theoretical conclusion.

D. **DIFFUSION COEFFICIENT AND CONCENTRATION DEPENDENCY**

The average diffusion coefficient \( D \) of Pontamine dye in Polyox solution was found to be \( 3.07 \times 10^{-7} \text{cm}^2/\text{sec} \) for the 1 mm tube and \( 5.09 \times 10^{-7} \text{cm}^2/\text{sec} \) for the 2 mm tube. The diffusion coefficient of dye in water is reported as \( 3.1 \times 10^{-5} \text{cm}^2/\text{sec} \) by Reejhsinghani et al. [39]. This value of \( D \) was over the concentration range of \( 0 \leq C \leq 0.2 \text{ gm/lit} \). Since no published data are available for the diffusion coefficient of dye in Polyox solution, comparison of the results of this study is not possible.

In the theoretical analysis it was assumed that the diffusion coefficient is independent of concentration \( C \), but the present experimental study reveals that it is highly concentration dependent. This was first concluded in the experimental study of Taylor [45] with a Newtonian \((\text{KMnO}_4 - \text{H}_2\text{O})\) system. It was shown that the value of \( D \) decreases as concentration increases. To verify this point in the case of a non-Newtonian fluid, runs were made at two different dye concentrations of 100 and 200 ppm in the same tube and under the same experimental conditions. It was observed that the values of \( D \) obtained
were different. They were \( D = 0.096 \times 10^{-5} \) and \( 0.127 \times 10^{-5} \text{cm}^2/\text{sec} \) for the concentration of 200 and 100 ppm respectively. As mentioned earlier, the 200 ppm dye concentration was used in the 1 mm tube and 100 ppm in the 2 mm tube. Since the lower concentration was used in the 2 mm tube, the expected value of \( D \) should be higher which is in agreement with the present results. Thus the value, \( D = 3.07 \times 10^{-7} \text{cm}^2/\text{sec} \) in the smaller tube was over the concentration range of \( 0 \leq C \leq 0.2 \text{ gm/lit.} \) while \( D = 5.09 \times 10^{-7} \text{cm}^2/\text{sec} \) corresponds to larger tube where the concentration range was \( 0 \leq C \leq 0.1 \text{ gm/lit.} \)

E. **EFFECT OF TUBE SIZE**

Results from the measurements in the two different size tubes show reasonable agreement with the theoretical solutions. It can be deduced from these results that there is little effect of tube size on the dispersion phenomena in this case. However, using a smaller diameter tube than 1 mm, or 1 mm diameter tube for a highly non-Newtonian fluid might show some deviation in results. This is because the orientation of long chain polymer molecules in the small capillary tube might be quite influential. On the other hand, using a larger tube (5 mm) there might be a significant effect of natural convection on the dispersion phenomena due to concentration gradients. Such an effect in the case of a Newtonian fluid was treated qualitatively by Reejhsinghani et al. [39].

F. **EFFECT OF ENTRANCE LENGTH OF TUBE**

In the theoretical analysis of the problem of fluid dispersion, it was assumed that the flow is steady laminar flow whose velocity
profile is fully developed. These assumptions do not prevail in the experimental investigation. In the experimental case at \( t = 0 \), pure solvent enters the capillary tube at \( x = 0 \) and flow starts through the tube at the same time. Some time is necessary for the average velocity to reach its steady state value. An approximate solution for the startup flow of a Power Law model fluid in a tube is considered by Sestak and Charles [42]. Simple calculations showed that the time of transient velocity was negligibly small.

The maximum Reynolds's number in the dispersion measurements using a generalized Reynolds's number equation as given by Bird et al. [6], was about 5 for which the flow is laminar. The equation for the entrance length in the case of a Newtonian fluid was given by Christiansen [10] as

\[
L_e = 0.0575 D_t N_{Re}^2
\]  
(6.2-8)

where \( D_t \) is the diameter of the tube. It was also shown that the numerical constant in the above equation would be smaller than 0.0575 for pseudoplastic materials and greater that for dilatant fluids. Using the value of 0.0575, for the 2 mm tube, the entrance length would be about 0.06 cm with \( N_{Re} = 5 \). Thus entrance effects were considered unimportant.

C. EFFECT OF MEASUREMENT OF AVERAGE CONCENTRATION

The hypothesis given by Taylor considers the average concentration of solute as a function of axial position of the tube. By average concentration we mean the average concentration in a infinitesimally
thin section of the tube. In the experimental technique of this work, the average concentration of solute was measured at various axial positions using a 14 Cary spectrophotometer. It is practically impossible to measure a concentration in an infinitesimally thin section since the minimum height of the beam of light source is 7 mm for 14 Cary Spectrophotometer.

Many investigators in the past measured average concentration using this instrument and reported good agreement between their experimental results and theory, without considering the above effect. Even in the different technique used by French [18] of measuring counts (i.e. concentration) it was reported that the minimum size of the columnator through which the scintillation probe viewed and capillary tube should be 7 mm at least to allow for acceptable counting statistics.

As the concentration did not change appreciably over the 7 mm axial measurement length, it was felt that the error introduced by averaging the concentration over a small volume element of the tube rather than over a planar cross-section would be relatively minor.
CHAPTER VII
CONCLUSIONS

In the present experimental investigation, rheological and dispersion measurements were carried out for different aqueous polymeric solutions. The following conclusions are made as a result of the analysis of such measurements.

(1) Experimental data were obtained for laminar dispersion in capillary tubes. Wide ranges of dimensionless time ($\tau = 0.001$ to 4.0) and Peclet number ($N_{pe} = 200$ to $4.75 \times 10^5$) were investigated. Results obtained from displacement measurements with the non-Newtonian fluid (Dye - 1.0% Polyox) showed agreement to within $\pm 5\%$ of the numerical solution of the convective diffusion equation as well as with the approximate analytical solution given by Taylor-Fan for dimensionless time, $\tau$, greater than 0.7 and high values of Peclet numbers.

(2) The Taylor-Fan approximate solution imposed the condition that $\tau > 0.0682R^2/D$ or $\tau > 0.0682$ for the validity of their solution. This study showed $\tau > 0.7$ as the range of applicability for this solution.

(3) At high values of Peclet number, $N_{pe} (> 59038)$ for a fixed time ($\tau = 0.01$), it was found from experimental results that there is no effect of increasing $N_{pe}$ on the concentration distribution change of solute.

(4) Data on dispersion measurements were taken in two different size tubes. Tube size did not affect the results of the experiment.
when plotted non-dimensionally.

(5) In this investigation, the average value of diffusion coefficient, \( D \), for the non-Newtonian (Dye - Polyox) system was found to be \( 3.07 \times 10^{-7} \text{ cm}^2/\text{sec} \) over the concentration range \( 0 \leq C \leq 0.2 \text{ gm/lit.} \)
and \( 5.09 \times 10^{-7} \text{ cm}^2/\text{sec} \) for \( 0 \leq C \leq 0.1 \text{ gm/lit.} \). The value of the diffusion coefficient for the Newtonian (Dye - \( \text{H}_2\text{O} \)) system was reported by Reejhsighani et al. \[39\] as \( D = 3.1 \times 10^{-6} \text{ cm}^2/\text{sec} \) over the concentration range of \( 0 \leq C \leq 0.2 \text{ gm/lit.} \). The diffusion coefficient \( D \) for the non-Newtonian system studied is concentration dependent as in the case of the Newtonian system studied earlier by Taylor \[45\]. In both cases, the diffusion coefficient decreases with increasing concentration. Due to limited data, no exact relation between concentration and diffusion coefficient was found.
SUGGESTIONS FOR FURTHER STUDY

The problem of dispersion of solutes in a non-Newtonian laminar flow system was investigated in the present work. The validity of the numerical and analytical approximate solutions was checked experimentally for a particular range of dimensionless time and Peclet number. However, due to time limits and physical limitations of the apparatus, certain areas have not been investigated in as much depth as they perhaps should have been.

The following suggestions might be considered in future research of this type to understand more fully dispersion phenomena in circular tubes.

(1) Results at low Peclet numbers (<100) and high values of dimensionless time were not obtained in the present study. Aris' \[2\] modification of Taylor's solution becomes important in this range and should be explored.

(2) Reejhsighani et al. \[39\] indicated in their experimental study on dispersion in Newtonian fluid that natural convection may be significant in larger (>5 mm) tubes. It may be interesting to study dispersion in larger diameter tubes to determine if this effect is significant for non-Newtonian fluid.

(3) In the experimental phase of this study, the solution used did not possess highly non-Newtonian characteristics. In further research, it would be challenging to test fluids possessing greater non-Newtonian characteristics.

(5) The numerical solution for the complete convective diffusion equation in the case of the flow of a Newtonian fluid was done by Ananthakrishnan et al. [1]. Numerical solutions could be obtained for the cases of the Eyring and Ellis model non-Newtonian fluids.
APPENDIX A
APPENDIX A.1 DERIVATION OF EQUATIONS 3.2-5 and 3.2-6

The relation between the shear stress and shear rate for Power law is given by Eq. 3.1-4 as

\[ \tau_{rx} = - m \left( \frac{dV_x}{dr} \right)^n \]  (3.1-4)

Substituting Eq. 3.1-4 into Eq. 3.2-3 and rearranging, we have

\[ - r^{1/n} \left( \frac{\Delta P}{2mL_1} \right)^{1/n} = \frac{dV_x}{dr} \]  (A.1-1)

Considering \( \Delta P/L_1 \) as independent of \( r \), this differential equation can be integrated to obtain

\[ \frac{n}{n+1} r^{n} \left( - \frac{\Delta P}{2mL_1} \right)^{1/n} = V_x + C_1 \]  (A.1-2)

Using the boundary condition \( V_x = 0 \) at \( r = R \) gives

\[ C_1 = \frac{n}{n+1} R^{n} \left( - \frac{\Delta P}{2mL_1} \right)^{1/n} \]  (A.1-3)

and so

\[ V_x = \frac{n}{n+1} R^{n} \left( \frac{\Delta P}{2mL_1} \right)^{1/n} \left[ 1 - \left( \frac{r}{R} \right)^{n+1} \right] \]  (3.2-5)

This is the expression for the local velocity; the expression for the maximum velocity can be obtained by setting \( V_x = V_{\text{max}} \) when \( r = 0 \);
\[ v_{\text{max}} = \frac{n}{n+1} \frac{R^n}{n} \left( \frac{\Delta P}{2mL_1} \right)^{1/n} \]  
(A.1-4)

The average velocity can be calculated by summing up all the velocities over a cross-section and then dividing by the cross-sectional area

\[ \vec{V}_x = \frac{\int_0^{2\pi} \int_0^R V_x r dr d\theta}{\int_0^{2\pi} \int_0^R r dr d\theta} \]  
(A.1-5)

Substituting Eq. 3.2-5 into Eq. A.1-5 and integrating twice, we obtain

\[ \vec{V}_x = \frac{n}{n+1} \frac{R^n}{n} \left( \frac{\Delta P}{2mL_1} \right)^{1/n} \left[ \frac{r^2}{2} - \frac{1}{R^{n+1}} \left( \frac{n}{3n+1} \right) \frac{3n+1}{r^n} \right]_0^R \]  
\[ \frac{R^2}{2} \]  
(A.1-6)

which simplifies to

\[ \vec{V}_x = \frac{n}{3n+1} \frac{R^n}{n} \left( \frac{\Delta P}{2mL_1} \right)^{1/n} \]  
(3.2-6)
APPENDIX A.2  DERIVATION OF EQUATIONS 3.2-8 AND 3.2-9

The Eyring model fluid gives the relation between $\tau_{rx}$ and $\frac{dV_x}{dr}$ as

$$\tau_{rx} = A \sinh^{-1} \left( -\frac{1}{B} \frac{dV_x}{dr} \right) \quad (3.1-6)$$

At finite values of $\tau_{rx}$, this model predicts a pseudoplastic behavior but reduces asymptotically to Newtonian case with $\mu = \frac{A}{B}$ as $\tau_{rx}$ approaches to zero. Combining Eq. 3.1-6 with the momentum flux distribution given by Eq. 3.2-3, we have

$$\frac{dV_x}{dr} = -B \sinh \left( \frac{\Delta P}{2L_1} \frac{r}{A} \right) \quad (A.2-1)$$

Schenk and van Laar [41] defined a dimensionless pressure gradient

$$b = \left( \frac{R}{2A} \right) \left( \frac{dp}{dx} \right) = \left( \frac{R}{2A} \right) \left( \frac{\Delta P}{L_1} \right) \quad (A.2-2)$$

From Eqs. A.2-1 and A.2-2

$$\frac{dV_x}{dr} = -B \sinh \left( \frac{br}{R} \right) \quad (A.2-3)$$

Integrating,

$$V_x = -\frac{BR}{b} \cosh \left( \frac{br}{R} \right) + C_1 \quad (A.2-4)$$

Using the boundary condition that $V_x = 0$ at $r = R$, we find that

$$C_1 = \frac{BR}{b} \cosh b \quad (A.2-5)$$

and so
\[ V_x = \frac{BR}{b} \left( \cosh b - \cosh b \frac{r}{R} \right) \quad (3.2-8) \]

where \( \frac{r}{R} \).

Maximum velocity occurs at the centerline of the tube where \( r = 0 \)

i.e. \( \frac{r}{R} = 0 \):

\[ V_{\text{max}} = \frac{BR}{b} \left( \cosh b - 1 \right) \quad (A.2-6) \]

From Eq. A.1-5 the expression of mean velocity for this case is

\[ \bar{V}_x = \frac{2\pi}{\delta} \int_0^R \frac{BR}{b} \left( \cosh b - \cosh b \frac{r}{R} \right) r \, dr \, d\theta \quad \int_0^{2\pi} \int_0^R r \, dr \, d\theta \quad (A.2-7) \]

Simplifying,

\[ \bar{V}_x = \frac{\frac{BR}{b} \int_0^R \left( \cosh b - \cosh b \frac{r}{R} \right) r \, dr}{R^2/2} \quad (A.2-8) \]

Introducing \( r = \delta R \) and \( \frac{r}{R} = 0 \) when \( r = 0 \) and \( \frac{r}{R} = 1 \) when \( r = R \),

this becomes

\[ \bar{V}_x = \frac{2BR}{b} \int_0^1 \left( \cosh b - \cosh b \frac{\delta R}{R} \right) \frac{r}{R} \, dr \quad \delta \quad (A.2-9) \]

or

\[ \bar{V}_x = \frac{BRE}{b} \cosh b \quad (3.2-9) \]

where

\[ E = \left( 1 - \frac{2 \sinh b}{b \cosh b} + \frac{2}{b^2} - \frac{2}{b^2 \cosh b} \right) \quad (3.2-10) \]
In a circular tube the volumetric flow rate through a differential annulus between $r$ and $r + dr$ is

$$dq = 2\pi r V_x dr$$  \hspace{1cm} (A.3-1)

and so

$$q = \pi \int_0^R 2r V_x dr$$  \hspace{1cm} (A.3-2)

or

$$q = \pi \int_0^R r^2 V_x d(r^2)$$  \hspace{1cm} (A.3-3)

Integrating by parts gives

$$q = \pi \left[ V_x r^2 \right]_0^R - \int_0^R r^2 d(V_x)$$  \hspace{1cm} (A.3-4)

By the assumption that there is no slip, the term $V_x r^2$ can be eliminated and assuming that the fluid is in steady, laminar flow and time-independent, we can write

$$dV_x = - f (\tau_{rx}) dr$$  \hspace{1cm} (A.3-5)

From Eq. 3.3-2, we further have that

$$dr = \frac{R}{T_w} d\tau_{rx}$$  \hspace{1cm} (A.3-6)

Substituting Eqs. A.3-5 and A.3-6 into Eq. A.3-4 and neglecting $V_x r^2$ gives

$$q = \pi \int \frac{R^2 \tau_{rx}}{T_w^2} f (\tau_{rx}) \frac{R}{T_w} d\tau_{rx}$$  \hspace{1cm} (A.3-7)
or
\[
\frac{q}{\pi R^3} = \frac{1}{\tau_w^3} \int_{\tau_w}^{\tau_w} \tau_{rx}^2 f(\tau_{rx}) d\tau_{rx}
\]
(A.3-8)

Multiplying by \(\tau_w^3\) and differentiating with respect to \(\tau_w\),
\[
\frac{d}{d\tau_w} \left[ \frac{q\tau_w^3}{\pi R^3} \right] = \frac{d}{d\tau_w} \left[ \int_{\tau_w}^{\tau_w} \tau_{rx}^2 f(\tau_{rx}) d\tau_{rx} \right]
\]
(A.3-9)

or
\[
\frac{q\tau_w^3}{3\pi R^3} + \tau_w \frac{d}{d\tau_w} \left( -\frac{q}{\pi R^3} \right) = \tau_w^2 f(\tau_w)
\]
(A.3-10)

Substituting \((R\Delta P/2L_1)\) for \(\tau_w\) and \((-\frac{dV_x}{dr})_w\) for \(f(\tau_w)\) then gives
\[
3 \frac{q}{\pi R^3} + \frac{R\Delta P}{2L_1} \frac{d(q/\pi R^3)}{d(R\Delta P/2L_1)} = \left( -\frac{dV_x}{dr} \right)_w
\]
(A.3-11)

Since \(q = \pi R^2 \bar{V}_x\),
\[
\left( -\frac{dV_x}{dr} \right)_w = 3 \frac{\bar{V}_x}{R} + \frac{4\bar{V}_x}{R} \frac{d(4\bar{V}_x/R)}{d(R\Delta P/2L_1)} \frac{(R\Delta P/2L_1)}{(4\bar{V}_x/R)}
\]
(A.3-12)

which simplifies to
\[
\left( -\frac{dV_x}{dr} \right)_w = \frac{4\bar{V}_x}{R} \left[ \frac{3}{4} + \frac{1}{4n'} \right] = \left( 3n' + \frac{1}{4n'} \right) \frac{4\bar{V}_x}{R}
\]
(3.3-4)

where
\[
\frac{d}{d\ln \left( \frac{R\Delta P}{2L_1} \right)} n' = \frac{\frac{d}{d\ln \left( \frac{4\bar{V}_x}{R} \right)}}{d\ln \left( \frac{4\bar{V}_x}{R} \right)}
\]
(3.3-5)
Taking logarithms on both sides of Eq. 3.1-4

\[ \ln \tau_{rx} = \ln m + n \ln \left( - \frac{dV_x}{dr} \right) \]  
(A.3-13)

We find upon differentiating that

\[ \frac{d(\ln \tau_{rx})}{d\left[ \ln \left( - \frac{dV_x}{dr} \right) \right]} = n \]  
(A.3-14)

From Eq. 3.3-4

\[ \ln \left( - \frac{dV_x}{dr} \right)_w = \ln \left( \frac{3n' + 1}{4n'} \right) + \ln \left( \frac{4V_x}{R} \right) \]  
(A.3-15)

Differentiating w.r.t. \( \ln \tau_w \) and using Eq. A.3-14, we obtain

\[ \frac{1}{n} = \frac{1}{n'} + \frac{d\left[ \ln \left( \frac{3n' + 1}{4n'} \right) \right]}{d(\ln \tau_w)} \]  
(A.3-16)

Eq. A.3-16 may be generalized if \( \tau_{rx} \) is substituted for \( \tau_w \)
since \( n \) and \( n' \) are understood to refer to a particular shear stress,
regardless of whether this takes place at a tube wall or any point. So
after some simplification we have

\[ n = \frac{n'}{1 - \frac{1}{3n' + 1} \left\{ \frac{dn'}{d(\ln \tau_{rx})} \right\}} \]  
(3.3-6)
APPENDIX B
APPENDIX B.1  DERIVATION OF EQ. 4.1-5

At time $t = 0$, if the solute is distributed symmetrically, the concentration $c = f(x,r)$ and after time $t$, it will be

$$c = f(x - V_xt, r) \quad \text{(B.1-1)}$$

The amount of solute which lies between $r$ and $r + \delta r$ is constant during the flow and is equal to $2\pi r C_0'X\delta r$. The solute will be distorted in time to

$$x = V_mt \left( \frac{\cosh b - \cosh b \xi}{\cosh b - 1} \right) \quad \text{(B.1-2)}$$

The total amount of solute between $x$ and $x + \delta x$ is therefore,

$$2\pi C_0'X \left( -r \frac{dr}{dx} \right) \delta x$$

and from Eq. B.1-2

$$\xi \frac{dx}{dx} = \frac{1}{b^2} \left[ - \frac{(\cosh b - 1)}{\frac{1}{tV_m}} \sqrt{\left[ \cosh b - \frac{x}{tV_m} (\cosh b - 1) \right]^2 - 1} \right] \cosh^{-1} \left[ \frac{\cosh \frac{x}{tV_m}}{\cosh b - 1} \right] \quad \text{(B.1-3)}$$

Now from definition of $C_m$

$$C_m = 2C_0'X (-r \frac{dr}{dx}) \frac{\delta x}{\pi R^2} \delta x = \frac{2C_0'X (-r \frac{dr}{dx})}{R^2} \quad \text{(B.1-4)}$$

or

$$C_m = 2C_0'X \left( -\xi \frac{dx}{dx} \right) \quad \text{(B.1-5)}$$

Substituting Eq. B.1-3 into Eq. B.1-5 gives
\[ C_m = \frac{2(coshb - 1)c_0x}{b^2 tV_m} \frac{1}{\sqrt{[coshb - \frac{x}{tV_m}(coshb - 1)]^2 - 1}} \cosh^{-1}\left[\frac{coshb - \frac{x}{tV_m}(coshb - 1)}{tV_m}\right] \]

\[ 0 < x < tV_m \]  \hspace{1cm} (4.1-5)

and \[ C_m = 0 \] when \( x < 0 \) and \( x \geq tV_m \)  \hspace{1cm} (4.1-6)

As \( b \to 0 \), Eq. 4.1-5 reduces to

\[ C_m = \frac{C_0x}{tV_m} \]  \hspace{1cm} (4.1-3)

which is the solution for the Newtonian case.
APPENDIX B.2 DERIVATION OF EQ. 4.1-14

In this case,

\[\begin{align*}
C &= C'_0 , \quad x \leq 0 \\
C &= 0 , \quad x > 0
\end{align*}\]  \(\text{at } t \leq 0\) \hspace{1cm} (4.1-9)

The tracer is distorted by the velocity profile starting at \(t = 0\) and it is shown in Figure B.1.

The average concentration in the thin section between \(x = x'\) and \(x = x' + dx\) is

\[C_m = \frac{\pi r^2 C'_0 dx}{\pi R^2 dx} = \xi^2 C'_0\]  \hspace{1cm} (B.2-1)

From Eqs. 3.2-8 and A.2-6

\[\xi^2 = \left[ \frac{1}{b} \cosh^{-1} \left( \cosh b - \frac{x}{tV_m} (\cosh b - 1) \right) \right]^2\]  \hspace{1cm} (B.2-2)

Substituting Eq. B.2-2 into Eq. B.2-1:

\[C_m = C'_0 \left[ \frac{1}{b} \cosh^{-1} \left( \cosh b - \frac{x}{tV_m} (\cosh b - 1) \right) \right]^2 , \quad 0 < x < tV_m\]  \hspace{1cm} (4.1-14)

As \(b \to 0\), Eq. 4.1-14 reduces to Eq. 4.1-11 which is the expression for Newtonian fluid.
Fig. B1. Step input with no diffusion deformation of tracer by Eyring model fluid.
APPENDIX B.3 DERIVATION OF EQ. 4.2-24

The analytical solution of Eq. 4.2-23 is given in this appendix.

Eq. 4.2-23 is the second-order ordinary differential equation:

\[
\left( \frac{d^2 C}{d\xi^2} + \frac{1}{\xi} \frac{dC}{d\xi} \right) = S \left\{ \frac{1}{E} \left( 1 - \frac{\cosh b\xi}{\cosh b} \right) - 1 \right\} \tag{4.2-23}
\]

It can be simplified to

\[
\left( \frac{d^2 C}{d\xi^2} + \frac{1}{\xi} \frac{dC}{d\xi} \right) = \frac{S}{E \cosh b} \left[ (1-E) \cosh b - \cosh b\xi \right] \tag{B.3-1}
\]

Let \( \frac{dC}{d\xi} = V \); then \( \frac{d^2 C}{d\xi^2} = \frac{dV}{d\xi} \) and our equation becomes

\[
\frac{dV}{d\xi} + \frac{1}{\xi} V = \frac{S}{E \cosh b} \left[ (1-E) \cosh b - \cosh b\xi \right] \tag{B.3-2}
\]

This equation is first order linear and has the solution

\[
V(\xi) = \frac{1}{\xi} \left[ \frac{S}{E \cosh b} \int \xi \left( (1-E) \cosh b - \cosh b\xi \right) d\xi + C_1 \right] \tag{B.3-3}
\]

Integrating,

\[
V(\xi) = \frac{S}{\xi E \cosh b} \left[ \frac{\xi^2 \cosh b (1-E)}{2} - \frac{\xi \sinh b\xi}{b} + \frac{\cosh b\xi}{b^2} + C_1 \right] \tag{B.3-4}
\]

Using B.C. \( V = \frac{dC}{d\xi} = 0 \) at \( \xi = 1 \) the value of \( C_1 \) from Eq. B.3-4 is
\[ C_1 = \left[ \frac{\sinh b}{b} - \frac{\cosh b}{b^2} - \frac{(1-E)\cosh b}{2} \right] \]  

(B.3-5)

and so

\[ V = \frac{dC}{d\xi} = \frac{S}{E\cosh b} \left[ \frac{(1-E)\xi\cosh b}{2} - \frac{\sinh b}{b} + \frac{\cosh b}{b^2\xi} + \frac{\sinh b}{b^2} - \frac{\cosh b}{b^2\xi} \right] \]

- \frac{(1-E)\cosh b}{2\xi} \]

(B.3-6)

Integrating,

\[ C = \frac{S}{E\cosh b} \left\{ \frac{(1-E)\xi^2}{4} \frac{\cosh b}{b^2} - \frac{\cosh b}{b^2} + \frac{1}{b^2} \left( \ell n\xi + \frac{(b\xi)^2}{2.2!} + \frac{(b\xi)^4}{4.4!} + \frac{(b\xi)^6}{6.6!} \right) \right\} + C_2 \]

(B.3-7)

Using the B.C. that at \( \xi = 0 \), \( C = C_0 \)

\[ C_2 = C_0 + \frac{S}{Eb^2\cosh b} \]

(B.3-8)

then

\[ C = C_0 + \frac{S}{b^2E\cosh b} + \frac{S}{E\cosh b} \left\{ \frac{(1-E)\xi^2}{4} \frac{\cosh b}{b^2} - \frac{\cosh b}{b^2} + \frac{1}{b^2} \left( \ell n\xi + \frac{(b\xi)^2}{4} + \frac{(b\xi)^4}{96} + \frac{(b\xi)^6}{4320} \right) + \ell n\xi \left( \frac{\sinh b}{b} - \frac{\cosh b}{b^2} - \frac{(1-E)\cosh b}{2} \right) \right\} \]

(B.3-9)
or simplifying,

\[
C = C_0 + S \left[ \frac{1}{E} \left( \frac{1}{b^2 \cosh b} + \frac{(1-E)^2}{4} - \frac{\cosh b}{b^2 \cosh b} + \frac{1}{b^2 \cosh b} \left( \ln \xi + \frac{(b \xi)^2}{4} \right) \right) 
\right.

+ \left. \frac{(b \xi)^4}{96} + \frac{(b \xi)^6}{4320} \right) + \ln \xi \left( \frac{\tanh b}{b} - \frac{1}{b^2} - \frac{(1-E)}{2} \right) \right] 

(4.2-24)
From Eq. 4.2-27

\[ C'_m = 2 \int_0^1 C' \xi d \xi \quad (4.2-27) \]

Substituting Eq. 4.2-26 into Eq. 4.2-27 and simplifying, we have

\[ C'_m = \frac{2}{E} \left[ \frac{1}{b^2 \cosh b} \int_0^1 \xi d \xi + \frac{(1-E)}{4} \int_0^1 \xi^3 d \xi - \frac{1}{b^2 \cosh b} \int_0^1 \cosh b \xi d \xi \right. \]

\[ + \left. \frac{1}{b^2 \cosh b} \left( \int_0^1 \xi \ln \xi d \xi + \frac{b^2}{4} \int_0^1 \xi^3 d \xi + \frac{b^4}{96} \int_0^1 \xi^5 d \xi + \frac{b^6}{4320} \int_0^1 \xi^7 d \xi \right) \right] \]

\[ + \left( \frac{\tanh b}{b} - \frac{1}{b^2} - \frac{(1-E)}{2} \right) \int_0^1 \xi \ln \xi d \xi \right] \quad (B.4-1) \]

Integrating,

\[ C'_m = \frac{2}{E} \left[ \frac{1}{b^2 \cosh b} \left| \frac{\xi^2}{2} \right|_0^1 + \frac{(1-E)}{4} \left| \frac{\xi^4}{4} \right|_0^1 - \frac{1}{b^2 \cosh b} \left( \frac{\sinh b \xi}{b} - \frac{\cosh b \xi}{b^2} \right) \right|_0^1 \]

\[ + \frac{1}{b^2 \cosh b} \left[ \frac{\xi^2}{2} (\ln \xi - \frac{1}{2}) \right|_0^1 + \frac{b^2}{4} \left| \frac{\xi^4}{4} \right|_0^1 + \frac{b^4}{96} \xi^6 \right|_0^1 + \frac{b^6}{4320} \xi^8 \right|_0^1 \]

\[ + \left( \frac{\tanh b}{b} - \frac{1}{b^2} - \frac{(1-E)}{2} \right) \left[ \frac{\xi^2}{2} (\ln \xi - \frac{1}{2}) \right|_0^1 \right] \quad (B.4-2) \]

or

\[ C'_m = \frac{2}{E} \left[ \frac{1}{2b^2 \cosh b} + \frac{(1-E)}{16} - \frac{1}{b^3} \left( \tanh b - \frac{1}{b} + \frac{1}{b \cosh b} \right) \right. \]

\[ + \frac{1}{b^2 \cosh b} \left( \frac{b^2}{16} + \frac{b^4}{576} + \frac{b^6}{34560} - \frac{1}{4} \right) + \left( \frac{1}{4b^2} + \frac{(1-E)}{8} - \frac{\tanh b}{4b} \right) \]

\[ (4.2-28) \]
In the limiting case, when \( b \rightarrow 0 \), from Eq. 4.2-28, \( C_m' = 1/12 \)
for a Newtonian fluid.
APPENDIX B.5 DERIVATION OF EQUATION 4.2-33

From Eq. 4.2-21

\[
\frac{V_{x1}}{V_x} = \frac{1}{E} \left( 1 - E \cdot \frac{\cosh b \xi}{\cosh b} \right) \tag{B.5-1}
\]

Substituting this equation into Eq. 4.2-32 gives

\[
Q' = \frac{1}{E} \int_0^1 C'(\xi) \left( F - \frac{\cosh b \xi}{\cosh b} \right) \xi \, d\xi \tag{B.5-2}
\]

where \( F = (1-E) \).

Using the expression for \( C' \) from Eq. 4.2-26, we have

\[
Q' = \frac{1}{E} \left[ \int_0^1 \left( F - \frac{\cosh b \xi}{\cosh b} \right) \xi \left( \frac{1}{b^2 \cosh b} + \frac{F}{4} \xi^2 - \frac{\cosh b \xi}{b^2 \cosh b} + \frac{1}{b^2 \cosh b} \left( \frac{\ln \xi}{b} - \frac{1}{b^2} - \frac{F}{2} \right) \right) \, d\xi \right] \tag{B.5-3}
\]

or

\[
Q' = \frac{1}{E^2} \left[ \frac{F}{b^2 \cosh b} \int_0^1 \xi \, d\xi + \frac{F^2}{4} \int_0^1 \xi^3 \, d\xi - \frac{F}{b^2 \cosh b} \int_0^1 \xi \cosh b \xi \, d\xi \\
+ \frac{F}{b^2 \cosh b} \int_0^1 \frac{\ln \xi}{b} \xi \, d\xi + \frac{F b^2}{4b^2 \cosh b} \int_0^1 \xi^3 \, d\xi + \frac{F b^4}{96 b^2 \cosh b} \int_0^1 \xi^5 \, d\xi \\
+ \frac{F b^6}{4320 b^2 \cosh b} \int_0^1 \xi^7 \, d\xi + \left( \frac{\tanh b}{b} - \frac{1}{b^2} - \frac{F}{2} \right) F \int_0^1 \xi \ln \xi \, d\xi \right] \\
- \frac{1}{b^2 (\cosh b)^2} \int_0^1 \xi \cosh b \xi \, d\xi - \frac{F}{4 \cosh b} \int_0^1 \xi^3 \cosh b \xi \, d\xi + \frac{1}{b^2 (\cosh b)^2}
\]
\[\int_0^1 \frac{\cosh^2 b}{b^2 (\cosh b)^2} \, d\xi - \frac{1}{b^2 (\cosh b)^2} \int_0^1 \xi \ln \xi \cosh b \, d\xi - \frac{b^2}{4b^2 (\cosh b)^2} \]

\[\int_0^1 \frac{\cosh b}{96b^2 (\cosh b)^2} \, d\xi - \frac{b^4}{4320b^2 (\cosh b)^2} \int_0^1 \xi \cosh b \, d\xi \]

\[\int_0^1 \frac{\cosh b}{\cosh b} \, d\xi - \left\{ \left( \frac{\tanh b}{b} - \frac{1}{b^2} - \frac{F}{2} \right) \frac{1}{\cosh b} \right\} \int_0^1 \xi \ln \xi \cosh b \, d\xi \right\}

(B.5-4)

Integrating term by term and taking limits,

\[Q' = \frac{1}{E^2} \left[ \frac{F}{2b^2 \cosh b} + \frac{F^2}{16} - \frac{F}{b^3 \cosh b} \left( \sinh b - \frac{\cosh b}{b} + \frac{1}{b} \right) - \frac{F}{4b^2 \cosh b} \right.

+ \frac{F}{16 \cosh b} + \frac{Fb^2}{576 \cosh b} + \frac{Fb^4}{34560 \cosh b} - \frac{F}{4} \left( \frac{\tanh b}{b} - \frac{1}{b^2} - \frac{F}{2} \right)

- \frac{1}{b^3 \cosh^2 b} \left( \sinh b - \frac{\cosh b}{b} + \frac{1}{b} \right) - \frac{F}{4 \cosh b} \left\{ \frac{\sinh b}{b} - \frac{3}{b} \left[ \left( \frac{1}{b} + \frac{2}{b^3} \right) \cosh b \right. \right.

- \frac{2}{b^2} \sinh b - \frac{2}{b^3} \right\} \left\{ \frac{1}{b^2} - \frac{\cosh b}{b^3} + \frac{1}{b^2} \left( \frac{1}{b^2} + \frac{b^4}{16} + \frac{b^4}{8} \right) - \frac{\sinh b}{b} - \frac{\cosh b}{b^3} \right\}

- \frac{1}{b^2 \cosh^2 b} \left[ \frac{1}{b^2} - \frac{\cosh b}{b^3} + \frac{1}{b^2} \left( \frac{b^2}{4} + \frac{b^4}{96} + \frac{b^6}{4320} \right) \right] - \frac{1}{4 \cosh^2 b} \left\{ \frac{\sinh b}{b} - \frac{5 \cosh b}{b^2} \right\}

- \frac{3}{b} \left[ \left( \frac{1}{b} + \frac{2}{b^3} \right) \cosh b - \frac{2}{b^2} \sinh b - \frac{2}{b^3} \right] \left\{ \sinh b + \frac{5 \cosh b}{b^2} \right\}

+ \frac{20}{b^2} \left[ \frac{\sinh b}{b} - \frac{3}{b} \right] \left\{ \left( \frac{1}{b} + \frac{2}{b^3} \right) \cosh b - \frac{2 \sinh b}{b^2} - \frac{2}{b^3} \right\} \right\}

\left\{ \frac{\sinh b}{b} - \frac{7 \cosh b}{b^2} + \frac{42}{b^2} \left[ \frac{\sinh b}{b} - \frac{5 \cosh b}{b^2} + \frac{20}{b^2} \right] \frac{\sinh b}{b} - \frac{3}{b} \left[ \left( \frac{1}{b} + \frac{2}{b^3} \right) \cosh b \right. \right\}
\[
- \left( \frac{2 \sinh b}{b^2} - \frac{2}{b^3} \right) \left[ \left\{ \frac{1}{\cosh b} \left( \frac{\tanh b}{b^2} - \frac{1}{b^2} - \frac{F}{2} \right) \right\} \left[ \frac{1}{b^2} - \frac{\cosh b}{b^2} + \frac{1}{b^2} \left( \frac{b^2}{4} + \frac{b^4}{96} + \frac{b^6}{4320} \right) \right] \right] \\
\left( \frac{1}{b^2} - \frac{\cosh b}{b^2} + \frac{1}{b^2} \left( \frac{b^2}{4} + \frac{b^4}{96} + \frac{b^6}{4320} \right) \right] \\
\right) \\
\right) \\
\right) \\
\right) \\
\right) \\
\right) \\
\right)
\]

\[Q' = \frac{1}{E^2} \left[ \frac{F}{4b^2 \cosh b} + \frac{F^2}{16} + \frac{F}{16 \cosh b} + \frac{P^2}{\cosh b} \left( \frac{b^2 + 60}{34560} \right) - \frac{1}{b^3 \cosh b} \left( \frac{\sinh b}{b} \right) \left( \frac{\cosh b}{b} + \frac{1}{b} \right) \left( F + \frac{1}{\cosh b} \right) - \left\{ \frac{1}{\cosh b} \left( \frac{\tanh b}{b^2} - \frac{1}{b^2} - \frac{F}{2} \right) \right\} \left\{ \frac{1}{b^2} \right\} \left[ \frac{1}{b^2} - \frac{\cosh b}{b^2} + \frac{1}{b^2} \left( \frac{b^2}{4} + \frac{b^4}{1080} + F \cosh b \right) \right] - \frac{(1 + F \cosh b)}{4 \cosh^2 b} \left( \frac{\sinh b}{b} \right) \left( \frac{\cosh b}{b} + \frac{1}{b} \right) \left( F + \frac{1}{\cosh b} \right) - \frac{1}{b^2} \sinh 2b \right) \\
- \frac{3b}{2} \left[ \left( \frac{1}{b} + \frac{2}{b^3} \right) \cosh b - \frac{2}{b^2} \sinh b - \frac{2}{b^3} \right] \right) + \frac{1}{4b^4 \cosh^2 b} \left( b \sinh 2b \right) \\
- \frac{\cosh 2b}{2} - \frac{7}{2} + 4 \cosh b - \frac{b^4}{24} - \frac{b^6}{1080} \right) - \left[ \frac{87}{4320 b \cosh 2b} \left\{ b^2 \sinh b \right\} \left( 1 - b \tanh b \right) \\
- \frac{5b \cosh b + 20 \sinh b}{b} \left\{ \cosh b + \frac{2 \cosh b}{b^2} - \frac{2 \sinh b}{b} - \frac{2}{b^2} \right\} \right] \right) \\
+ \frac{b^2}{4320 \cosh b} \left( 7 - b \tanh b \right) \right)
\]

(Eq. B.5-5)

Rearranging, Eq. B.5-5 becomes Eq. 4.2-33

\[Q' = \frac{1}{E^2} \left[ \frac{F}{4b^2 \cosh b} + \frac{F^2}{16} + \frac{F}{16 \cosh b} + \frac{P^2}{\cosh b} \left( \frac{b^2 + 60}{34560} \right) - \frac{1}{b^3 \cosh b} \left( \frac{\sinh b}{b} \right) \left( \frac{\cosh b}{b} + \frac{1}{b} \right) \left( F + \frac{1}{\cosh b} \right) - \left\{ \frac{1}{\cosh b} \left( \frac{\tanh b}{b^2} - \frac{1}{b^2} - \frac{F}{2} \right) \right\} \left\{ \frac{1}{b^2} \right\} \left[ \frac{1}{b^2} - \frac{\cosh b}{b^2} + \frac{1}{b^2} \left( \frac{b^2}{4} + \frac{b^4}{1080} + F \cosh b \right) \right] - \frac{(1 + F \cosh b)}{4 \cosh^2 b} \left( \frac{\sinh b}{b} \right) \left( \frac{\cosh b}{b} + \frac{1}{b} \right) \left( F + \frac{1}{\cosh b} \right) - \frac{1}{b^2} \sinh 2b \right) \\
- \frac{3b}{2} \left[ \left( \frac{1}{b} + \frac{2}{b^3} \right) \cosh b - \frac{2}{b^2} \sinh b - \frac{2}{b^3} \right] \right) + \frac{1}{4b^4 \cosh^2 b} \left( b \sinh 2b \right) \\
- \frac{\cosh 2b}{2} - \frac{7}{2} + 4 \cosh b - \frac{b^4}{24} - \frac{b^6}{1080} \right) - \left[ \frac{87}{4320 b \cosh 2b} \left\{ b^2 \sinh b \right\} \left( 1 - b \tanh b \right) \\
- \frac{5b \cosh b + 20 \sinh b}{b} \left\{ \cosh b + \frac{2 \cosh b}{b^2} - \frac{2 \sinh b}{b} - \frac{2}{b^2} \right\} \right] \right) \\
+ \frac{b^2}{4320 \cosh b} \left( 7 - b \tanh b \right) \right)
\]

(4.2-33)

where \( F = (1-E) \).

For the Newtonian case when \( b \to 0 \), from Eq. 4.2-33, \( Q' = -1/96. \)
Differentiating Eq. 4.2-42 w.r.t. \( x_1 \) gives

\[
\frac{\partial C_m}{\partial x_1} = -\frac{C_0'}{2\sqrt{k\pi t}} \exp\left(-\frac{x_1^2}{4kt}\right)
\]  

(B.6-1)

Using Eq. 4.2-25 in Eq. 4.2-27, it becomes

\[
C_m = SC_m' + C_0
\]  

(B.6-2)

From Eqs. B.6-2 and 4.2-25

\[
C = C_m - S(C_m' - C')
\]  

(B.6-3)

Now using the definition of \( S \),

\[
S = \frac{R^2}{D} \left( \frac{\partial C_m}{\partial \eta_1} \right) = \frac{R^2 V_x}{D} \frac{\partial C_m}{\partial x_1}
\]  

(B.6-4)

Eq. B.6-3 becomes

\[
C = C_m - \frac{R^2 V_x}{D} \frac{\partial C_m}{\partial x_1} (C_m' - C')
\]  

(B.6-5)

Using Eqs. 4.2-42, B.6-1, 4.2-37 and the dimensionless quantities of Eq. 4.2-11, we find that

\[
C = 0.5 C_0' \text{erfc} \left( \frac{X' - \tau/2}{\sqrt{-2Q'T}} \right) + \frac{0.5 C_0'}{\sqrt{-2\pi Q'T}} \exp \left[ \frac{(X' - \tau/2)^2}{2Q'T} \right] (C_m' - C')
\]  

(B.6-6)
From Eq. 4.2-14

\[ C_b = \frac{\int_0^1 c(\xi) \frac{V_x}{V_x} (\xi) \frac{V_x}{V_x} \xi \, d\xi}{\int_0^1 \frac{V_x}{V_x} (\xi) \xi \, d\xi} \]  \hspace{1cm} (B.6-7)

and so using Eq. B.6-6,

\[
C_b = \frac{\int_0^1 0.5 C_0' \text{erfc} \left( \frac{X' - \tau/2}{\sqrt{-2Q'\tau}} \right) \frac{V_x}{V_x} \xi \, d\xi}{\int_0^1 0.5 C_0' \sqrt{-2Q'\pi\tau} \exp \left[ \frac{(X' - \tau/2)^2}{2Q'\tau} \right] (C_m' - C') \frac{V_x}{V_x} \xi \, d\xi}
\]

\[
= \frac{\int_0^1 \frac{V_x}{V_x} \xi \, d\xi}{\int_0^1 \frac{V_x}{V_x} \xi \, d\xi} \]  \hspace{1cm} (B.6-8)

Now for the Eyring model fluid

\[
\int_0^1 \frac{V_x}{V_x} \xi \, d\xi = \int_0^1 \frac{1}{E} \left( 1 - \frac{\cosh b \xi}{\cosh b} \right) \xi \, d\xi = \frac{1}{2E} - \frac{1}{Eb\cosh b} \left( \frac{\sinh b}{b} + \frac{1}{b} \right) \]  \hspace{1cm} (B.6-9)

Using definitions of \( C_m \) and \( Q \) from Eqs. 4.2-27 and 4.2-32 and substituting Eq. B.6-9 into Eq. B.6-8, Eq. B.6-9 becomes, after simplification
\[
\begin{align*}
C_b &= \frac{1}{Ebcoshb} \left( \sinh b - \frac{\cosh b}{b} + \frac{1}{b} \right) - \frac{0.5}{\sqrt{2\pi}Q'} \exp \left[ \frac{(X' - \tau/2)^2}{2Q'} \right] \left( Q' + \frac{C_m'}{2} \right) \\
&= \left[ \frac{1}{2E} - \frac{1}{Ebcoshb} \left( \sinh b - \frac{\cosh b}{b} + \frac{1}{b} \right) \right] \\
\end{align*}
\]

(4.2-45)

Eq. 4.2-16 is

\[
\frac{C_b}{C_0'} = 0.5 \operatorname{erfc} \left( \frac{x-V_x t}{\sqrt{4kt}} \right) + \frac{1}{96 \sqrt{\frac{\pi DT}{48R^2}}} \exp \left[ - \frac{(x-V_x t)^2}{4kt} \right]
\]

(4.2-16)

In terms of dimensionless quantities it becomes

\[
\frac{C_b}{C_0'} = 0.5 \operatorname{erfc} \left( \frac{X' - \tau/2}{\sqrt{\tau/48}} \right) + \frac{1}{96 \sqrt{\frac{\pi \tau}{48}}} \exp \left[ - \frac{(X' - \tau/2)^2}{\tau/48} \right]
\]

(B.6-10)

As \( b \to 0, \ C_m' = 1/12, \) and \( Q' = -1/96 \) and hence Eq. 4.2-45 reduces to Eq. B. 6-10 which is the expression for the Newtonian flow.
Fig. CI. Plot of average concentration versus length of the tube.

System: K2MnO4 - H2O
Tube size: 1 mm
Velocity: 0.2545 cm/sec
Time of flow (sec)

- ○: 100
- △: 150
- □: 230

Percent average concentration Cm
System: KMnO₄ - H₂O

Tube size: 1 mm
Velocity: 0.429 cm/sec
Time of flow (sec)

- ○ 80
- △ 100
- □ 120

Fig. C2. Plot of average concentration versus length of the tube.
System: KMnO₄ - H₂O

Tube size: 1 mm
Velocity: 1.27 cm/sec
Time of flow (sec)

○ 18
△ 23.2
□ 40

Fig. C3. Plot of average concentration versus length of tube.
System: Dye - Polyox
Tube size: 1 mm
Time of flow (sec) Velocity (cm/sec)

- Circle 7200 0.003008
- Triangle 15360 0.003008
- Square 28800 0.001929

Fig. D1. Plot of average concentration versus length of tube.
System: Dye - Polyox
Tube size: 1 mm
Velocity (cm/sec): 0.03008
Time of flow (sec):

\[ \triangle \quad 780 \]
\[ O \quad 1200 \]

Fig. D2. Plot of average concentration versus length of tube.
System: Dye - Polyox
Tube size: 1 mm
Velocity: 0.1800 cm/sec
Time of flow (sec)

- ○ 90
- △ 180
- □ 230
- • 230 (2 mm tube)
- ▽ 1440

Fig. D3. Plot of average concentration versus length of tube.
FIG. 24. Plot of average concentration versus length of tube.

System: Dye - Polyoxy
Tube size: 1 mm
Velocity: 0.429 cm/sec
Time of flow (sec)

- ○ 80
- △ 100
- □ 120

Percent average concentration Cm

Tube length (cm)
Fig. D5. Plot of average concentration versus length of tube.

System: Dye - Polyox
Tube size: 1 mm
Velocity: 1.27 cm/sec
Time of flow (sec):

- O 20
- △ 30
- □ 40

Percent average concentration g/cm³
System: Dye - Polyox
Tube size: 2 mm

Time of flow (sec)
0 20 40 120

Velocity (cm/sec)
1.1483 1.1483 0.4019

Percent average concentration $C_m$
5 10 20 30 40 50 60 70 80 90 95 98 99 99.8 99.9 99.99

Tube length (cm)
0 10 20 30 40 50 60 70 80 90 95 98 99 99.8 99.9 99.99

Fig. D6. Plot of average concentration versus tube length.
Fig. D7. Plot of average concentration versus length of tube.

System: Dye - Polyox
Tube size: 2 mm

<table>
<thead>
<tr>
<th>Time of flow (sec)</th>
<th>Velocity (cm/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>7200</td>
</tr>
<tr>
<td>△</td>
<td>13500</td>
</tr>
<tr>
<td>□</td>
<td>72000</td>
</tr>
</tbody>
</table>

Percent average concentration $C_{avg}$
System: Dye - Polyox
Tube size: 2 mm
Velocity: 0.0287 cm/sec
Time of flow (sec): 780 1200

Fig. D6. Plot of average concentration versus length of tube.
System: Dye - Polyox
Tube size: 2 mm
Velocity: 0.1579 cm/sec
Time of flow (sec)

○ 180
△ 230

Fig. D9. Plot of average concentration versus length of tube.
APPENDIX E. ERROR ANALYSIS OF EXPERIMENTAL MEASUREMENTS

Figure 26c is a plot of $C_m^+$ versus $(X'/\tau)$ or $C_m^+$ versus $\frac{x}{2V_xt}$.

A. Error estimates in $\frac{x}{2V_xt}$ term:

The time can be measured within a precision of $\pm 0.1\%$ and distance $\pm 4\%$. The volumetric flow rate precision was $\pm 2\%$ and the diameter of the tube $\pm 0.02\%$. Hence, the measurement of average velocity was reproducible to within $\pm 2.2\%$. Therefore, the error involved in the term $X'/\tau$ was $\pm 1.7\%$.

B. Error estimates in $C_m^+$:

The error in $C_m^+$ comes from the error in the measurement of distance from the inlet of the tube and from the error involved in the photometric measurements.

From Figure 23, the average deviations of $L'$ and $\tau$ were $\pm 12$ and $\pm 13\%$. The deviation in the value of $D = \frac{\tau R^2}{t}$ can be calculated as follows:

The square of the relative standard deviation in $D$ is given by

$$\left(\frac{\Delta D}{D}\right)^2 = \left(\frac{1}{D} \frac{\partial D}{\partial R}\right)^2 (\Delta R)^2 + \left(\frac{1}{D} \frac{\partial D}{\partial \tau}\right)^2 (\Delta \tau)^2 + \left(\frac{1}{D} \frac{\partial D}{\partial t}\right)^2 (\Delta t)^2$$

Substituting $D = 3.067 \times 10^{-7}$ cm$^2$/sec, $\tau = 0.01021$, $R = 0.052$ cm, $t = 90$ secs, $\Delta \tau = 0.00133$, $\Delta R = 0.000001$ cm, and $\Delta t = 0.09$ sec
\( \left( \frac{\Delta D}{D} \right)^2 = 0.173 \)

and

\( \left( \frac{\Delta D}{D} \right) = 0.131 \)

or

\( \left( \frac{\Delta D}{D} \right) = 13.1\% \)

The mixing zone length \( L \) is given by

\[
L = \frac{L'(\frac{3n+1}{n+1})}{D} R^2 \overline{v_x}
\]

The square of the relative standard deviation in \( L \) can be written as

\[
\left( \frac{\Delta L}{L} \right)^2 = \left( \frac{L}{\partial L/\partial L'} \right)^2 (\Delta L')^2 + \left( \frac{L}{\partial L/\partial R} \right)^2 (\Delta R)^2 + \left( \frac{L}{\partial L/\partial \overline{v_x}} \right)^2 (\Delta \overline{v_x})^2 + \left( \frac{L}{\partial L/\partial D} \right)^2 (\Delta D)^2 + \left( \frac{L}{\partial L/\partial n} \right)^2 (\Delta n)^2
\]

The measured value of \( L \) is 28.5 cm for this particular run and considering the above deviations in \( L', D, R, \) and \( \overline{v_x} \), it becomes 28.8 cm or \( \pm 1.1\% \) deviation. The corresponding values of \( \xi_m^+ \) are tabulated in column four below.
<table>
<thead>
<tr>
<th>Distance x, cm</th>
<th>X'/T</th>
<th>C_m+ (Expt.)</th>
<th>C_m+ (with ±1.1% deviation)</th>
<th>C_m+ (with ±3.4% photo. error)</th>
</tr>
</thead>
<tbody>
<tr>
<td>32</td>
<td>1.0198</td>
<td>4.98</td>
<td>6.2</td>
<td>6.37</td>
</tr>
<tr>
<td>27</td>
<td>0.8605</td>
<td>15.24</td>
<td>13.6</td>
<td>14.12</td>
</tr>
<tr>
<td>22</td>
<td>0.7011</td>
<td>27.66</td>
<td>26.0</td>
<td>26.94</td>
</tr>
<tr>
<td>17</td>
<td>0.5418</td>
<td>39.58</td>
<td>42.0</td>
<td>43.34</td>
</tr>
<tr>
<td>12</td>
<td>0.3824</td>
<td>54.64</td>
<td>60.0</td>
<td>61.85</td>
</tr>
<tr>
<td>7</td>
<td>0.2231</td>
<td>71.03</td>
<td>76.0</td>
<td>78.15</td>
</tr>
<tr>
<td>2</td>
<td>0.0637</td>
<td>82.29</td>
<td>87.0</td>
<td>89.70</td>
</tr>
</tbody>
</table>

Absorbance A is defined as

\[ A = \log_{10} \left( \frac{1}{T} \right) \]

where T is the transmittance. The experimental data of absorbance were converted to percent transmittance. The plot of %T versus concentration, ppm was made on semi-logarithmic paper and slope of 67.4 was found as the transmittance change in percent corresponding to a tenfold change in concentration.

According to Ewing [15], the precision of measurements can be given by the relation

\[ \text{percent relative error in analysis} = \frac{230}{1 \text{ percent absolute photometric error} \times \text{slope}} \]

Hence percent relative error in analysis was ±3.4% and values of C_m+ were tabulated in Table 5.
BIBLIOGRAPHY


40. Reynolds, O., Phil. Mag., 20 (1885).
CURRICULUM VITAE

The author was born in Sayama, India, on August 23, 1945. He finished his primary education in Sayama and graduated from E. M. High School, Borsad with Distinction, in March, 1962. He received a Bachelor's degree in Chemical Engineering from the M. S. University of Baroda, India, in June, 1968.

He joined the University of New Mexico in September, 1969, for graduate study leading to the Master of Science degree in Chemical Engineering. Upon graduation in June, 1971, he commenced working towards the Ph.D. degree in Chemical Engineering. During this period, he served as a graduate assistant and laboratory instructor. He acquired experience in both teaching and demonstrating Unit Operations laboratory and Control experiments. Experience in computer simulation of chemical processes was gained with programming languages such as FORTRAN IV, CSMP (Continuous System Modeling Program), and CHESS (Chemical Engineering Simulation System). His publications include two technical papers in the field of dispersion phenomena.

The author is a member of the American Chemical Society, the Society of Sigma Xi, and the American Institute of Chemical Engineers.