A STUDY OF THE BIVARIATE ANALYSIS
OF DISPERSED PHASE MIXING

by

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ABSTRACT

A method for the measurement of the bivariate drop volume-dye concentration distribution in a dispersed phase mixing vessel has been developed. The method involves extracting a sample of dispersed phase from the vessel and immediately coating it with an anticoalescence agent. The drops are then forced at a constant flow rate through a small capillary. A logarithmic photometer focused on the capillary through a microscope produces an output of rectangular pulses. The length of each pulse is a measure of the volume of the drop and the height of each pulse is a measure of dye concentration in the drop. The analysis of the photometer output is performed easily and quickly on the computer.

A volume balance containing a single mixing kernel to quantitatively describe the breakage and coalescence processes in a steady state mixing vessel is derived. Various space balances for the two dimensional experiment are investigated in the attempt to find a balance which would allow calculation of the mixing kernel from the experimental data. Three techniques to study the approximate calculation of the mixing kernel are developed and applied to several experiments. The uniqueness question for the mixing kernel in the two dimensional integral balance equation is investigated but not solved. The mixing kernels obtained by using the balance equation are still in question because this uniqueness question is unresolved and because the resulting kernel values seem unreasonable physically.

Methods for the approximate interpretation of the data from the steady state dye mixing experiment are suggested and a particular example of some of the possible interpretations is demonstrated. In this example four experiments are run with different residence times
in the vessel. The drop size distributions in the vessel for the experiments are compared with each other and with the log normal distribution. The development of the dye concentration marginal distribution with residence time is indicated. The homogenous equal drop size model is applied to the ratio of input to output concentration variance for the four experiments. For the different residence times the model fits well and indicates a mixing rate of the same order of magnitude as has been found by other investigators.
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<td>Likelihood ratio for probability density comparison</td>
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<tr>
<td>$\nu$</td>
<td>Drop mass; integration variable</td>
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<td>Breakage function defined in text</td>
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<td>$\rho(m',\nu)$</td>
<td>Coalescence function defined in text</td>
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<tr>
<td>$\tau$</td>
<td>Residence time in vessel</td>
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<td>$\Xi$</td>
<td>Log-likelihood function to be maximized</td>
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<td>$\phi_2$</td>
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<td>$\Delta$</td>
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CHAPTER 1

INTRODUCTION

Many industrially important chemical engineering processes, such as liquid-liquid extraction, emulsion polymerization, and oil-water reactions are carried out in dispersed phase reactors. The effects of breakage of drops on such processes has been investigated by Valentas and Amundson (21), and the effects of coalescence has been investigated by Rietema (16) and Curl (3,4). These studies show the importance of dispersed phase mixing. In the past the design and scale-up of these reactors has been based largely on empirical methods because an understanding of the underlying breakage and coalescence processes had not been attained. Recently, however, there have been various attempts both theoretical and experimental to further characterize the breakage and coalescence processes, as enumerated in Chapter 2.

The goal of this work is to develop an experimental method which will give more detailed information about the mixing process than any experiment before and to derive an equation which can be used to quantitatively predict the mixing function using the data of the experiment. This goal, then, could be considered as an attempt to bring together the experimental procedures for measurement of dispersed phase properties and the theoretical development of general equations.

Previous dispersed phase experiments have been concerned with measurements of various properties of the dispersed phase such as drop size distribution, interfacial area, or concentration variance. These are all particular characteristics of the underlying bivariate drop size-concentration distribution. The experimental technique developed in this
work will measure this bivariate distribution by drawing a sample from the vessel and forcing it through a capillary. The experiment itself involves a mixing vessel operating at steady state with feed streams of continuous phase water, oil with low dye concentration, and oil with high dye concentration. The experiment and the measurement technique are explained in Chapters 4 and 5.

Chapter 6 contains some approximate interpretations of the data from the above experimental system. Four experiments were performed with different residence times. The resulting marginal volume and marginal concentration distributions are compared for the different experiments. The ratios of the output to input concentration variance for different residence times are compared with the equal drop size model.

A volume balance equation which contains a single mixing kernel is derived in Chapter 3. Various other balances which could be used for the calculation of the mixing kernel are investigated. Various attempts were made to prove the uniqueness of the mixing kernel in the equation but no method was completely successful. Three methods to study the calculation of the mixing kernel from experimental data are presented. Chapter 7 contains the application of these methods to experimental data.
CHAPTER 2

LITERATURE SURVEY

The pertinent literature can generally be divided into three categories; the theoretical description of the mixing process, simplified theories of mixing with experimental measurements of mixing parameters and other measurements in dispersed systems. The simplified theories of mixing and related experiments are discussed first to give some indication of the initial investigations into the nature of dispersed phase mixing. Other measurements of particular properties of dispersed systems follow. In particular, the methods for measuring drop size distributions in stirred vessels are presented and discussed. Finally a discussion of the one general mixing model found in the literature is given.

2.1 Simplified Models

Rietema (16) discusses four basic simplified models of mixing in stirred vessels. These are the homogeneous equal drop size model, the circulation model, the dead corner model, and the Harga model. The circulation model is based on regions of breakage near the impeller and regions of coalescence in other parts of the vessel. The dispersed phase circulates between these two regions. The dead corner model postulates that most coalescences occur between drops in the vessel and large masses of dispersed phase stagnated in dead corners. Large drops then break from this mass and return to the drop system. In all experiments for the measurement of mixing rates the equal drop size model has been used in interpreting the results.

A theoretical discussion of this model is given by Curl (3). The
basic assumption of the model is that all drops are the same size. Coalescences are considered to occur randomly between two drops in the vessel. Redispersion of the two coalesced drops occurs instantaneously producing two drops of the same size (the size assumed in the vessel) and the same concentration. This concentration is the average of the concentrations in the two drops. Using this mixing model, he defines a parameter, $\omega_j$, as the number of dispersed phase volumes involved in coalescences per unit time. This parameter is essentially that which is measured in most experiments. Curl also develops a batch mixing equation and solves it for the case of mixing equal volumes of dispersed phase each containing different concentrations of a solute.

Madden and Damerell (11) studied the system of water dispersed in toluene in a 0.3 gal. vessel, stirred by a flat blade turbine. The mixing rate was determined by measuring the rate of disappearance of iodine in the continuous phase as it reacted with sodium thiosulfate in the dispersed phase. The experiment was started with pure water being dispersed in the iodine toluene solution. Then a small quantity of dispersed phase containing a high concentration of sodium thiosulfate was injected into the vessel. As the sodium thiosulfate spread throughout the dispersed phase, the rate at which the iodine was consumed changed. Using the random coalescence model, this rate of disappearance was converted into a mixing rate.

Experiments similar to those above were performed by Miller et al (14). Their system was oil dispersed in water. Instead of using a chemical reaction to follow the spread of reacting solute, they used light transmission to follow the spread of a light absorbing dye. The transmittance through the dispersion was related to the variance of dye
concentration in the drops. The experiment was started with the oil dispersed in water in the agitated vessel. Additional dispersed phase containing dye was then introduced into the mixing vessel. The plot of light transmission versus time obtained from the experiment was then interpreted using the homogeneous model of Curli. Mixing rates were measured in this manner for a variety of vessels, impellers, phase fractions, dispersed phase properties, and power inputs. The dependency of mixing on each of these variables was correlated.

Hillestad (7) also measured coalescence rates using a light transmission technique. The experimental technique was similar to that of Miller et al. Instead of following the spread of dye on the vessel, Hillestad follows the course of the ferric chloride-potassium ferri-cyanide reaction in aqueous drops dispersed in an organic continuous phase. The light transmission output was calibrated and the experimental measurements were used to calculate mixing rates. The method of calibration and the subsequent calculation of mixing rates appear questionable to this author.

Mixing rates in a continuous flow system were measured by Groothius and Zuiderweg (5). Their experimental apparatus consisted of a stirred tank to which was fed two streams of dispersed phase of different densities, one heavier and one lighter than the continuous phase water. The density of the lighter stream was adjusted such that if a drop from this stream coalesced with any drop of density heavier than water the resultant drop would be heavier than water. The output stream was then separated into two fractions of dispersed phase, one heavier than water and one lighter than water. The mixing rate in the vessel was deduced from the change in dispersed phase fraction heavier than water as it
passes through the vessel.

Howarth (8) measured coalescence frequency by measuring the rate of change of interfacial area when the stirring speed has been changed instantaneously from one value to a lower one. The model used to interpret this data is based upon the assumption that the turbulence is isotropic and that the decay of turbulence in the vessel is virtually instantaneous. That is, when the stirrer speed is changed, the turbulence in the vessel changes rapidly from one isotropic state to another in comparison to the rate of coalescence in the vessel. The usual equal drop size model is employed to develop a relationship between coalescence rate as the dependent variable and two independent variables. These are the average drop size in the vessel and the rate of change in interfacial area per unit time at the instant of change in turbulence. According to the author this method allows varying average drop size and power inputs somewhat independently.

Negligible mixing was reported for water dispersed in benzene by Matsuzawa and Miyauchi (13). Shinnar (18) also found negligible mixing for certain values of stirrer speed using a Shellwax water system, whereas, for other stirrer speeds, mixing rates were much higher. Using the theory of isotropic turbulence, he postulated the prevention of coalescence to be caused by the turbulent fluctuations in the vessel. He related this phenomenon to stirrer speed and thus explains the phenomenon of no mixing at certain stirrer speeds and higher mixing rates at other speeds.

2.2 Other Measurements in Dispersed Systems.

The measurement of the interfacial area by light transmission and the measurement of drop size distributions by photographic techniques.
microscopic inspection, Coulter counters, and light scattering are the primary physical measurements made on dispersed systems. Here only the methods for measuring drop size distribution will be discussed, since they indicate previous methods for measuring drop size distribution.

A typical example of the determination of drop size distribution by photography is given in an article by Chen and Middleman (2). The drops were photographed in the tank with the camera focused on a plane midway between the tank wall and its axis. The cylindrical glass tank was surrounded by a square Plexiglass tank, which served as a constant temperature bath and allowed pictures to be taken without optical distortion. The drops were measured directly from the negatives, using a 32 power traveling microscope. The system was checked by measuring a known distribution of glass beads in the vessel. This experiment indicated an agreement within 5% and also a necessity of counting at least 300 drops to obtain accurate results.

Shinnar (18), for example, describes a method for obtaining drop size distribution by direct microscopic observation. His experiment involved mixing Shellwax in a heated vessel. A sample of the dispersion is removed from the vessel and cooled quickly. The solidified wax drops were then measured under a microscope. For each distribution presented, he counted approximately 1000 drops. Other methods, such as coating the outside of drops with a polymer (12), have been suggested for obtaining drop size distributions by microscopic inspection.

A Coulter Counter was used by Sprow (19) to measure drop size distributions of an emulsion of methyl isobutyl ketone in salt water. In his system a sample was withdrawn from the stirred vessel and immediately diluted from a phase fraction of 25% to one of 0.05 to 0.5% phase fraction. At this dilution, the drop size distribution could be measured
using the Coulter Counter. This device measures drop sizes by measuring the change in electrical resistance through a small aperture as the non-conducting drop passes through it. The change in resistance is related to drop size by calibration.

Light scattering was used by Lindsey et. al. (10) to measure drop size distribution in a batch stirred vessel. For this measurement, a special light scattering cell is used with the dispersion being pumped to this cell continuously. The drop size distribution is related to the plot of the product of light intensity times scattering angle squared versus the scattering angle. To obtain the drop size distribution itself, the Worthy differential analysis of the intensity versus scattering angle curve must be performed.

All of the above methods have basic limitations. They all work best at low phase fraction. The light scattering technique and the Coulter Counter operate best with very small drops. The photographic and microscopic inspection techniques are very time consuming. Finally none of the above techniques allows another variable such as concentration of dye in the drop to be measured.

2.3 General Mixing Model

Valentas and Anundson (20) derive a number balance for a dispersed phase system in a mixing vessel. They consider the number of drops entering and leaving a differential mass range $m'$ to $m'+ dm'$ in the vessel by breakage, coalescence, and flow.

The number input into the mass range by flow is determined by the input number of drops per unit time $n_A$ and the input number distribution $a(m',t)$. The number output by flow from this mass range is found from
the drop size distribution in the vessel $N(t) A(m', t)$ and the escape frequency. The escape frequency, $f(m')$, is defined as the fraction of droplets of the vessel contents with mass between $m'$ and $m' + dm'$ flowing out per unit time. In most cases, $f(m')$ is constant, i.e. the output distribution is the same as the distribution in the vessel.

The breakage process is characterized by the breakage frequency $g(m')$ and the breakage kernel $\nu(m') \beta(m': \nu)$. The breakage frequency $g(m')$ is defined to be the fraction of droplets of the reactor contents, with mass between $m'$ and $m' + dm'$, disappearing through breakage per unit time. Upon breakage a droplet of mass $m'$ gives rise on the average to $\nu(m')$ smaller droplets whose sizes are distributed according to the probability density function $\beta(m': \nu)$. Here $\beta(m': \nu) d\nu$ is the fractional number of droplets with mass between $\nu$ and $\nu + d\nu$ formed upon breakage of a droplet of mass $m'$.

The function $h(m')$ and $\lambda(m', \nu)$ are used to characterize the coalescence process. The coalescence frequency, $h(m')$, is defined as the fraction of droplets of the reactor contents, with mass between $m'$ and $m' + dm'$ involved in collisions per unit time. Since not all collisions produce coalescence, the coalescence efficiency function $\lambda(m', \nu)$ is introduced.

These functions are then combined to give the following integrodifferential equation as the balance over an arbitrary mass range in the vessel:
\[
\frac{d}{dt} \left[ N(t)A(m',t) \right] = n_a \alpha(m',t) \\
\text{accumulation in mass range} \\
+ \int_m^1 \nu(\nu) g(\nu) \beta(m';\nu) N(t)A(m',t) d\nu \\
\text{flow into mass range} \\
+ \int_0^{m'} \lambda(m'-\nu,\nu) h(m'-\nu) N(t)A(m'-\nu,t) h(\nu) N(t)A(\nu,t) d\nu \\
\text{breakage into mass range} \\
+ \int_0^{m'} \lambda(m'-\nu,\nu) h(m'-\nu) N(t)A(m'-\nu,t) h(\nu) N(t)A(\nu,t) d\nu \\
\text{coalescence into mass range} \\
- \left[ f(m') + g(m') + h(m') \omega(m',t) \right] N(t)A(m',t) \\
\text{flow from mass range} \\
\text{breakage from mass range} \\
\text{coalescence from mass range} \\
\text{where} \\
\omega(m',t) = \int_0^{m'} \lambda(m',\nu) h(\nu) N(t) A(\nu,t) d\nu \\
\text{2.1}
\]

This equation was then used to determine the effect of various choices of mixing functions on the drop size distribution in the vessel. To make this type analysis useful in real systems the functions \( h, \lambda, g, \beta, f, \) and \( \nu \) would have to be measured or otherwise ascertained for such systems. Measurement of each function in a separate specialized experiment would be a difficult task and would not guarantee its applicability to a general system.

If equation 2.1 itself were to be used to measure the mixing functions, the number of these functions could be reduced by combining some
of them to make more complicated functions. In particular $h(m')$
$h(\nu) \lambda (m', \nu)$ could be written as $\pi(m', \nu)$ and $g(\nu) \beta(m'; \nu)$
could be written as $\theta(m', \nu)$. The function $f$ can be considered a con-
stant as might be expected for real systems. This would then leave
three functions $\nu$, $\theta$, and $\pi$ to be determined.
DEVELOPMENT OF BALANCE EQUATIONS

Valentas' equation (2.1) could be simplified such that mixing is described by three functions $\psi$ and $\theta$ for breakage and $\tau$ for coalescence. The purpose of this chapter is to reduce the number of functions describing mixing to one. Various balances for the dye mixing are developed and discussed. The uniqueness of the mixing kernel is investigated and three methods to study the calculation of this kernel are presented.

3.1 Derivation of Volume Balance

It is possible to simplify the expression of a balance equation further by considering other spaces, e.g. volume, area, or diameter distributions using volume, area, or diameter as the independent variables. The volume balance using drop volume as the independent variable will now be developed. The use of a volume balance should help simplify the kernel description of breakage because in a number description of breakage the number of drops is not conserved whereas in a volume description of breakage volume is conserved. This may allow elimination of $\psi$, the function describing the variable increase in the number of drops caused by breakage. Coalescence, however, is basically a number process and its description in a volume balance may be more complicated.

For the development of a volume balance, consider a CSTR of volume, $V$, and dispersed phase ratio $\phi_2$, operating at a steady state, with an input volume flow rate, $Q$, having a dispersed phase ratio $\phi_1$. The input enters with a volume distribution $p_0(V)$ and the volume distribution in the vessel is $p(V)$. It is assumed that the vessel is
homogeneous, i.e. that \( p(v) \) applies everywhere approximately in the vessel and that the mixing kernels also are approximately the same everywhere. This assumption may appear to be false because it is known that most of the breakage occurs near the stirrers, but if a drop must make three or four passes through the stirrer before it breaks (this implies that its coalescence rate is small) then the system can be considered approximately homogeneous. Here homogeneity means that the time average distributions of drops in any two small volumes in the vessel are approximately the same. Also it will be assumed that the exit volume distribution is the same as the distribution in the vessel; this is the same as the assumption that \( f \) is a constant in the Valentas model and is true in many real systems. Figure 3.1 shows this system.

![Schematic Drawing of System](image)

**Figure 3.1**

The volume balance is formed for an arbitrary drop volume range \( dv \) in the vessel. The volume in this volume range in the vessel is \( Vx p(v)dv \) and since the system is operating at steady state, this volume must not change with time. Hence, the inflow and outflow from this
volume range must be zero. There are three ways that volume is transferred into and out of this volume range, dv, i.e. by flow, coalescence, and breakage. Flow carries volume into and out of the vessel and thus into and out of a volume range, dv, in the vessel, whereas breakage and coalescence transfers volume between volume ranges in the vessel. Breakage shifts volume from a larger volume range to smaller volume ranges and coalescence transfers volume from smaller volumes to larger volumes. Figure 3.2 shows the processes involved in a balance in a volume range dv.

Processes Involved in Mixing

Figure 3.2

3.1.1 Flow Terms

The volume fraction of input dispersed phase with volume size dv is \( p_o(v) \) dv from the definitions of \( p_o(v) \). The flow rate into the
volume range $dv$ in the vessel is then $Q \phi_1 p_0(v) \, dv$. Similarly that flowing out of the volume range $dv$ in the vessel is simply $Q \phi_1 p(v)$ as it was assumed that the exit volume distribution was the same as the distribution in the vessel.

3.1.2 Coalescence Terms

For this reactor only binary coalescences, which would depend in part upon the product of the number probabilities of the two drops sizes involved, are assumed. Number probabilities are used because coalescence is basically a number process, i.e. it occurs between two drops, not between fractional volumes of drops. The number probability function is related to the volume probability function by the following relation.

$$f_n(v) = \frac{P(v)}{V C_L} \quad 3.1$$

where

$$C_L = \int_0^{\infty} \frac{P(v)}{V} \, dv$$

Then the total number of drops in size range $dv$ is:

$$n(v) = N f_n(v) \, dv \quad 3.2$$

where $N$ is the total number of drops in the vessel and $N = \frac{V \phi_2}{\bar{V}}$

where

$$\bar{V} = \int_0^{\infty} V f_n(v) \, dv = \frac{1}{C_L}$$

Hence

$$n(v) = \sqrt{\phi_2} \, \frac{P(v)}{V} \, dv \quad 3.3$$
Then defining \( \delta'(v', v'') \) to be the velocity coalescence cross-section product, i.e. the coalescence efficiency times the relative velocity collision cross-section product as defined in gas kinetic theory, it is possible to write the transfer of volume when two drops of size \( v' \) and \( v'' \) coalesce. The volume transferred into the size range \( v \) to \( v + dv \) where \( v = v' + v'' \) by this coalescence is given below.

\[
\text{Flux} = \frac{v' \delta'(v', v'')}{v'} \frac{n(v') n(v'')}{v'}
\]

or

\[
\text{Flux} = v' \int \frac{\phi_2 \delta'(v', v'')}{v'} \frac{p(v') p(v'')}{v'} dv' dv''
\]

Defining the coalescence kernel as shown below gives the final expression for the flux into volume range \( v = v' + v'' \) by coalescence of drops of volume \( v' \) and \( v'' \).

\[
K_c(v', v'') = \frac{\phi_2 \delta'(v', v'')}{v' v''}
\]

\[
\text{Flux} = \int \phi_2 v K_c(v', v'') p(v') p(v'') dv' dv''
\]

It is noticed that this coalescence kernel is symmetric, i.e. \( K_c(v', v'') = K_c(v'', v') \). This is an important property used later.

The total flux into a volume range \( dv \) is the integral over all \( v' \) and \( v'' \) such that \( v' + v'' = v \). To evaluate this integral, the following transformation is used

\[
v'' = v - v'
\]

\[
v' = v'
\]
This implies that

\[ dv'dv'' = dv'dv \]

The input into the volume range is then given by

\[ \text{Flux in} = \sqrt{2} \int_0^\infty v K_c(v, v-v') p(v') p(v-v') dv'dv \]  

3.9

This integral is taken from 0 to \( v/2 \) instead of to \( v \) in order not to count each coalescence twice. By symmetry, it is evident that the flux also can be calculated from the equation

\[ \text{Flux in} = \frac{1}{2} \sqrt{2} \int_0^v K_c(v, v-v') p(v') p(v-v') dv'dv \]  

3.10

or

\[ \text{Flux in} = \frac{1}{2} \sqrt{2} \int_0^\infty K_c(v, v-v') p(v') p(v-v') dv'dv \]  

3.11

since

\[ p(v) = 0 \quad v \leq 0 \]

The flux out of the volume range \( dv \) by coalescence is the flux caused by the coalescence of drops in the interval with drops outside the interval. The total flux out by coalescence is

\[ \text{Flux out} = \sqrt{2} \int_0^\infty v K_c(v, v') p(v) p(v') dv'dv \]  

3.12

3.1.3 Breakage Terms

A breakage function \( K_B(v, v') \) \( dv' \) is defined to be the volume flux from drop volume range \( v \) into drop volume range \( v' \) per unit time per unit volume of drop volume \( v \). Immediately it is noted that \( K_B(v, v') = 0 \)
for \( v' > v \) because it is impossible for breakage of drop volume \( v \) to cause a flux into a volume range larger than \( v \). The volume rate of breakage of drops of volume \( v \) is simply the integral of the breakage function over all \( v' \) into which it can break, i.e.

\[
\omega(v) = \int_{0}^{v} K_B(v, v') \, dv'
\]  

The reciprocal of \( \omega(v) \) is then the time required for one volume of drops of volume \( v \) to break. Also the function:

\[
\beta(v'; v) = \frac{K_B(v, v')}{\omega(v)}
\]

is the breakage probability density function given a drop volume \( v \). This means that if one volume of drop volume \( v \) breaks, \( \beta(v'; v) \, dv' \) is the fraction of this volume which breaks into the volume range \( v' \).

The flux into a volume range \( dv \) from a volume range \( dv' \) by breakage is then

\[
\int_{v}^{\infty} \phi_2 K_B(v', v) p(v') \, dv' \, dv
\]

When all the fluxes of volume ranges \( dv' \) which are greater than \( v \) are summed, the following integral gives the total flux into the volume range \( dv \) by breakage.

\[
\text{Flux in} = \int_{v}^{\infty} \phi_2 K_B(v', v) p(v') \, dv' \, dv
\]

Similarly, the volume flux out of the volume range \( dv \) and into the volume range \( dv' \) is given by:

\[
\int_{v}^{\infty} \phi_2 K_B(v, v') p(v) \, dv' \, dv
\]
When all the fluxes of volume range $v$ into volume ranges $v'$ less than $v$ are summed, the following integral gives the total flux from volume range $dv$.

$$\text{Flux out} = \int v \phi_2 \int_0^v K_B(v,v') p(v) dv' dv \quad 3.18$$

3.1.4 Final Balance

All the terms that contribute fluxes to the balance on the volume range $v$ to $v + dv$ are summarized below.

Flow:
- Input $Q \phi_1 p_0(v) dv$
- Output $Q \phi_1 p(v) dv$

Coalescence:
- Input $\int v \phi_2 \int_0^v K_c(v,v-v') p(v') p(v-v') dv' dv$
- Output $\int v \phi_2 \int_0^\infty K_c(v,v') p(v) p(v') dv' dv$

Breakage
- Input $\int v \phi_2 \int v K_B(v',v) p(v') dv' dv$
- Output $\int v \phi_2 \int_0^v K_B(v,v') p(v) dv' dv$

Since the CSTR is operated at steady state, the sum of fluxes in minus the sum of fluxes out must equal zero; then putting this statement in equation form gives the final balance shown below.
\begin{align*}
W_r \left[ p(v) - p_o(v) \right] &= \int_v^\infty K_B(v',v) p(v) \, dv' \, dv \\
&\quad + \int_0^v K_c(v, v-v') p(v') p(v-v') \, dv' \\
&\quad - \int_0^v K_B(v, v') p(v) \, dv' \quad - \int_0^\infty K_c(v, v') p(v) p(v') \, dv'
\end{align*}

where

\[ W_r = \frac{Q \phi_i}{V \phi_2} \]

Two properties of the kernels are now used to combine them into one kernel. Since \( K_B(v, v') = 0 \) if \( v' \geq v \) and \( K_c(v, v') = K_c(v', v) \), the mixing kernel can be defined as follows:

\[
K(v, v') = \begin{cases} 
K_B(v, v') & \text{if } v > v' \\
K_c(v, v') & \text{if } v' \geq v
\end{cases}
\]
The regions for breakage and coalescence are shown in Figure 3.3.

![Diagram showing regions for breakage and coalescence](image)

**Mixing Kernel**

**Figure 3.3**

This kernel is substituted into the equation (3.19) to give equation (3.21). Each term in the equation is numbered and its integration path in the \( v-v' \) space is shown in Figure 3.3.

\[
W_r [P(v) - P_0(v)] = \int_0^v K(v, v-v') p(v-v') p(v') dv'
\]

\[
- \int_0^v K(v, v') p(v) p(v') dv' - \int_v^\infty K(v, v') p(v') p(v) dv'
\]

\[
+ \int_v^\infty K(v, v') p(v') dv' - \int_0^v K(v, v') p(v) dv'
\]

Equation (3.21)
Thus an equation is developed with one unknown two dimensional kernel. If by experiment the input and output distributions were known, it still would not be possible to determine the mixing kernel as will be shown below. Assume that \( K_0(x, y) \) is a known solution to equation 3.22. Then another solution could be considered as this solution plus a perturbation, i.e.

\[
K(x, y) = K_0(x, y) + a K'(x, y)
\]

where \( K'(x, y) \) = perturbation of solution

\[ a = \text{constant} \]

Substituting this into equation 3.22 gives

\[
0 = \int_{0}^{V} V K'(x, V-x) p(x) p(V-x) \, dx - \int_{0}^{V} V K'(x, V) p(x) p(V) \, dx
\]

\[
-\int_{V}^{\infty} V K'(V, x) p(V) p(x) \, dx + \int_{0}^{\infty} V K'(x, V) p(x) \, dx - \int_{0}^{V} V K'(V, x) p(V) \, dx
\]

But this is just the equation describing batch mixing and it would be expected that there would exist a mixing kernel for this equation to the accuracy of measurement of the distribution. Thus to determine this kernel at least some other interactory process must be added to the equation to give bivariate analysis and hence a two dimensional equation.

3.2 Development of Two Dimensional Equations

In order to develop a two-dimensional equation a two dimensional experiment must be performed and the added quantity in the two dimensional experiment must interact in the mixing process. Of the processes that might be included are reaction in the dispersed phase, mass transfer from the dispersed phase, or dye dispersion in the dispersed phase;
the last is the easiest experimentally. However, the dye must not be surface active or it will affect the mixing process itself.

A schematic of the process is the same as in Figure 1 except the distributions are now two dimensional in volume and concentration, i.e. \( p(v) \) changes to \( p(v,c) \) and \( p_0(v) \) changes to \( p_0(v,c) \). There are, as before, many balances which can be written on this system with different independent variables, e.g. volume, area, moles, concentration, etc. and various distributed quantities, volume, number, etc. Several balances will be developed and compared.

3.2.1 Volume Distributed Over Volume and Concentration

Consider a volume balance in an area \( dv \, dc \) in the volume-concentration space. The following input and output relations apply:

Flow

\[
\begin{align*}
\text{Input} & \quad Q \phi_1 p_0(v,c) \, dv \, dc \\
\text{Output} & \quad Q \phi_1 p(v,c) \, dv \, dc
\end{align*}
\]

3.23a

3.23b

Breakage

\[
\begin{align*}
\text{Input} & \quad \int_0^{\infty} K(x,v) p(x) \, dx \, dv \, dc \\
\text{Output} & \quad \int_0^{V} K(v,x) p(v) \, dx \, dv \, dc
\end{align*}
\]

3.23c

3.23d

Coalescence

\[
\begin{align*}
\text{Input} & \quad \int_0^{\infty} K(x,v-x) p(x,y) p(v-x, \frac{c_v}{v-x}) \, dx \, dy \, dv \, dc
\end{align*}
\]

3.23e
Output \( \Phi_2 \int_0^\infty \int_0^\infty K(x, y) p(x, y) p(v, c) \, dy \, dx \, dv \, dc \)  
\( + \Phi_2 \int_0^\infty \int_0^\infty K(v, x) p(x, y) p(v, c) \, dy \, dx \, dv \, dc \) \( \text{3.23f} \)

The flow and breakage terms follow directly from the previous equation because the dye concentration distribution is not affected by these processes. Instantaneous mixing of the dye upon coalescence is assumed in developing the equation and the coalescence terms. This is not a bad assumption because the time between interactions is relatively large. The volume input into an area in the volume-concentration space by coalescence of two drops of volume \( v' \) and \( v'' \) respectively and concentration \( c' \) and \( c'' \) respectively is given by the following expression.

\[ V \Phi_2 \int_0^\infty K_c(v'; v'') p(v', c') p(v'', c'') \, dv' \, dc' \, dv'' \, dc'' \] \( \text{3.24} \)

To obtain the total volume flux into the volume concentration area \( dv \, dc \) the above expression must be integrated over all \( v' \) and \( v'' \) such that \( v = v' + v'' \) and over all \( c' \) and \( c'' \) such that

\[ c = \frac{c' v' + c'' v''}{v' + v''} \] \( \text{3.25} \)

The transformation of variables then is

\( v'' = v - v' \)
\( v' = v' \)
\( c' = c' \)
\( c'' = \frac{c v - c' v'}{v - v'} \) \( \text{3.26} \)

Use of the Jacobian of the transformation gives
\[ d \nu' d \delta' d \gamma' d \zeta' = \frac{\nu}{\nu-\nu'} \, d \nu' d \delta' d \gamma' d \zeta' \] 3.27

The total volume flux into the area \( d \nu \, d \delta \) is then

\[ \text{Flux in} = \int_{0}^{\frac{\nu}{\nu-\nu'}} \int_{0}^{\frac{\nu^2}{\nu-\nu'}} K_c(x, \nu-x) p(x, \gamma) p(\nu-x, \frac{\nu-\nu}{\nu-x}) d\gamma d\nu d\delta d\zeta \] 3.28

The expression for volume flux out of the volume-concentration area \( d \nu \, d \delta \) by coalescence is easily derived in the same manner.

Combining all the input and output terms such that input minus output equals zero, gives the following equation.

\[ W_r \left[ p(\nu, \zeta) - p(\nu, \delta) \right] = \int_{\nu}^{\nu'} K(\nu, \zeta) p(\nu, \zeta) d\zeta - \int_{\nu}^{\nu'} K(\nu, \zeta) p(\nu, \delta) d\zeta \] 3.29

\[ + \int_{\nu}^{\nu'} \int_{\nu}^{\nu'} K(\nu, \nu-x) p(x, \gamma) p(\nu-x, \frac{\nu-\nu}{\nu-x}) d\gamma d\zeta \]

\[ - \int_{\nu}^{\nu} \int_{\nu}^{\nu} K(\nu, \gamma) p(\nu, \gamma) p(\nu, \delta) d\gamma d\zeta - \int_{\nu}^{\nu} \int_{\nu}^{\nu} K(\nu, \gamma) p(\nu, \gamma) p(\nu, \zeta) d\gamma d\zeta \]

Figure 3.4 shows how the coalescence and breakage processes redistribute volume in the volume-concentration space. Coalescence transfers volumes to some average points in the concentration dimension and to higher values in the volume dimension as indicated by the dashed lines.
Breakage causes volume to be transferred only in the volume dimension and only to lower values.

Volume Transfer in C-V Space

Figure 3.4

This is now a two dimensional equation to determine a two dimensional function, $K(v,v')$. If $p_0(v,c)$ and $p(v,c)$ are measured, the function, $K(v,v')$ may possibly be determined. Since it is known that the total volume transferred per unit time out of all areas in the $v$-$c$ space by each of the mechanisms flow, breakage, and coalescence must equal the flow into all areas for each of these mechanisms respectively, it is possible to check the equations for consistency. For example, the integral over all $v$ and $c$ of the breakage flux in must equal the integral over all $v$ and $c$ of the breakage flux out. The details of this check are given in Appendix I. The problems of methods of determining $K(v,v')$ and the question of uniqueness will be discussed later.
Other forms of this balance can now be easily developed.

3.22 Number Distribution Over Volume and Concentration

If \( r_v(v, c) \) is the input number distribution and \( r(v, c) \) is the reactor number distribution then it is known that

\[
\frac{Q \delta_v p(v, c) dv dc}{V} = \eta_A r_v(v, c) dv dc
\]

\[
\frac{V \delta_v p(v, c) dv dc}{V} = N r(v, c) dv dc
\]

or

\[
p(v, c) = \frac{V}{V_v} r_v(v, c)
\]

\[
p(v, c) = \frac{V}{V} r(v, c)
\]

Substituting these relations into the equation gives the volume balance in terms of number distributions.

\[
W_v \left[ h(v, c) - \frac{V}{V_v} r_v(v, c) \right] = \int_{V}^{\infty} K(x, v) r(x, c) dx - \int_{0}^{V} K(v, x) r(v, c) dx
\]

\[
+ \frac{1}{V} \int_{0}^{\frac{V}{V}} \int_{0}^{C} v x K(x, v-x) r(x, y) r(v-x, \frac{CV-xy}{V-x}) dy dx
\]

\[
- \frac{1}{V} \int_{0}^{\infty} \int_{0}^{C} v x K(x, v) r(x, y) r(v, c) dy dx - \frac{1}{V} \int_{0}^{\infty} \int_{0}^{C} v x K(x, v) r(x, y) r(v, c) dy dx
\]
3.2.3 Volume Distributed Over Volume and Moles of Dye

Instead of concentration of dye in the drops the total moles in the drop could be considered as the other independent variable. In a similar manner a balance could be made over an area \( dv \, dm \) in the volume-mole space using the volume probability distribution with volume and moles as independent variables. The resulting equation using the same single mixing kernel is given below.

\[
W_r [S(v,m) - S_0(v,m)] = \int_{0}^{\infty} K(x,v) S(x, \frac{y}{V}) \, dx - \int_{0}^{Y} K(v,x) S(v,m) \, dx
\]

\[
+ \frac{1}{V} \int_{0}^{\infty} \int_{0}^{\infty} v K(x,v-x) S(x,y) S(y, \frac{m-x}{V}) \, dy \, dx
\]

\[
- \int_{0}^{\infty} \int_{0}^{\infty} v K(x,v) S(x,y) S(y,m) \, dy \, dx - \int_{0}^{\infty} \int_{0}^{\infty} v K(v,x) S(x,y) S(v,m) \, dy \, dx
\]

This balance could also have been written using the functions \( K_c \) and \( K_b \) and this balance is used with these functions later. The transfer of volume in the \( v-m \) space is different than that in the \( v-c \) space and can be represented by vector addition for coalescence and vector multiplication by a number less than one for breakage. The transfer of volume in the \( v-m \) space is shown in Figure 3.5.
3.2.4 Dye Mass Distributed Over Volume and Moles

This balance is developed from the previous one by a transform of variables because the space of the balance remains the same. Let \( q_o (v, m) \) and \( q (v, m) \) be the input and vessel dye mass distributions respectively. The basic relation holding in the vessel is

\[
g \, q(v, m) \, dv \, dm = V \phi_2 \, \frac{m}{V} \, S(v, m) \, dv \, dm
\]

3.34

where \( g = \) mass of dye in the vessel.

Then

\[
S(v, m) = \bar{c} \, \frac{V}{m} \, q(v, m)
\]

3.35
where \( \bar{c} \) = average concentration in the vessel.

Substituting this relation into the previous balance gives

\[
W_t[q(v, m) - q_o(v, m)] = \int_0^{\infty} K(x, v) q(x, \frac{x}{v}) \, dx - \int_0^{\infty} K(v, x) q(v, m) \, dx
\]

\[
+ \bar{c} \int_0^{\infty} \int_0^{\infty} \frac{vx(v-x)}{y(m-y)} K(x, v-x) q(x, y) q(v-x, m-y) \, dy \, dx
\]

\[
- \int_0^{\infty} \int_0^{\infty} v K(x, v) q(x, y) q(v, m) \, dy \, dx - \int_0^{\infty} \int_0^{\infty} v K(v, x) q(x, y) q(v, m) \, dx \, dy
\]

The above balances as well as others were developed in an effort to find a suitable distribution and phase space to be used to determine the mixing function. However no phase space allowed a description of the process which gave a simple relation for the transfer from finite areas in the phase space. Figure 3.6 shows the v-c space divided into finite squares. It is noticed that the description of breakage in this space is simple but the coalescence transfer is quite complicated, i.e. the description of breakage between squares is described directly between squares, however, the coalescence between two squares gives a very unusual region in the space. Other spaces gave similar difficulties. The equations developed were inspected for their simplicity when used in an approximation scheme such as the use of the trapezoidal rule to approximate the integrals. No simplification could be found.
3.3 Existence, Uniqueness, and Other Properties of the Equations

Existence and uniqueness of solutions of integral equations are difficult to prove; for complicated integral equations they are almost impossible. However the following indicates some of the thoughts on this subject. The existence of a kernel is assumed because physically such a function should exist to satisfy the balance in the vessel.

Assuming that one solution of the equation exists the following relation is substituted into the v-c equation (Equation 3.29).

\[ K(v,x) = K_0(v,x) + \alpha K'(v,x) \]  

where \( K_0 \) is the known solution

\( K \) is another solution

\( \alpha \) is a constant multiplier

Substituting equation 3.37 into equation 3.29 and using the fact that \( K_0 \) is a solution of equation 3.29 gives
\[ 0 = \int_{v}^{\infty} K'(x,v) p(x,v) \, dx - \int_{0}^{v} K'(v,x) p(v,c) \, dx \\
+ \int_{0}^{x} \int_{0}^{c} \frac{v^2}{v-x} K'(x,v-x) p(x,y) p(v-x, \frac{cv-xv}{v-x}) \, dy \, dx \tag{3.38} \\
- \int_{0}^{v} K(x,v) p(x,y) p(v,c) \, dy \, dx - \int_{0}^{v} K'(v,x) p(x,y) p(v,c) \, dy \, dx \]

It is noticed that the flow terms have been removed from the balance and hence it is a balance written for a batch reactor. But no physical all positive (thus also all negative) kernel can fit this equation because any batch mixing will tend to change the concentration distribution until all drops have the same concentration. In fact this says that in the part of the kernel which describes coalescence there must be a negative region and a positive region. How to proceed to prove that the only \( K' \) satisfying the batch equation is \( K' = 0 \) is not obvious at present. It is interesting to note the following: Let \( K' = K'^+-K'^- \) where \( K'^+ \geq 0 \) and \( K'^- \geq 0 \) and for any \( x \) and \( y \) either \( K'^+ (x,y) = 0 \) or \( K'^- (x,y) = 0 \). Letting the batch equation be the operator \( \mathcal{L} \), the following must be true

\[ \mathcal{L} \{ K'^+ \} = \mathcal{L} \{ K'^- \} \tag{3.39} \]

This then says that the operator \( \mathcal{L} \) must transform two mutually exclusive all positive \( K' \)'s into the same function.

The equation can also be transformed into a conditional balance
in the following manner:

From Equation 3.21 the following results:

\[
\left[ W_r + \int_0^\infty k(v,x) \, dx + \int_0^v \nu k(x,v) p(x) \, dx + \int_v^\infty k(x,v) p(x) \, dx \right] = \frac{W_r \, P(\nu) + \int_0^\infty k(x,v) p(x) \, dx + \int_0^v \nu k(x,v) x p(x) p(v-x) \, dx}{P(\nu)} \tag{3.40}
\]

Then from Equation 3.29 the equation below is found:

\[
W_r \, p(v,c) + \int_0^\infty k(x,v) p(x) \, dx + \int_0^v k(x,v) p(x) p(v-x) \frac{c v x}{v-x} \, dx = \frac{P(v,c) \left[ W_r + \int_0^\infty k(x,v) \, dx + \int_0^v \nu k(x,v) p(x) \, dx + \int_v^\infty k(x,v) p(x) \, dx \right]}{P(v)} \tag{3.41}
\]

Substituting the first equation into the second equation gives the marginal balance.

\[
0 = W_r \left[ p(v,c|v) - p(c|v) \right] / P(v) + \int_0^\infty k(x,v) p(x) \left[ p(c|x) - p(c|v) \right] \, dx \tag{3.42}
\]

\[
+ \int_0^v k(x,v-x) p(x) p(v-x) \frac{c v x}{v-x} \int_0^\infty p(y|x) p(c v x/y | v-x) \, dy - p(c|v) \, dx
\]

From this equation it can be seen that no information is obtained if \( C \) is not distributed, i.e. if \( p(c|v) = p(c) = \delta(c-c_0) \).

Also of interest is the equation which results when Equation 3.33 is transformed using a moment generating function. In this transformation \( K \) is divided into \( K_B \) and \( K_C \) as given below:
\[ O = W_r \left[ S_0(v, m) - S(x, m) \right] + \int_0^\infty K_b(x, v) S(x, \frac{m}{v}) \, dx \]
\[ - \int_0^v K_b(v, y) S(y, m) \, dy + \frac{1}{2} \int_0^\infty \int_0^\infty v K_c(x, v-y) S(x, y) S(v-x, m) \, dy \, dx \]
\[ - \int_0^\infty \int_0^\infty v K_c(x, v) S(x, y) S(v, m) \, dy \, dx \]

Now multiply through by \( e^{\theta v + \phi m} \) and integrate in equation 3.43

\[ O = W_r [M(a, b) - M(c, d)] + \int_0^\infty \int_0^\infty K_b(x, v) S(x, y) [e^{\theta v} M(x, y) - e^{\phi x} M(y, x)] \, dy \, dx \]
\[ + \int_0^\infty \int_0^\infty v K_c(x, v) S(x, y) S(v, y) [e^{\theta v} M(x, \phi) M(\phi, y) - e^{\phi x} M(\phi, v)] \, dy \, dv \]

This form of the equation was used to try to investigate uniqueness as well as used in one of the approximation methods. The moment generating transformation of some of the other equations were developed, but this one allowed a polynomial approximation of the kernel to be applied without requiring the evaluation of unusual moments of the distribution.

3.4 Approximate Calculation of the Kernel

Since there appeared to be no simple way to approximate the integral equations to allow extraction of unassumed kernels and since the data obtained from the experiment is the volume and concentration of
each drop in the sample, it was decided that the best way to accomplish the goal of calculating unassumed mixing function was to simulate the mixing process on the computer and calculate the necessary mixing functions to best fit the observed data. Two methods of best fitting the data are attempted, least squares estimation and a pseudo-maximum likelihood estimation. In addition, an assumed polynomial form is substituted into the moment generating function equation and the constants of this assumed form are evaluated.

3.4.1 Least-Squares Estimation of Kernel

The first method, which uses least-squares estimation of the mixing kernel, is developed by writing volume balances over finite squares in the volume-concentration space. The space is divided into \( n^2 \) squares with the squares representing the larger drops extending to hypothetical infinity as shown in Figure 3.7. The divisions in the volume are adjusted such that a prescribed percentage of the volume lies in the upper infinite interval and that \( n \) is odd.

![Division of Volume-Concentration Space](Figure 3.7)
The volume probability for each square is calculated from the sample from the vessel. Thus the flow out term for each square is just the volume flow rate of dispersed phase times the probability of each square, e.g. flow out of the $ij$th square is

$$Q \phi_i P_{ij}$$

Similarly the flow into the $ij$th square is

$$Q \phi_i P_{oij}$$

The breakage and coalescence kernel is divided into $(n-1)/2 + 1$ squares as shown in Figure 3.8. It isn't necessary that the number of divisions be $(n-1)/2 + 1$ but it could be $(n-1)/m_d + 1$ when this is an integer. Thus there will be $m_d$ divisions in the probability space for each division in the kernel space for all divisions except the divisions which extends to infinity. It is noticed that the top square is missing from both the breakage and coalescence kernels. In the case of breakage this value is omitted since no information can be obtained about it because it represents breakage volume flux from the infinite interval into itself. Thus the same term would be added and subtracted from the balance on each of the infinite squares. Information on the other breakage kernel values along the diagonal can be obtained as long as $m_d$ is greater than one. The top square in coalescence kernel is omitted because very few drops are included in the upper $P\%$ of size and thus considering coalescences among these would not add significant transfer to the process and the value obtained most likely would not be very accurate.
Breakage and Coalescence Kernel

Figure 3.8

For breakage, each drop is considered individually, i.e. the volume flux possible when each drop breaks is considered. Suppose a drop falls in the $k, l$ th square shown in Figure 3.7, and its volume probability in the total sample is $P_d$. This drop can contribute volume flux to all squares of the same concentration and smaller volume. For example the volume transfer from the $k, l$th square to the $m, l$ th square is given by the relation:

$$V \phi_2 K_{k,m}^B P_d$$

3.47

The square in the breakage kernel which is associated with the $k,m$ volume ranges is affected as shown in Figure 3.8. Thus the quantity $V \phi_2 K_{k,m}^B P_d$ is subtracted from the balance on the $k, l$ th square and added to the $m, l$ th square. This process is repeated for each drop and the coefficient of each of the $K$'s for each of the squares is calculated.
The coalescences values are calculated in a similar manner. The coalescences of all possible combinations of drops in the sample is formed and the resulting volume fluxes are calculated. For example if drops of volume \( v_1 \) with volume probability \( P_e \) in the \( w, x \) th square shown in Figure 3.7 coalesced with drops of volume \( v_2 \) with volume probability \( P_f \) in the \( y, z \) th square; the volume flux into the \( u, v \) th square is then given by the following relation

\[
V \phi_2 (v_1 + v_2) K_{w,y}^c P_e P_f
\]

And the flux out of the \( w, x \) th square is:

\[
V \phi_2 v_1 K_{w,y}^c P_e P_f
\]

and out of the \( y, z \) th square the volume flux is

\[
V \phi_2 v_2 K_{w,y}^c P_e P_f
\]

The coalescence kernel involved is selected depending upon the sizes coalescing and for the particular example used above, the required value of the coalescence kernel is shown in Figure 3.8.

Thus for each of the squares in the probability space there is obtained an equation as shown below.

\[
Q \phi_1 \left[ P_{ij} - P_{oi,j} \right] = V \phi_2 \left[ \sum_{k=1}^{m} B_{ij,k} K_{k,m}^B + \sum_{w=1}^{y} C_{iw,w,y} K_{w,y}^c \right]
\]

Making a row vector, \( \vec{K} \), of all the kernel values times \( V \phi_2/Q \phi_1 \), the above equation can be written as

\[
\vec{d} = A \vec{K}
\]

Here \( \vec{d} \) is a row vector of the \( P_{ij} - P_{oi,j} \), and \( A \) is the necessary matrix relating the two vectors.
The vector \( \hat{d} \) and the matrix \( A \) are both determined from data and the vector \( K \) is calculated such that \( (\hat{d} - A K)^T (\hat{d} - A K) \) is minimized subject to the condition that \( K \geq 0 \). This is just a quadratic programming problem.

### 3.4.2 Pseudo-Maximum Likelihood Estimation of Kernel

The second method involves a maximum likelihood method of estimation. For this method the integral equation (equation 3.29) is written in the following form.

\[
p(v,c) = \frac{P(v,c) + \int_0^{v_x} \frac{K(v,x)}{W_x} p(x,c) dx + \int_0^{v_x} \frac{K(x,v)}{W_x} p(x,v) dx}{1 + \int_0^{v_x} \frac{K(v,x)}{W_x} dx + \int_0^{v_x} \frac{K(x,v)}{W_x} p(x,v) dx + \int_0^{v_x} \frac{K(x,x)}{W_x} p(x,x) dx}
\]

Or this equation can be written on terms of input and output volume fluxes as given below.

\[
P_{ij} = \frac{P_{bij} + F_{ij} B_{in} + F_{ij} C_{in}}{1 + \frac{1}{P_{ij}} F_{ij} B_{out} + \frac{1}{P_{ij}} F_{ij} C_{out}}
\]

Again if the same divisions as in the least square methods are used, the fluxes for each square are functions of the kernel \( K \)'s. The assumption that the \( P_{ij} \) values are correct for the right hand side of the above equation allows it to be written as a conditional probability, i.e.

\[
P_{ij}^{nk} = \frac{P_{ij} + F_{ij} B_{in} + F_{ij} C_{in}}{1 + \frac{1}{P_{ij}} F_{ij} B_{out} + \frac{1}{P_{ij}} F_{ij} C_{out}}
\]
Paralleling the maximum likelihood method in statistics, a good estimate of the \( \eta \) vector would be one which maximized the following log-likelihood function:

\[
\Phi = \sum_{ij} P_{ij} \ln P_{ij} \mid k
\]

The method chosen to find the maximum was the pattern search (22). This method searches in the \( K \) space for the maximum of the likelihood function subject to the restriction \( K \geq 0 \) and \( \sum_{ij} P_{ij} = 1 \).

### 3.4.3 Polynomial Fit of Kernels

The last method used to determine the mixing functions uses the following equation, equation 3.44, as its starting point.

\[
M(\Theta, \Phi) - M(\Theta, \Phi) = \int_{0}^{\infty} \frac{K(x)}{W_r} S(x) \left[ e^{\Theta M_x(x)} - e^{\Theta M_x(x)} \right] dx
\]

\[
+ \int_{0}^{\infty} \frac{K(x)}{W_r} S(x) S(x) \left[ e^{\Theta (V+x)} M_x(x) - e^{\Theta (V+x)} M_x(x) \right] dx dv
\]

Polynomial functional forms are then assumed and substituted into the equation and the coefficients of the various powers of \( \Theta \) and \( \Phi \) are equated to give equations in the moments of the measured distribution. These equations could also be obtained by simply multiplying the original balance equation by the desired powers of \( v \) and \( m \) and integration over \( v \) and \( m \). The forms thought suitable for the coalescence and breakage kernels are given below. Each term in the breakage kernel is composed of a rate part, some power of \( x \), and a beta distribution type function. The coalescence function is composed of symmetric functions which in—
crease with increasing size of the drops.

\[
\frac{K_c(v,x)}{W_r} = B_0 V(x-V) + B_1 VX(x-V) + B_2 VX^2(x-V) + B_3 V(x-V)^2 + B_4 VX(x-V)^2
\]

\[
K_c(v,x) = C_0 + C_1 (V+x) + C_2 (V^2+x^2) + C_3 VX
\]

As an example, the coefficients of terms of \( \Theta \) to the first power and \( \Theta \) to the zero power will be calculated.

**Breakage**

\[
\int_0^\infty \left[ B_0 V(x-V) + B_1 VX(x-V) + B_2 VX^2(x-V) + B_3 V(x-V)^2 + B_4 VX(x-V)^2 \right] S(x) (x-V) dx \, dv
\]

\[
= -\frac{1}{12} \sqrt{v} B_0 - \frac{1}{12} \sqrt{v} B_1 - \frac{1}{12} \sqrt{v} B_2 - \frac{1}{20} \sqrt{v} B_3 - \frac{1}{20} \sqrt{v} B_4
\]

**Coalescence**

\[
\int_0^\infty \left[ C_0 + C_1 (V+x) + C_2 (V^2+x^2) + C_3 VX \right] S(x) S(V) dx \, dv
\]

\[
= \sqrt{v} C_0 + 2 \sqrt{v} \sqrt{v} C_1 + 2 \sqrt{v} \sqrt{v} C_2 + \sqrt{v} \sqrt{v} C_3
\]

And finally the resulting equation in the moments of the distribution is

\[
\sqrt{V} \sqrt{V} = -\frac{1}{12} \sqrt{v} B_0 - \frac{1}{12} \sqrt{v} B_1 - \frac{1}{12} \sqrt{v} B_2 - \frac{1}{20} \sqrt{v} B_3 - \frac{1}{20} \sqrt{v} B_4
\]

\[
+ \sqrt{v} C_0 + 2 \sqrt{v} \sqrt{v} C_1 + 2 \sqrt{v} \sqrt{v} C_2 + \sqrt{v} \sqrt{v} C_3
\]

This process is then repeated for all powers of \( \Theta \) and \( \Theta \) such that the
sum of the powers was less than or equal to three. This gives nine
equations to solve for nine unknowns. It should be noted that these
equations involve moments up to the eighth power. The equations can be
written in linear form assuming $\mathbf{Z}^t = (B, C)$

$$\mathbf{X} = \mathbf{H} \mathbf{Z}$$  \hspace{2cm} 3.62

The solution is simply obtained.

$$\mathbf{Z} = \mathbf{H}^{-1} \mathbf{X}$$  \hspace{2cm} 3.63

where $\mathbf{X}$ is the vector of left hand sides, e.g. $\mathbf{\nu} - \mathbf{\nu}_0$.  

CHAPTER 4

EXPERIMENTAL APPARATUS AND PROCEDURES

The purpose of the experimental apparatus is to provide the necessary information for the analysis of the dispersed phase mixing occurring in a paddle stirred, baffled mixing vessel. Since the analysis of this system is based primarily upon a population balance model, the system should be designed to closely approximate the assumptions involved in this model. The information deemed necessary for the qualitative and quantitative interpretation of the mixing phenomena is also primarily dependent upon the population balance model used in this analysis.

The basic experiment involves the baffled stirred tank to which is fed two streams of dispersed phase (the oil phase) and a stream of continuous phase (the water phase). Each of the two dispersed streams has a different concentration of a dye (9-9' biflourene). The drops of the oil are then mixed by the agitator and leave through the exit stream.

The measurements necessary for the interpretation of the experiment are the input flow rates of all three streams, the size distribution of the input oil drops of the two oil streams, and the size-concentration distribution of the oil drops in the vessel. The input flow rates are measured with rotameters. The input size distribution is generated to be one of all the same size with this size determined by counting the number of drops per second and dividing the flow rate by this number. A particular apparatus was designed to generate the equal size drops and count them. The size concentration distribution in the vessel is measured by a specially designed technique. This involves drawing a sample from the vessel and immediately coating it with an anti-
coalescence agent. This sample is then forced through a small capillary and using a photometer and subsequently the computer, the drop size and concentration of each drop in the sample is determined. Other parameters of interest are the stirring speed and the physical properties of the liquids.

4.1 Flow System

The basic flow system is shown in Figure 4.1. It consists of three streams from the storage tanks to drop generators and then to the mixing vessel. Two streams leave the vessel; one going to the waste fluids tank and the other to the sampling system. Of critical importance is the choice of materials in the flow system. All components must be made of materials which will not contaminate the oil or the water phases. Also the mixing vessel must be designed such that its inside faces are wetted by the continuous phase water, and it also must be designed with no dead corners where the accumulation of dispersed phase can take place. The system is sized to handle larger flow rates than are used in the actual experiments of this report.

4.1.1 Pumping System and Rotameters

The pumping system associated with each of the three thirty-five gallon stainless steel storage tanks is exactly the same. It consists of a gear pump driven by a one-sixth horsepower explosion proof reversible motor on the bottom exit from the tanks. This pump when in operation during an experiment causes the fluid to flow through a twenty-five pound back pressure valve in a recyle loop back to the storage tank. An output line connected to the recyle loop on the high pressure side of the back pressure valve gives a constant pressure source for flow through
the sintered stainless-steel filter to the rotameters and finally to
the drop generators. The exit side of the gear pump is also provided
with a valve to the outside. This allows the tank to be emptied easily
for cleaning or the pump could be reversed in direction and this then
becomes an input for filling the tanks with fluid especially the oils.

From the pumping systems the flow goes to the Schutte Koerting
rotameters which contain their own needle valves. These rotameters
can be used to measure various flow rates by simply changing the ball
floats and tubes. The rotameters were calibrated for the particular
fluids used in each and the calibrations are given in Appendix V.1.

4.1.2 Drop Generators

From the rotameters the flow continues to the drop generators
which were designed to produce oil drops of approximately equal size in
water. Following the production of the drops in the tube, electrical
probes inserted into the glass tubes count the rate of production of the
drops. A diagram of the drop generators is given in Figure 4.2. The
drop generators consist of a stainless steel tee into which a twenty
gauge hypodermic needle was inserted from one side and a Venturi glass
tube from the other. The water flows into the tee and around the
needle, pulling off drops of oil as it comes from the needle. After
leaving the needle, the drops pass between two platinum probes in the
glass. These probes are connected to a circuit which measured the
change in resistance as the drop passed between them. The electrical
circuit used is given below in Figure 4.3.
The voltage across the 500k resistor is amplified through Sanborn amplifiers and recorded on paper recorder. A sample of the output is given in Figure 4.4.

4.1.3 **Mixing Vessel and Exit System**

The mixing vessel is a cylindrical vessel with an inside diameter of about four and three-eighths inches and a height of five and one-half inches. It is composed of stainless steel top and bottom plates, two glass cylinders each two and one-quarter inches high, and a stainless steel center ring of one inch thickness. The two glass cylinders are inserted into machined grooves in the top and bottom plates respectively and into the center ring. The whole assembly is then held together by six bolts from the top plate to the bottom plate. The seals between the glass and the stainless plates and center rings are made with O-rings. This is shown in Figure 4.5. The stirrer shaft enters the mixing vessel through the top plate to which the bearing housing for the
(Chart Speed 120 mm/sec)

Output of Drop Generators

Figure 4.4
MIXING VESSEL
FIGURE 4.5
stirrer shaft is attached. An O-ring seal is used on the stirrer shaft also. All operational input and outputs for the vessel during an experiment are through the six ports in the center ring. As the experiment is now set up, four of these ports are used; two for inputs from the drop generators, one for output to the waste storage tank and one for the sampling probe. The top plate also contains an exhaust tube for removing the air from the vessel before starting the experiment. This tube has an air chamber attached to it to maintain a relatively constant pressure in the vessel when a sample is being withdrawn. The bottom plate also has an exhaust tube to facilitate cleaning the vessel without dismantling it. The vessel is held on the frame of the experiment by connections to the top of the bearing housing.

The vessel is equipped with four equally spaced baffles which extend into the vessel about .437 inches, or one-tenth the diameter of the vessel. The top and bottom of each baffle were cut at a 45° angle to avoid dead corners in the vessel. The stirrer is a standard stainless-steel paddle type with six paddles equally spaced around the diameter. The diameter of the stirrer is 2 inches and each paddle is 0.4 inches high and 0.5 inches long. The stirrer is driven by a 1/4 horsepower totally enclosed motor with a Zero-max transmission to allow variation of stirrer speed. The calibrations of the transmission is given in Appendix V.2.

A pressure gauge in the exit stream indicates the pressure in the vessel. This pressure is generated by a 10 psi back pressure valve in this stream. In series with this back pressure valve is an ordinary valve which allows by-passing of the valve to facilitate cleaning or to operate at a lower pressure. The exit stream empties into the waste storage tank from which the fluids are discarded.
4.2 **Sampling System**

The principle of the sampling system is to remove a sample of dispersed phase from the vessel and force it at a constant rate through a capillary smaller than the smallest drop of interest in the vessel. A photometer focused on the capillary will then measure the size of the drop and concentration of the light absorbing dye in the drop. The basic sampling system consists of a sampler which draws a sample of the dispersion from the vessel and coats it with an anticoalescence agent, the sample holding section which holds the sample and forces it through the capillary at a constant rate, and the microscope assembly which focuses the photometer on the capillary. All components must be composed of materials upon which the oil drops will not coalesce. The sampler must be designed such that no significant amount of anticoalescence agent can escape into the vessel. And finally, the system must maintain a constant flow rate while the dispersed phase sample is being pumped through the capillary.

4.2.1 **Sampler**

A cross-section of the sampler is shown in Figure 4.6. When in operation, the sampler is placed through a port in the center ring of the vessel. It is of critical importance that the surfactant holes be far enough away from the entrance to insure no back mixing of the surfactant into the vessel. In fact, the sampler had to be revised to insure this. In Appendix II the possible effects of surfactant (Tween 40) are investigated in detail and it is concluded that this leakage is negligible. The sampler has an inside dimension of 7/32" and when in operation its stroke was about 4 1/2". The volume displaced behind the piston is about
26% of that displaced in front of the piston. In Figure 4.7 is shown the sampler connected to the surfactant feed system. During the inward stroke of the sampler, the valve is adjusted such that surfactant can be drawn from the surfactant reservoir into the chamber behind the piston. While the piston is moving outward, the valve is adjusted such that the surfactant from this chamber flows into the annulus of the cylinder and out the surfactant holes in the sampler. The sample then continues through the center of the piston shaft and into the capillary glass tubing. In fact there is always some flow through the sampler and into the glass capillary tubing during the operation of the experiment.

The sampler is driven at a constant rate by the oil-air sampler drive assembly shown in Figure 4.8. The sampler is connected to the two way piston cylinder which is powered by oil from the oil-air tanks. When the piston is to be propelled out, oil-air tank #1 is connected to the air line and oil-air tank #2 is opened to the atmosphere. For piston travel in the reverse direction, oil-air tank #1 is opened to the atmosphere and air pressure is applied to oil-air tank #2. The air pressure supplied to these tanks was about 60 psi. The rate of travel of the piston is controlled by the Hoke needle valve which meters the oil as the piston travels. The on-off control of the piston is controlled by solenoid valves connected to a push switch. Thus when a sample is to be drawn, oil-air tank #1 is connected to the air line and oil-air tank #2 is opened to the atmosphere. The speed of piston travel is selected by the metering valve. Finally the push switch is depressed propelling the sampler and a sample is drawn.

4.2.2 Sample Holding Section
SURFACTANT FEED SYSTEM FOR SAMPLER
FIGURE 4.7

FROM AIR LINE

OIL AIR TANK NO. 1

OIL AIR TANK NO. 2

SOLENOID VALVE

ROKE NEEDLE VALVE WITH VERNIER ADJUSTMENT

PUSH BUTTON SWITCH

TWO WAY PISTON CYLINDER

CONNECTED TO SAMPLER DRIVE ATTACHMENT

SAMPLER DRIVE ASSEMBLY
FIGURE 4.8
The sample proceeds through glass capillary tubing to the sample holding section shown in Figure 4.9. While the sample is being drawn, glass capillary stopcock #1 is set for straight through operation and glass capillary stopcock #2 is set for discharge into the side arm. Hamilton Stopcock #1 is set for discharge into the waste storage tank and Hamilton Stopcock #2 is set for drawing water from the water bottle into the syringe. As the sample proceeds into the sample reservoir, whose volume is about one-third that of the sampler, glass capillary stopcock #1 is changed such that the flow from the sampler is diverted into the waste storage tank via the side arm. Following this glass stopcock #2 is turned to an off position, allowing the drops in the sample reservoir to settle towards the top. When the drops have settled out, glass capillary stopcock #2 is set for straight through operation and Hamilton stopcock #2 is adjusted for straight through operation. The constant drive mechanism for the syringe is started and the sample is forced up through the capillary embedded in plastic. The constant flow rate through the capillary can be varied by changing syringes or changing gears in the constant drive mechanism.

Hamilton stopcock #1 permits materials to be injected into the sample holding section for such things as cleaning the system or calibrating the photometer-microscope assembly. Hamilton stopcock #2 when connected between the water bottle and the syringe allows refilling of the syringe after a sample has been forced through the capillary. The capillary is formed by pulling a 3mm glass tubing down to the desired size capillary, usually in size range .075 to .40mm. This fragile capillary is then placed between two microscope slides and the space between them is filled with epoxy. Of particular importance in the
SAMPLE HANDLING SECTION
FIGURE 4.9

MICROSCOPE ASSEMBLY
FIGURE 4.10
measurement of drop volume, is the constant flow rate through capillary. Pressure drop changes in the capillary caused by viscosity changes and interfacial area changes as the drops move through could cause flow variations by expansion and contraction of such things as air bubbles. The possible effects of air bubbles in the system and the teflon tube connecting the syringe to Hamilton Stopcock #2 are investigated in Appendix III. It is found that the teflon tube does not have a significant effect nor do air bubbles less than 0.2 mm³ in volume.

4.2.3 **Microscope Assembly**

As the drops pass through the capillary, a microscope is focused on it as shown in Figure 4.10. The light source for the microscope is a six volt D.C. lamp with the current coming from the D.C. power supply. The concave mirror focuses additional light on the pinhole. The beam splitter, which simultaneously focuses the capillary for the photometer and the eye, allows viewing of the capillary while an experiment is in operation. The iris allows the field of view seen by the photometer to be varied, and in operation this iris is very nearly closed allowing the photometer to see only the center of the capillary tube. Through the optical filter, the photometer sees only the light of wavelength near the maximum adsorption for the dye used. A spectrograph of the dye is given in Appendix IV. The shape of the drop as it passes through the capillary is also of interest. Figure 4.11 is a photograph of a drop as it is passing through the capillary. This photograph was taken with a Polaroid camera, using a flash unit to supply the light through the microscope.

4.3 **Photometer and Data Transformation**
Drop Passing Through Capillary

Figure 4.11
The output of the photometer is the logarithm of the light intensity as the drops pass through the capillary. This output is recorded on analog tape in the FM mode. This data is then digitized using an analog to digital converter.

4.3.1 **Photometer and Analog Computer**

The photometer operates at constant photo-current by means of a feed-back circuit to the dynode voltage. The dynode voltage across the tube then varies with light intensity to approximately the 6.6 power (6). The logarithm of the voltage output of the photo-multiplier is extracted using the exponential characteristics of silicon diffused transistor in the feed-back loop of an operational amplifier as explained by Paterson (15). The output of the photometer should then be proportional to dye concentration.

The output of the photometer is then put through an analog computer to multiply the signal, balance it to zero, and filter out the high frequency noise. The diagram of analog components is given below in Figure 4.12.

![Analog Components](Figure 4.12)
The output of this system is linear in the range of dye concentrations used in the experiments. A graph of voltage output vs concentration is given in Appendix V. 3. This linearity was checked for several successive days and it remained very good. This means that the microscope assembly as well as the electronics maintain the linearity very well.

A typical graph of the output from this unit is shown in Figure 4. 13. This graph was printed with a paper recorder of relatively slow frequency response and in fact this graph does not show the magnitude of the noise. In order to detect if the signal to noise ratio is low enough to determine the lowest concentration level, it was necessary to look at the signal on an oscilloscope. The feedback capacitance allows adjustment to reduce the high frequency noise but it also reduces frequency response for measuring the smaller drops. The .005 mfd capacitor is a compromise for these two goals.

4.3.2 Data Recording

In operation this voltage varies between +1.0 volts and -1.0 volts and is recorded on an Ampex SP 300 tape recorder in the FM mode. The tape recorder is put in the record mode when the constant drive syringe is started. Another signal is recorded on a different channel indicating the experimental sample number, where the sample starts (usually about 5 seconds before the first drop reaches the capillary), and where it ends (after all but a few small drops have passed through the capillary). The speed of the tape was varied to allow a multiplication factor in the analog to digital conversion operation. Usually the tape speed while recording was 1 7/8 inches per sec. The characteristics of the recorder are linear between +1.0 volts and it has a frequency response of 312 cps for a tape speed of 1 7/8 inches per second. The
Digital Drops
Typical Photometer Output
Figure 4.13
usual care of cleaning the tape heads is necessary to insure proper operation.

The analog tape is then replayed at a different speed and the data converted to digital data on an analog to digital converter. For each experimental sample the signal translated to digital tape is that contained between the start and stop markers on the different analog channel. Usually three to eight are stored on digital tape. The usual replay speed is 15 inches per second giving a multiplication factor of eight. The A to D converter has two levels of accuracy, 6 bit and 10 bit information and two densities (and thus frequencies) of recording (40,000 or 15,000 samples per second in the six bit mode and half these in the ten bit mode). The digital tape speed is constant at 75 in per sec. The first data recorded was made using six bit information, but it was decided that this didn't allow enough accuracy and the final runs were using 10 bit information. Below in Figure 4.14, is given a sketch of how 10 bit information is stored on seven track tape.

| 0 0 0 1 0 1 1 | ←First Four Bits of Number
| 1 1 1 0 1 0 1 | ←Second Six Bits of Number
| 1 0 0 1 0 0 1 |
| 0 1 0 1 1 0 0 |

Parity Bit

10 Bit Data on Tape

Figure 4.14

The first number of Figure 4.14, when reconstructed would be the binary number 1011110101 or in hexadecimal this number would be 2F9. One page of hexadecimal numbers taken from a magnetic tape recorded at 40,000
(actually 20,000 in 10 bit mode) samples per second, is shown in Figure 4.15. Among these numbers it is noticed that two drops are represented. These drops are indicated in Figure 4.13, the paper record of the signal. One of the problems encountered with the use of the particular A to D converter employed is its lack of a buffer. Thus to make record gaps, as is required by the IBM 360 computer for magnetic tape reading routines, some of the data must be omitted. This causes either 0.5% or 1.3% of the data to be omitted. An analysis of the error thus caused is included in Appendix VI. With the data in this form it is ready for analysis by the computer.

4.4 Preparations

The oil used as the dispersed phase in these experiments was a mixture of Dowtherm-E and Shell #3747 Base Oil. These two were chosen because they will give the possibility of varying the density, since Dowtherm is heavier than water and #3747 Base Oil was lighter than water. Also they are similar to kerosene with a low coalescence rate allowing the assumption of uniformity in the mixing vessel to be approximately valid. The mixture used in the experiments is 39.1% Dowtherm-E and 60.9% by volume #3747 Base Oil, which gave this mixture a density just slightly lighter than water. No attempt was made to measure or control any other property; only an effort was made to maintain the properties of this fluid constant throughout the experiments. It was prepared in oil storage tank #2, by using sticks calibrated for the tanks. To avoid contamination, the oil was pumped directly from the drums by running the pumps in reverse. The mixture was stirred in one tank by the pump and a stainless rod, until it was uniform. After standing for several days, some of this oil was pumped into oil-storage tank #3.
The dye (9-9' biflourene) was recrystallized from a 95% alcohol and 5% toluene mixture to remove impurities as suggested in a paper by Miller et al. As indicated previously, Appendix IV contains a spectrograph of the purified dye. The extinction coefficient of the dye was calculated to be $2.5 \times 10^{-4}$ liters/cm/mole. This dye was added to oil storage tank #3 to give a concentration of about 0.5 mg/ml and the concentration in oil storage tank #2 was made to be about 0.1 mg/ml. A test was run on the viscosity of the two solutions to try to detect a difference. No significant difference in viscosity was found between the 0.1 mg/ml solution and the 0.5 mg/ml solution.

The water phase used in the experiment was a 0.001 N solution of Na$_3$PO$_4$ in distilled water with the salt Na$_3$PO$_4$ serving a dual purpose. It provided an electrolyte so that the drop generators could count the drops and it kept the glass and stainless steel clean. This cleanliness was particularly critical in the vessel where the walls must always be wetted by the continuous water phase and in the sample reservoir of the sample holding section where oil drops tended to stick to the sides of the glass. A test was made to determine if the salt caused any great change in the coalescence rates of the oil drops and it was concluded that there was no significant effect. If there were a minor effect it would be included in the physical properties and held constant throughout the experiment.

The water in the water bottle of the sample holding section was a 0.05 N solution of Na$_3$PO$_4$ to insure that no drops stuck to the walls in the sample reservoir and especially in the capillary, where very small drops sticking to the walls would produce a wildly varying electrical output.
After trying various surfactants at different concentrations, it was concluded that Tween 40 at 2.9% provided the best protection. To this Tween 40 solution was added a small amount of methylene blue, which provided a colored marking for the sample as it flowed into the sample holding section. The actual sample to be measured was then selected from the center sections of the blue material. The activity of this solution to prevent coalescence seemed to decline with age and constant checks had to be made to see if the solution was satisfactory. The check is accomplished most easily because any coalescence which occurs shortly before the drops enter the capillary is easily detected in the output of the photometer as shown in Appendix VII.
CHAPTER 5

CALCULATION OF DISTRIBUTIONS AND TEST OF SAMPLING SYSTEM

The data from the experiment is a digital tape, which contains the digitized output signal of the photometer for several experimental samples. Each sample is stored as a file with from 15 to 50 records. This data is then interpreted using the IBM 360 computer to give the concentration and size for each drop in the sample. This requires reading the numbers from the tape, converting them into integers, and measuring the height and length of each of the pulses in the digitized signal. These measured drops are used to form the bivariate volume distribution of volume and concentration as well as other bivariate and marginal volume distributions. Also various comparisons and tests were performed on samples from the same experiment as well as on samples from different experiments with the same experimental conditions.

4.1 Calculation of Data and Distributions

The data is read from the tape using an assembly language subroutine (see Appendix VIII) in a FORTRAN IV program. This subroutine reads one record at a time, storing one line from the tape per byte in the computer. Thus the first two lines in Figure 4.14 would be stored as 00001011 in one byte and 00110101 in another. The subroutine then shifts the four digits in the first byte two bits to the right into the second byte forming a ten bit integer in two bytes of storage. Two byte integers are the smallest that FORTRAN IV can use. These numbers then are ready for the main program. The subroutine listing also contains a control section which positions the tape at the first end of file marker, i.e. before the start of the first sample.
Using the subroutine, the main program (see Appendix IX) reads the records of a file in succession. The first part of each file contains the digitized output of the photometer with water flowing through the capillary. The computer uses this section to form a base line. After the base line has been established, the computer, reading the digitized photometer output in succession, continuously tests to see if the output has deviated from the base line by a prescribed amount. If such a deviation is detected, the computer counts the number of digital samples and accumulates the sum of the sample values until the signal is again within the prescribed band of the base line. The concentration of the drop is then calculated by dividing the accumulated sum by the total number of samples. The volume of the drop is just a multiple of the number of samples counted. These values are stored if the volume of the drop is larger than a particular value. Drops smaller than the inside diameter of the capillary would cause an approximate rectangular pulse but any measurement of the number of samples and thus volume associated with such a drop would be meaningless. Whenever a sample is found to be within the prescribed band of the base line, this sample is averaged into the base line, weighting the previous value very heavily. The averaging allows the computer to compensate for base line drift.

Occasionally stray signals enter the recording equipment at one point or another. Normally these appear on the analog tape as fluctuations of magnitude larger than $\pm 1$ volt. Hence when they are translated they usually appear as 000 hex or 3FF hex on the tape. If these fluctuations are below the base line (3FF hex) they are averaged into the base line, causing no particular harm, because of the small amount of fluctuation. If, however, a number of 000 hex is found, the computer omits
that area of tape by considering it to be base line. It should be noted that these fluctuations are very rare.

The program is designed to combine any group of the files (experimental samples) into a single group and thus gives a combined sample for further calculations. It then calculates seven different volume distributions from the drops formed. These distributions are found by dividing the particular space into regions and determining how much volume belongs in each region. The distributions calculated are for the volume-concentration space, log volume-concentration space, volume-mole space, volume-concentration with p% above a certain value, volume marginal, log volume marginal and concentration marginal. Some of these measured distributions are given in Figures 5.1 - 5.6. For this experiment, Experiment #5 in Table 6.1, the flow rates were the following: water 35.6, low concentration oil 4.6 cc/min and the high concentration oil was about 13.4. The stirrer speed was not measured. It is noticed that the average concentration compares rather well with the flow rates and that the high and low concentration components are at approximately the proper proportion. In most experiments the average concentration was within 5% of the expected value. A distribution with p% above a certain size will be given in the next section. Besides distribution data various other properties of the sample such as volume and concentration averages second and cross moments of the distribution, and maximum and minimum values of concentration, moles, and volume. The program can also store the drop data on cards or in the permanent disk storage of the computer for future use.

4.2 Tests of Data
<table>
<thead>
<tr>
<th>Volume (mm²)</th>
<th>Concentration (Probabilities x 10³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.98 0.0</td>
<td>0.0 0.0 0.0 0.0 0.0 0.0 3.82 0.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 2.89</td>
<td></td>
</tr>
<tr>
<td>0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 2.37</td>
<td></td>
</tr>
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<tr>
<td>0.0 1.42 0.0 1.36 2.74 2.81 2.72 7.28 4.41 1.27 2.72 8.69</td>
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<tr>
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</tr>
<tr>
<td>7.21 1.62 1.67 4.66 10.6 14.7 30.8 6.45 53.3 23.0 2.61 19.4</td>
<td></td>
</tr>
<tr>
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</tr>
<tr>
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Volume Distribution in Volume-Concentration Space
Figure 5.1
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<th>0.0</th>
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<td>8.54</td>
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<td>0.94</td>
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<td>4.73</td>
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<td>0.04</td>
<td>0.09</td>
<td>0.0</td>
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<td>0.23</td>
<td>0.09</td>
<td>0.09</td>
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**Concentration**

(Probabilities \(\times 10^3\))

*Volume Distribution in Log-Volume-Concentration Space*

**Figure 5.2**
<table>
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<tr>
<th>Volume (mm$^3$)</th>
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<th>0.0</th>
<th>0.0</th>
<th>0.0</th>
<th>0.0</th>
<th>0.0</th>
<th>0.0</th>
<th>3.82</th>
<th>0.0</th>
<th>2.89</th>
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<td>5.00</td>
<td>10.5</td>
<td>24.3</td>
<td>21.0</td>
<td>8.15</td>
<td>4.77</td>
<td>1.73</td>
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</tr>
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<td>0.0</td>
<td>0.0</td>
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<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>1.13</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
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<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Moles
(Probabilities x 10$^3$)
Volume Distribution in Volume-Moles Space

Figure 5.3
Several samples were taken from the vessel for each experiment performed. It is of interest to determine if two samples taken from the same experiment are statistically from the same distribution. Since there are no good statistical tests designed for continuous two dimensional distributions, the distribution was considered to be multinomial in that each square in the volume concentration space had a certain number probability associated with it. The statistical comparison is then made between the derived multinomial number distributions for two samples, using the likelihood ratio test.

The likelihood ratio test for comparison of two multinomial number distributions will be derived below. The two distributions contain $N_1$ and $N_2$, drops respectively with the number of drops belonging to the $i$ th square in the volume concentration space for the first distribution being $n_{1i}$. Similarly for the second distribution this number is $n_{2i}$. The likelihood function for the two distribution is given below.

$$L.F. = \prod_{i=1}^{m_p} P_{1i}^{n_{1i}} P_{2i}^{n_{2i}} \sum_{i=1}^{m_p} P_{ji} = 1 \quad j = 1, 2 \quad 5.1$$

Where $P_{1i}$ and $P_{2i}$ is the probability of the drop belonging to the $i$ th square in the first and second distributions respectively, $m_p$ equals number of squares in the v-c plane.

The likelihood ratio is then ratio of the maximum of the likelihood function under the hypothesis to be tested to the maximum of the likelihood function unrestricted by the hypothesis. The hypothesis to be tested is the following.

$$P_{1i} = P_{2i} \quad \text{for all } i \quad 5.2$$
The maximum of the likelihood function under this hypothesis is then:

$$L.F_{\text{res. max}} = \prod_{i=1}^{m_p} \left( \frac{n_{1i} + n_{2i}}{N_1 + N_2} \right)^{n_{1i} + n_{2i}}$$  \ \ [5.3]$$

And the maximum of the likelihood function unrestricted is:

$$L.F_{\text{max}} = \prod_{i=1}^{m_p} \left( \frac{n_{1i}}{N_1} \right)^{n_{1i}} \left( \frac{n_{2i}}{N_2} \right)^{n_{2i}}$$  \ \ [5.4]$$

Then the likelihood ratio becomes:

$$\lambda_L = \frac{\prod_{i=1}^{m_p} \left( \frac{n_{1i} + n_{2i}}{N_1 + N_2} \right)^{n_{1i} + n_{2i}}}{\prod_{i=1}^{m_p} \left( \frac{n_{1i}}{N_1} \right)^{n_{1i}} \left( \frac{n_{2i}}{N_2} \right)^{n_{2i}}}$$  \ \ [5.5]$$

Since it is known that $-2\ln \lambda_L$ is distributed nearly Chi squared with $m_p - 1$ degrees of freedom, this is the quantity usually calculated.

This test is applied to several combination of samples from the same experiment (see Appendix X for computer program). Using six divisions in volume and six divisions in concentrations (thirty-six squares), various samples from the same experiment were compared. The value of $-2 \ln \lambda_L$ ranged from 55 to 700. The test yielded values in the same range when two samples from different experiments having the same experimental conditions were compared, and when samples taken at different sampling speeds were compared. According to the test, the hypothesis that the two samples are from the same distribution is rejected. However, because the experimental samples contained a large number of drops, the likelihood ratio test is very critical. Also from previous light transmission ex-
periments, it is known that the distribution of size in a particular volume in the vessel varies significantly with time at very low frequencies of the range 0.1 sec\(^{-1}\). Since the process of drawing a sample requires less than one second, the sample will not be an average of the distribution variation in a particular volume. Hence variations in the distributions of samples taken at different times are expected.

Since there are variations in experimental samples, the true distribution in the vessel is approached as more experimental samples are combined to calculate the distribution. The size distributions of each of two single samples are compared with the distribution calculated from three samples in Figure 5.7. Figure 5.8 shows the comparison of a distribution calculated from two samples compared with that calculated from three samples. It is noticed that the distributions generally approach a single distribution as more samples are considered.
CHAPTER 6

APPROXIMATE INTERPRETATION OF EXPERIMENTS

The apparatus described previously can be used to perform many experiments which would give approximate information about dispersed phase mixing. For example, the effects of stirrer speed on mixing and drop size distribution could easily be measured. Direct qualitative information about the mixing kernel could possibly be obtained at very low residence times, i.e. when very little breakage or coalescence has taken place. Many other possible qualitative experiments could be performed. In order to illustrate possible experiments, four experiments with varying residence times are given below.

6.1 The Experiments

The experimental apparatus was run for four different experiments with approximately the same dispersed phase fraction, the same ratio of oil stream flows, and the same stirrer speed. The only parameter varied was the flow rates to the vessel and hence the residence times. The input data for these experiments is given in Table 6.1 under Experiment Numbers 1, 2, 3, and 4. The input drop size distribution was not measured for these experiments, but it was noted that the drop volume entering was quite different for each of the four experiments.

For each experiment four samples were drawn and the volume and concentration for each drop was measured for all four experiments. These measurements included 2114 drops, 2254 drops, 2819 drops, 2981 drops for the four experiments respectively. The usual drop volume concentration distributions were calculated. Figure 6.1 contains the log volume marginal for each of the experiments. The concentration marginal distri-
bution is given in Figure 6.3. The probabilities listed in the ordinate of Figures 6.1 and 6.3 are not that of the true probability function, but rather these probabilities represent those that are correct for a histogram plotted through the points shown in the figures. Figure 6.4 contains a plot of the ratio of the output concentration variance to that of the input concentration variance versus the residence time in the vessel.

Table 6.1

<table>
<thead>
<tr>
<th>Exp No.</th>
<th>Water cc/mm</th>
<th>Light Dye cc/mm</th>
<th>Dark Dye cc/mm</th>
<th>Stirrer Speed rpm</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>91.0</td>
<td>11.2</td>
<td>7.3</td>
<td>195</td>
</tr>
<tr>
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</tr>
<tr>
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<td>30.0</td>
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<td>2.5</td>
<td>195</td>
</tr>
<tr>
<td>5</td>
<td>35.6</td>
<td>4.6</td>
<td>13.4</td>
<td>?</td>
</tr>
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<td>6</td>
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<td>3.7</td>
<td>244</td>
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<tr>
<td>7</td>
<td>44.0</td>
<td>5.5</td>
<td>3.6</td>
<td>244</td>
</tr>
</tbody>
</table>

6.2 Discussion

The data for the drop volume distribution, Figure 6.1, shows some scatter in the large drop range caused by the large effect of a few large drops. The distributions of the all four experiments are approximately the same, although the distribution of the fourth experiment seems to indicate that the drops were somewhat smaller in this experiment. This may be caused by the difficulty in controlling the very low flows with the present rotameter values. The input drop size may explain
MARGINAL CONCENTRATION DISTRIBUTION

FIGURE 6.3
CURVE OF EQUATION 6.1

CONCENTRATION VARIANCE RATIO VS. RESIDENCE TIME
FIGURE 6.4
some of the variations between distributions, but it would be expected that at such high residence times the input drop size distribution would not have a major effect. It is interesting to note that a log normal distribution would probably fit this data fairly well as indicated in Figure 6.2. Dispersed phase drop size distributions have often been fitted to log normal distributions. This is in contrast to the distribution measured in a previous experiment and shown in Fig. 5.5.

The shift in the marginal concentration distribution as the residence time increases is shown in Figure 6.3. If there is a definite secondary maximum between the central peak and the maximum concentration as seems to be indicated by the concentration distributions, then this would tend to imply that there was substantial coalescence between two drops of approximately equal volume and concentrations of the average concentration and the maximum concentration respectively. Such peaks, however, could result from other coalescence patterns. The increasing height of the central peak and the decreasing height of the minimum and maximum and maximum concentration levels with increasing residence time is expected.

Figure 6.4 shows the decrease in concentration variance ratio with increasing residence time. If the equal drop size model of Curl were to be used in a continuous system, the variation of concentration variance ratio, $C_r$, would vary as shown in equation (6.1) below

$$C_r = \frac{1}{1 + \frac{1}{2} \omega_i \tau}$$  \hspace{1cm} (6.1)

The curve calculated for $\omega_i = 0.54 \text{ sec}^{-1}$ is shown in Figure 6.4. This indicates that this model can be used to relate concentration variance in the range of mixing times studied. However, to say that
this fit implies that most of the drops coalescing are near the average in size is overextending the data. In fact, the sketchy results of the next section seem to indicate that this is not true.

Using the power coefficient of Rushton (17) the power input into the vessel is calculated to be 0.254 horsepower per 1000 gallons. A mixing rate of 0.54 sec\(^{-1}\) with a power input of 0.256 horsepower per 1000 gallons is the same order of magnitude as would be expected if Miller's (14) data were extrapolated to such a low power input.
CHAPTER 7
INTERPRETATION OF EXPERIMENTS USING METHODS OF KERNEL APPROXIMATION

The approximation methods developed in Chapter 3 have been applied to some measured distributions. The least-squares method was applied a number of times to two different distributions in slightly different ways. Various tests were made on this method and different functional relationships for the kernel were tried. The polynomial fit was also tried for two different distributions, but the pseudo-maximum likelihood method was only tried on one distribution. The distribution on which all three methods were attempted is given in Figure 7.1.

These approximation methods were tried with the knowledge that the uniqueness of the kernel solutions is not known. Also if uniqueness were known there is no knowledge of the effect of experimental error on the calculated kernels. Because of these difficulties the results presented below are to be viewed with skepticism.

7.1 The **Least-Squares** Method

7.1.1 Methodology

The computer program used to calculate the least-squares fit of the kernel is given in Appendix XI. The computer program first reads the necessary input information from computer storage where the drop volume-concentration data is stored and from the cards upon which other pertinent information such as number of squares in the distribution is punched.

The drop volume-concentration distribution is developed. First the computer determines the drop volume such that p% of the total dispersed volume is above this volume. In calculating the distribution
VOLUME - CONCENTRATION DISTRIBUTION WITH 5% ABOVE 0.813

FIGURE 7.1
the computer can randomly select some of the drops to be eliminated from the distribution and further calculations. This will allow the effect of small variations of distribution on kernel values to be ascertained. After the distribution is computed, it is printed out on the line printer.

While the distribution is being calculated the coefficients of the breakage kernel values are also being computed. In this computation each drop is considered individually. For example if a drop belonged to the \( k, l \)th square, the flux from this square into all smaller squares of the same concentration (e.g. the \( m, l \)th square) will have to be considered. Thus from the coefficient of \( B_{k,m} \) in the balance equation on the \( k, l \)th square the appropriate factor (this factor is the probability of the drop \( P_d \), when no form for breakage is assumed) is subtracted and to the coefficient of \( B_{k,m} \) in the balance equation on the \( m, l \)th square the appropriate factor is added. These coefficients, \( B_{k,l,m} \), are stored in the breakage array.

Since the computer time expended in considering all possible coalescences between drops in the sample would be excessive, the coalescences are performed on a randomly selected group of drops of the experimental sample. The number of drops that could be used in a reasonable amount of computer time for coalescence computation was about 500. Suppose two drops from the selected group have volumes \( v_1 \) and \( v_2 \) respectively and belong to the \( w, x \)th and \( y, z \)th square respectively. When they coalesce they will belong to the \( u, v \)th square; thus to the coefficient of \( C_{w,y} \) in the balance on the \( u, v \)th square is added the appropriate factor. (When no form for the coalescence is assumed this factor is the product of the sum of the volumes of the two drops and the
probabilities of each drop in the selected sample, e.g. \((v_1 + v_2)\)x \(P_e P_f \). \(P_e \) is calculated to be \(v_1 \) divided by the total dispersed phase volume in the selected group. Similar appropriate factors are subtracted from the coefficient of \(K_{w,y}^c \) in the balances on the \(w \), \(x\)th and \(y \), \(z\)th squares. The coefficients \(C_{i,j,w,y} \) are stored in the coalescence array.

To complete the information necessary for the least squares method, the input probability distribution must be calculated. The input distribution is just two points in the volume concentration space, and it is calculated from the flow rates of the two oil streams and the output of the drop counters. The volume of the drops of each stream is calculated by dividing the flow rate of that stream by the frequency of drops for that stream. The concentration for each stream is known since it is the maximum or minimum concentration in the experimental sample (at very large residence times this may not be true, but such residence times were never used in these experiments). Finally, the probability associated with each of the two points in the volume-concentration space is the flow rate of the drops represented by that point divided by the sum of the two flow rates.

The resulting equation for each square is equation 3.51 or:

\[
Q \phi_i [P_{i,j} - P_{o,ij}] = V \phi_2 \left[ \sum_{k,m} B_{i,j,k,m} K_{k,m}^\theta + \sum_{w,y} C_{i,j,w,y} K_{w,y}^c \right]
\]

Or, as stated before, this can be written as:

\[
\vec{d} = A \vec{K}
\]
where \( \bar{d}^t = \{ p_{ij} - p_{0,ij} \} \) for all \( i,j \)

\[
\bar{K}^t = \frac{\sum_{i,j} \phi^2_i}{\sum_{i,j} \phi^2_i} \left( \begin{array}{c} \phi^d_i \phi^c_{ij} \\
\phi^d_{ij} \phi^c_{ij} 
\end{array} \right)
\]

\( A \) is the matrix of \( B_{ij,k,m} \) and \( C_{ij,w,y} \)

Since \( p_{ij}, p_{0,ij}, B_{ij,k,m}, \) and \( C_{ij,w,y} \) are known, the vector \( \bar{d} \), and the matrix \( A \) are known. The vector \( \bar{d} \) has dimensions \( in \times n^2 \) and \( K \) has dimensions \( 1 \times \left[ \left( \frac{n-1}{m_d} + 2 \right) \left( \frac{n-1}{m_d} + 1 \right) - 2 \right] \)

Here \( n \) is the number of divisions along each side of the volume-concentration space and \( m_d \) is the number of divisions in the volume coordinate of the distribution per division in the volume coordinates of the kernel space. In most of the calculations \( n \) was equal to 9 and \( m \) to 2, giving \( \bar{d} \) dimensions \( 1 \times 81 \) and \( \bar{K} \) dimensions of \( 1 \times 28 \). Hence \( A \) has dimensions \( 28 \times 81 \).

In the least-squares estimation of \( \bar{K} \) in the linear equations (3.52), the function (quadratic form) to be minimized is \( (d - A \bar{K})^t (d - A \bar{K}) \). That is a \( \bar{K} \) is chosen such that

\[
\bar{d}^t \bar{d} - 2 \bar{d}^t A \bar{K} + \bar{K}^t A^t A \bar{K}
\]

is minimized. Defining \( T \) to be \( A^t A \) and \( h \) to be \( d^t A \) the problem is
the minimization

\[ \Omega = -2\mathbf{h} + \mathbf{K}^T \mathbf{K} \] 7.2

or maximization of the function

\[ -\Omega = 2\mathbf{h} - \mathbf{K}^T \mathbf{K} \] 7.3

The best least squares fit is then the point at which

\[ -\nabla \Omega = 0 \] 7.4

or

\[ -\nabla \Omega = 0 = \mathbf{h} - \mathbf{T} \mathbf{K} \]

The best least squares fit is then

\[ \mathbf{K} = \mathbf{T}^{-1} \mathbf{h} \] 7.5

However, it is known that \( \mathbf{K} \) must be positive; this gives the following quadratic programming problem. Maximize

\[ -\Omega = 2\mathbf{h} - \mathbf{K}^T \mathbf{K} \]

subject to:

\[ \mathbf{K} \geq 0 \] 7.6

From this it can be seen that for calculating the true minimum or the constrained minimum, the vector \( \mathbf{d} \) and the matrix \( A \) are not needed. Hence the computer program calculates the square matrix \( T \) and the vector \( \mathbf{h} \) directly from the values \( P_{i,j} \), \( P_{ij} \), \( B_{i,j,k,m} \), and \( C_{i,j,k} \).

The usual methods of quadratic programming requires inverting the \( T \) matrix many times. Since in most cases the \( T \) matrix is nearly
singular, many inversions introduce much inaccuracy. Thus a derivative method was used to find the maximum i.e. the differential equation

\[ \frac{d\tilde{K}}{dt} = (\tilde{h} - T\tilde{K}) \]

was integrated using Euler's method subject to the constraint

\[ \tilde{K} \geq 0 \]

until the steady state had been found. When this point has been found, it satisfies the Kuhn-Tucker conditions, the necessary and sufficient conditions for the maximization of a positive definite quadratic form with linear constraints.

Euler's method in the program uses the following recursion formula.

\[ \tilde{K}_{i+1} = \tilde{K}_i + (\tilde{h} - T\tilde{K}_i) \Delta t \]

If any \( K_{j,i+1} < 0 \), that \( K_{i,i+1} \) is set equal to zero. The iteration is continued until the quantity

\[ \sum_j |K_{j,i,i+1} - K_{j,i}| \]

is less than a certain small value, 0.0001. After the constrained \( \tilde{K} \) vector is calculated it is printed out.

Other quantities are also calculated and printed out. These include the \( T \) matrix itself, the true minimum calculated from the equation,

\[ \tilde{K} = T^{-1}\tilde{h} \]

the confidence intervals on the values at the true minimum, the sum of squares for the constrained minimum and the true minimum and the eigen-
valves of the matrix $T$. In calculation of $T^{-1}$ the maximum pivot method for Gauss-Jordan (1) reduction is used. The eigenvalues and eigenvectors of the $T$ matrix were determined by using the Jacobi iteration method (1).

### 7.1.2 Results

The least-squares method as applied to the first distribution was somewhat different than that described above. It does not consider the coalescences of large drops, those in the upper p%, with smaller drops, i.e., the last column in the coalescence kernel in Figure 3.8 is omitted. Also the drops used in coalescence calculations are not randomly selected; rather the computer chooses one out of every three or four drops. This program did not contain most of the extra calculations such as the unconstrained least-squares fit, etc.

Figures 7.2, 7.3, 7.4, and 7.5 contain kernels with unassumed forms calculated from the same distribution except that different drops were chosen in the coalescence computation. The upper range of volume contained 4% of the distribution and the lowest range of volume contained the most dispersed phase volume. For this experiment, Experiment #6 in Table 6.1, the flow rates were: water 29.6 cc/min, low concentration oil 4.05 cc/min, and high concentration oil 3.65 cc/min. The input frequency of drops of low concentration was 20 per second and of the high concentration drops it was 25 per second. The stirrer speed was 244 rpm. Figure 7.6 contains the kernel calculated from the same experiment except that the distribution was computed with 2% of the dispersed phase volume in the upper range of volume.

The least-squares method was applied as described above to the distribution shown in Figure 7.1. The flow rates for this experiment,
Kernel Calculated Using Every Third Drop Starting with the First One in Coalescence Computation.

Figure 7.2

Kernel Calculated Using Every Fourth Drop Starting with Third Drop in Coalescence Computation.

Figure 7.3
Kernel Calculated Using Every Fourth Drop Starting with the Second One in Coalescence Computation.

Figure 7.4

Kernel Calculated Using Every Fourth Drop Starting with the First One in the Coalescence Computation.

Figure 7.5
Coalescence  

Breakage

Kernel Calculated Using Every Fourth Drop Starting with the First Drop for Coalescence Computation.

Figure 7.6
Experiment #7 in Table 6.1, were: water 44.0 cc/min, low concentration oil 5.5 cc/min, and high concentration oil 3.6 cc/min. The stirrer speed was 244 rpm. The input frequency of the low concentration oil was 31 drops per second and that of the high concentration oil was 15 drops per second. From the distribution it is noticed that most of the drops lie in lower four volume size ranges of the distribution.

Since in the previous experiment, the all positive kernels contained a group of zeros, it was decided that perhaps a better fit could be obtained if functional forms were applied to the kernels. The following form was used for breakage.

$$K_{(x,y)}^B = b x^{(d-2)} (x-v) y$$  \hspace{1cm} 7.10

Here $x$ is the size breaking and $v$ is the size broken into. The power factor was chosen to be $d-2$ to give $d$ the meaning of the power of the rate of breakage of volume $x$, i.e., rate of breakage of volume $x$ is $x^d$. The remaining portion of the factor, $(x-v) v/x^2$ is simply a probability distribution since

$$\int_0^x \frac{(x-v)v}{x^2} dv = \frac{1}{2}$$  \hspace{1cm} 7.11

This form was chosen because a power function for breakage and a beta type distribution for the resulting drops were thought reasonable. Two forms were tried for the coalescence kernel

$$K_{(x,y)}^C = c (v^f + x^f)^e$$  \hspace{1cm} 7.12

$$K_{(x,y)}^C = \alpha (vx)^f/(v+x)^e$$
The first form is similar to the collision kernel used in gas kinetic theory if \( f \) is chosen to be 1/3 and \( e \) is chosen to be 3. The second form was chosen to fit more closely the unassumed kernels.

Again \( a, b, \) and \( c \) are divided into squares the same as was \( K \).

In applying the breakage kernel to the drop distribution, the flux from each drop to each square of size smaller than the drop had to be calculated separately. Consider a drop of size \( X \) breaking into the square of size range \( v_1 \) to \( v_2 \); the size \( X \) belongs to square \( k \) and \( v_1 \) to \( v_2 \) is the square \( m \). To calculate the flux into square \( m \) and out of square \( k \), the proper \( b \) is chosen and the form integrated to give:

\[
Flux = b_{k,m} X^{d-2} \int_{v_i}^{v_f} \int_{v_1}^{v_2} (x-v) d\nu d\nu_1 \nu_1 \nu_2
\]

\[
= b_{k,m} X^{d-2} \left[ \frac{xv^2}{2} - \frac{v^3}{3} \right]_{v_1}^{v_2} \nu_1 \nu_2
\]

\[
= b_{k,m} X^{d-2} \left\{ \frac{x(\Delta v)^2 [m^2-(m-\eta)^2]}{2} - \frac{(\Delta v)^3 [m^3-(m-\eta)^3]}{3} \right\}
\]

This allows the calculation of the coefficient of \( b_{k,m} \) and it is stored in the array \( B_{ijkm} \) as was the coefficient of \( K^B_{ijkm} \) before.

The factor used in determining the coefficients of \( C_{wy} \) is similar to that of the calculation of the coefficient of \( K^c_{wkm} \), i.e., the flux into square \( u, v \) is:

\[
\text{Flux in} = C_{w,1} (v_i + v_f) (v_i^f + v_f^f) e P_e P_f
\]

The flux out terms have the same factor variation as the flux in term.

Similarly, the flux in and flux out terms are modified when coalescence
has the form assumed in equation 7.12.

Figures 7.7 to 7.10 contain the calculated factors $b$ and $c$ obtained for the breakage form (equation 7.10) and the first coalescence form (equation 7.11). Figures 7.11 and 7.12 contain results obtained using the breakage form (equation 7.10) and the second coalescence form (equation 7.12). The parameters used in each of the forms is indicated in the figure. For all of these forms the additional information such as eigenvalues and eigenvectors were calculated. These were not important because the true minimum could not be determined since the matrix was too singular to be inverted.

7.1.3 Discussion

From the results it can be seen that the least-squares method does not give good results as indicated by the number of zeros in the kernels. However some physical interpretation can be obtained from these kernels if these kernels do represent reality. All the kernels calculated seem to suggest that the breakage function increases rapidly with volume, i.e. that almost all the breakage occurs in the upper five volume percent of the dispersed phase. This rapid increase is demonstrated in Figures 7.5 and 7.6 where the upper range of volume was changed from 4% to 2%. Also it is noticed that in almost all cases the values for coalescence in the range of the most probable drop size are zero or very small. This suggests that the most probable drop size is involved the least in coalescence. Similar phenomena to this is discussed by Shinnar (18). Other more detailed interpretations are possible, but it is thought that such interpretations are unwarranted.

Some of the weaknesses of the least-squares method are shown in these results. Figures 7.10, 7.11, and 7.12 show the effect of chang-
### Multiplying Factors for Assumed Kernel Forms

#### 500 Random Drops for Coalescence

\[
\begin{align*}
\text{Coalescence} & \\
& \begin{array}{cccc}
0.0 & 0.0 & .24 \\
1.2 & 0.0 & .15 \\
0.0 & 0.0 & 0.0 & 0.0 \\
.2 & 0.0 & 0.0 & 0.0 & 0.0
\end{array} \\
\text{Breakage} & \\
& \begin{array}{cccc}
0.0 & 11.2 \\
.006 & .04 & 11.0 \\
.006 & .08 & 16 & 8.9 \\
0.0 & 0.0 & .04 & 0.07 & 3.5
\end{array}
\end{align*}
\]

\[d = 4.0 \quad f = 1/3 \quad e = 2.0\]

**Figure 7.7**

#### 300 Random Drops for Coalescence

\[
\begin{align*}
\text{Coalescence} & \\
& \begin{array}{cccc}
0.0 & 0.0 & .060 \\
.042 & .26 & .038 \\
0.0 & 0.0 & 0.0 & 0.0 \\
.4 & 0.0 & 0.0 & .075 & 0.0
\end{array} \\
\text{Breakage} & \\
& \begin{array}{cccc}
0.00 & 7.56 \\
.005 & .048 & 7.66 \\
.013 & .148 & .194 & 6.36 \\
0.0 & 0.0 & .085 & .082 & 2.5
\end{array}
\end{align*}
\]

\[d = 3.0 \quad f = 1/3 \quad e = 0.0\]

**Figure 7.8**
Multiplying Factors for Assumed Kernel Forms.
300 Random Drops for Coalescence.

\[ d = 3.0 \quad f = \frac{1}{3} \quad e = 2.0 \]

Figure 7.9

Multiplying Factors for Assumed Kernel Forms.
200 Random Drops for Coalescence.

\[ d = 3.0 \quad f = \frac{1}{3} \quad e = 2.0 \]

Figure 7.10
Multiplying Factors for Assumed Kernel Forms.
250 Random Drops for Coalescence.

\[ d = 3.0 \quad f = 1/3 \quad e = 2.0 \]

**Figure 7.11**

---

### Coalescence

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### Breakage

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### Coalescence

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</table>

### Breakage

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<td>0.034</td>
<td>0.467</td>
</tr>
<tr>
<td>0.170</td>
<td>1.49</td>
</tr>
</tbody>
</table>

Multiplying Factors for Assumed Kernel Forms.
250 Random Drops for Coalescence.

\[ d = 3.0 \quad f = 1/3 \quad e = 0.0 \]

**Figure 7.12**
ing the assumed form for the coalescence kernel upon the calculation of the breakage kernel. However, it is noticed from Figures 7.9 and 7.10 that the number of drops considered in coalescence does not significantly affect the results. The major weakness of this method is the zeros in the kernel. These occur if the true minimum lies outside the all positive region. Since $T$ is positive definite, there is only one minimum and if some non-realizable negative solution is the dominant solution, this method may find this one as the solution.

7.2 Psuedo-Maximum Likelihood Method

7.2.1 Methodology

The computer program used to implement the psuedo-maximum likelihood method is given in Appendix XII. The first part of the program is quite similar to that of the least squares. The same data is read from computer file storage and from the punched deck. Both the input and the output probability distributions are calculated in exactly the same manner, having the same option of omitting some drops randomly in the output distribution. Also the drops used in forming the coalescence kernel are selected in the same manner.

In the least squares method, two coefficient matrices $C_{ijw}$ and $B_{ijkm}$ were calculated. When the product of $C_{ijw}$ times $K_{wy}^c$ was summed over all $w$ and $y$, \( \sum_{w,y} C_{ijw} K_{wy}^c \), this sum represented the input volume flux minus the output flux due to coalescence for a particular square. However looking at equation 3.55

\[
P_{ij1k} = \frac{P_{oi} + F_{ij}^\theta + F_{ij}^\phi}{1 + \frac{1}{P_{ij}} F_{ij}^{\theta \text{out}} + \frac{1}{P_{ij}} F_{ij}^{\phi \text{out}}} \tag{3.55}
\]
it can be seen that the fluxes in and out by both coalescence and
breakage will have to be calculated separately. The computer program
accomplishes this goal by having four coefficient arrays instead of two.
Thus for example $F_{ij}^{Bin}$ is represented by the following equation.

$$F_{ij}^{Bin} = \sum_{k,m} B_{i,j,k,m}^{\cdot h} K_{k,m}^{B}$$  \hspace{1cm} 7.17

Also the element of the output arrays are calculated such that:

$$\frac{1}{P_{ij}} F_{ij}^{Cout} = \sum_{w,y} C_{ij,w,y}^{\cdot out} K_{wy}^{C}$$ \hspace{1cm} 7.18

i.e. the elements are the coefficients used to calculate the output for
a particular square divided by the probability of that square. Finally
equation 3.55 can be written as:

$$P_{ij,k} = \frac{P_{ij} + \sum_{k,m} B_{i,j,k,m}^{i,h} K_{k,m}^{B} + \sum_{w,y} C_{ij,w,y}^{i,h} K_{wy}^{C}}{1 + \sum_{k,m} B_{i,j,k,m}^{out} K_{k,m}^{B} + \sum_{w,y} C_{ij,w,y}^{out} K_{wy}^{C}}$$ \hspace{1cm} 7.19

In the calculation of the two breakage arrays, each drop is considered
individually as in the least squares method. The same factor ($P_d$ since
no forms were assumed) is added to the appropriate element of both the
$B^{bin}$ and the $B^{out}$ arrays instead of added and subtracted from appro-
priate elements of the $B$ array as in the least squares method. Simil-
arily the appropriate factors are added to the elements of $C^{in}$ and $C^{out}$.
These factors are the same as those calculated in the least squares
method with no form assumed for the kernel. In order to make the arrays \( \mathbf{C}^{\text{out}} \) and \( \mathbf{B}^{\text{out}} \) contain the correct value for equation 7.19, each element of these arrays is divided by the probability of the square to which it pertains, i.e. the algorithm below is used for all \( i, j, k, \) and \( m \).

\[
\mathbf{B}_{ijkm}^{\text{out}} = \frac{\mathbf{B}_{ijkm}^{\text{out}}}{P_{ij}}
\]

\[
\mathbf{C}_{ijkm}^{\text{out}} = \frac{\mathbf{C}_{ijkm}^{\text{out}}}{P_{ij}}
\]

Having calculated the arrays \( P_{ij}, P_{oij}, B^{\text{in}}, B^{\text{out}}, C^{\text{in}}, \) and \( C^{\text{out}} \), it is possible, given \( K \), to calculate the log likelihood function, i.e.

\[
\Phi = \sum_{ij} P_{ij} \ln P_{ij|k}
\]

with the condition

\[
\sum_{ij} P_{ij|k} = 1
\]

or this can be written as

\[
\Phi = \sum_{ij} P_{ij} \ln \left[ \frac{P_{oij} + \sum_{km} B_{ijkm}^{\text{in}} K_{km}^{\text{B}} + \sum_{wy} C_{ijwy}^{\text{in}} K_{wy}^{\text{C}}}{1 + \sum_{km} B_{ijkm}^{\text{out}} K_{km}^{\text{B}} + \sum_{wy} C_{ijwy}^{\text{out}} K_{wy}^{\text{C}}} \right]
\]

\[
\sum_{ij} P_{ij|k} = 1
\]

Using the maximum likelihood methods of statistics as a guide, it would seem desirable to use the computer to find the \( \mathbf{K} \) which maximizes \( \Phi \) subject to equation 7.21. Since neither the \( \mathbf{K} \) associated with the maximum nor the gradient of \( \Phi \) can be found directly, some search method will have to be used. The pattern search as described by Wilde and Beightler (22), probably the most efficient method, was implemented.
on the computer.

This method involves starting at some point and checking in which direction a finite change of each variable will give an increase in the object function. A new point is then projected in the direction of increasing object function and a search is again performed around this point. Another projection is made and the processes continue building a pattern with acceleration in the directions of increasing object function. If the projected point has an object function greater than that of the last point, this last point is used as a starting point for a new pattern. If a point is reached where no increase in object function can be found by changes in any variable, then the size of the change of variable is reduced and an attempt to start building a pattern is made. When the size of the change of variable has reached a certain small value and still no increase in object function can be found, the search is complete.

The object function used in this search was not equation 7.22, since it is difficult to impose the condition of equation 7.21 on it. Instead an object function which placed heavy penalty on deviating from condition 7.21 was devised, i.e. the object function was:

\[ \Gamma = \sum_{i,j} P_{ij} \ln P_{ij/k} - 1000 (1 + \sum_{i,j} P_{ij})^2 \]  \hspace{1cm} 7.23

The search method restrained the values from becoming negative; in fact, the values always had to be assigned a small positive value to prevent from becoming zero (the computer cannot extract the logarithm of zero) for some and . In order to follow the search method the new point was printed out each time it was found.
7.2.2 Results

The computer program was applied to the experiment whose probability distribution is represented in Figure 7.1. After an extensive amount of computer time was used, the program, which started at a point where all K's were one, reached a point where one value was increasing indefinitely. The values at this point are shown in Figure 7.13.

7.2.3 Discussion

Nothing can be said about the physical interpretation of these results because the true value predicted by the method was never reached. At the point when the program was stopped, there were still six values changing in addition to the one increasing without bound.

The method itself has one overwhelming difficulty; it took more than a reasonable amount of IBM 360 computer time to search the K space from the values of all K's equal to one to the values indicated in Figure 7.13.

7.3 Polynomial Fit of Kernels

7.3.1 Methodology

The main equation used in developing the polynomial fit of the data is equation 3.57

\[
M(\theta, \phi) - M_0(\theta, \phi) = \int_0^\infty \int_0^\infty \frac{K_b(x, y)}{W_r} S(x) S(y) \left[ e^{\theta x} M_x(y) - e^{\theta y} M_x(\theta) \right] dx dy
\]

\[
+ \int_0^\infty \int_0^\infty \frac{K_c(x, y)}{W_r} S(x) S(y) \left[ e^{\theta x} M_x(\theta) M_y(y) - e^{\theta y} M_x(\theta) \right] dx dy
\]  

\[3.57\]
<table>
<thead>
<tr>
<th></th>
<th>Coalescence</th>
<th>Breakage</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%</td>
<td>161.3 11.3</td>
<td>8.5 10.2</td>
</tr>
<tr>
<td></td>
<td>0.0 0.0 0.0</td>
<td>2.1 4.4 0.8</td>
</tr>
<tr>
<td></td>
<td>3.3 0.0 0.0 0.0</td>
<td>0.1 1.9 1.1 1.1</td>
</tr>
<tr>
<td></td>
<td>7.8 10.3 1.8 25.2 29.3</td>
<td>0.2 0.2 0.5 0.8 0.5</td>
</tr>
</tbody>
</table>

Kernel Calculated Using Pseudo-Maximum Likelihood

Figure 7.13
The polynomial assumed forms for the breakage and coalescence are:

\[
\frac{K_B(x,v)}{W_r} = B_0 v(x-v) + B_1 vx(x-v) + B_2 v^2 x^2(x-v) + B_3 v(x-v)^2 + B_4 vx(x-v)^2
\]
\[
\frac{K_C(x,v)}{W_r} = C_0 + C_1 (x+v) + C_2 (v^2 + v^3) + C_3 x v
\]

These equations are substituted into equation 3.57 and the integrations in this equation are performed for various powers of \( \Theta \) and \( \Phi \) when the moment generating function and the exponential functions have been expanded in a power series.

The various powers of theta and phi considered and the resulting equations are listed below.

\[
\Theta^1 \Phi^0
\]
\[
\overline{V} - \overline{V}_0 = -\frac{1}{2k} \overline{V}^2 B_0 - \frac{1}{2k} \overline{V}^2 B_1 - \frac{1}{2k} \overline{V}^2 B_2 - \frac{1}{2k} \overline{V}^2 B_3 - \frac{1}{2k} \overline{V}^2 B_4
\]
\[
+ \overline{V}^2 C_0 + 2 \overline{V}^3 C_1 + 2 \overline{V}^4 C_2 + \overline{V}^5 C_3
\]
\[
\Theta^0 \Phi^1
\]
\[
\overline{m} - \overline{m}_0 = -\frac{1}{2} \overline{m} \overline{V}^2 B_0 - \frac{1}{2} \overline{m} \overline{V}^2 B_1 - \frac{1}{2} \overline{m} \overline{V}^2 B_2 - \frac{1}{2} \overline{m} \overline{V}^2 B_3 - \frac{1}{2} \overline{m} \overline{V}^2 C_4
\]
\[
+ \overline{m} \overline{V} C_0 + (\overline{V}^3 + 2 \overline{V} \overline{m} \overline{V}) C_1 + (\overline{V}^4 + 2 \overline{V} \overline{m} \overline{V}^2) C_2 + \overline{V}^5 \overline{m} \overline{V} C_3
\]
\[
\Theta^1 \Phi^0
\]
\[
\overline{mV} - \overline{m}_0 \overline{V}_0 = \frac{7}{60} \overline{mV} + B_0 - \frac{7}{60} \overline{mV} B_1 - \frac{7}{60} \overline{mV} B_2 - \frac{1}{60} \overline{mV} B_3 - \frac{1}{60} \overline{mV} B_4
\]
\[
+ (\overline{m} \overline{V} + 2 \overline{m} \overline{V} \overline{m}) C_0 + (\overline{m} \overline{V} + 2 \overline{m} \overline{V} + 3 \overline{V} \overline{m} \overline{V}) C_1 + (\overline{V}^3 \overline{m} + 2 \overline{V} \overline{m} \overline{V} + 2 \overline{V} \overline{m} \overline{V}^2) C_2 + (\overline{V}^4 \overline{m} + 2 \overline{V} \overline{m} \overline{V} + 2 \overline{V} \overline{m} \overline{V}^2) C_3
\]
\[
\Theta^0 \Phi^2
\]
\[
\overline{m^2} - \overline{m}_0^2 = -\frac{7}{120} \overline{m} \overline{V} \overline{V} B_0 - \frac{7}{120} \overline{m} \overline{V} \overline{V} B_1 - \frac{7}{120} \overline{m} \overline{V} \overline{V} B_2 - \frac{1}{120} \overline{m} \overline{V} \overline{V} B_3 - \frac{1}{120} \overline{m} \overline{V} \overline{V} B_4
\]
\[
+ (\overline{m} \overline{V} + \overline{m} \overline{V} + \overline{m} \overline{V} + \overline{m} \overline{V}) C_0 + (\overline{m} \overline{V} + \overline{m} \overline{V} + \overline{m} \overline{V} + \overline{m} \overline{V}) C_1
\]
\[
+ (\overline{m} \overline{V} + \overline{m} \overline{V} + \overline{m} \overline{V} + \overline{m} \overline{V} + \overline{m} \overline{V} + \overline{m} \overline{V}) C_2 + (\overline{m} \overline{V} + \overline{m} \overline{V} + \overline{m} \overline{V} + \overline{m} \overline{V}) C_3
\]
\[ \Theta' \phi^0 \]
\[ \vec{V}^2 - \vec{V}_0^2 = -\frac{7}{40} \vec{V}^2 B_0 - \frac{7}{40} \vec{V}^2 B_1 - \frac{7}{40} \vec{V}^2 B_2 - \frac{1}{30} \vec{V}^2 B_3 - \frac{1}{30} \vec{V}^2 B_4 + \frac{3}{5} \vec{V}^2 C_0 + \frac{3}{5} (\vec{V}^2 + \vec{V}_0^2) C_1 + \frac{3}{5} (\vec{V}^2 + \vec{V}_0^2) C_2 + \frac{3}{5} \vec{V}^2 \vec{V}_0^2 C_3 \]

\[ \Theta' \phi^1 \]
\[ \vec{V}^2 - \vec{V}_0^2 = -\frac{1}{45} \vec{V}^2 B_0 - \frac{1}{45} \vec{V}^2 B_1 - \frac{1}{45} \vec{V}^2 B_2 - \frac{2}{520} \vec{V}^2 B_3 - \frac{2}{520} \vec{V}^2 B_4 + (\frac{1}{5} \vec{V}_0^2 C_0 + (\frac{1}{5} \vec{V}^2 + \frac{1}{5} \vec{V}_0^2) C_1 + (\frac{1}{5} \vec{V}^2 + \frac{1}{5} \vec{V}_0^2) C_2 + (\frac{1}{5} \vec{V}^2 + \frac{1}{5} \vec{V}_0^2) C_3 \]

\[ \Theta' \phi^2 \]
\[ \vec{V}^2 - \vec{V}_0^2 = -\frac{1}{45} \vec{V}^2 B_0 - \frac{1}{45} \vec{V}^2 B_1 - \frac{1}{45} \vec{V}^2 B_2 - \frac{2}{840} \vec{V}^2 B_3 - \frac{2}{840} \vec{V}^2 B_4 + (\vec{V}^2 + \vec{V}_0^2) C_0 + (\vec{V}^2 + \vec{V}_0^2) C_1 + (\vec{V}^2 + \vec{V}_0^2) C_2 + (\vec{V}^2 + \vec{V}_0^2) C_3 \]

\[ \Theta' \phi^3 \]
\[ \vec{V}^2 - \vec{V}_0^2 = -\frac{1}{45} \vec{V}^2 B_0 - \frac{1}{45} \vec{V}^2 B_1 - \frac{1}{45} \vec{V}^2 B_2 - \frac{2}{2520} \vec{V}^2 B_3 - \frac{2}{2520} \vec{V}^2 B_4 + (\vec{V}^2 + \vec{V}_0^2) C_0 + (\vec{V}^2 + \vec{V}_0^2) C_1 + (\vec{V}^2 + \vec{V}_0^2) C_2 + (\vec{V}^2 + \vec{V}_0^2) C_3 \]
These equations can then be solved to determine the unknown coefficients as discussed in Chapter 3. The solution of the equation is:

$$\hat{Z} = H^{-1} \hat{X}$$

where $$\hat{Z}^t = [B, C]$$

$$\hat{X} = \text{left hand sides of equations 7.24}$$

$$H = \text{coefficients of } \hat{Z} \text{ in 7.24}$$

The computer program which performs these calculations is given in Appendix XIII. It first reads the output drop volume-concentration distribution from the computer storage and the input flow rates and drop frequencies from the card reader.

It then converts this data to a volume-mole distribution and computes all the output moments necessary for the system of linear equations by summing these values for each individual drop. Having computed all the moment information the matrix $H$ is tabulated and inverted using the maximum pivot method (1). The input moments are calculated and this information is used to determine $\hat{X}$. Finally the result $\hat{Z}$ is computed.

7.3.2 Results

This method was applied to the same two distributions as was the least squares method. The resulting kernels for the first experiment, Experimental Number 6, was:

$$\frac{K_0(x,y)}{W_1} = -959.6V(x-V) + 975.7Vx(x-V) - 2.32Vx^2(x-V) - 1.26V(x-V)^2 + 3Vx(x-V)^2$$

$$\frac{K(x,y)}{W_1} = 925.4 - 882.7(x+V) - 329.0(V^2x^2) + 2576.6xV$$
The results for the second experiment, the one whose distribution is plotted in Figure 7.1 are:

\[
\frac{K_r(x, y)}{W_r} = 5219.9 V(x-y) - 38970 Vx(x-y) + 124940 Vx^2(x-y)
+ 76377 V(x-y)^2 - 132170 Vx(x-y)^2
\]

7.26

\[
\frac{K_e(x, y)}{W_r} = -5757.5 + 9455.4 (V+x) + 1924.5 (x+y)^2 - 5729.7 x y
\]

7.3.3 Discussion

The results indicate that these functions have both positive and negative values in the range of interest which would not be expected in the physical system. Hence no physical interpretation could be obtained from these results.

The calculation of the coefficients involves moments to the eighth power; since these moments are difficult to measure accurately, errors in the results can be expected. The choice of the form of the kernels is, of course, crucial in finally obtaining results that are physically meaningful. Thus the choice of the form for the kernels calculated above may not be good.

7.4 Summary of Approximation Methods

The quantitative calculation of mixing kernels would have to be described as questionable. The big question is uniqueness of the calculated kernels. If the kernels are unique then all methods would approximate the kernel however roughly. But since uniqueness is not known, the approximations of the kernels must be considered in this light.
CHAPTER 8

SUMMARY AND SUGGESTIONS FOR FURTHER WORK

8.1 Summary

A method for the measurement of the bivariate drop volume-dye concentration distribution of the dispersed phase drops in a mixing vessel was developed. This method involved extracting a sample of the dispersed phase from the vessel, immediately coating the drops with an anticoalescence agent and forcing the drops through a small capillary. A photometer was focused on the capillary through a microscope. The output of the photometer, which consisted of a series of rectangular pulses, was digitized and then analyzed quickly and easily on the computer. In this analysis the computer determined the volume of a drop by measuring the length of the pulse and the concentration of dye in the drop by measuring the height of the pulse.

This measurement method was used to study the mixing in a vessel which was part of a steady state experimental system. To this vessel were fed three streams; the continuous phase water and two streams of the dispersed phase containing different concentrations of light absorbing dye. The dispersed phase input streams were fed to the vessel as drops of known size. As these drops coalesce and break, they change volume and dye concentration giving the bivariate distribution.

A volume balance in a differential drop volume range in the vessel was derived. The description of coalescence and breakage in this balance was accomplished with a single mixing kernel. This kernel was then used in a balance in a differential drop volume dye concentration area for the steady state experiment. This balance and others were
investigated in an effort to find some method of calculating the mixing kernel from these equations given the input and vessel bivariate distributions. Three methods to study the calculation of the kernel were developed and applied to several measured distributions. Since uniqueness of the mixing kernel was never proven and since the calculated kernel values appear unreasonable, the calculation methods are questionable.

A series of experiments with different residence times was run to obtain approximate interpretations of the data. The resulting volume marginal distributions were compared with each other and with the log-normal distribution. The development of the concentration profile was shown by the concentration marginals. The ratio of input to output concentration variance was plotted versus residence time. The equal drop size model seemed to fit this data very well with a mixing rate of 0.5 m $\text{min}^{-1}$. This mixing rate was of the same order of magnitude as found by other investigators (14).

8.2 Suggestions for Further Work

The suggestions for future work can be divided into further study of methods for using the balance equations to calculate mixing kernels and further experimental investigations into the nature of mixing.

Further attempts at proving the uniqueness of the kernel in the balance equation would be of value. The least-squares method, the most promising for calculating the mixing kernel, should be studied more extensively. In particular a bivariate distribution could be generated using a known kernel and the least-squares method applied to see how well this kernel was calculated. Other methods of calculating the kernel should be investigated.
Other approximation interpretations of the mixing data may involve experiments with all conditions the same except input drop volume. This should be a good test of Shinnar's theory (18) of coalescence stabilized dispersions. From the experiments of this work, it was noticed that the drop volume distribution in some cases appears to be log normal. The investigation of experimental conditions which give rise to particular drop volume distributions would be of interest. Also an effect of the drop volume distribution on mixing might be detected. Finally the effect of dispersed phase density on mixing might be investigated with the hope of determining under what experimental conditions settling becomes important in the coalescence process. Many other such investigations are possible.

Also minor modifications in the experiment would be in order. The seal between the stirrer shaft and the vessel probably should be converted to a mechanical seal. The back pressure in the outlet stream from the vessel probably should be replaced by something better if many high residence time experiments are performed. Also different size hypodermic needles should be obtained for use in the drop generators. This would allow counting the drops over a much wider range of fluid velocities. In future experiments, the dye concentration in the oil phases should be at least doubled to eliminate the necessity of a high feedback capacitance in the last stage of the analog section. Also a slight modification in the computer program which calculates the drop volume and concentration would eliminate the frequency response problem entirely.
BIBLIOGRAPHY


APPENDIX 1

CHECK OF BALANCE EQUATIONS

As a check of the balance equations, the integral over \( v \) and \( c \) in the volume concentration balance should be equal for the flow terms, the breakage terms, and the coalescence terms. That is, the total flow into the vessel should equal the total flow out, etc. For the flow and breakage terms this fact is quite evident, i.e.

\[
Q \phi, \int_0^\infty \int_0^c p(v,c) \, dc \, dv = Q \phi, = Q \phi, \int_0^\infty \int_0^c p(v,c) \, dc \, dv
\]

and

\[
\int_0^\infty \int_0^c \int_v^\infty k_B(x,v) p(x,c) \, dx \, dc \, dv = \int_0^\infty \int_0^c \int_0^v k_B(v,x) p(v,c) \, dx \, dc \, dv
\]

since \( k_B(v,x) = 0 \quad x \geq v \)

For coalescence it is necessary to show that

\[
\int_0^\infty \int_0^c \int_0^v \int_0^x \frac{v^x y(x,v-x) p(x,y) p(v-x)}{x(v-x)^2} \, dx \, dy \, dc \, dv
\]

\[
= \int_0^\infty \int_0^c \int_0^v \int_0^x \frac{v^x y(v,x) p(v,c) p(x,y)}{vx} \, dy \, dx \, dc \, dv
\]
Perform the integrals of $y$ and $c$ to get the following relation to prove.

$$\int_0^\infty \int_0^\infty \frac{v r(x, v-x) p(x) p(v-x)}{x(v-x)} \, dx \, dv = \int_0^\infty \int_0^\infty \frac{v r(y, y-x) p(y) p(v-x)}{v x} \, dx \, dv$$

This equation is easily shown to be true from the following

$$\int_0^\infty \int_0^\infty \frac{v r(x, v-x) p(x) p(v-x)}{x(v-x)} \, dx \, dv = \frac{1}{2} \int_0^\infty \int_0^\infty \frac{v r(x, v-x) p(x) p(v-x)}{x(v-x)} \, dx \, dv$$

using the transformation

$z = v-x$

$x = x$
APPENDIX II

POSSIBLE EFFECTS OF TWEEN 40 SEEPAGE INTO VESSEL

In considering what effect seepage from the sampler of Tween 40 will have on the system, the most difficult problem is that of defining a level of concentration of Tween 40 at which it has a significant effect on coalescence. In trying to solve this problem the data of Lang (9) was used, although it isn't very applicable, because he uses a single drop and somewhat different fluids. Lang found that .00244 millimolar concentration had no significant effect on coalescence rates. In his case this corresponds to a interfacial area per molecule of 66.7 $\text{ag}^2$.

As an example for comparison, consider the case of 20% dispersed phase of average drop size of .25 mm$^3$ in the reactor vessel which has a volume of 1440 cc$^3$. The volume of 3% Tween 40 solution injected into the sample tube when a sample is drawn is 1 cc.

Calculations of the possible concentrations and interfacial area per molecule for various amounts of seepage follow.

<table>
<thead>
<tr>
<th>Percentage of material seeping into vessel</th>
<th>Concentration in vessel</th>
<th>Area available per molecule</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>millimolar</td>
<td>ag$^2$/molecule</td>
</tr>
<tr>
<td>100</td>
<td>.015</td>
<td>16.2</td>
</tr>
<tr>
<td>10</td>
<td>.0015</td>
<td>162</td>
</tr>
<tr>
<td>1</td>
<td>.00015</td>
<td>1620</td>
</tr>
</tbody>
</table>

Thus even if 10% of the surfactant got into the vessel no significant effect should be found.
APPENDIX III

POSSIBLE EFFECTS OF VISCOSITY SURFACE TENSION ON FLOW RATE THROUGH CAPILLARY

Both viscosity and surface tension can cause pressure fluctuations in the lines of the syringe drive. These pressure fluctuations could thus cause variations in flow rate by expansion and contraction of air bubbles in the system or by the teflon connecting tube.

Pressure fluctuations are caused by the differing viscosity of the water and oil as it flows through the capillary. The magnitudes of these fluctuations are now calculated.

The following data for the capillary and fluids are now given.

\[ R = 0.025 \text{ cm} \]
\[ L = 2 \text{ cm} \]
\[ Q = 2.2 \text{ mm}^3/\text{sec} \]
\[ \mu_{\text{water}} = 0.01 \text{ g} \text{m}/\text{cm/ sec} \]
\[ \mu_{\text{oil}} = 0.035 \text{ g} \text{m}/\text{cm/ sec} \]

The Reynolds No. is first checked to show that the flow is laminar.

\[ Re = \frac{Q \rho}{\pi DP} = 2.8 \]

Use Hagen Poiseuille Law to show fluctuations

\[ \Delta P_{\text{flow}} = \frac{8LQ}{\pi R^4} \mu \]

125
thus

\[ \Delta P_{\text{fluc}} = \frac{8QL}{\pi R^4} (N_\text{oil} - N_\text{water}) \]

\[ \Delta P_{\text{fluc}} = 6.78 \times 10^2 \text{ dynes/cm}^2 \]

Pressure fluctuations are also caused by the change on the radius of curvature of the drops as they enter the capillary section.

\[ \Delta p = 2 \sigma \left( \frac{1}{R_2} - \frac{1}{R_1} \right) \]

\[ R_1 = 0.1 \text{ cm} \]

\[ R_2 = 0.025 \text{ cm} \]

\[ \sigma = 51.0 \text{ dynes/cm} \]

\[ \Delta p = 30.6 \times 10^2 \text{ dynes/cm}^2 \]

Thus the two pressure fluctuations are of the same magnitude.

Now the variation in volume caused by the teflon expansion is calculated. The physical dimensions of the tube are given below
Length = 12"
I.D. = .06"
Wall thick = .03"

For calculating the change in volume the following formula is used.

\[ \Delta V = \frac{2\pi R^3 L \Delta P}{TM} \]

\[ M = \text{modulus of elasticity} \]
\[ = 6 \times 10^4 \]

\[ \Delta V = 0.0027 \text{ mm}^3 \]

Calculate the size drop of air in the line which would cause a change of drop size of .002 mm³.

For this the following formula was used

\[ \frac{\Delta V}{V} = \frac{\Delta P}{P} \]

or

\[ V = \frac{P \Delta V}{\Delta P} \]

\[ V = 0.203 \text{ mm}^3 \]

this size drop is easily observable
APPENDIX IV

SPECTROGRAPH OF DYE
APPENDIX IV

CALIBRATIONS

V.1 Rotameter Calibrations
V.2 Zeromax Transmission Calibrations
V.3 Photometer Linearity
Appendix V.1  Rotameter #1

Water with \( \frac{1}{4} \) 15-6-5 tube and glass float

![Graph showing flow rate vs. rotameter reading.](image-url)
Appendix V.1 Rotameter HZ
Light oil with 5/15-6.5 tube and 5.5 float

Flow Rate (cm/min)

Rotameter Reading
(center of float)
Appendix V.1: Rotameter #3

Dark Oil with 8 15-6-5 tube and s.s. float

Flow Rate (c.c./min)

Rotameter Reading (center of float)
Appendix V.2 Zeromax Calibration

Stator Speed (rpm)

Zeromax Reading

0 5 10 15 20 25 30

0 100 200 300 400
Appendix V.3 Photometer Linearity
APPENDIX VI

ERROR CAUSED BY RECORD GAP

\[
\frac{T_m - t}{T_m + T_s} \quad \text{t = time of a drop and } T_m > t > T_s
\]

The probability of a drop not being caught by the record gap is

Thus the probability of being caught is

\[
\frac{T_s + t}{T_m + T_s}
\]

The output distribution of times, \( f_{out}(t) \), is then related to the input distributions of time by the formula

\[
\frac{T_m}{T_m + T_s} f_{out}(t) = \frac{T_m - t}{T_m + T_s} f_{in}(t) + \frac{2T_s}{T_m + T_s} \int_t^{t+T_s} \frac{2t - \varepsilon}{t} f_{in}(\varepsilon) d\varepsilon + \frac{t-T_s}{T_m + T_s} f_{in}(t+T_s)
\]

fraction totally in \( T_m \)

fraction partially in \( T_s \)

135
or
\[ f_{\text{out}}(t) = \left(1 - \frac{t}{T_m}\right) f_{\text{in}}(t) + 2 \phi \int_{t}^{t+T_s} (2 - \frac{\varepsilon}{t}) f_{\text{in}}(\varepsilon) d\varepsilon \]

\[ + \frac{t - T_s}{T_m} f_{\text{in}}(t + T_s) \]

where \( \phi = \frac{T_s}{T_m + T_s} \)

then
\[ t_{\text{out}} = t_{\text{in}} (1 - \phi) \]

For these experiments \( \phi = 0.013 \) for a sampling rate of 40,000 and \( 0.005 \) for a sampling rate of 15,000. Since most experiments were run at 15,000, the error is definitely negligible.
APPENDIX VII

COALESCEENCE OF DROPS IN CAPILLARY

Drop Coalescence
APPENDIX VIII

ASSEMBLY LANGUAGE SUBROUTINES

Two subroutines are listed. CORCT reads number from the tape and stores them. POSTAP rewinds the tape and positions it at the first end of file mark.

This subroutine reads the data from the magnetic tape and un-scrambles the bit data in the memory of the computer. This subroutine is called by the statement CALL CORCT (REG, NBR, EDF). Here REG is an INTEGER*2 array into which the numbers from the tape is stored. NBR, also INTEGER*2, is the location into which the number of bytes in the record read is stored. EOF is the label to which control is returned when an end of file mark is found.

The statement CALL POSTAP in a fortran program causes the tape to be rewound and positioned at the first end of file mark. In using this subroutine the device number 2 must be reserved for the tape drive unit.
1 CORCT CSECT
2 ENTER 12,SA=SAVE
3* USING *,12
4* STM 14,12,12(13)
5* LR 12,15
6* LA 15,SAVE
7* ST 15,8(13)
8* ST 13,4(15)
9* LR 13,15
10 L 2,0(1) ADDRESS OF REGION
11 ST 2,REGION
12 L 2,4(1) ADDRESS OF COUNT
13 LH 2,0(2) LOAD COUNT
14 STH 2,RECLTH STORE COUNT
15 LR 2,1 KEEP POINTER
16 LA 1,=A(ERRRTN) ADD OF ERROR ROUTINE
17 L 15,=V(SETOERR)
18 BALR 14,15
19 L 3,REGION
20 READ 2,(3),RECLTH,EXIT=EOF
21+ CNOP 0,4
22+ ST 3,**+12 THE DATA ADDRESS
23+ L 15,=V(READ)
24+ BAL 1,**+36 BRANCH AROUND CONSTANTS
25+ DC A(3) DATA ADDRESS
26+ DC A(RECLTH) ADDRESS OF LENGTH
27+ DC A(**+20) MODIFIER BITS
28+ DC A(**+12) LINE NUMBER
29+ DC A(**+4) LDN POINTER
30+ DC F'2' LOGICAL DEVICE NUMBER
31+ DC F'0' LINE NUMBER
32+ DC B'00000000000000000000000000000000' MODIFIER BITS
33+ BALR 14,15 BRANCH TO SUBROUTINE
34+ LTR 15,15
35+ BNZ EOF
36 BADREC L 11,REGION
37 USING INAREA,11
38 LH 7,RECLTH
39 L 1,4(2)
40 STH 7,0(1)
41 LA 6,2
42 LA 4,6
43 SR 7,6
44 ZFROLP LH 0,INAREA(4)
45 SRDL 0,6
46 SRL 0,2
47 SDL 0,6
48 STH 0,INAREA(4)
49 BXLE 4,6,ZFROLP
50 RETURN L 13,SAVE+4 RESTORE GR,13
51 RETURN (14,12),T,RC=0
52* LM 14,12,12(13) RESTORE THE REGISTERS
53* MVI 12(13),X'FF' SET RETURN INDICATION
54* LA 15,0(0,0) LOAD RETURN CODE
55* BR 14 RETURN
SOURCE STATEMENT

56  EOF  EXIT  4
57+EOF  L  13,4,(13)
58+  LM  14,12,12,(13)
59+  LA  15,4
60+  BR  14
61  ERRRTN  LM  14,12,12,(11)
62  LA  13,SAVE
63  SPRINT  '0**** BAD RECORD FOUND'
64+  CNOP  0,4
65+  L  15,=V(SPRINT)
66+  BAL  1,=*+26+((L'*##2+1)/2*2) AROUND CONSTANTS
67+  DC  A(*+22) DATA ADDRESS
68+  DC  A(*+16) LENGTH
69+  DC  A(*+8) MODIFIER BITS
70+  DC  F'0' LINE NUMBER
71+  DC  B'00000000000000000000000000000000' MODIFIER BITS
72+  DC  Y(L'*##2) LENGTH
73+##2  DC  C'0**** BAD RECORD FOUND'
74+  BALR  14,15 BRANCH TO SUBROUTINE
75  B  BADREC RETURN TP SUBROUTINE
76  DS  OF
77  SAVE  DS  18F
78  REGION  DS  F
79  RECLTH  DS  H
80  LTOG
81  =A(ERRRTN)
82  =V(SETOERR)
83  =V(READ)
84  =V(SPRINT)
85  PPOSTAP  CSECT.
86  ENTER  12,SA=SAVE1
87+  USING *,12
88+  STM  14,12,12,(13)
89+  LR  12,15
90+  LA  15,SAVE1
91+  ST  15,8,(13)
92+  ST  13,4(15)
93+  LR  13,15
94  WRITE  2,RTS,3,ACC
95+  CNOP  0,4
96+  L  15,=V(WRITE)
97+  BAL  1,=*+38 BRANCH AROUND CONSTANTS
98+  DC  A(RTS) DATA ADDRESS
99+  DC  A(*+28) LENGTH
100+  DC  A(*+20) MODIFIER BITS
101+  DC  A(*+12) LINE NUMBER
102+  DC  A(*+4) LDN POINTER
103+  DC  F'2' LOGICAL DEVICE NUMBER
104+  DC  F'0' LINE NUMBER
105+  DC  B'00000000000000000000000100000000' MODIFIER BITS
106+  DC  Y(3)
107+  BALR  14,15 BRANCH TO SUBROUTINE
108  WRITE  2,FEEOF,3,ACC
109+  CNOP  0,4
110+  L  15,=V(WRITE)
APPENDIX IX

MAIN PROGRAM TO INTERPRET DATA

The main program which calculates the drop volume-dye concentration distribution and other related information is listed on the following pages. The computer symbols for this program and the program in Appendix X are listed together since many are the same.
<table>
<thead>
<tr>
<th>Computer Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Array of tape data.</td>
</tr>
<tr>
<td>ACON</td>
<td>Average concentration.</td>
</tr>
<tr>
<td>ADS</td>
<td>Average drop size (mm³).</td>
</tr>
<tr>
<td>BASE</td>
<td>Base line.</td>
</tr>
<tr>
<td>BB</td>
<td>Weighting factor for base.</td>
</tr>
<tr>
<td>BLOG</td>
<td>Largest log of volume.</td>
</tr>
<tr>
<td>CDIST</td>
<td>Volume-concentration distribution.</td>
</tr>
<tr>
<td>CLDIST</td>
<td>Log volume-concentration distribution.</td>
</tr>
<tr>
<td>CLOG</td>
<td>Log volume difference.</td>
</tr>
<tr>
<td>CMAR</td>
<td>Concentration marginal distribution.</td>
</tr>
<tr>
<td>COAD</td>
<td>Volume times concentration.</td>
</tr>
<tr>
<td>COAD2</td>
<td>Volume times concentration squared.</td>
</tr>
<tr>
<td>CONCL</td>
<td>Minimum concentration.</td>
</tr>
<tr>
<td>CONCLE</td>
<td>Minimum concentration.</td>
</tr>
<tr>
<td>CONCM</td>
<td>Maximum concentration.</td>
</tr>
<tr>
<td>CONCZ</td>
<td>Concentration difference ratio.</td>
</tr>
<tr>
<td>CONT</td>
<td>Concentration difference</td>
</tr>
<tr>
<td>CORCT</td>
<td>Read subroutine.</td>
</tr>
<tr>
<td>CSDT</td>
<td>Volume-concentration distribution.</td>
</tr>
<tr>
<td>CSQD</td>
<td>Log likelihood for bivariate distribution.</td>
</tr>
<tr>
<td>CSQDC</td>
<td>Log likelihood for concentration marginal.</td>
</tr>
<tr>
<td>CSQDV</td>
<td>Log likelihood for volume marginal.</td>
</tr>
<tr>
<td>CVC</td>
<td>Volume concentration correlation.</td>
</tr>
<tr>
<td>C1</td>
<td>First moment of concentration.</td>
</tr>
<tr>
<td>C2</td>
<td>Second moment of concentration.</td>
</tr>
<tr>
<td>C3</td>
<td>Third moment of concentration.</td>
</tr>
</tbody>
</table>
DC  Increment in concentration.
DCC  Increment in concentration.
DCH  Increment in concentration.
DCT  Number concentration marginal.
DENI  Log of probability.
DENJ  Log of probability.
DIST  Volume-concentration distribution.
DLV  Increment in log-volume.
DLVV  Increment in log-volume
DM  Increment in moles.
DMAX  Largest drop volume found.
DMIN  Smallest drop volume measured.
DPC  Percent of volume in upper volume range.
DRM  Volume of drop for upper range.
DST  Number probability distribution.
DV  Increment in volume.
DVM  Increment in volume.
DVT  Number volume marginal.
DVV  Increment in volume.
FAC  Analog multiplication factor by tape speed
FCON  Concentration.
FCONC  Array with maximum and minimum concentration.
FREQ  Frequency of digital samples.
FRT  Flow rate through capillary.
FSF  Contains FSF
I  Iteration variable.
IBASE  Integer of BASE.
IE Iteration variable.
IKT Iteration variable.
INBR Numbers per tape record.
IPRT INBR-24.
ISREC Number of files skipped.
ITMZ Iteration variable.
IYT Iteration variable.
IZT Iteration variable.
I Iteration variable.
J Iteration variable.
JCC Subscript.
JCCC Subscript.
JCLC Subscript.
JKK Subscript.
JKKK Subscript.
JLV Subscript.
JMM Subscript.
JNN Subscript.
JVV Subscript.
K Iteration variable.
KGB Dummy variable.
KLEV Concentration at a point
KLEV1 Concentration at a point.
KLEV2 Concentration at a point.
KLEV3 Concentration at a point.
KOLT Drop count difference.
KONC Array of drop concentrations.
NORG  Number of record groups.
NOS   Number of skipped drops.
NSSB  Number of samples to set base.
NSSBS NSSB stored.
NSPDA Indicator variable for punch.
NSTDA Indicator variable for store.
NVT   Number of drops per increment.
OPT   Output format.
OPTA  Output format.
OPTB  Output format.
OPTM  Output format.
POSTAP Tape positioning subroutine.
SDR   Smallest drop to be measured.
SLOG  Log of smallest drop.
SMC   Second moment concentration.
SMCAV Second moment concentration average volume.
SMV   Second moment volume.
SMVAC Second moment volume average concentration.
SOAD  Volume of drop.
SOAD2 Volume of drop squared.
SOAD3 Volume of drop cubed.
SOEK  Size of each count.
STOT  Total volume of oil.
SUM   Summing variable.
S1    Sum of volumes.
S1C1  Sum of volume times concentration.
S1C2  Sum of volume times concentration squared.
$S_2$  
Sum of volume squared.

$S_{2C1}$  
Sum of volume squared times concentration.

$S_3$  
Sum of volume cubed.

$TMC$  
Third moment concentration.

$TMV$  
Third moment volume.

$TNUM$  
Total number of drops.

$TOTZ$  
Sum of number of drops.

$TVOL$  
Total counts of oil.

$UNUM$  
Log of $TOTZ/TNUM$.

$VLMAR$  
Log volume marginal.

$VMAR$  
Volume marginal.

$ZMOL$  
Maximum moles in a drop.

$ZHOLE$  
Moles per drop.
INTEGER *2 A(15050), NBR, LEN

DIMENSION KONT(6000), ZMOLE(6000), DIST(32, 32), MDST(32, 32), LMQOL(40)

DIMENSION OTP(20), KNGC(10000), CDIST(32, 32), FCONC(2), CLDST(32, 32)

DIMENSION VMAP(30), VLMAP(30), CMAP(30), OPTM(20)

DIMENSION CSDLT(32, 32), OPTA(20), OPTB(20)

572 FORMAT (611, 3F12.4)
571 FORMAT (25(1X, 7E14.6))
52 FORMAT (1C18/1D18)
17 FORMAT (311, 2F10.4)
117 FORMAT (?2I4)
23 FORMAT (1111)
07 FORMAT (20A4)
52 FORMAT (2F15.6)
57 FORMAT (1115, 5F14.6)
5 FORMAT (81S, 5F8.4)

DATA ESF, LEN, MOD/*ESF*, 3, 129/
READ(5, 5) NBR, NSSB, NLEV, NOS, NDIM, NBJ, NORG, NMA, RB, FPT, FAC, FREO, SDR
READ(5, 17) NSPDA, NSTDA, NDIP, NPC, DPM
NSSBS=NSSB

LT=0
KOUNT=0
MOLES=0
MKONT=0
NOS=0
CONCM=0.0
CONCL=100.0
ZMQOL=0.0
DO 74 I=1, 44
74 LMOL(I)=0
BASE=0.0
NOR=0
L=0
NKS0=SDR*FREQ/(2.0*FRT*FAC*NOS)
SOEK=FRT*FAC*NOS*2.0/FREQ
CALL POSTAP

IF(NOD.NE.0) GO TO 73
CALL CORCT(A, NBR, 622)
INR=NBR/2
NOD=NOD+1
DO 23 I=4, INR, 25
IF(I.GT.1004) GO TO 24
BASE=BASE+4(I)/40.0
GO TO 23
24 IBASE=BASE
KLEV=A(I)-IBASE
IF(KLEV.LE.NLFV) GO TO 26
LT=LT+1
FCON=FCONA+KLEV
GO TO 23
26 BASE=BASE*30.0+A(I))/30.0
CONTINUE
FCONC(NQG)=FCON/LT
IF(NOD.EQ.1) GO TO 28
WRITE (6, 32) (FCONC(I), I=1, 2)
1TMZ=0
READ(5,93) ISFEC
71 IF(ISFEC.GE.ISFEC) GO TO 70
CALL WRITE(ESE,LEN,MOD,0,2)
ITMZ=ITVZ+1
GO TO 71
70 CALL CORCT(A,NBR,SBR)
INBR=NBR/2
IPRT=INBR/2
WRITE(5,711) (A(I),I=1,25)
WRITE(4,711) (A(I),I=IPRT,INBR)
NOR=NOR+1
IF(NOR.GT.1) NSSS=4
IF(NOR.GT.1) GO TO 30
20 DO 30 I=4,NSSS
BASE=BASE+A(I)/(NSSS+0.0001)
IBASE=BASE
30 DO 60 I=NSSS,INBR,NOS
IF(A(I).EQ.0) GO TO 50
IF(A(I).EQ.1023) GO TO 50
KLEV1=IBASE-A(I)
IF(KLEV1.LE.KLEV) GO TO 40
KOUNT=KOUNT+1
MOLES=MOLES+KLEV1
GO TO 50
40 IF(KOUNT.LT.NKSD) GO TO 51
L=L+1
KONT(L)=KOUNT
ZMOLE(L)=MOLES
KONC(L)=MOLES/KOUNT
IF(KOUNT.GT.KONT) MKONT=KOUNT
IF(KONC(L).GT.CONCM) CONCM=KONC(L)
IF(KONC(L).LT.CONCL) CONCL=KONC(L)
50 IF(KLEV1.GT.50) GO TO 50
BASE=(BB*BASE+A(I))/(BB+1.0)
IBASE=BASE
50 KOUNT=3
MOLES=0
60 CONTINUE
WRITE(6,572) L,MKONT,NBR,IBASE,NOR,KOUNT,CONCM,CONCL
GO TO 70
80 NO5=NO5+1
IF(NO5.GE.NO5) GO TO 63
NOR=0
NSSS=NSSS
BASE=0.0
GO TO 73
53 CONTINUE
STOT=0.0
S1=0.0
C1=0.0
S2=0.0
S1C1=0.0
C2=0.0
S3=0.0
S2C1=0.0
SIC2=0.0
C3=0.0
DO 78 I=1,L
SOAD=KONT(I)*S0EK
S0AD2=S0AD*S0AD
S0AD3=S0AD2*S0AD
CONCZ=(KCONC(I)-CONCL)/(CONCM-CONCL)
COAD=S0AD*CONCZ
COACZ=COAD*CONCZ
STOT=STOT+S0AD
S1=S1+S0AD
C1=C1+COAD
S2=S2+S0AD
S1C1=S1C1+S0AD*COAD
C2=C2+COAD2
S3=S3+S0AD2*S0AD
S2C1=S2C1+S0AD2*COAD
S1C2=S1C2+S0AD*COACZ
C3=C3+COAD*CONCZ
ZMOLF(I)=ZMOLF(I)-KONT(I)*CONCL
IF (ZMOLF(I),GT,0.0) ZMOL=ZMOLF(I)
IF(KONT(I),LE,LMOL(I)) GO TO 78
DO 72 I=2,40
IF (KONT(I),LT,LMOL(I)) GO TO 77
72 LMOL(I+1)=LMOL(I)
I=I+1
77 LMO=LMOL(I-1)
CONTINUE
SUM=0.0
DO 53 I=0,38
I=I-1
SUM=SUM+LMOL(I)*S0EK/STOT
IF(SUM,GT,0.0,AND,LMO,LE,LMOL(I-1)) GO TO 54
53 CONTINUE
54 LMO=LMOL(I-1)
IF(DM.I,GT,0.0) LMO=DM/S0EK
DO 21 I=1,NDM
VMAR(I)=0.0
VMLAR(I)=0.0
CMAR(I)=0.0
KAR=NTP
IF(NDIM,GT,NDIM) KAR=NDIM
DO 85 I=1,KAR
DO 85 J=1,KAR
CDIST(I,J)=0.0
CDST(I,J)=0.0
CLOST(I,J)=0.0
85 MDST(I,J)=0
DCM=(COACM-CONCL)/(NDIM-0.001)
DVM=(LMV-NMD)/(NDIM-1.001)
DC=(COACM-CONCL)/(NDIM-0.001)
DM=ZMOL/(NDIM-0.001)
DV=(MMNT-NMD)/(NDIM-0.001)
DIV=(MKT-NMD)/(NMA-0.001)
DCG=(COACM-CONCL)/(NMA-0.001)
BLOG = ALCG (MKONT + 0.0001)
SLOG = ALCG (NKSD + 0.0001)
DLV = (BLOG - SLOG) / (NDIM - 0.0001)
DLVV = (BLOG - SLOG) / (NMA - 0.001)
KTOT = ?
DO 90 I = 1, L, 1
KZT = KONT(I)
KTOT = KTOT + KZT
CLOG = ALCG (KZT + 0.0001) - SLOG
CONT = KCONC(I) - CONCL
KOLT = KZT - NKSC
JKK = CLOG / DLV
JMMM = ZMOLE(I) / DM
JCC = CONT / DC
JNN = KOLT / DV
JVV = KOLT / DVV
JLVC = CLOG / DLVV
JCCLC = CONT / DCC
JKKK = KOLT / VM
JCCC = CONT / DCV
IF (JKKK .GE. NDIP) JKKK = NDIP - 1
VMAR(JVV + 1) = VMAR(JVV + 1) + KONT(I)
VLMAR(JLV + 1) = VLMAR(JLV + 1) + KONT(I)
CMAR(JCLC + 1) = CMAR(JCLC + 1) + KONT(I)
CODIST (JKK + 1, JCC + 1) = CODIST (JKK + 1, JCC + 1) + KONT(I)
CODST (JKKK + 1, JCCC + 1) = CODST (JKKK + 1, JCCC + 1) + KZT
CLUDST (JNN + 1, JCC + 1) = CLDIST (JNN + 1, JCC + 1) + KONT(I)
CLUDST (JKK + 1, JMMM + 1) = CLDIST (JKK + 1, JMMM + 1) + KONT(I)
TVOL = KTOT
DO 25 I = 1, NMA
VMAR(I) = VMAR(I) / TVOL
VLMAR(I) = VLMAR(I) / TVOL
CMAR(I) = CMAR(I) / TVOL
KGB = NDIP
IF (NDIM .GT. NDIP) KGB = NDIM
DO 95 I = 1, KGB
DO 95 J = 1, KGB
CSDT(I, J) = CSST(I, J) / TVOL
CLUDST(I, J) = CLDIST(I, J) / TVOL
CLUDST(I, J) = CLDIST(I, J) / TVOL
CLUDST(I, J) = CLDIST(I, J) / TVOL
ADST = S1 / STOT
SMV = S2 / STOT
TMV = S3 / STOT
CVC = S1C1 / STOT
SMC = C2 / STOT
TMC = C3 / STOT
ACONC = C1 / STOT
SMVAC = S2C1 / STOT
SMVAC = S1C2 / STOT
DMAX = MKONT * SOEK
DRM = LMO * SOEK
DMIN = (NKSD) * SOEK
WRITE (5, 87) MKONT, DMAX, DMIN, DRM, CONCM, CONCL
WRITE (6, 87) L, ADS, SMV, TMV, CVC, SMVAC
WRITE(6,97) NKSD,ACON,SMC,THC,SMCAV,STOT
READ (5,7) (CTP(I),I=1,20)
WRITE (6,OTP) ((CLUD(I,J),J=1,NDIM),I=1,NDIM)
WRITE (6,OTP) ((CLUD(I,J),J=1,NDIM),I=1,NDIM)
WRITE (6,OTP) ((CLUD(I,J),J=1,NDIM),I=1,NDIM)
READ(5,7) (OPTM(I),I=1,20)
WRITE(6,OPTM) (VMAR(I),I=1,NMA), (VMAR(I),I=1,NMA), (CMAP(I),
I=1, NMA)
READ (5,7) (OPTA(I),I=1,20)
WRITE(6,OPTA) ((CSOT(I,J),J=1,NDIP),I=1,NDIP)
IF (NSP(a,LT,1) GO TO 18
WRITE(4,717) (KONT(I),KONC(I),I=1,L)
IF (NSTD(a,LT,1) GO TO 19
READ (5,7) (OPTR(I),I=1,20)
WRITE(7,97) L,DMAX,DMIN,ADS,SMV,CVC
WRITE(7,97) L,CONCL,CONCM,SOEK,TVOL,STOT
WRITE(7,92) (LMOL(I),I=1,20)
WRITE(7,OPTR) (KONT(I),KONC(I),I=1,L)
CONTINUE
END
APPENDIX X

PROGRAM TO TEST DATA
   The program which applies the likelihood ratio test to different experimental samples is given in the following pages. The symbols for this program are listed in Appendix IX since many symbols are the same in the two programs.
IMPLICIT REAL*8 (A-E, I-Z)
INTEGER*2  NBR
DIMENSION KCNT(66), CONC(6000), LMCL(40), FCCCA (2), DST(2,20,20)
DIMENSION NIFS(2,20), OPTA(20)
DIMENSION AVT(2,20), NCT(2,20), DVT(2,20), CCT(2,20)
FORMAT(2F15.6)
FORMAT(3(E5F15.6))
FORMAT(I1C)
FORMAT(2F15.6)
FORMAT (2CA4)
FORMAT (E15.5)
IZT=0
IYT=2
READ(5,11C) NCCy
READ (5,7) (OPTA(I), I=1,20)
CO 115 MIT=1,ACC
NSSE=NSSE
READ(5,5) NBR, NNESS, NLEV, NGS, NOIM, ACC, NCG, NMA, PB, FT, FAC, FREC, SCF
LT=0
KCLNT=0
MCLES=C
MKCNT=0
NCG=C
CCMCM=C.C
CCACL=10CC00.C
CC 74 I=1,C
LMCL(I)=C
BASE=C.C
NCR=C
L=C
NKS=SDR*FREC/(2.0*FT+FAC*NGS)
SOE=FT+FAC*NGS*2.0/FREO
INER=NBR/2
IF (IZT.GE.1) GC TC 104
  CALL PCSTAP
  CONTINUE
IF(NCC.NE.C) GC TC 70
  CALL CCRCT(A, NBR, &?)
ACC=NCC+1
  GC 23 I=4, INBR, 25
  IF(I.GT.1CC4) GC TC 24
  BASE=BASE+A(I)/40.0
  GC TC 23
  IBASE=BASE
  KLEV=A(I)-IBASE
  IF (KLEV.LF.NLEV) GC TC 26
  LT=LT+1
  FCCCA=FCCCA+KLEV
  GC TC 23
  BASE=IBASE+C.C+A(I)/31.0
  CONTINUE
  FCCA(NCC)=FCCCA/LT
  IF (NCC.NE.1) GC TC 28
  WRITE (6,52) (FCCC(I), I=1,2)
  CALL CCRCT(A, NBR, &E)
NCR=NCR+1
IF(NCR GT 1) NSSP=4
IF(NCR GT 1) GC TO 30
20 Base=Base+A(I)/(NSSE+C.C0C1)
IEASE=Base
30 DO 60 I=NSSP,INPS,ACS
KLEV3=A(I+1)-IEASE
KLEV1=A(I)-IEASE
KLEV2=A(I-1)-IEASE
IF(KLEV1.LE.KLEV.AND.(KLEV2.LE.KLEV.OR.KLEV2.LE.KLEV1)) GO TO 40
KCNT=KCNT+1
MCLES=MCLES+KLEV1
GO TO 60
40 IF(KCNET LT AKSC) GO TO 50
L=L+1
KCNT(L)=KCNT
CCNC(L)=MCLES/(KCNT+C.C0C1)
IF(KCNET(L).LE.LMKCL(I)) GC TO 78
60 DC 72 I=2,4C
IF(KCNET(L).LT.LMKCL(I1)) GC TO 77
72 LMKCL(I1-1)=LMKCL(I1)
I1=I1+1
77 LMKCL(I1-1)=KCNT(L)
80 CONTINUE
IF(KCNET.GT.MKNET) MKNET=KCNET
IF(CCNC(L).GT.CNCY) CNCY=CCNC(L)
IF(CCNC(I1).LT.CNCY) CNCY=CCNC(L)
KCNET=0
MCLES=0
IEASE=(BB+BASE+A(I))/(BB+1.C)
IPASE=BASE
60 CONTINUE
GO TO 70
80 NCC=NCC+1
IF(NCC.GE.NCR) GC TO 63
NCR=C
NSSP=NSSPS
BASE=C.C
GO TO 70
63 CONTINUE
IZT=IZT+1
IF(IZT.GE.2) GC TO 121
IZT=2
GO TO 122
121 IYT=1
122 CONTINUE
GC 48 I=1,ACIN
GC 48 J=1,ACIN
NIES(IYT,T,J)=C
CST(IYT,I,J)=C.C
IF(IZT.GT.1) GC TO 41
LST=L
LMC=LMKCL(4C-AMA)
EMIN=AKSC*SCEK
CV=(LNC*AKSD)/(NCIV-C.C001)*SCEK
CONCLE=CONCL
DC=(CCCLCM/CONCL)/(NCIV-C.C001)

41 DC 42 I=1,1
JN=(KCNT(I)*SCEK-C*1N)/DV+1.0
JC=(CCCLCM-CONCL)/CC+1.0
IF (JN.LT.1) JN=1
IF (JC.LT.1) JC=1
IF (JN.GT.NCIM) JN=NCIM
IF (JC.GT.NCIM) JC=NCIM
NIES(IYT,JV,JC)=NIES(IYT,JV,JC)+1

42 CST(IYT,JV,JC)=CST(IYT,JV,JC)+1.0/L
IF (LT.LT.2) CC TC 46
CC 49 IKT=1,2
WRITE(6,CFTA) ((CST(IKT,I,J),J=1,NCIM),I=1,NCIM)

TNLK=L+LST
CSQD=C.C

CC 47 I=1,NCIM
DO 47 J=1,NCIM

TCTZ=NIES(1,I,J)+NIES(2,I,J)
IF(NIES(2,I,J),AE,C) CENJ=DLCG(CST(2,I,J))
IF(NIES(1,I,J),AE,C) CENJ=DLCG(CST(1,I,J))
IF(TOTZ,AE,C,C) UNLY=DLCG(TOTZ/TNUM)

47 CSQD=CSQD+2.0*(TSTZ+UNLY-NIES(1,1,J)*CENJ-NIES(2,1,J)*DENJ)
WRITE(6,CFTA) (CST(IKT,I,J),J=1,NCIM),I=1,NCIM

DC 154 K=1,2
DC 152 I=1,NCIM

ACT(K,I)=C
NVT(K,I)=C

CST(K,I)=C.C

CV(K,I)=C.C

DO 153 J=1,NCIM

CST(K,I)=CST(K,I)+CST(K,J,I)
CV(K,I)=CVT(K,I)+CST(K,I,J)
NVT(K,I)=NVT(K,I)+NIES(K,T,J)
ACT(K,I)=ACT(K,I)+NIES(K,J,I)

154 WRITE(6,CFTA) (CST(K,I),I=1,NCIM)
WRITE(6,CFTA) (CV(K,I),I=1,NCIM)

CQSDV=C.C
CQSCC=C.C

DC 156 I=1,NCIM

TCTZ=NVT(1,I)+NVT(2,I)
TCTV=ACT(1,I)+ACT(2,I)
IF(NVT(1,I),AE,C) DENJ=DLCG(CVT(1,I))
IF(NVT(2,I),AE,C) DENJ=DLCG(CVT(2,I))
IF(TOTZ,AE,E,0) UNLY=DLCG(TCTZ/TNUM)

CQSCV=CQSCV+2.0*(NVT(1,I)*DENJ*NVT(2,I)*DENJ-TCTZ*UNLY)
IF(NCT(2,I),AE,C) DENJ=CCLC(CCT(2,I))
IF(NCT(1,I),AE,C) DENJ=CCLC(CCT(1,I))
IF(TCTY,AE,E,0) UNLY=DLCG(TCTY/TNUM)

156 CQSCC=CQSCC+2.0*(NCT(1,I)*DENJ*NCT(2,I)*DENJ-TCTY*UNLY)
WRITE(6,163) CQSCV,CQSCC

115 LST=L
CONTINUE

END
APPENDIX XI

LEAST SQUARES PROGRAM

The following pages contain a listing of the program used to apply the least squares method to the experimental data. The subroutine RANDU, as called by this program, is listed in IBM SSP manual.
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADS</td>
<td>Average drop size.</td>
</tr>
<tr>
<td>AJCK</td>
<td>Variable used in matrix inversion.</td>
</tr>
<tr>
<td>BET</td>
<td>Kernel value at all positive minimum.</td>
</tr>
<tr>
<td>BETA</td>
<td>Kernel value at minimum.</td>
</tr>
<tr>
<td>BI</td>
<td>Used in eigenvector calculation.</td>
</tr>
<tr>
<td>BIGA</td>
<td>Pivot in matrix inversion.</td>
</tr>
<tr>
<td>BIN</td>
<td>Breakage flux in.</td>
</tr>
<tr>
<td>BL</td>
<td>Coefficients for breakage out.</td>
</tr>
<tr>
<td>BR</td>
<td>Coefficients for breakage in.</td>
</tr>
<tr>
<td>BOU</td>
<td>Breakage flux out.</td>
</tr>
<tr>
<td>CIN</td>
<td>Coalescence flux in.</td>
</tr>
<tr>
<td>CLDST</td>
<td>Volume-concentration distribution.</td>
</tr>
<tr>
<td>CO</td>
<td>Coefficients for coalescence in.</td>
</tr>
<tr>
<td>COEF</td>
<td>Array of coefficients in.</td>
</tr>
<tr>
<td>CONCL</td>
<td>Minimum concentration</td>
</tr>
<tr>
<td>COMCM</td>
<td>Maximum concentration</td>
</tr>
<tr>
<td>COU</td>
<td>Coalescence flux out</td>
</tr>
<tr>
<td>CSA</td>
<td>Cosine for rotation in eigenvector calculation.</td>
</tr>
<tr>
<td>CTDST</td>
<td>Distribution calculated by pseudo-maximum likelihood method.</td>
</tr>
<tr>
<td>CTP</td>
<td>Upper percent of distribution.</td>
</tr>
<tr>
<td>CU</td>
<td>Coefficients for coalescence out.</td>
</tr>
<tr>
<td>CVC</td>
<td>Volume concentration correlation.</td>
</tr>
<tr>
<td>DCC</td>
<td>Concentration increment.</td>
</tr>
<tr>
<td>DEL</td>
<td>Estimate of variance.</td>
</tr>
<tr>
<td>DELTS</td>
<td>Size of increment for search stop.</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>DELTT</td>
<td>Step size in search.</td>
</tr>
<tr>
<td>DIVF</td>
<td>Divisor in program.</td>
</tr>
<tr>
<td>DMAX</td>
<td>Largest drop volume.</td>
</tr>
<tr>
<td>DMIN</td>
<td>Smallest drop volume.</td>
</tr>
<tr>
<td>DRM</td>
<td>Drop volume for upper percent.</td>
</tr>
<tr>
<td>DV</td>
<td>Volume increment.</td>
</tr>
<tr>
<td>DUV</td>
<td>Volume increment.</td>
</tr>
<tr>
<td>FACTE</td>
<td>Breakage factor.</td>
</tr>
<tr>
<td>FAIN</td>
<td>Array of input probabilities.</td>
</tr>
<tr>
<td>FRAT</td>
<td>Factor in program.</td>
</tr>
<tr>
<td>FRT12</td>
<td>Flow rate in of light oil (cc/min).</td>
</tr>
<tr>
<td>FRT13</td>
<td>Flow rate in of dark oil (cc/min).</td>
</tr>
<tr>
<td>HOLDI</td>
<td>Factor in matrix inversion.</td>
</tr>
<tr>
<td>HOLDK</td>
<td>Factor in matrix inversion.</td>
</tr>
<tr>
<td>I</td>
<td>Iteration variable.</td>
</tr>
<tr>
<td>IE</td>
<td>Iteration variable.</td>
</tr>
<tr>
<td>INTG</td>
<td>Number of distribution increments per kernel increment.</td>
</tr>
<tr>
<td>IR1</td>
<td>Subscript used in matrix inversion.</td>
</tr>
<tr>
<td>IR2</td>
<td>Subscript used in matrix inversion.</td>
</tr>
<tr>
<td>ITER</td>
<td>Iteration variable.</td>
</tr>
<tr>
<td>IVI</td>
<td>Subscript.</td>
</tr>
<tr>
<td>IVJ</td>
<td>Subscript.</td>
</tr>
<tr>
<td>IX</td>
<td>Number used in RANDU.</td>
</tr>
<tr>
<td>IY</td>
<td>Number used in RANDU.</td>
</tr>
<tr>
<td>IT1</td>
<td>Iteration variable.</td>
</tr>
<tr>
<td>IT2</td>
<td>Iteration variable.</td>
</tr>
</tbody>
</table>
12 Iteration variable.
13 Iteration variable.
14 Iteration variable.
15 Iteration variable.
16 Iteration variable.
17 Iteration variable.
J Iteration variable.
JC1 Subscript.
JCJ Subscript.
JKK Subscript.
JLL Subscript.
JVI Subscript.
JVJ Subscript.
JZC Subscript.
JZK Subscript.
K Subscript.
KC Subscript.
KDIUS Divisions in kernel space.
KDIV KDIUS + 1.
KMTS KDIUS + 1.
KONC Array of drop concentrations.
KONT Array of drop counts.
KV Subscript.
L Number of drops in sample.
LKY Subscript.
LKZ Subscript.
M Subscript.
MVV  Subscript.
NDIMS Number of divisions in distribution space.
ND2  Number of kernel values
ND3  ND2-1.
NFC  Number of drops considered in coalescence.
NFD  NFC-1.
NOSD Number of skipped drops.
NO2  Number of drops per second of light oil input.
NO3  Number of drops per second of dark oil input.
NRU  Sorting array.
NST  Starting value for RANDU.
NT   Iteration variable.
NVV  Subscript.
OPTB Format storage array.
OPTT Format storage array.
OPTZ Format storage array.
P8   Power in breakage assumed form.
PIPC Power in coalescence assumed form
POPC Power in coalescence assumed form
PRAB Probability of drop.
PRBI Probability of drop.
PROBJ Probability of drop times assumed form factor.
PROVI Probability of drop timed drop volume.
PROVJ Probability of drop times drop volume and assumed form factor.
Q    Number used in eigenvector calculation.
RANDU Randon number subroutine.
SAVB Storage of BETA.
SBETA  Storage of BETA.
SCI    Concentration of drop
SCJ    Concentration of drop.
SCMX   Variable in search.
SIZ2   Volume of light oil input drop.
SIZ3   Volume of dark oil input drop.
SLV    Drop volume array for coalescence.
SLC    Drop concentration array for coalescence.
SMAX   Variable in search.
SMV    Second moment volume.
SNA    Sine of rotation in eigenvalue calculation.
S0EK   Size of each count.
SP     Variable in eigenvalue calculation.
SPI    Variable in eigenvalue calculation.
SPQ    Variable in eigenvalue calculation.
STOT   Total volume of oil in sample.
STPRO  Probability sum.
STUC   Sum of squares at constrained maximum.
STUG   Value of sum of kernel difference.
STUM   Value of squares at maximum.
STUR   SUML storage.
SUM    Summing variable.
SUML   Summing variable.
SV     Drop volume.
SVI    Drop volume in coalescence.
SVJ    Drop volume in coalescence.
TCDR   Total volume involved in coalescence
<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEST</td>
<td>Test variable for quadratic search.</td>
</tr>
<tr>
<td>TEST1</td>
<td>Test variable for quadratic search.</td>
</tr>
<tr>
<td>TOSUM</td>
<td>Variable in eigenvalue calculation.</td>
</tr>
<tr>
<td>TVOL</td>
<td>Total counts of oil.</td>
</tr>
<tr>
<td>TVRE</td>
<td>Total counts skipped.</td>
</tr>
<tr>
<td>YFL</td>
<td>Variable output of RANDU.</td>
</tr>
<tr>
<td>YM</td>
<td>Dummy array and confidence intervals.</td>
</tr>
<tr>
<td>YPS</td>
<td>Array for least squares.</td>
</tr>
</tbody>
</table>
IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION CDEF(50,50),YPS(50),IR1(50),IR2(50),YM(50),BETA(50)
DIMENSION FR(6,6,14,16), GO(6,6,16,16), OPTT(201), OPTZ(20)
DIMENSION CLOST(32,32), NPARU(6000), SVL(4000), SLG(4000), BST(50)
DIMENSION KONT(6000), KONG(6000), BT(50,50), LMOL(20), OPTB(20)

173  FORMAT(3F12.4)
550  FORMAT(10I5,6)
16  FORMAT(210,3F10.4,5I5)
279  FORMAT(401L6,6)
34  FORMAT(10X,1AHPIVOT IS TOO SMALL)
87  FORMAT(1115,5E14.6)
52  FORMAT(10I8/10I8)
7  FORMAT(20A4)
901  FORMAT(110)
READ(5,16) NDIMS,KDIUS,CTR,PRTL2,PRTL3,NO2,NO3,NOSD,NST,NFC
READ(5,172) PIPC,ROPC,PB
READ(7,87) L,DMAX,DMIN,ADS,SMV,CVC
READ(7,87) L,CONCL,CONCH,SOEK,TVOL,STOT
READ(7,52) (LMOL(I),I=1,20)
READ(5,7) (OPTB(I),I=1,20)
READ(7,OPT6) (KONT(I),KONG(I),I=1,L)
SUM=0.0
DO 51 IE=1,10
   I=20-IE+1
   SUM=SUM+LMOL(I)/TVOL
IF (SUM.GT.CTR.AND. LMOL(I-1).NE.LMOL(I)) GO TO 67
51  CONTINUE
67  DVR=LMOL(I-1)*SOEK
WRITE(6,97) L,DMAX,DMIN,DRM,ADS,STOT
KNTS=KDIUS+1
DO 57 J=1,NDIMS
   DO 56 K=1,KNTS
      CLOST(I,J)=0.0
   END DO
   DO 57 K=1,KNTS
   GO TO 57
57  CONTINUE
56  DCC=(CONCL-CONCL)/(NDIMS-0.0001)
DV=DRM/(NDIMS-1.0001)
DV=DRM/(KDIUS-0.0001)
DO 84 I=1,L
54  NRU(I)=0
TVRE=O.0
IX=NST
NT=0
121  IF (NT.GE.NOSD) GO TO 66
CALL RANDU(IX,IY,YFL)
IX=IX
K=YFL+L+1.0
IF (NRU(K),NE.0) GO TO 121
NT=NT+1
NRU(K)=1
TVRE=TVRE+KONT(K)
GO TO 121
119 IF(JCV.GE.NDIM) NCV=0
120 GOTO 119
121 IF(JCV.GT.1) GOTO 122
122 CALL RANU(IX, IY, IYL)
123 DO 124 J=1, L
124 IF(NRUI(J).NE.1) GO TO 123
125 DO 126 J=1, L
126 IF(NRUI(J).NE.1) GO TO 125
127 DO 128 J=1, L
128 IF(NRUI(J).NE.1) GO TO 127
129 DO 130 J=1, L
130 IF(NRUI(J).NE.1) GO TO 129
131 CONTINUE
132 CONTINUE
133 READ (5, 7) (OPTT(I), I=1, 20)
134 WRITE (6, OPTT) ((CLOST(I, J), I=1, NDIM), J=1, NDIM)
135 TCV=TCRD+SOEK
136 NFD=NFC-1
137 DO 138 I=1, NFD
138 SVI=SLV(I)
139 SCI=SLC(I)
140 PROB=SVI/TCV
141 PROVI=SVI*PROB
142 JV1=SVI/DOV+1.0
143 IF(JV1.LE.NDIM) GO TO 148
144 JV1=NDIM
145 J=J+1
146 CONTINUE
147 NCF=1
148 DO 149 J=1, NCF
149 IF(JC.J.GT.NDIM) JC.J=NDIM
150 K=K+1
151 DO 153 J=1, NCF
152 IF(JV1.L.E.NDIM) JV1=NDIM
153 J=J+1
154 CONTINUE
155 IF(JV1.L.E.NDIM) GO TO 131
JVJ=NDIMS
IVJ=KDIOUS+1
131 IF(JVJ+JVJ-2*NDIMS) 132,117,117
132 JCJ=SCJ/DOC+1.0
IF(JCJ.GT.NDIMS) JCJ=NDIMS
KV=(SVI+SVJ)/DOV+1.0
IF(KV.GT.NDIMS) KV=NDIMS
KC=(SCI*SVI+SCJ*SVJ)/(SVI+SVJ)/DOC+1.0
IF(KC.GT.NDIMS) KC=NDIMS
PROBJ=(SVJ*SVI)*POPC/(SVJ*SVI)^*IPC*SVJ/TCV
PROVJ=SVJ*PROBJ
CONTINUE
117 CONTINUE
124 CONTINUE
KDIOUS=KDIOUS+1
DO 55 I=1,NDIMS
DO 55 J=1,NDIMS
DO 55 I2=2,KDIV
C0I(I2-1,12-1,1,K)=2.0*COI(I2-1,12-1,1,K)
I3=I2-1
DO 55 I4=1,13
55 CONTINUE
CONTINUE
IF(JJLL.GE.NDIMS) JJLL=NDIMS-1
IF (JKK.GE.NDIMS) JKK=NDIMS-1
CLOST(JKK+1,1)=CLOST(JKK+1,1)-FRT12/(FRT12+FRT13)
CLOST(JJLL+1,NDIMS)=CLOST(JJLL+1,NDIMS)-FRT13/(FRT12+FRT13)
ND2=(KDIOUS+1)*(KDIOUS+1)-1+KDIV
DO 45 I=1,ND2
50 CONTINUE
YPS(I)=0.0
50 CONTINUE
DO 45 J=1,ND2
DO 44 I1=1,13
IF(I1,EO,KDIV,AND,12,EO,KDIV) GO TO 44
44 CONTINUE
LKZ=LKZ+1
LKY=0
DO 46 I3=1,KDIV
DO 46 I4=1,13
46 CONTINUE
IF(I3,EO,KDIV,AND,14,EO,KDIV) GO TO 134
46 CONTINUE
LKZ=LKZ+1
LKYY=LKY
DO 47 I3=1,KDIV
DO 47 I4=1,13
47 CONTINUE
LKY=LKY+1
DO 48 I5=1,NDMS
DO 48 I6=1,NDMS
IF (LKZ.EQ.1) YPS(LKY)=YPS(LKY)+BR(I3,I4,I5,I6)*CLOST(I5,I6)
48 COEFF(LKZ,LKY)=COEFF(LKZ,LKY)+CO(I1,I2,I5,I6)*BR(I3,I4,I5,I6)
47 COEFF(LKY,LKZ)=COEFF(LKZ,LKY)
44 CONTINUE
DO 42 I1=1,KDIV
DO 42 I2=1,I1
LKZ=LKZ+1
LKY=LKY+1
DO 43 I3=1,KDIV
DO 43 I4=1,I3
LKY=LKY+1
DO 43 I5=1,NDMS
DO 43 I6=1,NDMS
43 COEFF(LKZ,LKY)=COEFF(LKZ,LKY)+BR(I1,I2,I5,I6)*BR(I3,I4,I5,I6)
42 CONTINUE
TEST1=10000.0
DELT1=100.0
DO 221 I=1,ND2
221 BETA(I)=0.0
DO 210 I=1,1000
DO 211 J=1,ND2
YH(J)=0.0
212 YH(J)=YH(J)-COEFF(J,K)*BETA(K)
211 YH(J)=YH(J)+YPS(J)
TEST=0.0
DO 213 J=1,ND2
SBETA=BETA(J)+YH(J)*DELT1
IF (SBETA.LT.0.0) SBETA=0.0
TEST=TEST+ABS(BETA(J)-SBETA)
213 BETA(J)=SBETA
IF (TEST.GE.2.0) TEST1=TEST1+TEST1
IF (TEST.LE.0.01) DELT1=DELT1/2.0
IF (TEST.LE.0.00001) GO TO 214
TEST1=TEST
214 CONTINUE
READ(5,7) (OPTZ(I),I=1,20)
WRITE(6,OPT7) (BETA(I),I=1,ND2)
WRITE(6,901) 1
DO 263 I=1,ND2
DO 263 J=1,ND2
263 BETA(I,J)=COEFF(I,J)
STUS=0.0
STUR=0.0
STUM=0.0
DO 252 I=1,ND2
STUS=STUS+YPS(I)*BETA(I)
242 STUM=STUM+BETA(I,K)*STUM+BETA(K)*STUM
252 WRITE(5,OPTZ) (BETA(I,J),J=1,ND2)
DO 101 I=1,ND2
101 IR1(I)=0
101 IR2(I)=0
DO 31 K=1,ND2
B1GA=0.0
DO 32 I1=1,ND2
DO 32 I2=1,ND2
DO 33 I11=1,IK
DO 33 I21=1,K
IF(11.EQ.IP1(I11)).OR.I2.EQ.IP2(I21)) GO TO 32
33 CONTINUE
IF(B1GA.CT.PABS(COEF(I1,I2))) GO TO 32
B1GA=PABS(COEF(I1,I2))
TR1(K)=11
TR2(K)=I2
32 CONTINUE
IF(F1GA.LT.0.0000001) WRITE(6,34)
B1GA=COEF(IP1(K),IP2(K))
DO 35 J=1,ND2
C0EF(I1(K),J)=COEF(I1(K),J)/B1GA
C0EF(I1(K),TR2(K))=1.0/B1GA
DO 31 I=1,ND2
AJ CK=COEF(I,TR2(K))
IF(I.EQ.IR1(K)) GO TO 31
COEF(I,TR2(K))=-AJ CK/B1GA.
DO 31 J=1,ND2
IF(J.NE.TR2(K)) COEF(I,J)=COEF(I,J)-AJ CK*COEF(TR1(K),J)
31 CONTINUE
DO 36 J=1,ND2
DO 37 I=1,ND2
37 YM(IR2(I))=COEF(IR1(I),J)
DO 36 I=1,ND2
DO 38 J=1,ND2
38 YM(IR1(J))=COEF(I,IR2(J))
DO 33 J=1,ND2
33 COEF(I,J)=YM(J)
2 BET(I)=0.0
DO 3 I=1,ND2
DO 3 J=1,ND2
3 BET(I)=BET(I)+C0EF(J,I)*YPS(T)
DO 1 I1=1,ND2
1 YM(I1)=0.0
WRITE (A,OPTZ) (BET(I),I=1,ND2)
SUM=0.0
DO 4 I3=1,ND3S
4 SUM=SUM+CL0ST(I3,I4)*CL0ST(I3,I4)
STUR=SUM
STUC=SUM
STUG=0.0
DO 6 I=1,ND2
DO 141 J=1,ND2
STUG=STUG+(BETA(I)-BET(I))*BI(I,J)*(BETA(J)-BET(J))
141 STUC=STUC+BET(I)*BI(I,J)*BET(J)
STUC=STUC-2.0*YPS(I)*BET(I)
SUMI = SUMI - VPS(I)*DEL(I)
DEL = SUMI / (NOIVS*NDIMS*ND2)
DO 8 I = 1, ND2
8 YM(I) = DSORT(COEF(I, I)*DEL)
WRITE(6, 275) YM(I), I = 1, ND2
STUM = STUM + STUP - 2.0*STUS
WRITE(6, 275) STUM, SUMI, STIC, STUC
SP = 0.0
TOSUM = 0.0
DO 510 I = 1, ND2
SP = SP + BI(I, I)*3I(I, I)
DO 510 J = 1, ND2
TOSUM = TOSUM + BI(I, J)*3I(I, J)
COEF(I, J) = 0.0
IF(I, EQ, J) COEF(I, J) = 1.0
CONTINUE
ND3 = ND2 - 1
DO 511 ITER = 1, 25
DO 512 I = 1, ND3
II = I + 1
DO 512 J = II, ND2
Q = BI(I, J) - BI(J, J)
IF(DABS(Q), GT, 1.0D-10) GO TO 513
CSA = 0.70722
SNA = CSA
GO TO 514
513 IF(DABS(BI(I, J)), LT, 1.0D-10) GO TO 512
P = 2.0*BI(I, J)*Q/DABS(Q)
SP = DSORT(P*P + Q*Q)
CSA = DSORT((1.0 + DABS(Q)/SPQ)/2.0)
SNA = P/(2.0*CSA*SPQ)
514 CONTINUE
DO 515 K = 1, ND2
HOLDK = COEF(K, I)
COEF(K, I) = HOLDK - CSA - COEF(K, J)*SNA
515 COEF(K, J) = HOLDK + SNA - COEF(K, J)*CSA
DO 516 K = 1, ND2
IF(K, GT, J) GO TO 517
YM(K) = RI(I, K)
BI(I, K) = CSA*YM(K) + SNA*BI(J, K)
IF(K, EQ, J) RI(J, K) = SNA*YM(K) - CSA*BI(J, K)
GO TO 516
517 HOLDI = BI(I, K)
BI(I, K) = CSA*HOLDI + SNA*BI(J, K)
BI(J, K) = SNA*HOLDI - CSA*BI(J, K)
CONTINUE
516 YM(J) = -CSA*YM(J) + SNA*YM(I)
DO 518 K = 1, J
IF(K, GT, I) GO TO 510
HOLDK = RI(K, I)
BI(K, I) = CSA*HOLDK + SNA*BI(K, J)
BI(K, J) = SNA*HOLDK - CSA*BI(K, J)
GO TO 518
519 BI(K, J) = SNA*YM(K) - CSA*BI(K, J)
CONTINUE
512 BI(I,J)=0.0
SPI=0.0
DO 520 I=1,ND2
  YPS(I)=BI(I,1)
520 SPI=SPI+YPS(I)*YPS(I)
WRITE(6,550) ITER,SP,SP1
IF((1.0-SP/SP1).LT.0.001) GO TO 521
511 SP=SPI
521 WRITE(6,507) (YPS(I),I=1,ND2)
DO 777 I=1,ND2
  WRITE(6,507) (COEF(I,J),J=1,ND2)
777 CONTINUE
END
APPENDIX XII

PSUEDO-MAXIMUM LIKELIHOOD PROGRAM

The following pages contain a listing of the program used to implement the psuedo-maximum likelihood method on the computer. The computer symbols of this program are listed in Appendix XI since many are the same as in that program.
IMPLICIT INTEGER(A-H,O-Z)
DIMENSION COEF(50,50), YM(50), BET(A50), OPTT(20), OPTZ(20)
DIMENSION BNP(4,6,6,16,16), RL(6,6,16,16), CO(6,6,16,16), CUN(6,6,16,16)
DIMENSION CLST(32,32), NPU(6000), SLV(6000), SLC(6000), FAIN(32,32)
DIMENSION KON(6000), KONC(6000), LMOL40, OPT8(20), CTDST(32,32)

16 FORMAT (211C,3F10.4,5F15)
17 FORMAT (1115,5F14.6)
32 FORMAT (1016/1018)
309 FORMAT (2F12.6)
7 FORMAT (20A4)
336 FORMAT (4D14.5)

READ(5,16) NDIMS, KDIUS, CTR, FRTI2, FRTI3, NO2, NO3, NOSD, NST, NFC
READ(7,97) LMOL, DMOL, DMN, ADS, SLV, CVC
READ(7,37) CLST, CON, CONC, SOK, TVOL, STOT
READ(7,52) (LMOL(I), I=1,20)
READ(5,7) (OPT8(I), I=1,20)
READ(7,OPT8) (CON(I), CONC(I), I=1,L)

SUM=0.0
DO 51 IE=1,19
I=20-IE+1
SUM=SUM+LMOL(I)/TVOL
IF (SUM.SGT.CTP.AND. LMOL(I-1).NE.LMOL(I)) GO TO 67
51 CONTINUE

DMC=LMOL(I-1)*SOK
WRITE(6,97) DMCL, DMOL, DMN, ADS, SLV
KMTS=KDIUS+1
DO 97 I=1,NDIMS
DO 57 J=1,NDIMS
CMST(I,J)=0.0
DO 57 K=1,KMTS
DO 57 L=1,KMTS
BL(J,K)=0.0
CU(J,K)=0.0
CO(I,K)=0.0
57 CONTINUE

CMC=(CONC-CONC)/NDIMS-0.0001
DVM=DMC/(NDIMS-1.0001)
DVE=DMC/KDIUS-0.0001
DO 84 I=1,L
84 NPU(I)=0
TVRE=0.0
IX=NST
NT=0
121 IF (NT.GE.NOSD) GO TO 64
CALL RANDUX(IX, IY, YFL)
IX=IY
K=YFL*L+1.0
IF (NPU(K).NE.0) GO TO 121
NT=NT+1
NPU(K)=1
TVRE=TVRE+KON(K)
GOTO 121
66 NT=0
FCOR=0.0
CALL RANDU(IY, IV, YFL)
  IX=IV
  K=YFL*L+1.0
  IF(NRU(K).NE.0) GO TO 122
  NT=NT+1
  NRU(K)=2
  SLC(NT)=KONC(K).CONC1
  SLV(NT)=KONT(K)*S0EK
  TCR=TCR+KONT(K)
  IF(NT.LT.NFC) GO TO 122
  TVOL=TVOL-TVRE
  INTG=(NDIMS-1)/KDIUS
  DO 123 J=1,L
    IF(NRU(J).NE.0) GO TO 123
    PRAB=KONT(J)/TVOL
    SV=KONT(J)*S0EK
    JZK=SV/TVOL+1.0
    JZC=(KONC(J)-CONCL)/DCC+1.0
    IF(JZK.GT.NDIMS) JZK=NDIMS
    IF(JZC.GT.NDIMS) JZC=NDIMS
    CLDST(JZK,JZC)=CLDST(JZK,JZC)+PRAB
    MVV=JZK+INTG-1)/INTG
    DO 119 I=1,JZK
      IF(I.EQ.JZK) GO TO 119
      NVV=I+INTG-1)/INTG
      BL(MVV,NVV,JZK,JZC)=BL(MVV,NVV,JZK,JZC)+PRAB
      BR(MVV,NVV,JZK,JZC)=BR(MVV,NVV,JZK,JZC)+PRAB
    119 CONTINUE
    READ (5,7) (OPTT(I),I=1,20)
    WRITE (6,6) OPTT((CLDST(I,J),I=1,NDIMS),J=1,NDIMS)
    TCV=TCV+S0EK
    NFO=NFO-1
    DO 124 I=1,NFO
      SVI=SLV(I)
      SCI=SLC(I)
      PROBI=SVI/TCV
      PROVI=SVI*PROBI
      JVI=SVI/TVOL+1.0
      JVI=SVI/TVOL+1.0
      IF(JVI.LE.NDIMS) GO TO 129
      JVI=NDIMS
      IVI=KDIUS+1
    129 JCI=SCI/DCC+1.0
    IF(JCI.GT.NDIMS) JCI=NDIMS
    K=I+1
    DO 124 J=K,NFO
      SVJ=SLV(J)
      SCJ=SLC(J)
      JVI=SVJ/TVOL+1.0
      IVI=SVJ/TVOL+1.0
      IF(JVI.LE.NDIMS) GO TO 131
      JVI=NDIMS
      JVI=KDIUS+1
    131 IF(JVI+JVI-2*NDIMS).GT.132,117,117
132  JCJ = SCJ / DCC + 1.0
  IF (JCJ .GT. NDTMS) JCJ = NDTMS
  KV = (SVI + SVJ) / DVV + 1.0
  IF (KV .GT. NDTMS) KV = NDTMS
  KC = (SCJ * SVJ + SCJ * SVJ) / (SVI + SVJ) / DCC + 1.0
  IF (KC .GT. NDTMS) KC = NDTMS
  PROBJ = SVJ / TCJ
  PROVJ = SVJ * PROBJ
  C01(IIVJ, IVJ, KV, KC) = C01(IIVJ, IVJ, KV, KC) + PROBJ * PROBJ + PROJ * PROBJ
  CU1(IIVJ, IVJ, JVI, JCI) = CU1(IIVJ, IVJ, JVI, JCI) + PROVI * PROBJ
  CU1(IIVJ, IVJ, JVI, JCJ) = CU1(IIVJ, IVJ, JVI, JCJ) + PROVJ * PROBI

117  CONTINUE
124  CONTINUE

DO 55 I = 1, NDTMS
DO 55 K = 1, NDTMS
DO 55 J = 2, NDTMS
C01(I2-1, I2-1, I, K) = 2.0 * C01(I2-1, I2-1, I, K)
CU1(I2-1, I2-1, I, K) = 2.0 * CU1(I2-1, I2-1, I, K)
I3 = I2 - 1
DO 55 J = 1, I3
C01(I2, I4, I, K) = C01(I2, I4, I, K) + C01(I4, I2, I, K)
CU1(I2, I4, I, K) = CU1(I2, I4, I, K) + CU1(I4, I2, I, K)
ND2 = K02US + 1.0 * K02US + 1.0
S1Z2 = FRT12 * 1000.0 / (60.0 * ND2)
S1Z3 = FRT13 * 1000.0 / (60.0 * ND2)
JKK = S1Z2 / OVV
JLL = S1Z3 / OVV
IF (JLL .GE. NDTMS) JLL = NDTMS - 1
IF (JKK .GE. NDTMS) JKK = NDTMS - 1
DO 300 I = 1, NDTMS
DO 300 K = 1, NDTMS
DIVF = CLOSE(T(J, I)
IF (DIVF .EQ. 0.0) DIVF = 1.0D-10
DO 300 J = 1, NDTMS
DO 300 J = 1, NDTMS
CU1(K, 11, I, J) = CU1(K, 11, I, J) / DIVF
BL(K, 11, I, J) = BL(K, 11, I, J) / DIVF
DO 301 I = 1, NDTMS
DO 301 J = 1, NDTMS
301  FAIN(J, I) = 0.0
FAIN(JKK + 1, I) = FRT12 / (FRT12 + FRT13)
FAIN(JLL + 1, NDTMS) = FRT13 / (FRT12 + FRT13)
READ (5, 7) (OPTB(I), I = 1, 20)
READ(5, OPTB) (BETA(I), I = 1, ND2)
READ(5, 309) DELT, DELTS
READ(5, 7) (OPTZ(I), I = 1, 20)
I7 = 1
DO 310 I = 1, ND2
310  YM(I) = BETA(I)
329  SCMX = -1.0D+20
318  CONTINUE
I4 = 0
I4 = 0
314  CONTINUE
I5 = 0
313 CONTINUE
SMAX=0.0
STPRO=0.0
DO 303 I=1,NDIMS
LI=303 J=1,NDIMS
BIN=0.0
ROU=0.0
CIN=0.0
COU=0.0
LKZ=0
LKZ=ND2/2
DO 304 K=1,KMTS
DO 304 IL=1,K
IF(IL.EQ.KMTS) GO TO 357
LKZ=LKZ+1
LKZ=LKY+1
BIN=BIN+PI(K,IL,I,J)*BETA(LKZ)
ROU=ROU+PL(K,IL,I,J)*BETA(LKZ)
CIN=CIN+PI(K,IL,I,J)*BETA(LKZ)
COU=COU+PL(K,IL,I,J)*BETA(LKZ)
CONTINUE
304 CONTINUE
FRAT=FAUH(IL,J)+BIN+CIN)/(1.0+ROU+COU)
COSTH(IL,J)=FRAT
STRO=STRO+FRAT
IF(FRAT.LE.0.0) FRAT=1.00-15
SMAX=CMSTH(IL,J)*DLOG(FRAT)+SMAX
303 CONTINUE
SMAX=SMAX-1000.0*(1.0-STRO)*(1.0-STRO)
IF(I4.EQ.0.0) GO TO 314
IF(SMAX.GT.SVMAX) GO TO 311
I5=I5+1
IF(I5.GE.2) GO TO 315
BETA(I4)=BETA(I4)-DELT*2.0
IF(BETA(I4).LT.0.0) GO TO 315
GO TO 313
315 I6=I6+1
SMAX=SVMAX
BETA(I4)=BETA(I4)+DELT
311 I4=I4+1
SVMAX=SMAX
IF(I4.GT.NO2) GO TO 316
BETA(I4)=BETA(I4)+DELT
GO TO 314
316 CONTINUE
I7=I7+1
IF(I7.LE.10) GO TO 342
I7=1
WRITE(6,OPTT)((CIDS(I,J),I=1,NDIMS),J=1,NDIMS)
342 CONTINUE
WRITE(6,536) SMAX,SCMX,SVMAX,STRO
WRITE(6,OPTZ) (BETA(I),I=1,ND2)
IF(SMAX.LT.SCNX) GO TO 327
IF(I6.GE.NO2) GO TO 331
DO 317 I=1,ND2
SAVB = BETA(I)
BETA(I) = 2.0 * BETA(I) - Y(I)
IF(BETA(I), LE, 0.0) BETA(I) = 0.00000001

317 Y(I) = SAVB
SCM = SMAX
GO TO 318

327 DO 328 I = 1, ND2
328 BETA(I) = Y(I)
GO TO 329

331 DO 332 I = 1, ND2
332 Y(I) = BETA(I)
DELT = DELT / 2.0
IF(DELT, LT, DELS) GO TO 319
GO TO 329

319 CONTINUE
WRITE (6, OPTT) (CTOS(T, I), I = 1, NDIMS), (J = 1, NDIMS)
END
APPENDIX XIII

POLYNOMIAL FIT PROGRAM
The following pages contain the program which calculates
the coefficients of the polynomial kernels. It essentially forms
and solves equation 7.24.
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADS</td>
<td>Average drop size</td>
</tr>
<tr>
<td>AJCK</td>
<td>Variable in matrix inversion.</td>
</tr>
<tr>
<td>BETA</td>
<td>Unknown constants of polynomial</td>
</tr>
<tr>
<td>BIGA</td>
<td>Pivot in matrix inversion.</td>
</tr>
<tr>
<td>COEF</td>
<td>Coefficient matrix.</td>
</tr>
<tr>
<td>CONC</td>
<td>Array of drop concentrations.</td>
</tr>
<tr>
<td>CONCL</td>
<td>Lowest concentration</td>
</tr>
<tr>
<td>CONCM</td>
<td>Maximum concentration.</td>
</tr>
<tr>
<td>CVC</td>
<td>Concentration volume correlation.</td>
</tr>
<tr>
<td>DMAY</td>
<td>Maximum drop volume</td>
</tr>
<tr>
<td>DMIN</td>
<td>Minimum drop volume</td>
</tr>
<tr>
<td>FRTI2</td>
<td>Flow rate of light oil.</td>
</tr>
<tr>
<td>FRTI3</td>
<td>Flow rate of dark oil.</td>
</tr>
<tr>
<td>I</td>
<td>Iteration variable.</td>
</tr>
<tr>
<td>IR1</td>
<td>Subscript in matrix inversion.</td>
</tr>
<tr>
<td>IR2</td>
<td>Subscript in matrix inversion</td>
</tr>
<tr>
<td>I1</td>
<td>Subscript in matrix inversion</td>
</tr>
<tr>
<td>I21</td>
<td>Subscript in matrix inversion</td>
</tr>
<tr>
<td>J</td>
<td>Iteration variable.</td>
</tr>
<tr>
<td>K</td>
<td>Iteration variable.</td>
</tr>
<tr>
<td>KONT</td>
<td>Array of drop counts</td>
</tr>
<tr>
<td>L</td>
<td>Number of drops.</td>
</tr>
<tr>
<td>LMOL</td>
<td>Array of largest drops.</td>
</tr>
<tr>
<td>ND2</td>
<td>Nine.</td>
</tr>
<tr>
<td>NO2</td>
<td>Number of drops of light oil per second.</td>
</tr>
<tr>
<td>NO3</td>
<td>Number of drops of dark oil per second.</td>
</tr>
<tr>
<td>OPTB</td>
<td>Format storage.</td>
</tr>
</tbody>
</table>
PRO Probability of a drop.
PROG1 Input probability.
PROG2 Input probability.
SMV Second moment volume.
SOEK Size of each count.
STOT Total dispersed volume ($mm^3$).
TVOL Total dispersed counts.
VL Volume of drop.
VL2 Volume of drop squared.
VL3 Volume of drop cubed.
VL4 Volume of drop to 4th power.
VL5 Volume of drop to 5th power.
VL6 Volume of drop to 6th power.
VL7 Volume of drop to 7th power.
VM Array of volume moments.
VOL1 Input drop volume.
VOL2 Input drop volume.
YM Array of left hand sides.
ZM Moles of drop.
ZMM Moles of drop squared.
ZMMM Moles of drop cubed.
ZMOUb Moles of input drop.
IMPLICIT REAL*8 (A-H,O-Z)
INTEGER CONC
DIMENSION COEF(10,10), VM(10), IPC(10), IP2(10), VM(10,5), BETA(10)
DIMENSION KONT(4000), CONC(4000), ZMOLE(4000), LMOL(20), OPT8(20)

7 FORMAT (20A4)
52 FORMAT (10I2/10I2)
87 FORMAT (11I15,5F14.4)
34 FORMAT (10X,1AHPIVOT IS TOO SMALL)
73 FORMAT (5D15.5/5D15.5)
35 FORMAT (2F10.4,2I10)

READ(7,87) L, DMAX, EMIN, AGS, SMV, CVC
READ(7,87) L, CONCL, CONCM, SOEK, TVOL, STOT
READ(7,52) (LMOL(I), I=1,20)
READ(7,57) (OPT8(I), I=1,20)
READ(7,57) (KONT(I), CONC(I), I=1,L)
DO 762 I=1,L

762 ZMOLE(I)=KONT(I)*(CONC(I)-CONCL)
READ (5,35) FRTI2,FRTI3,N02,N03
ND2=9
DO 10 I=1,9
DO 10 J=1,9
VM(I,J)=0.0
10 COEF(I,J)=0.0
DO 20 I=1,L
PRO=KONT(I)/TVOL
ZM=ZMOLE(I)*SOEK
ZMM=ZM*ZM
ZMMM=ZM*ZMM
VL=KONT(I)*SOEK
VL2=VL*VL
VL3=VL2*VL
VL4=VL3*VL
VL5=VL4*VL
VL6=VL5*VL
VL7=VL6*VL

VM(1,2)=VM(1,2)+ZM*PRO
VM(2,1)=VM(2,1)+VL*PRO
VM(3,1)=VM(3,1)+VL2*PRO
VM(2,2)=VM(2,2)+ZM*VL*PRO
VM(1,3)=VM(1,3)+ZMM*PRO
VM(1,4)=VM(1,4)+ZMMM*PRO
VM(2,3)=VM(2,3)+ZMM*VL2*PRO
VM(3,2)=VM(3,2)+ZM*VL*PRO
VM(4,1)=VM(4,1)+VL3*PRO
VM(5,1)=VM(5,1)+VL4*PRO
VM(4,2)=VM(4,2)+VL3*ZM*PRO
VM(3,3)=VM(3,3)+VL2*ZMM*PRO
VM(2,4)=VM(2,4)+VL*ZMMM*PRO
VM(6,1)=VM(6,1)+VL5*PRO
VM(5,2)=VM(5,2)+VL4*ZMM*PRO
VM(4,3)=VM(4,3)+VL3*ZMM*PRO
VM(3,4)=VM(3,4)+VL2*ZMMM*PRO
VM(7,1)=VM(7,1)+VL6*PRO
VM(6,2)=VM(6,2)+VL5*ZM*PRO
VM(5,3)=VM(5,3)+VL4*ZMM*PRO
VM(4, 4) = VM(4, 4) + VL3*ZMM*PR
VM(8, 1) = VM(3, 1) + VL7*PR
VM(7, 3) = VM(7, 2) + VL6*ZMM*PR
VM(6, 3) = VM(6, 3) + VL5*ZMM*PR
VM(5, 4) = VM(5, 4) + VL4*ZMM*PR
VM(9, 1) = VM(9, 1) + VL7*VL
VM(8, 2) = VM(8, 2) + VL7*ZMM*PR
VM(7, 3) = VM(7, 3) + VL6*ZMM*PR
VM(6, 4) = VM(6, 4) + VL5*ZMM*PR

CONTINUE
DO 21 I = 1, 3
  COEF(1, I) = -VM(1 +4, I) / 12.0
  COEF(2, I) = -VM(I +3, 2) / 12.0
  COEF(3, I) = -VM(I +5, 1) / 120.0 * 7.0
  COEF(4, I) = -7.0 * VM(I +4, 2) / 69.0
  COEF(5, I) = -7.0 * VM(I +3, 3) / 120.0
  COEF(6, I) = VM(I +6, 1) / 45.0
  COEF(7, I) = -VM(I +5, 2) / 15.0
  COEF(8, I) = -VM(I +4, 3) / 15.0
  COEF(9, I) = -VM(I +3, 4) / 45.0
DO 22 I = 4, 5
  COEF(1, I) = VM(I +1, 2) / 20.0
  COEF(2, I) = VM(I +1, 3) / 20.0
  COEF(3, I) = VM(I +3, 4) / 30.0
  COEF(4, I) = VM(I +2, 2) / 15.0
  COEF(5, I) = VM(I +1, 3) / 30.0
  COEF(6, I) = -31.0 * VM(I +4, 1) / 2520.0
  COEF(7, I) = -31.0 * VM(I +3, 2) / 280.0
  COEF(8, I) = -31.0 * VM(I +2, 3) / 280.0
  COEF(9, I) = -31.0 * VM(I +1, 4) / 2520.0
DO 22 I = 6, 7
  COEF(1, I) = VM(2, 1) * VM(2, 1)
  COEF(1, I) = 2.0 * VM(3, 1) * VM(2, 1)
  COEF(1, I) = VM(3, 1) * VM(3, 1)
  COEF(2, I) = VM(3, 1) * VM(2, 2)
  COEF(2, I) = VM(4, 1) * VM(1, 2) + VM(2, 1) * VM(3, 2)
  COEF(2, I) = VM(3, 1) * VM(3, 2) + VM(2, 2)
  COEF(2, I) = VM(2, 1) * VM(3, 2)
  COEF(2, I) = VM(2, 1) * VM(1, 2)
  COEF(3, I) = VM(3, 1) * VM(3, 1) / 2.0
  COEF(3, I) = VM(3, 1) * VM(3, 1) + VM(3, 1) * VM(4, 1) / 2.0
  COEF(3, I) = VM(3, 1) * VM(3, 1) + VM(3, 1) * VM(5, 1) / 2.0
  COEF(3, I) = VM(3, 1) * VM(4, 1) / 2.0
  COEF(4, I) = VM(1, 2) * VM(3, 1) + 2.0 * VM(2, 1) * VM(2, 2)
  COEF(4, I) = VM(4, 1) * VM(4, 1) + VM(3, 2) + 3.0 * VM(3, 1) * VM(2, 2)
  COEF(4, I) = VM(4, 1) * VM(4, 1) + 2.0 * VM(2, 1) * VM(4, 2) + VM(3, 1) * VM(3, 2) +
2 * VM(4, 1) * VM(2, 2)
  COEF(5, I) = VM(4, 1) * VM(2, 2) + 2.0 * VM(3, 1) * VM(3, 2)
  COEF(5, I) = VM(4, 1) * VM(3, 2) + VM(5, 1) * VM(2, 3) / 2.0
  COEF(5, I) = VM(4, 1) * VM(4, 2) + VM(2, 2) * VM(3, 2) + VM(1, 3) * VM(4, 1) / 2.0
  COEF(5, I) = VM(3, 2) * VM(2, 2)
  COEF(5, I) = VM(1, 2) * VM(3, 2) + VM(2, 2) * VM(3, 2) + VM(1, 3) * VM(3, 1) * VM(3, 2) +
2 + VM(3, 2) * VM(2, 2)
  COEF(5, I) = VM(1, 2) * VM(3, 2) + VM(2, 2) * VM(3, 2) + VM(1, 3) * VM(3, 1) * VM(3, 1) * VM(3, 1) / 2.0
  COEF(5, I) = VM(2, 1) * VM(3, 1) * VM(3, 1) / 2.0
  COEF(5, I) = VM(1, 2) * VM(2, 2) + VM(1, 3) * VM(2, 2) / 2.0
  COEF(6, I) = VM(4, 1) * VM(4, 1) + VM(1, 2) / 2.0 + VM(3, 1) * VM(3, 1) * VM(3, 1) / 2.0
  COEF(6, I) = VM(4, 1) * VM(5, 1) * VM(5, 1) / 3.0 + 5.0 * VM(3, 1) * VM(4, 1) / 3.0
COEFF(6,8) = 2.0*VM(6,1)*VM(2,1)/3.0 + VM(5,1)*VM(3,1) + 2.0*VM(4,1)*
2 VM(4,1)/3.0
COEFF(6,9) = 2.0*VM(5,1)*VM(3,1)/3.0 + VM(4,1)*VM(4,1)/2.0
COEFF(7,6) = VM(4,1)*VM(1,2)/2.0 + 3.0*VM(3,1)*VM(2,2)/2.0 + 3.0*
2 VM(2,1)*VM(3,2)/2.0
COEFF(7,7) = VM(5,1)*VM(1,2)/2.0 + 2.0*VM(4,1)*VM(2,2)/3.0*VM(3,1) +
2 VM(3,2) + 3.0*VM(2,1)*VM(4,2)/2.0
COEFF(7,8) = VM(6,1)*VM(1,2)/2.0 + 3.0*VM(5,1)*VM(2,2)/2.0 + 2.0*VM(4,1) +
2 VM(3,2)/2.0 + 3.0*VM(2,1)*VM(5,1)/2.0 + 3.0*VM(3,1)*VM(4,2)/2.0
COEFF(7,9) = VM(5,1)*VM(2,2)/2.0 + 1.5*VM(4,1)*VM(3,2) + 1.5*VM(3,1)*
2 VM(4,2)
COEFF(8,6) = VM(2,1)*VM(2,3) + VM(3,2)/VM(1,2) + VM(2,2) + VM(3,1)
2 * VM(1,3)/2.0
COEFF(9,7) = VM(2,1)*VM(3,3) + 3.0*VM(2,2)*VM(3,2) + 1.5*VM(3,1)*VM(2,3)
2 + VM(1,2)*VM(4,2) + VM(4,1)*VM(1,3)/2.0
COEFF(8,8) = VM(2,1)*VM(4,3) + 2.0*VM(2,2)*VM(4,2) + VM(4,1)*VM(2,3) +
2 VM(3,2)*VM(3,3) + VM(1,2)*VM(5,2) + VM(1,3)*VM(5,1)/2.0 + VM(3,1)*
3 VM(3,3)/2.0
COEFF(9,9) = VM(3,1)*VM(3,3) + VM(3,2) + VM(3,2) + VM(4,2) + VM(2,2)
2 VM(4,1)*VM(2,3)/2.0
COEFF(9,6) = VM(1,4)*VM(2,1)/6.0 + VM(2,2) + VM(1,3)/2.0 + VM(2,3)*VM(1,2)
2 / 2.0
COEFF(9,7) = VM(3,1)*VM(1,4)/6.0 + VM(2,1)*VM(2,4)/6.0 + VM(1,2)*VM(3,3)
2 / 2.0 + VM(2,3) + VM(2,2) + VM(1,3)*VM(3,2)/2.0
COEFF(9,8) = VM(3,2)*VM(2,3) + VM(1,2)*VM(4,3) + VM(4,2)*VM(1,3)
2 VM(2,2)*VM(3,3)/2.0 + (VM(1,4)*VM(4,1) + VM(2,1)*VM(3,4))/6.0
COEFF(9,9) = VM(3,3)*VM(2,2) + VM(3,2) + VM(2,2) + VM(3,1)*VM(2,4)
2 / 6.0
DO 101 I = 1, ND2
101 IR1(I) = 0
IR2(I) = 0
DO 31 K = 1, ND2
BIGA = 0.0
DO 32 I = 1, ND2
32 CONTINUE
IF (BIGA.GT.0.0 .AND. I2.EQ.IP2(I21)) GO TO 32
BIGA = DABS(COEFF(I1, I2))
IR1(K) = 1
IR2(K) = I2
DO 33 K = 1, ND2
33 CONTINUE
IF (BIGA.LT.0.0 .AND. I2.EQ.IP2(I21)) WRITE(6,34)
DO 83 J = 1, ND2
83 CONTINUE
COEFF(IR1(K), J) = COEFF(IR1(K), J) / BIGA
COEFF(IR1(K), IP2(K)) = 1.0 / BIGA
DO 31 I = 1, ND2
31 CONTINUE
AJCK = COEFF(I, IP2(K))
IF (I.EQ.IP1(K)) GO TO 31
COEFF(I, IP2(K)) = -AJCK / BIGA
DO 31 J = 1, ND2
31 CONTINUE
IF (J.NE.IP2(K)) COEFF(I, J) = COEFF(I, J) - AJCK*COEFF(IR1(K), J)
DO 36 J=1,ND2
   DO 37 I=1,ND2
      YM(IR2(I)) = COEF(IR1(I), J)
   DO 36 I=1,ND2
   DO 39 J=1,ND2
      YM(IR1(J)) = COEF(I, IR2(J))
   DO 38 J=1,ND2
   COEF(I, J) = YM(J)
   PROG1 = FRT12/(FRT12+FRT13)
   PROG2 = FRT13/(FRT12+FRT13)
   VOL1 = FRT12/NO2*1000.0/60.0
   VOL2 = FRT13/NO3*1000.0/60.0
   ZMOLI = VOL2*(CONCM-CONCL)
   YM(1) = VM(2,1) - VOL1*PROG1 - VOL2*PROG2
   YM(2) = VM(1,2) - ZMOLI*PROG2
   YM(3) = VM(3,1) - VOL1*VOL1*PROG1 - VOL2*VOL2*PROG2
   YM(4) = VM(2,2) - ZMOLI*VOL2*PROG2
   YM(5) = VM(1,3) - ZMOLI*ZMOLI*PROG2
   YM(6) = VM(4,1) - VOL1*VOL1*VOL1*PROG1 - VOL2*VOL2*VOL2*PROG2
   YM(7) = VM(3,2) - ZMOLI*VOL2*VOL2*PROG2
   YM(8) = VM(2,3) - ZMOLI*ZMOLI*VOL2*PROG2
   YM(9) = VM(1,4) - ZMOLI*ZMOLI*ZMOLI*PROG2
   DO 84 I=1,9
   DO 84 J=1,9
   BETA(I) = COEF(I, J)*YM(J)
WRITE (6,73) (BETA(I), I=1,9)
END
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<thead>
<tr>
<th>NAME AND ADDRESS</th>
<th>DATE</th>
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<td>S. K. Reddy</td>
<td>4/17/77</td>
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<td>S. Pellegom</td>
<td>5/23/77</td>
</tr>
<tr>
<td>E. Eng</td>
<td>Noon 3/28</td>
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