

THE UNIVERSITY OF CALGARY

AN EXPERIMENTAL STUDY OF DIFFUSION IN THE BITUMEN-TOLUENE SYSTEM

by

VIERA OBALLA

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES IN PARTIAL

FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

DEPARTMENT OF CHEMICAL AND PETROLEUM ENGINEERING

CALGARY, ALBERTA, CANADA

FEBRUARY, 1987

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ISBN 0-315-35916-1

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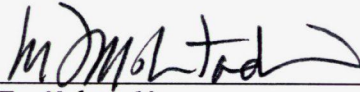
submitted by Viera Oballa in partial fulfillment of the
requirements for the degree of Master of Science in Engineering



Dr. R.M. Butler, Supervisor/Committee Chairman
Department of Chemical and Petroleum Engineering



Dr. W.Y. Svrcek
Department of Chemical and Petroleum Engineering



Dr. F. Mohtadi
Department of Chemical and Petroleum Engineering



Dr. R.D. Rowe
Department of Mechanical Engineering

87-03-27

date

ABSTRACT

Diffusion in the toluene-bitumen system was studied by a method in quasi steady state (diaphragm cell method) and non-steady state (free diffusion method). In both cases an optical method using radiation in the near infra-red region was employed to measure the bitumen concentration. For the in-situ concentration measurements (free diffusion method), a pulsed GaAlAs laser was used as the light source with a silicon semiconductor diode detector.

Diaphragm Cell Method:

Experimental diffusion coefficients of maltenes and asphaltenes, as well as bitumen in toluene at various concentrations are reported. All of the curves attain a maximum in the middle range concentrations. Precipitation of asphaltenes in the diaphragm was observed during the experiments with bitumen.

The precipitate blocked some of the active pores and reduced the area open to diffusion. This occurrence made the results unreliable.

Free Diffusion Method:

The concentration distribution curves differed markedly from the normal S-shape associated with constant diffusivity; this was particularly noticeable for bitumen concentrations above 60 volume percent.

The overall diffusion coefficient was calculated as a function of concentration. It was found to vary by an order of magnitude over the concentration range (0-100%). It climbed from low values at each end of the range to a maximum of $4.8 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at about 54 volume percent bitumen.

The observations can be explained by considering the effect of viscosity and also the difference in the size of bitumen components and toluene molecules.

ACKNOWLEDGEMENTS

I would like to express my gratitude to my supervisor, Dr. R.M. Butler, for this challenging thesis topic, his confidence in me and his guidance throughout the duration of this study.

I wish to express my thanks to all my colleagues, in particular, Mr. C.T. Yee and Mr. K. Chung with whom I had numerous informative and enlightening discussions.

The financial support of the Department of Chemical and Petroleum Engineering and the Alberta Oil Sands Technology and Research Authority (AOSTRA) is gratefully appreciated.

Special thanks to Mr. B. Raybould for helping to put the laser together, Mr. C.T. Yee for drawing the circuit diagrams and Patricia Stuart for typing this manuscript and for her understanding.

I would like to dedicate this thesis to the two men in my life - my husband Mike and my son Miroslav for their encouragement and support.

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NOMENCLATURE

A	cross-sectional area normal to the concentration gradient
AS	absorbance, dimensionless
B	diaphragm cell constant [cm^{-2}]
C	concentration; mass per volume of solution [g/cm^3]
D	diffusion coefficient [cm^2/s]
$\bar{D}$	integral diffusion coefficient [cm^2/s]
d	thickness of the absorbing layer [cm]
J	diffusional flow [cm^3/s]
ℓ	thickness of the diaphragm [cm]
q	amount of diffusing substance [g]
t	time [s]
V	volume of the diaphragm cell compartment [cm^3]
X	volume fraction
y	vertical direction

Subscripts

Greek Symbols

A	asphaltenes	ϵ	absorptivity coefficient [cm^2/g]
B	bitumen		
b	bottom compartment		
f	final		
i	initial		
m	maltenes		
S	solvent (toluene)		
t	top compartment		

CHAPTER ONE

INTRODUCTION

With the diminution of conventional oil reserves, attention has turned to heavy oil production and enhanced oil recovery (EOR). Alberta possesses abundant reserves of heavy oils and tar sands. Different methods have been tried to produce the heavy oil from the ground. Most of them are based on reducing the oil's high viscosity and increasing its mobility. The use of gases (CO_2 , light hydrocarbons) or liquids (C_5 and heavier hydrocarbons, light oil fractions) in EOR, as well as heavy oil production has been proposed by a number of researchers. However, very little research has been done to understand the occurring mass transport phenomena. Only a few experimental values of the diffusion coefficient of bitumen into various organic substances are available in the published literature. All of these were obtained in a very narrow concentration range or for a single concentration and were assumed to be constant. Such an assumption may misrepresent the role of diffusion during the recovery of bitumen.

To clarify this, more experimental data are necessary. Therefore, the objective of this work was to investigate the diffusion of bitumen into toluene; how the concentration and permeability affects the diffusivity.

There are several theories for the estimation of diffusion coefficients, e.g. Eyring's theory, the hydrodynamic theory, etc. However, none of these theories is quite satisfactory in predicting the correct diffusivities because a number of arbitrary assumptions had to be introduced into the theoretical treatment of kinetic phenomena in liquids.

Eyring's theory of absolute reaction rates assumes a cubic lattice configuration model for a fluid in liquid state. The diffusion occurs in a series of jumps from "hole to hole" which are scattered in the lattice [22].

The hydrodynamic theory is based on the Nernst-Einstein equation [23]. It describes the diffusion process of large spherical molecules or particles in a continuum using Stokes law. However, difficulties arise for smaller solute molecules, straight chain molecules, concentrated solutions, etc. Due to these problems, several semi-empirical equations have been proposed which have a number of restrictions [24], e.g. Wilke-Chang correlation for infinite dilute solutions [25].

On the basis of molecular theory there is a strong belief of a close relationship between diffusion and viscosity. The Stokes-Einstein equation relates the diffusion coefficient to viscosity as being inversely proportional to each other. Many authors [12, 26, 27] discuss the relationship between viscosities and diffusion coefficients for various mixtures. Very often it is assumed that the product of viscosity η and diffusion

coefficient D is a constant. This can be done for ideal mixtures, but as soon as there is a slight deviation from ideality, the relationship does not hold anymore [28]. Onsanger [26] classifies systems of concentrated solutions into 3 groups:

- a) For systems which obey Raoult's law, $D\eta$ is a linear function of composition.
- b) For solutions of non-polar liquids with considerable deviations from Raoult's law, $D\eta/(x_1\partial\mu_1/\partial x_1)$ varies linearly with concentration, x , (μ is a chemical potential).
- c) Mixtures of polar liquids with no defined relationship between D and viscosity.

Tyrell [29] suggests that $D\eta^p = \text{constant}$, where p is a parameter. Its value is less than 1 (often about 0.6) and depends on the considered system.

Diffusivity can be measured experimentally by methods which belong to two basic groups.

- 1) Steady state or quasi steady state methods, in which the diffusion flux has a constant value. One of the most popular methods in this group is the "Diaphragm Cell Method".

- 2) Unsteady state methods which can be divided into two subgroups according to selected boundary conditions used in solving the second Fick's Law equation.
- a) Free diffusion methods (infinite boundary conditions).
 - b) Restricted diffusion methods (concentration changes at the boundaries during an experiment).

In the methods from the second group, the concentration distribution must be measured in-situ if diffusivity is to be found as a function of concentration. This poses some problems, especially for a substance so complex as bitumen.

The initial experiments which are described in this thesis were carried out using the diaphragm cell method. Results obtained with this technique were difficult to interpret because of the extreme variation of diffusivity with concentration and also because of the tendency for the diaphragm to become partially plugged by deposited asphaltenes. Another problem was that progress was slow because only limited information was obtained from lengthy experiments.

As a result of the above problems, it was decided to switch to a technique based on free diffusion methods and results from this were much more interesting and informative.

CHAPTER TWO

LITERATURE REVIEW

2. Literature Review

When solutions having different concentrations are brought into contact, at constant temperature and pressure, the molecules intermingle. Eventually, at equilibrium, a uniform concentration prevails. This process is called diffusion. The driving forces in such processes are concentration gradients.

Many studies have been made of the diffusion of various electrolytes and non-electrolytes [12,20]. However, the diffusion of various solvents into bitumen has been studied only by a few researchers and the information is very limited. In the work described here, diffusion in the bitumen-toluene system has been studied; since bitumen consists of various size molecules, attention will also be paid to mass transfer in systems with varying molecular sizes.

2.1 Diffusion in systems with large solute molecules

Some of the earliest work was carried out in this field, has been with polymers. Different methods, mostly optical, were used to measure the concentration or concentration gradient as a function of distance [1,2].

Hayes and Park [3] used the micro-interferometric technique to study the benzene-rubber system. They observed a strong dependence of the diffusion coefficient on concentration. Their results showed a maximum in the intermediate concentration range. A similar diffusion coefficient-concentration curve was observed by Hutcheon et al [4] during diffusion of different kinds of solvents (ethyl acetate, propyl acetate, isopropyl acetate, butyl acetate, triacetin and acetone) into polyvinyl-acetate.

Funk [5] studied the dissolution of tar sand bitumen using low-molecular weight paraffinic solvents at ambient temperature. The experimental data were obtained by three different methods:

- spinning disc technique
- liquid-fluidized bed, and
- direct particle size analysis of the insolubles.

The effective diffusion coefficients for n-pentane, n-heptane and n-decane bitumen systems were determined using the spinning disc technique. The numerical values are $1.41 \times 10^{-7} \text{ cm}^2/\text{s}$, $1.21 \times 10^{-7} \text{ cm}^2/\text{s}$ and $6.5 \times 10^{-9} \text{ cm}^2/\text{s}$ respectively. Actually, the values represent the diffusion of the deasphalted oil (maltenes) into the respective paraffinic solvents. The leached out layer of asphaltenes was examined by particle size analysis.

Fu and Philips [6] measured diffusivities of volatile

hydrocarbons (pentane, hexane, heptane, isohexane, 2,2 dimethylbutane, cyclohexane, benzene, toluene and octane) in Athabasca bitumen using a method which involves diffusion of a hydrocarbon from a bitumen-hydrocarbon solution into a flowing stream of nitrogen. The hydrocarbon concentration in the mixture with nitrogen was determined by gas chromatography.

They found that the diffusivity decreased with increasing molecular weight of the hydrocarbon. However, the presence of branching and ring-shaped structures had a far more significant effect in decreasing the diffusivity than did increasing molecular weight. Their results range from $1.45 \times 10^{-7} \text{ cm}^2/\text{s}$ for pentane to $2.82 \times 10^{-8} \text{ cm}^2/\text{s}$ for 2,2 dimethylbutane. The value of the diffusion coefficient for a toluene/bitumen system was found to be $7.78 \times 10^{-8} \text{ cm}^2/\text{s}$. The average initial concentration of a hydrocarbon in the bitumen solution was about $5 \times 10^{-2} \text{ g/cm}^3$ and the temperature was $23 \pm 1.5^\circ\text{C}$.

The relationship between diffusion of n-pentane asphaltenes and pore size was studied by Baltus [7] using track-etched mica membranes with tetrahydrofuran as solvent. The diffusion cell and the procedure used were similar to a diaphragm cell method [8]. The diffusion of various n-pentane asphaltene fractions differing in molecular weight was measured as a function of pore radius of the track-etched membranes (80-220 Å). Gel permeation chromatography was used to analyse the diffusion

samples. Baltus concluded that the diffusion coefficient decreased (16.1×10^{-7} - 2.71×10^{-7} cm²/s) with increasing molecular weight of asphaltenes fractions (2×10^3 - 64×10^3) at constant pore radius.

CHAPTER THREE

DIAPHRAGM CELL METHOD

3.1 Steady State Theory

The diaphragm cell method is based on the assumption of a quasi steady-state in the diffusion process. This implies that the concentration gradient within the diaphragm may be assumed constant.

In this work, the modified diaphragm cell of Stokes [8] was used. The apparatus consisted of two compartments divided by a horizontal sintered glass diaphragm. The pores of the diaphragm should be such that no convection is allowed, but, at the same time, they must be large enough for the molecules to pass freely. It is very important to maintain a uniform concentration in each compartment.

The amount diffusing through the diaphragm in an interval dt will be

$$dq = \frac{DA}{\ell} (C_b - C_t) dt \quad 3.1$$

D = diffusion coefficient [$\text{cm}^2 \cdot \text{s}^{-1}$]

A = crosssectional area normal to the concentration gradient [cm^2]

ℓ = diaphragm thickness [cm]

C_b = bottom compartment concentration; mass of bitumen per volume of solution [g.cm^{-3}]

C_t = top compartment concentration; mass of bitumen per volume of solution [g.cm^{-3}]

The above equation is completely valid only if the concentration in the top and bottom compartments does not change (boundary conditions for solving Fick's second law equation). However, in the diaphragm cell, these concentrations vary slowly with time. This change can be expressed as follows:

$$V_t \frac{dC_t}{dt} - \frac{DA}{\ell} (C_b - C_t) dt = 0 \quad 3.2 A$$

$$V_b \frac{dC_b}{dt} + \frac{DA}{\ell} (C_b - C_t) dt = 0 \quad 3.2 B$$

V_t = volume of cell's top compartment [cm^3]

V_b = volume of the cell's bottom compartment [cm^3]

Combining equations 3.2 A and 3.2 B and integrating results in:

$$\frac{d(C_b - C_t)}{dt} = -BD (C_b - C_t) \quad 3.3$$

B = diaphragm cell constant [cm^{-2}]

$$\frac{C_{bf} - C_{tf}}{C_{bi} - C_{ti}} = \exp(-BDt) \quad 3.4$$

where

$$B = \frac{A}{\ell} \left(\frac{1}{V_b} + \frac{1}{V_t} \right)$$

C_{bf}, C_{tf} = final concentrations

C_{bi}, C_{ti} = initial concentrations

The error resulting from the quasi-steady state assumptions was estimated by Mills et al [9]. They found that if the diaphragm volume is 10% of the total cell volume, the error due to the above approximation is about 3%.

An assumption that the diffusion coefficient is a constant was made in the integration of equation 3.3. However, for many liquids, including the present system, the diffusion coefficient varies with concentration and therefore, the measured diffusion coefficient is not valid for the specified initial concentration C_{bi} , but for the range $C_{bi}-C_{ti}$. Such a diffusion coefficient is called an average or integral coefficient. The relationship between the integral and differential diffusion coefficient is discussed by Gordon [10].

$$\bar{D} = \frac{1}{C_{mb} - C_{mt}} \int_{C_{mt}}^{C_{mb}} D dC$$

$$C_{mb} = \frac{C_{bf} + C_{bi}}{2} \quad C_{mt} = \frac{C_{tf} + C_{ti}}{2} \quad 3.5$$

$\bar{D}$ = integral diffusion coefficient [$\text{cm}^2 \cdot \text{s}^{-1}$]

3.2 Experimental

A "Suncor Coker Feed Bitumen" and (spectrophotometric grade) toluene were used in all experiments. All experiments were

carried out at a temperature of 25°C. A summary of the bitumen's measured properties is shown in Table 1.

Table 1: Properties of Suncor Coker Feed Bitumen

Density [kg/m ³] at 20°C	1017.8
Viscosity [Pa.s] at 25°C	31.1
Asphaltenes [mass %]	14.11

3.2.1 Concentration Measurement

An optical method was employed to determine the intensity of a transmitted light beam passing through a layer of bitumen -, maltenes -, and asphaltenes - toluene mixtures. The Lambert-Beer law (see Appendix A) was used to calculate the bitumen concentration. In the diaphragm cell method, the concentration of bitumen was also measured by evaporation of the solvent (toluene).

3.2.1.1 Perkin-Elmer Spectrophotometer

A Perkin-Elmer spectrophotometer (UV and visible region) was used to measure the absorbance of samples from the diaphragm cell. The absorptivity coefficient was determined beforehand using solutions of known concentration. Because there is a strong light absorbance in the visible region, the absorptivity at 800 nm (near infrared region) was chosen for analysis. The calibration curves for maltenes, asphaltenes, as well as

bitumen are plotted in Figures. 1,2 and 3 respectively.

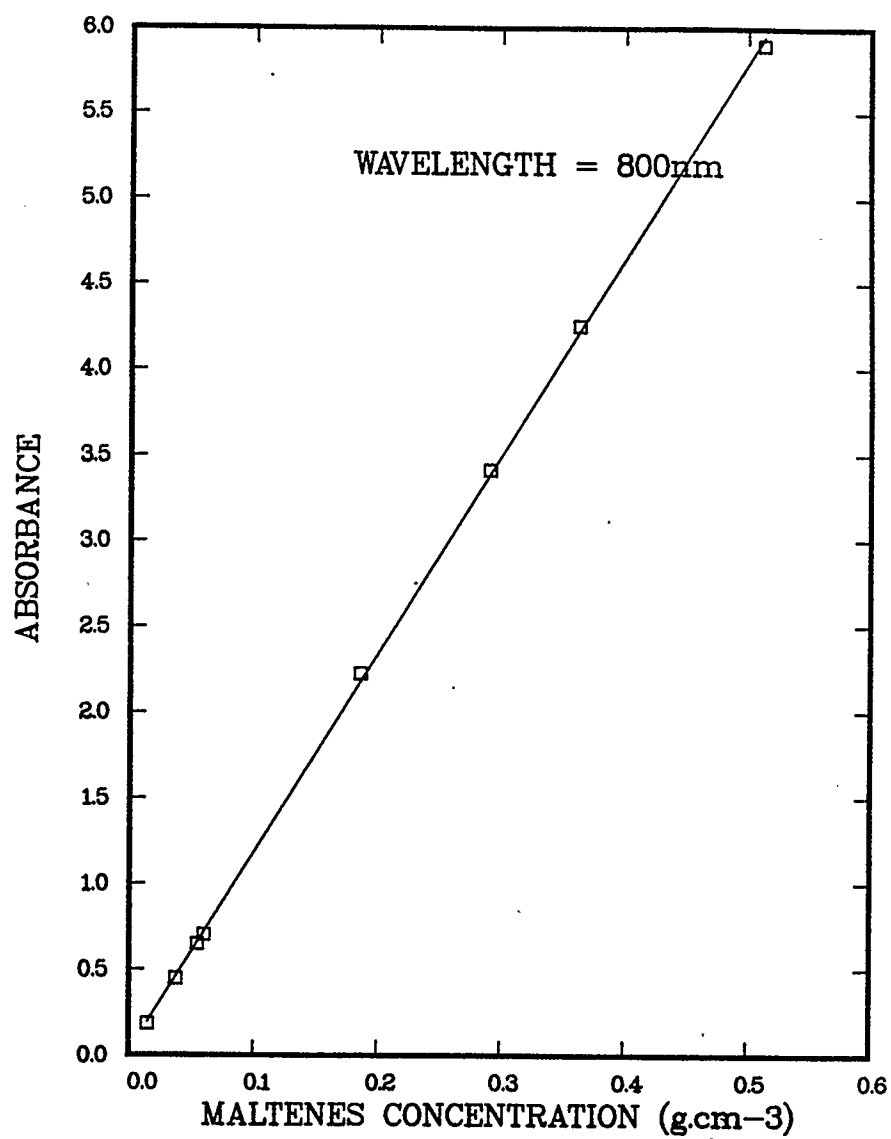


FIGURE 1: CALIBRATION CURVE FOR MALTENES/TOLUENE MIXTURES

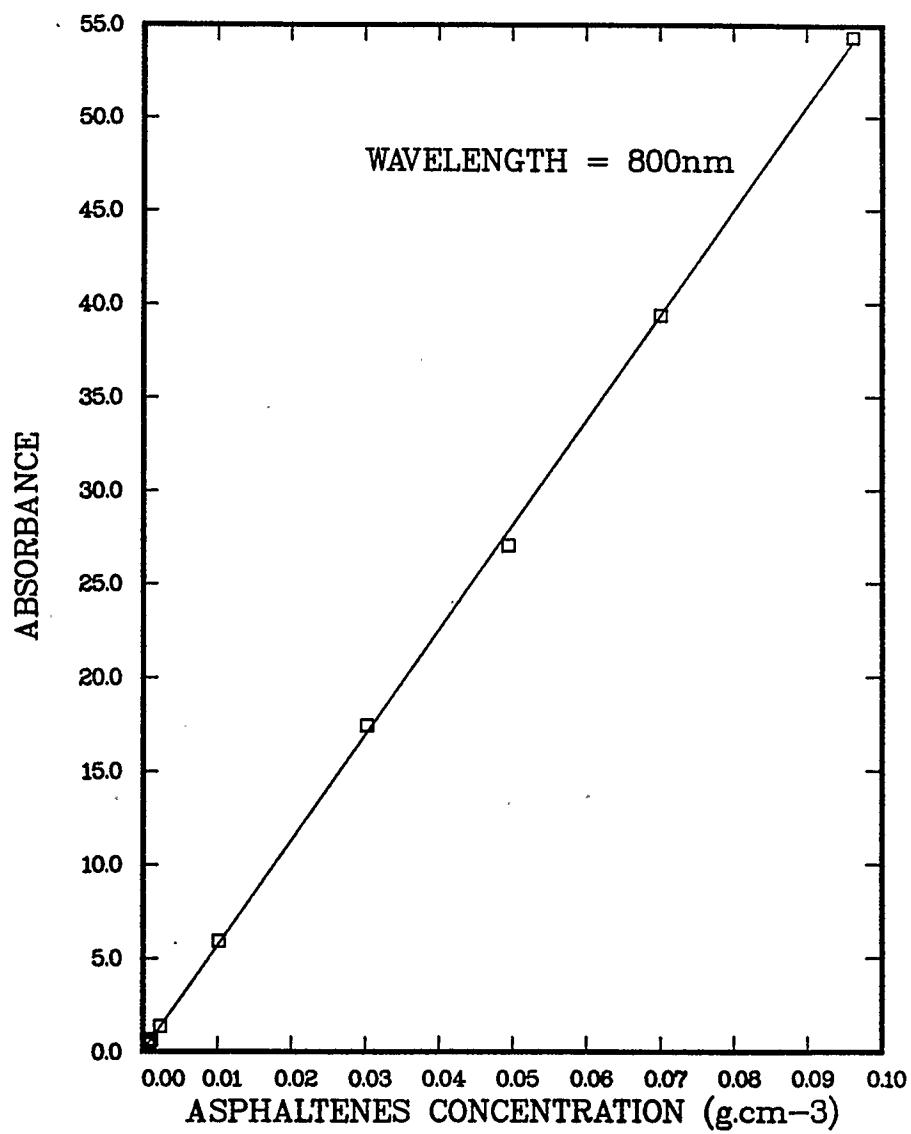


FIGURE 2: CALIBRATION CURVE FOR ASPHALTENES/TOLUENE MIXTURES

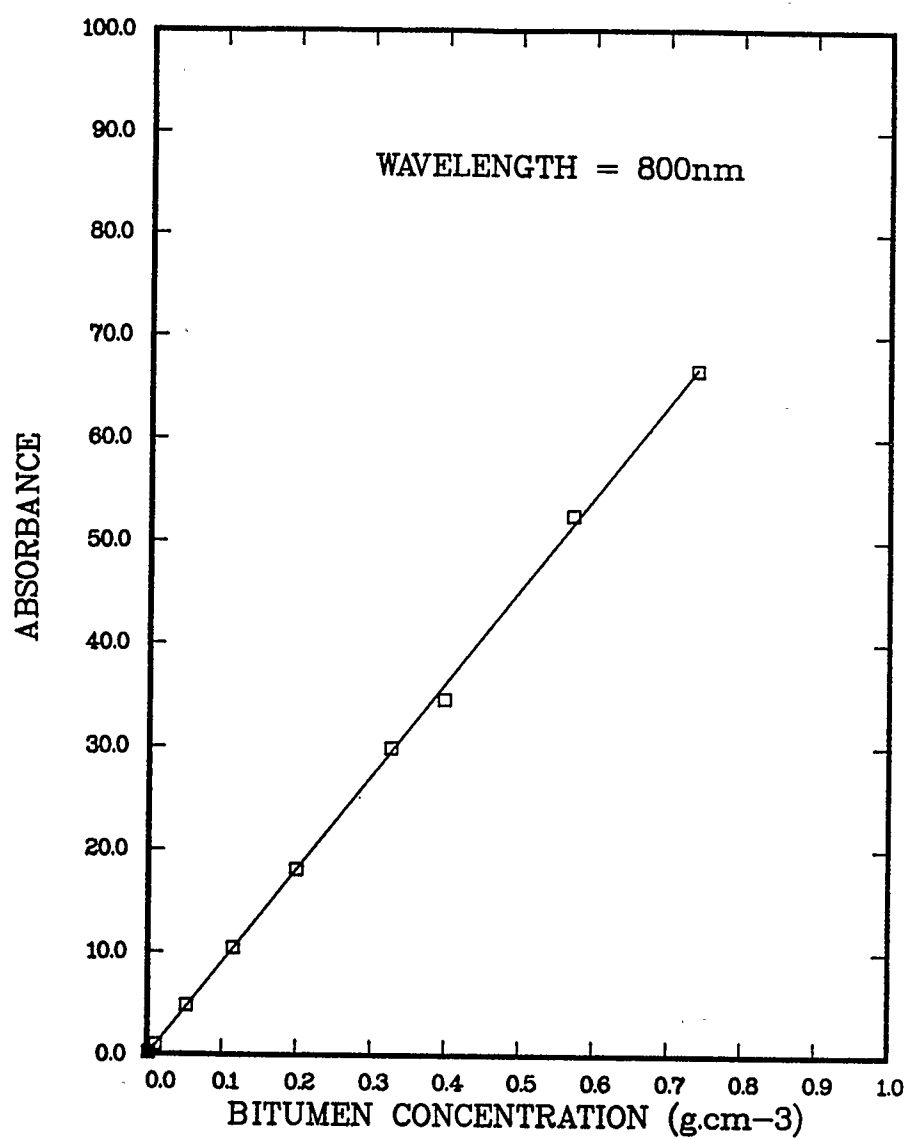


FIGURE 3: CALIBRATION CURVE FOR BITUMEN/TOLUENE MIXTURES

Table 2 shows the absorptivity coefficients for all 3 materials.

Table 2: Absorptivity Coefficients at 800 nm

Compound	Absorptivity coefficient [cm ² /g]
maltenes	11.73
asphaltenes	565.36
bitumen	90.61

The mass percentage of n-pentane asphaltenes in the bitumen determined by the Syncrude method [11] was 14.11 (average value of 6 experiments).

The amount of asphaltenes can also be calculated from eq. 3.6 if the maltenes' and asphaltenes' absorptivity coefficients and bitumen concentration are known and the absorbance of bitumen is measured.

$$AS_{\text{Bitumen}} = [\epsilon_A C_A + \epsilon_M (C_B - C_A)] \cdot d \quad (3.6)$$

AS = absorbance, dimensionless

C_A = concentration; mass of asphaltenes per volume of solution

C_B = concentration; mass of bitumen per volume of solution

ϵ_A = absorptivity of asphaltenes [cm².g⁻¹]

ϵ_M = absorptivity of maltenes [cm².g⁻¹]

d = thickness of the absorbing layer [cm]

Equation 3.6 basically says that the absorbance of a compound is a sum of the absorbance of each component contained in the compound.

The concentration of asphaltenes in the bitumen which is calculated from eq. 3.6 is 14.27%. This value agrees very well with that reported above for measurements using the Syncrude method.

The absorbances of maltenes, asphaltenes and bitumen at 800 nm wavelength do not depend on the concentration of a single component (there is no peak at this wavelength) but all components contribute to it. Assuming that the qualitative composition of maltenes and asphaltenes does not change drastically, this method can be used for a "fast" determination of the amount of asphaltenes without prior bitumen separation.

To test this (idea), the amounts of asphaltenes in two other types of bitumen (Cold Lake and Athabasca) were also determined. The error in both cases was within 1.5% (Suncor Coker feed bitumen values for ϵ_M and ϵ_A were used in calculations).

3.2.2 Apparatus

The diaphragm cell was constructed according to Stokes [8]. It consists of two compartments, which are divided by a sintered glass diaphragm (Fig. 4). It had the following parameters:

. Diaphragm

- type : coarse sintered glass
- diameter : 3 cm
- thickness : 3 mm
- pore volume: 0.307 ml

. Volume of the top compartment : 45.16 ml

. Volume of the bottom compartment: 44.58 ml

The volume of both compartments and the diaphragm were measured by weighing the cell with the various parts filled with distilled water at 20°C.

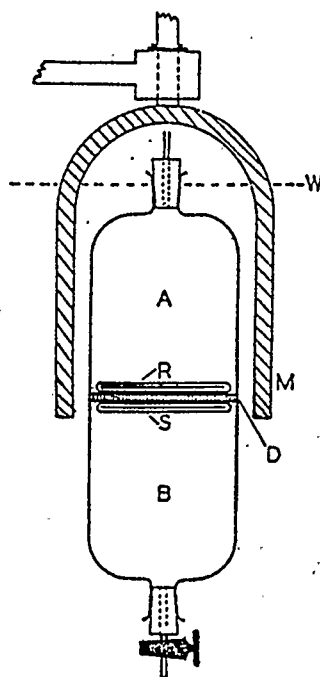


FIGURE 4: DIAPHRAGM CELL [8]

- A, B - top and bottom compartment
- R, S - stirrer
- M - magnet
- W - water level

3.2.3 Procedure

The bottom compartment was filled with the more concentrated solution (higher density) and placed into a water bath for a few hours to achieve temperature equilibrium. After equilibrium has been attained, the top compartment was rinsed several times and filled with the solvent. After several hours of prediffusion, the solution from the top compartment was pipetted out, the compartment rinsed and filled again with a fresh solvent at the same temperature as the mixture in the bottom compartment. Care was taken during pipetting out the solution not to disturb the liquid in the diaphragm. After 2-3 days of diffusion, the contents of both compartments were removed and the bitumen concentrations measured.

Both compartments were stirred continuously. A floating stirrer in the bottom compartment and a sinking stirrer in the top compartment were barely touching the diaphragm from both sides. The stirring effect was achieved by using a rotating magnet.

Note: During a prediffusion a quasi-steady state is reached in the diaphragm. The time needed to achieve it can be estimated from $\ell^2/\pi^2 D$ [12].

when ℓ is diaphragm thickness [cm]

D is diffusion coefficient [$\text{cm}^2 \cdot \text{s}^{-1}$]

3.2.4 Calibration of the Diaphragm Cell

It is very difficult to measure the effective cross-sectional area of the diaphragm and therefore the cell factor B must be determined by calibrating the cell with a solution of known diffusion coefficient. The binary system of 0.5 N HCl-water was used for the cell calibration.

Since the cell constant depends on the rate of stirring, the cell was calibrated at various rates of stirring. At low stirring rates, stagnant layers are built in the vicinity of the diaphragm and additional mass transfer resistances are created. At high stirring rates, the liquid is forced through the diaphragm which causes a convectational mass transfer and, as a consequence, high apparent values of diffusion coefficients.

The concentration of HCl was determined by titration with 0.5 N NaOH using phenolphthalein as an indicator. The integral diffusion coefficient of 0.5 N HCl used in the calculation is $3.09068 \times 10^{-5} \text{ cm}^2/\text{s}$ [10].

It can be seen from Fig. 5 that above 85 rpm there appeared to be a forced mass transfer of liquid through the diaphragm. A stirrer speed of 66 rpm, which lies in the region where the cell factor is independent of the stirring rate, was chosen for the actual experiments ($B=0.1513 \text{ cm}^{-2}$).

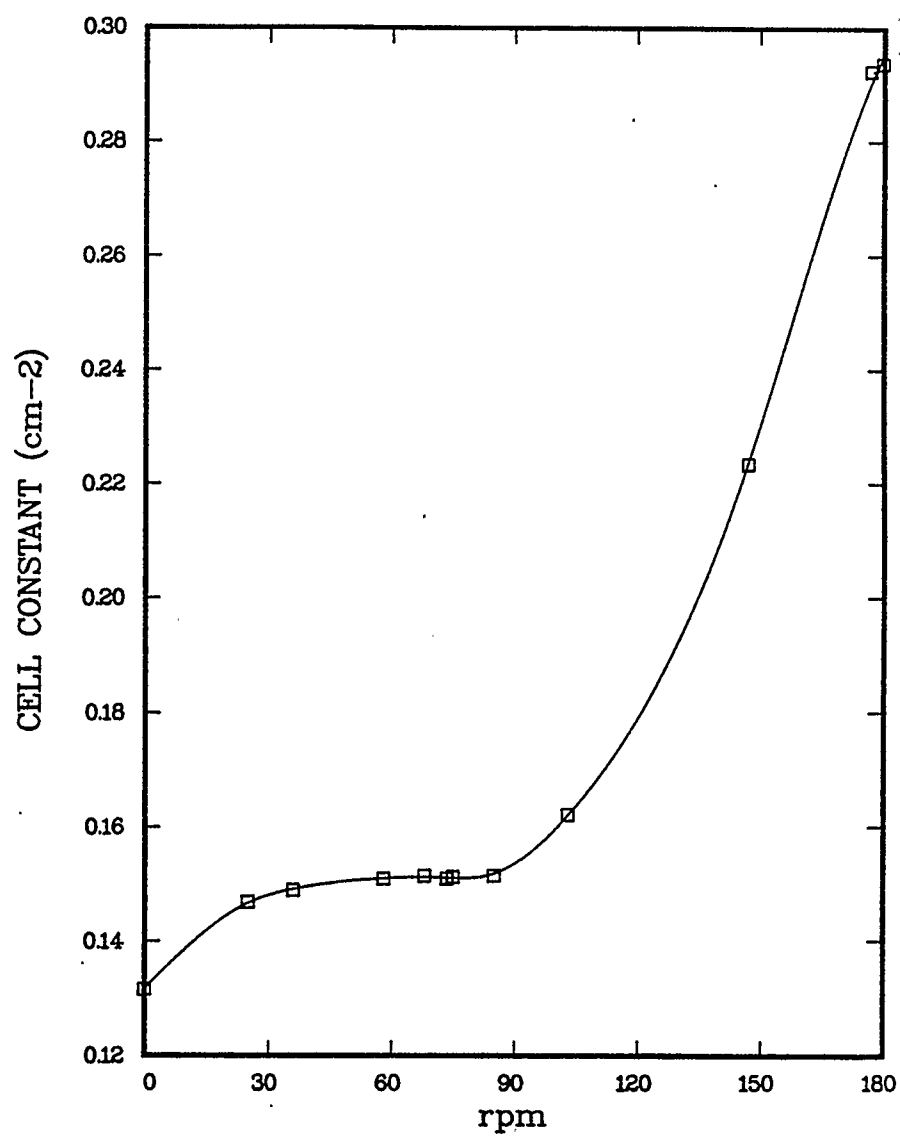


FIGURE 5: CALIBRATION CURVE FOR THE DIAPHRAGM CELL

3.3 Experimental Data

Bitumen is a mixture of various hydrocarbons and can be divided into different fractions. The n-pentane extraction method described in the Syncrude manual [11] was employed to separate the asphaltenes from saturates, aromatics and resins. The last three fractions were considered as one pseudocomponent - maltenes. Because the properties of maltenes and asphaltenes differ considerably (e.g. molecular weight, absorptivity, viscosity, etc.), it was also necessary to study the diffusion process of both pseudocomponents independently.

3.3.1 Maltenes-Toluene and Asphaltenes-Toluene Mixtures

In all experiments, the initial solute concentration in the top compartment was equal to zero. This diminished the relative analytical error [21]. The results are summarized in Tables 3 and 4.

Table 3: Experimental Data for Maltenes-Toluene Mixtures

Initial Concentration [g/cm ³]	Top Compartment Concentration [g/cm ³]	Bottom Compartment Concentration [g/cm ³]	Diffusion Time [hrs]
0.05629	0.00342	0.05306	42.1
0.18911	0.00419	0.18487	40.6
0.31260	0.00834	0.30276	41.8
0.37688	0.01455	0.36379	43.0
0.51444	0.00834	0.50817	43.1

Table 4: Experimental Data for Asphaltenes-Toluene Mixtures

Initial Concentration [g/cm ³]	Top Compartment Concentration [g/cm ³]	Bottom Compartment Concentration [g/cm ³]	Diffusion Time [hrs]
0.0105	0.0005	0.0010	41.9
0.0299	0.0017	0.0281	25.0
0.0477	0.0057	0.0419	41.6
0.0680	0.0075	0.0529	42.6
0.0879	0.0007	0.0871	40.5

3.3.2 Bitumen-Toluene Mixtures

Bitumen was considered as one pseudo-component. There was a possibility of bitumen fractionation due to different mobilities of various molecules. This could change the composition of bitumen mixture in the top and bottom compartments. Because the spectrophotometric method is not an absolute method (calibration is needed), a gravimetric method was also chosen to determine the bitumen concentration in the mixture by evaporating the toluene. The results of these experiments are in Table 5. Columns 2 and 3 show values of concentration determined by a spectrophotometer while columns 4 and 5 indicate concentration values determined by the evaporation of toluene.

Table 5: Experimental Data for Bitumen-Toluene Mixtures

Initial Concentration [g/cm ³]	Final Concentration [g/cm ³]			
	Spectrophotometer		Evaporation	
Bottom	Top	Bottom	Top	Bottom
0.0109	0.0025	0.0086	0.0024	0.0081
0.0560	0.0077	0.0510	0.0082	0.0482
0.1152	0.0032	0.1106	0.0042	0.1108
0.1996	0.0045	0.1973	0.0065	0.1925
0.2489	0.0032	0.2456	0.0055	0.2429
0.3264	0.0062	0.3159	0.0093	0.3160
0.3977	0.0083	0.3732	0.0112	0.3859
0.4887	0.0118	0.4608	0.0140	0.4712
0.5706	0.0071	0.5518	0.0095	0.5594
0.6441	0.0056	0.6346	0.0073	0.6351
0.7380	0.0111	0.7256	0.0133	0.7201
0.8071	0.0081	0.8673	0.0093	0.7752

It can be seen from Table 5 that there are discrepancies between the concentrations measured by using a spectrophotometer and those obtained by evaporation. When the concentration is calculated from absorbance values, it is assumed that the bitumen composition is the same as that in the solutions used for calibration. However, the discrepancies in Table 5 show that not all of the asphaltenes diffused into the top compartment. First it was assumed that the asphaltenes which do not diffuse into the top compartment remain dissolved in the bottom compartment solution. Later a precipitation of asphaltenes in the diaphragm was observed.

The percentage of diffused asphaltenes was calculated from the data in Table 5 using equation 3.6. The results for solutions in both compartments are shown in Table 6.

Table 6: The Percentage of Asphaltenes in Solute in the Top and Bottom Cell Compartment

Initial Conc. [g _B /cm ³]	Final Percentage of Asphaltenes	
	Top Compartment	Bottom Compartment
0.0109	14.4	15.1
0.0560	13.35	15.23
0.1152	10.47	14.27
0.1996	9.48	14.66
0.2489	7.39	14.47
0.3264	8.8	14.25
0.3977	9.89	13.71
0.4887	11.59	13.81
0.5706	10.18	14.03
0.6441	10.53	14.23
0.738	11.65	14.37
0.8071	12.14	---

The initial percentage of asphaltenes in bitumen was $\approx$ 14.25%. Probably within the experimental error, the ratio of asphaltenes to maltenes remained unchanged in the bottom compartment. However, except for one experiment, the ratio was smaller in the bitumen which diffused to the top compartment.

3.4 Results and Discussion

Integral diffusion coefficients for maltenes-toluene and asphaltenes-toluene mixtures were calculated from the experimental data using eq. 3.4. The values are shown in Tables 7 and 8.

Table 7: Integral Diffusion Coefficients for Maltenes-Toluene Mixtures

Initial Conc. [g _M /cm ³]	$\bar{D} * 10^5$ [cm ² /s]	Corresponding Bitumen Concentration [g _B /cm ³]
0.0563	0.5674	0.0656
0.1883	0.2067	0.2196
0.3099	0.2439	0.3614
0.3769	0.3442	0.4395
0.5144	0.1408	0.5999

Table 8: Integral Diffusion Coefficients for Asphaltenes-Toluene Mixtures

Initial Conc. [g _A /cm ³]	$\bar{D} * 10^5$ [cm ² /s]	Corresponding Bitumen Concentration [g _B /cm ³]
0.0105	0.4291	0.0736
0.0299	0.9078	0.2101
0.0478	1.2230	0.3357
0.0682	1.0892	0.4789
0.0881	0.0791	0.6182

The third column in each table lists the concentration of simple bitumen solutions which would contain the same concentration of maltenes or asphaltenes shown in the first column.

Although bitumen consists of maltenes and asphaltenes fractions, it is regarded here as one pseudo-component. The calculated integral diffusion coefficients are in Table 9. Column 2 shows diffusion coefficients ($\bar{D}_{sp}$) which were calculated from concentrations that were determined by the spectrophotometric

method. The concentrations which were determined by evaporation of toluene were used in the calculation of the diffusion coefficients ($\bar{D}_{ev}$) in column 3.

Table 9: Integral Diffusion Coefficients for Bitumen-Toluene Mixtures

Initial Conc. [g _B /cm ³]	$\bar{D}_{sp} \cdot 10^5$ [cm ² /s]	$\bar{D}_{ev} \cdot 10^5$ [cm ² /s]
0.0109	2.4624	2.5745
0.0560	1.2801	1.4382
0.1152	0.2350	0.3061
0.1996	0.1976	0.2857
0.2489	0.111	0.1932
0.3265	0.1688	0.2529
0.3977	0.1850	0.2436
0.4888	0.2079	0.2415
0.5706	0.1107	0.1453
0.6441	0.0751	0.0970
0.7380	0.1296	0.1553
0.8071	0.0793	0.1059

The integral diffusion coefficients for all three materials are not much smaller than the diffusion coefficients which are normally found for ordinary liquids, although one might expect very small values because of the high viscosity, especially for asphaltenes.

There is a considerable scatter and apparent inconsistency in integral diffusion coefficients.

Although considerable effort was expended in trying to correlate and rationalize the data shown in Tables 7, 8 and 9, this

was not found to be possible. It was concluded that the data variability possibly resulted from the variable degrees of plugging of the diaphragm combined perhaps with variations in the size of the asphaltene molecular agglomeration in the various solutions.

In general, the diaphragm cell method proved to be unsatisfactory and it was decided to switch to another experimental technique.

CHAPTER FOUR

FREE DIFFUSION METHOD

Due to the unforeseen difficulties with the diaphragm cell method (asphaltenes precipitation in the diaphragm) a free diffusion method was developed to measure the diffusivity in the toluene/bitumen system.

4.1 The Diffusion Equation

In the modelling of the diffusion process, which is discussed below, the following assumptions are made:

- the system is contained in a static cell with a fixed volume
- the liquid with the lower density is above the heavier liquid (no gravitational effects)
- bitumen is one pseudocomponent (diffusion in a binary mixture)
- one dimensional mass transfer
- infinite medium (for boundary condition)
- no volume change on mixing
- constant temperature and pressure

The rate of transfer of diffusing toluene through a unit area is described by equation 4.1 which is due to Fick [13].

$$J_S = -D_S \frac{\partial X_S}{\partial y} \quad 4.1$$

J_S = rate of transfer of toluene through a unit area
[cm s⁻¹]

D_S = diffusion coefficient of toluene [cm².s⁻¹]

X_S = volume fraction of toluene at y

y = vertical direction

This diffusional flow of toluene is counteracted by the diffusion of bitumen into the solvent (eq. 4.2).

$$J_B = -D_B \frac{\partial X_B}{\partial y} \quad 4.2$$

J_B = rate of transfer of bitumen through a unit area
[cm.s⁻¹]

D_B = diffusion coefficient of bitumen [cm².s⁻¹]

X_B = volume fraction of bitumen at y

Due to the mass conservation in the system, the sum of both flows must be equal to zero. It is obvious from the above assumptions that the diffusion coefficient of toluene D_S is equal to the diffusion coefficient of bitumen D_B .

$$\text{i.e. } D_S = D_B = D_{BS}$$

The rate of solvent volume accumulation in the system is expressed through the continuity equation 4.3.

$$\frac{\partial X_S}{\partial t} = - \frac{\partial J_S}{\partial y} - \frac{\partial J_B}{\partial y} = \frac{\partial}{\partial y} \left(D_{BS} \frac{\partial X_S}{\partial y} \right) \quad 4.3$$

The overall diffusion coefficient D_{BS} is a material property that describes the mobility of either component in the mixture. It depends on temperature, pressure and composition of the system.

4.2 Solution of the Diffusion Equation

Numerous methods can be used to solve the continuity equation 4.3. Analytical solution methods are applicable to solve the linear form of the diffusion equation and boundary conditions (constant diffusion coefficient). They can be also used when the diffusion coefficient is not constant, but the dependance on concentration and/or time must be described by an algebraic function.

Numerical methods can be used to solve any form of the diffusion equation and boundary conditions as well. However, the final results are only approximations to the correct solution.

When the diffusion coefficient depends on concentration

only, the partial differential equation (PDE) 4.3 can be reduced to an ordinary differential equation (ODE) by using the Boltzman transformation [13]. This transformation is valid only for infinite and semi-infinite boundary conditions and the following initial condition:

$$\begin{array}{ll} X_S = X_\infty & y > 0 \\ X_S = 0 & y < 0 \end{array} \quad t = 0$$

A new variable z is introduced which depends on distance and time.

$$z = y/\sqrt{t} \quad 4.4$$

Then the concentration-distance and time gradients are:

$$\frac{\partial X_S}{\partial y} = \frac{1}{t^{1/2}} \cdot \frac{dX_S}{dz} \quad 4.5$$

$$\frac{\partial X_S}{\partial t} = - \frac{y}{2t^{3/2}} \cdot \frac{dX_S}{dz} \quad 4.6$$

Substituting equations 4.5 and 4.6 into equation 4.3 results in ODE 4.7.

$$\frac{d}{dz} \left(D_{BS} \frac{dX_S}{dz} \right) = - \frac{z}{2} \frac{dX_S}{dz} \quad 4.7$$

Integrating equation 4.7 with respect to z and substituting z in the resulting equation with y and t , the following equation

is obtained.

$$D_{BS} = -\frac{1}{2t} \cdot \frac{dy}{dX_S} \int_0^{X_1} y dX_S \quad 4.8$$

where X_1 can be any concentration between 0 and X_∞ .

To satisfy the boundary and conservation of mass conditions, the integral $\int_0^{X_\infty} y dX_S$ must be equal to zero.

The trapezoidal rule was used to approximate the value of the integral. In the calculation of the diffusivities from the experimental data which are described later, the derivative in eq. 4.8 was calculated by using a fifth degree central difference formula.

To assess the degree of accuracy in the approximation of the integral and the derivative, a fictitious problem with a constant diffusion coefficient was chosen. The concentration distribution was calculated from an exact solution of Fick's Second Law equation with infinite boundary conditions. These concentrations were used as input data and values of diffusion coefficients were calculated from eq. 4.8.

The type of method used to evaluate the integral did not affect the results (the Trapezoidal rule and Simpson rule were both tried). However, the degree of the polynomial used to calculate the derivative influenced the final results. The diffusion coefficient-concentration curve attained a humped shape

when a second degree central difference formula was used (Figure 6). The distance between two neighbouring points i and $i+1$ was chosen to be the same as the distance between the two scanning points in all experiments (i.e. 0.5 mm). By increasing the degree of the polynomial, the function $D = f(c)$ approached an almost constant value.

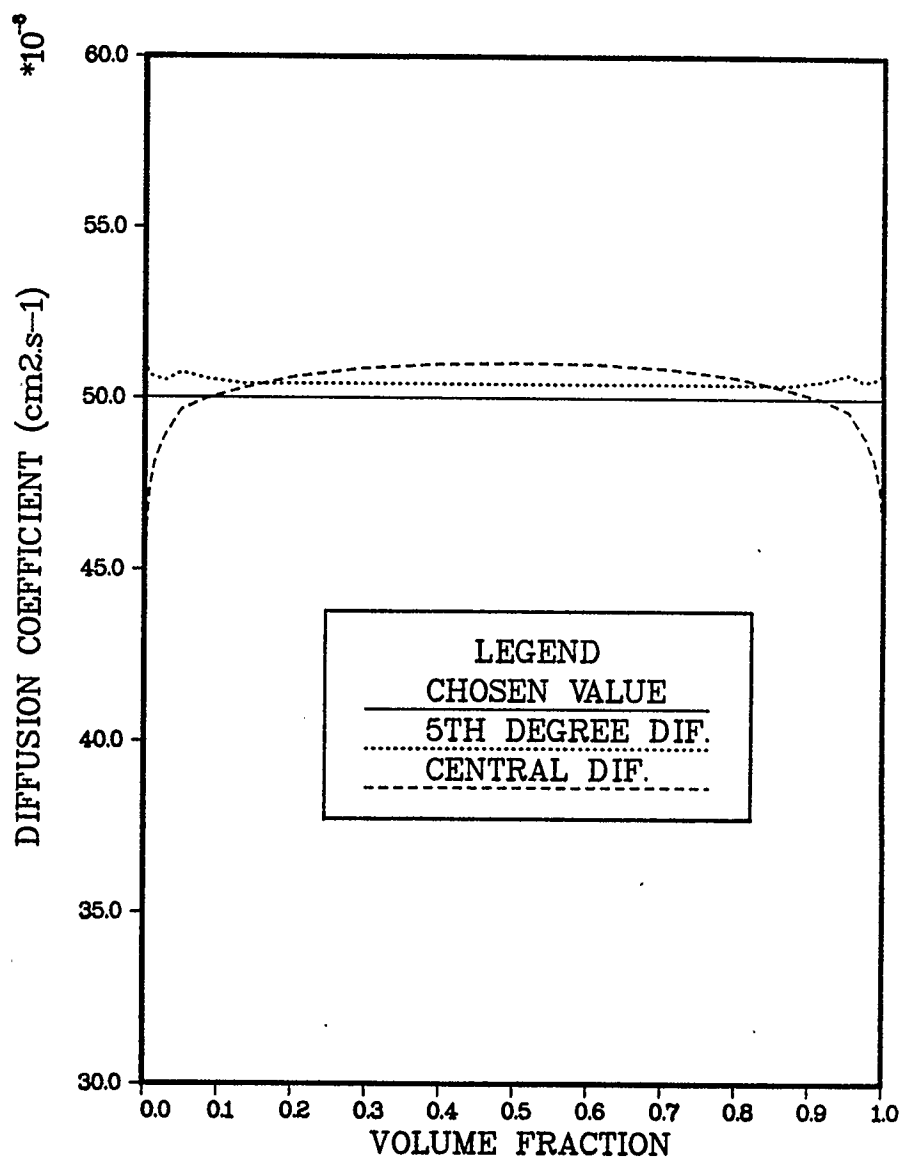


FIGURE 6: ERROR ANALYSIS

4.3 In-situ Concentration Measurements

No analytical instrument is available commercially that can be used to measure the absorbance or intensity of the transmitted light through the dark bitumen solutions in-situ. Therefore a "PROTOTYPE" had to be designed and constructed with the co-operation of Mr. B. Raybould of the Department of Chemical and Petroleum Engineering, University of Calgary.

A pulsed GaAlAs Laser served as a source of monochromatic light. (see description in Appendix B) It emits radiation at 853 nm. The intensity of the transmitted light beam was measured by a silicon detector.

A pulsed laser was chosen because the emitted light intensity is much higher than that of a continuous wave (CW) laser. A 100% concentration of bitumen can be measured by a spectrophotometer only if the absorbing bitumen layer is less than 0.015 cm. With the "PROTOTYPE", the thickness of the bitumen layer can be as high as 0.035 cm.

The intensity of the emitted light can be varied. In all experiments, the laser was operated at about 60% of its maximum intensity. At higher intensity, the silicon detector became saturated. However, a set of calibrated monochromatic filters could be used to absorb the radiation passing through the less concentrated solutions and prevent the detector from becoming saturated.

A description of GaAlAs semi-conductors and silicon detectors is in the Appendix B. Also in the Appendix B are the technical data for the laser and detector which were used together with circuit diagrams.

Bitumen concentration was calculated from the measured values of light intensity using the Lambert-Beer law (Appendix A). The absorptivity coefficient E was determined beforehand with solutions of known bitumen concentration in a 1cm kyvette. The calculated value of the absorptivity coefficient at 853 nm is $72.3 \text{ cm}^2/\text{g}$. The value obtained from spectrophotometric measurements at 850 nm (max. wavelength value available) is $77.63 \text{ cm}^2/\text{g}$. Considering that the accuracy of the spectrophotometer at 850 nm is not 100% (end of the scale - error due to the pen movement, etc.), the "PROTOTYPE" is capable of determining the in-situ concentration of bitumen within approximately the same experimental error as the commercial spectrophotometer.

Bitumen is a complex substance containing molecules of different sizes and types (the light absorbance varies with each molecule type) which move at various velocities during the diffusion process. This phenomenon causes bitumen fractionation, i.e. the composition of bitumen as well as the absorptivity coefficient are different from the original bitumen composition. Since it is not possible to measure the degree of fractionation in-situ and calculate the "real" bitumen concentration, then the concentration is actually a product of the "real" concentration

and the change in the absorptivity coefficient.

4.4 Experiments

The mass transfer process was studied in three different experimental systems:

- . toluene - bitumen (T - B)
- . toluene - bitumen solution (T - BS)
- . bitumen solution - bitumen (BS - B)

and various cell gaps.

4.4.1 Apparatus

The schematic diagram of the set-up is on Fig. 7.

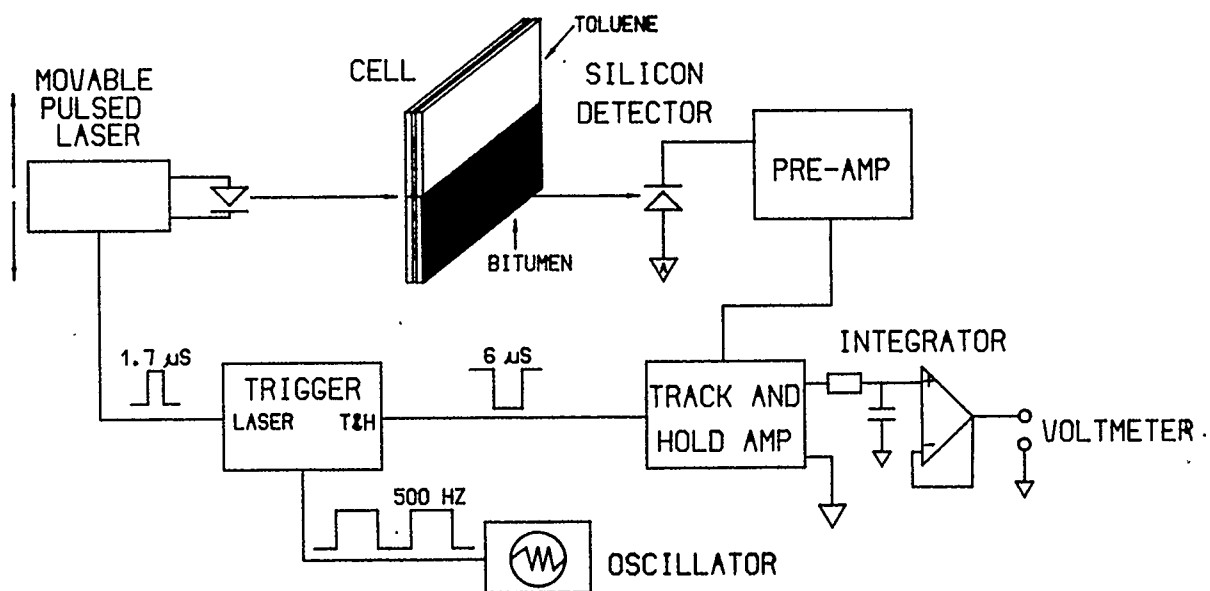


FIGURE 7: A SCHEMATIC DIAGRAM OF THE EXPERIMENTAL SET-UP

The GaAlAs Laser - Silicon detector system ("PROTOTYPE") has already been described in section 4.3.3 and Appendix B.

The mass transfer process took place in a cell which consisted of two vertical optical glass plates (10 cm wide, 20 cm high and 0.3 cm thick). A metal shim was placed between the plates to produce a uniform gap between them. In experiments in which pure bitumen was used in the bottom half of the cell, the metal shim was placed between the plates only in the vertical direction. The cell was sealed on the two vertical sides with monosodium silicate and held together with clamps. In experiments with the bitumen solution at the bottom of the cell (rather than pure bitumen), a metal shim was also placed between the plates at the bottom and the cell was sealed on all sides except the top.

4.4.2 Procedure

The cell was filled first with the denser substance to a height of about 10 cm. The cell was filled from the bottom with bitumen at elevated temperature ($\approx 50^{\circ}\text{C}$).

Numerous problems were encountered during the filling of the cell. However, the following method eventually proved successful. A metal box with a tubing soldered to the bottom was sealed to the bottom of the cell with a silicon sealant (the height of the box was approximately 2 cm). The box must fit the

cell exactly to avoid leakage. A bitumen reservoir was connected to the box and the whole set-up was placed inside an oven. The static head was chosen in such a way that air in the cell was displaced slowly by bitumen.

When the cell was filled quickly, air became trapped in the bitumen and created undesirable effects. When the bitumen reached the prescribed height, the cell was cooled, the metal box removed and the bottom of the cell was cleaned and sealed.

When the solution was the denser substance, it was injected from a side of the cell through a tiny hole that was sealed afterwards.

In carrying out an experiment, the cell was supported in a holder vertically between the laser and the detector. Since the dispersion angle of the beam is 10° , it was necessary to have the laser and the detector as close as possible for maximum utilization of the emitted radiation. To ensure that the laser and detector were aligned properly and that the absorbing layer was uniform, the filled part was scanned in a vertical direction before the diffusion process was started. Only when the intensity of the transmitted light was constant at each scanning point was the top of the cell filled with toluene or the bitumen solution. The scanning procedure was repeated every hour during the initial stages of the run and, later on, every three hours. To minimize the possibility of an experimental error due to the

slight initial irregularities of the interface, each experiment lasted 48 hrs. This was long enough to allow solvent to penetrate over a distance of 1-2 cm. All experiments were carried at a temperature of $20 \pm .5^{\circ}\text{C}$.

4.4.3 Experimental Data

First the diffusion process was studied in a toluene/bitumen system with the glass plates 0.0074, 0.0086, 0.0097 and 0.0127 cm apart. The concentration distribution curves are presented in two ways. The concentration-distance curves for Runs 13, 14 and 17 are shown in Figs. 8, 9 and 10. The common intersection of all concentration curves at various times was chosen as the zero distance. The concentration dependance on $y/\sqrt{t}$ for Runs 7, 15 and 25 is shown in Figs. 11, 12 and 13. Here the points represent concentrations measured at various times. The smoothed full line shows concentration values which were used in the subsequent calculation of diffusion coefficients. The conditions for the runs are specified in the figures.

Concentration values at 540 min. were used in diffusion coefficient calculations. These values are shown in Tables 10, 11, 12 and 13.

$b = .0097 \text{ cm}$ RUN 13

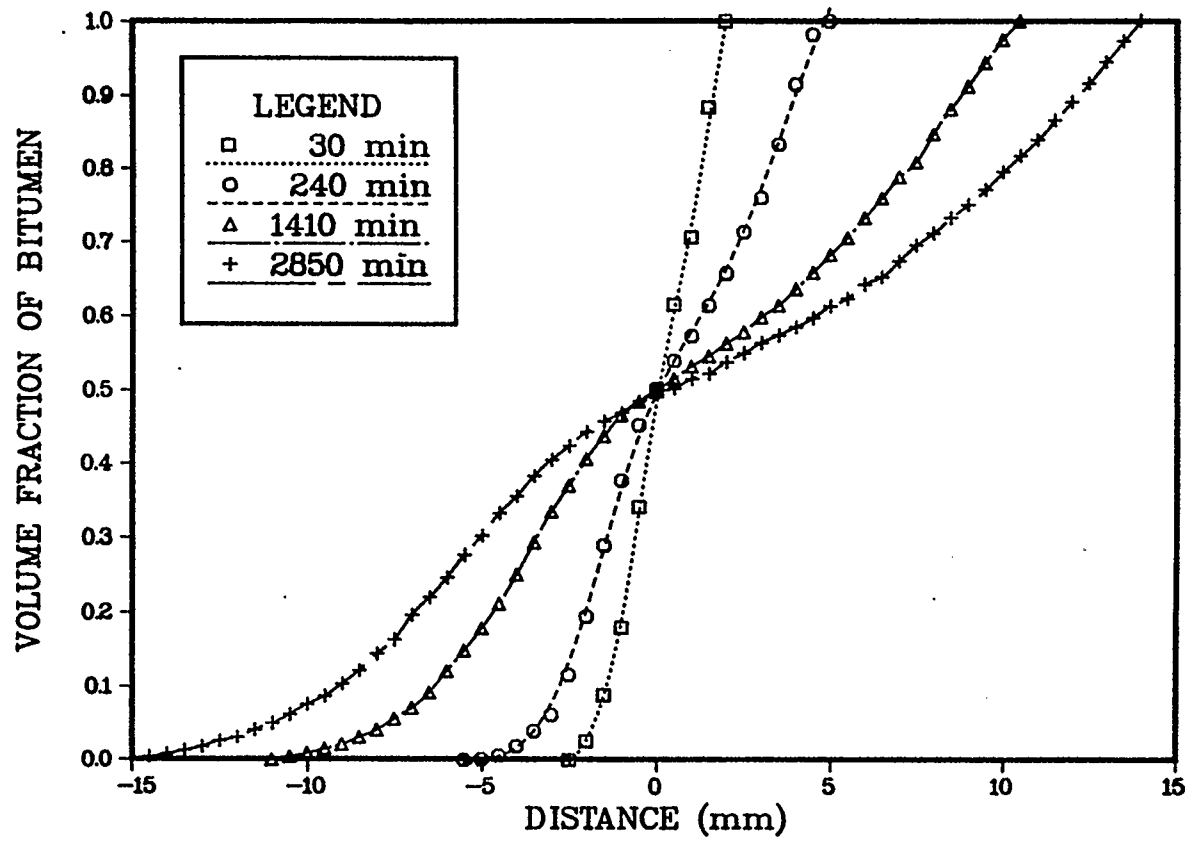


FIGURE 8: CONCENTRATION-DISTANCE CURVES RUN 13

$b = .0086 \text{ cm}$ RUN 14

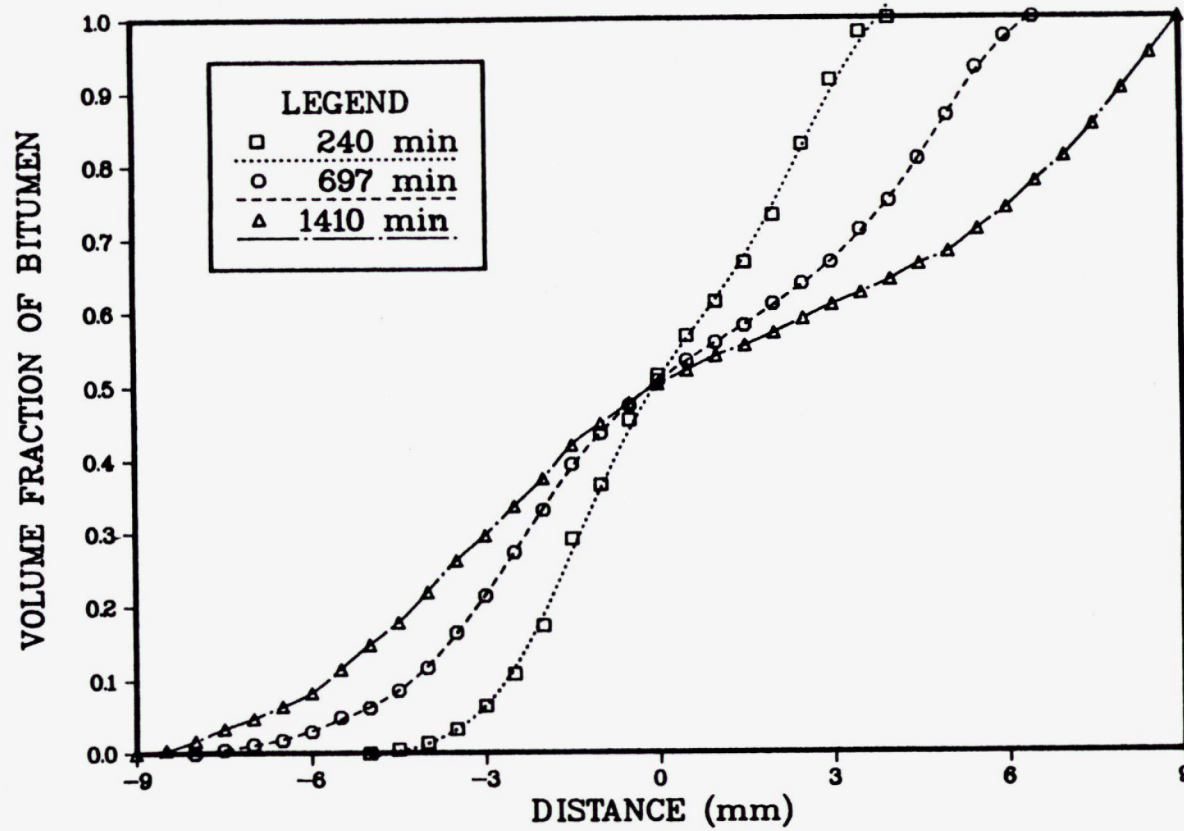


FIGURE 9: CONCENTRATION-DISTANCE CURVES RUN 14

$b = .0127 \text{ cm}$ RUN 17

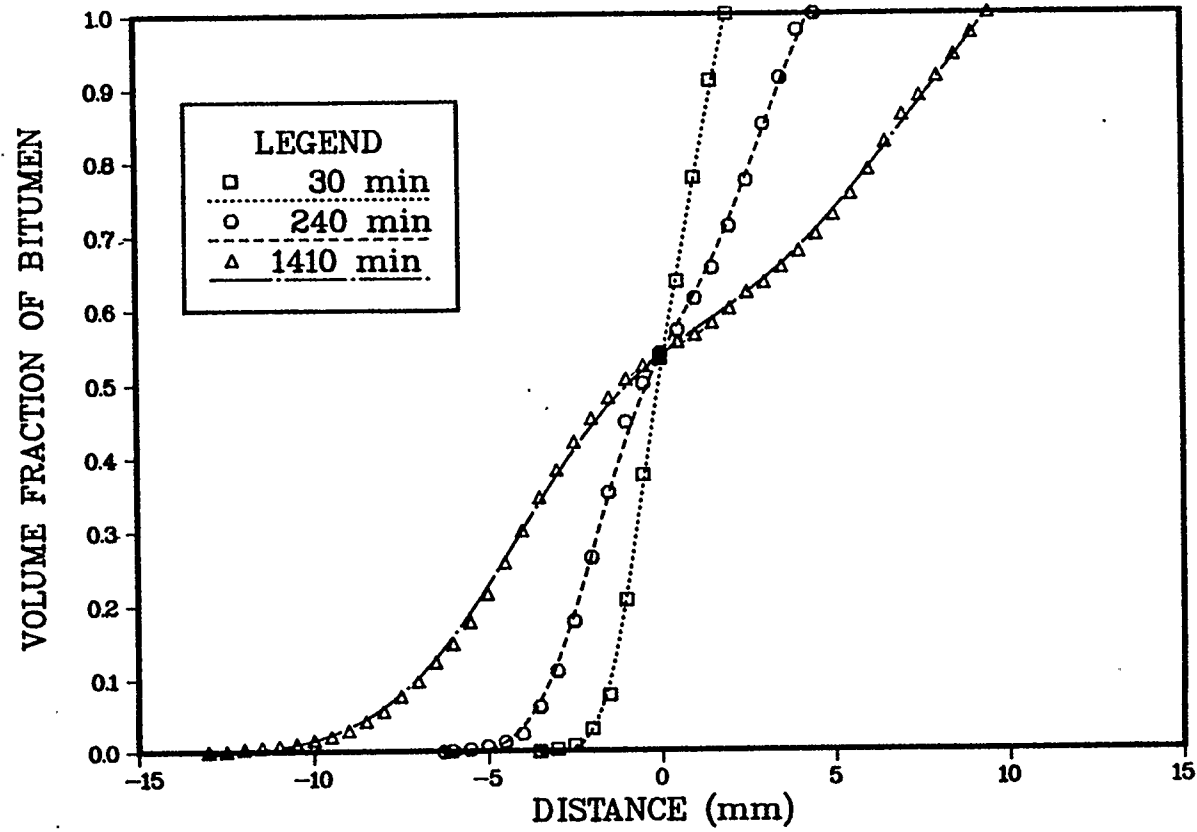


FIGURE 10: CONCENTRATION-DISTANCE CURVES RUN 17

$b = .0086 \text{ cm}$ RUN 7

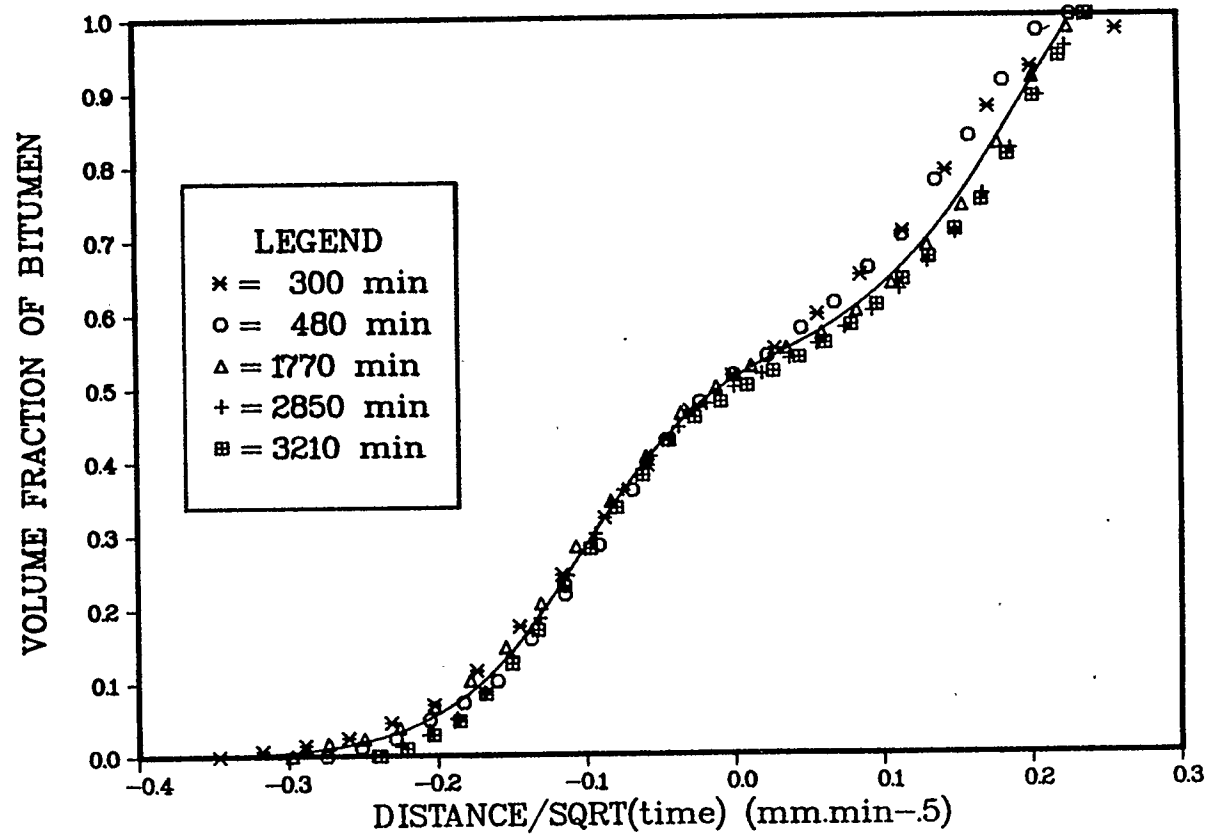


FIGURE 11: CONCENTRATION DEPENDANCE ON $y/\sqrt{t}$ RUN 7

$b = .00747 \text{ cm}$ RUN 15

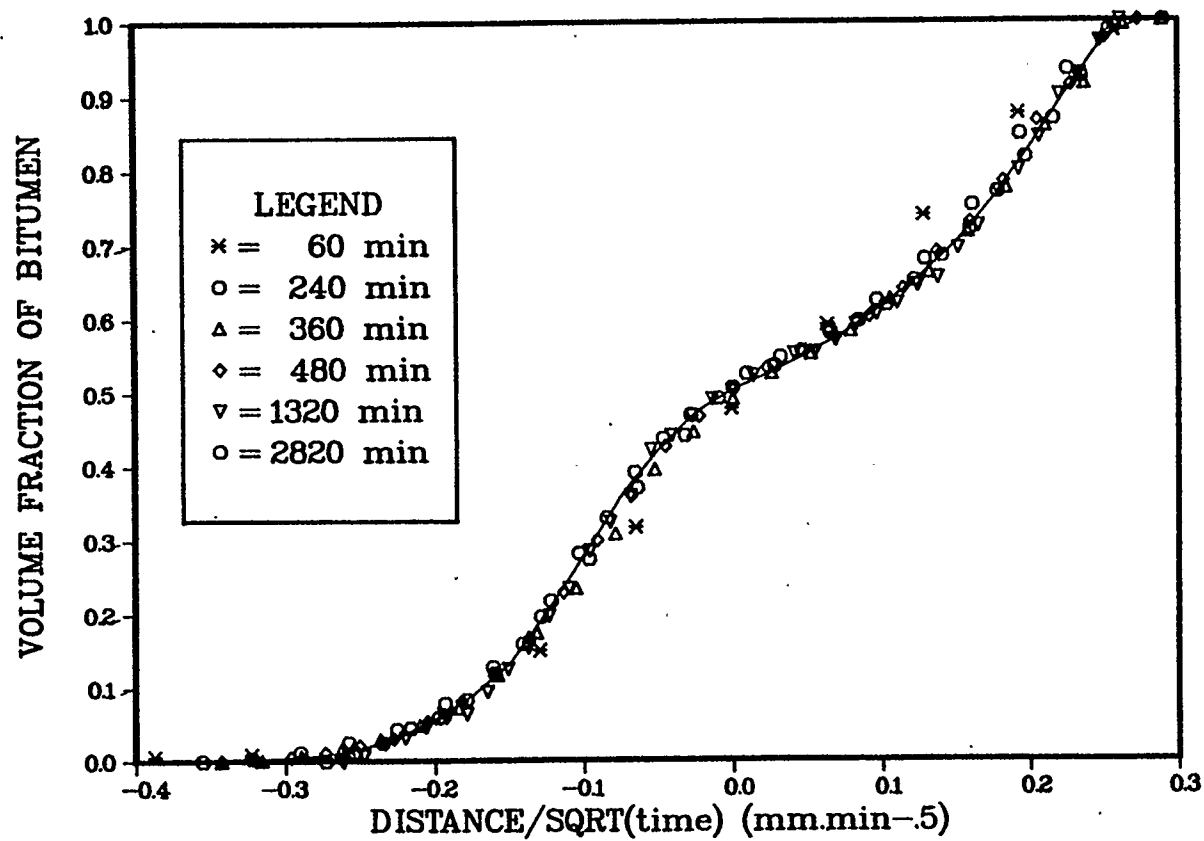


FIGURE 12: CONCENTRATION DEPENDANCE ON $y/\sqrt{t}$ RUN 15

$b = .0127\text{cm}$ RUN 25

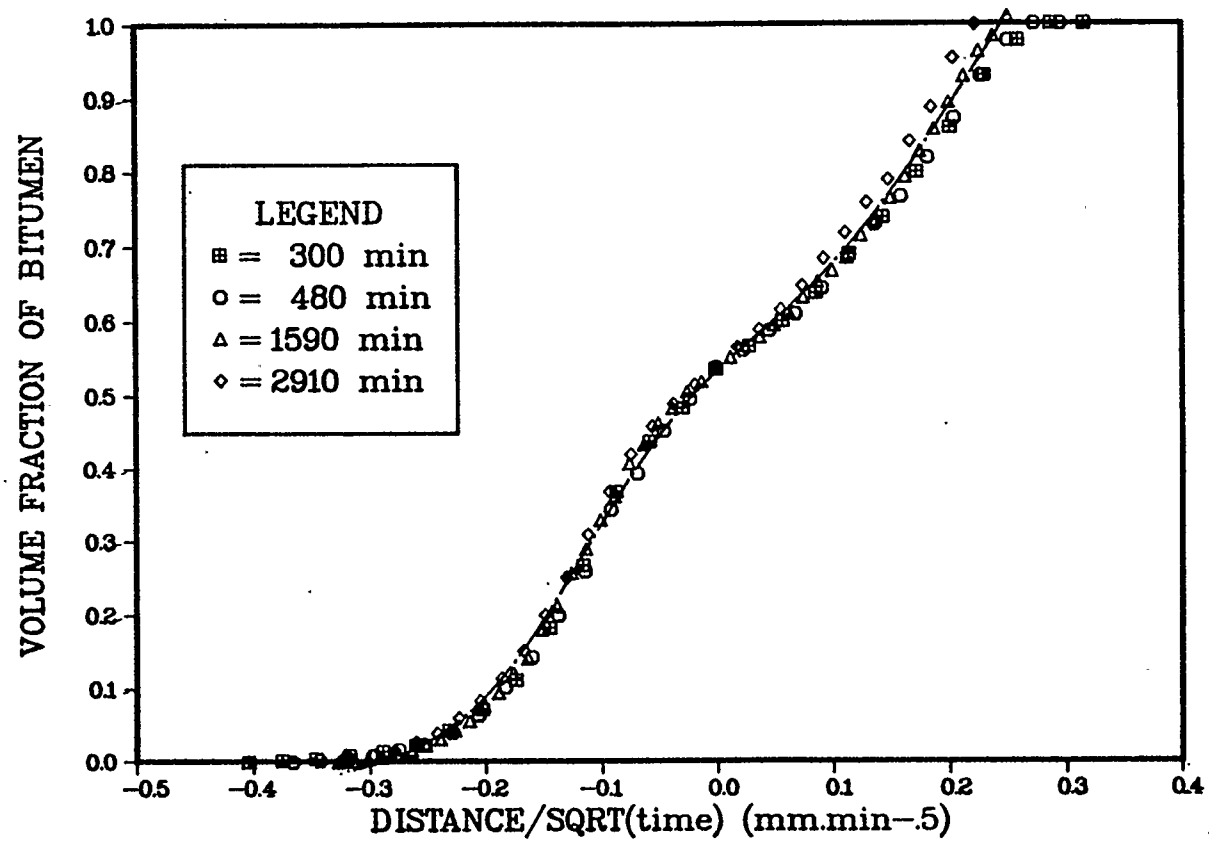


FIGURE 13: CONCENTRATION DEPENDANCE ON $y/\sqrt{t}$ RUN 25

Table 10: Smoothed concentration values for Run 15

$$b = .0074 \text{ cm}$$

Distance [mm]	Concentration at 540 min. [g _B /cm ³]
-10.0000	0.0000
- 9.5000	0.0001
- 9.0000	0.0002
- 8.5000	0.0005
- 8.0000	0.0011
- 7.5000	0.0022
- 7.0000	0.0044
- 6.5000	0.0081
- 6.0000	0.0145
- 5.5000	0.0246
- 5.0000	0.0406
- 4.5000	0.0634
- 4.0000	0.0955
- 3.5000	0.1385
- 3.0000	0.1930
- 2.5000	0.2591
- 2.0000	0.3270
- 1.5000	0.3909
- 1.0000	0.4413
- 0.5000	0.4817
0.0000	0.5074
0.5000	0.5272
1.0000	0.5481
1.5000	0.5716
2.0000	0.5990
2.5000	0.6314
3.0000	0.6669
3.5000	0.7072
4.0000	0.7579
4.5000	0.8170
5.0000	0.8815
5.5000	0.9351
6.0000	0.9887

Table 11: Smoothed concentration values for Runs 7 and 14

$$b = .0086 \text{ cm}$$

Distance [mm]	Concentration at 540 min. [g _B /cm ³]
-10.0000	0.0001
- 9.5000	0.0001
- 9.0000	0.0003
- 8.5000	0.0007
- 8.0000	0.0014
- 7.5000	0.0027
- 7.0000	0.0052
- 6.5000	0.0096
- 6.0000	0.0167
- 5.5000	0.0282
- 5.0000	0.0451
- 4.5000	0.0703
- 4.0000	0.1039
- 3.5000	0.1489
- 3.0000	0.2052
- 2.5000	0.2728
- 2.0000	0.3412
- 1.5000	0.4000
- 1.0000	0.4480
- 0.5000	0.4857
0.0000	0.5153
0.5000	0.5383
1.0000	0.5602
1.5000	0.5848
2.0000	0.6128
2.5000	0.6451
3.0000	0.6828
3.5000	0.7261
4.0000	0.7758
4.5000	0.8320
5.0000	0.8934
5.5000	0.9508
6.0000	0.9900

Table 12: Smoothed concentration values for Run 13

$$b = .0097 \text{ cm}$$

Distance [mm]	Concentration at 540 min. [g _B /cm ³]
- 9.5000	0.0001
- 9.0000	0.0003
- 8.5000	0.0006
- 8.0000	0.0013
- 7.5000	0.0025
- 7.0000	0.0049
- 6.5000	0.0091
- 6.0000	0.0162
- 5.5000	0.0277
- 5.0000	0.0448
- 4.5000	0.0703
- 4.0000	0.1048
- 3.5000	0.1510
- 3.0000	0.2091
- 2.5000	0.2787
- 2.0000	0.3485
- 1.5000	0.4067
- 1.0000	0.4532
- 0.5000	0.4897
0.0000	0.5178
0.5000	0.5406
1.0000	0.5624
1.5000	0.5864
2.0000	0.6146
2.5000	0.6475
3.0000	0.6850
3.5000	0.7283
4.0000	0.7780
4.5000	0.8338
5.0000	0.8922
5.5000	0.9502
6.0000	0.9923

Table 13: Smoothed concentration values for Runs 17 and 25

$$b = .0127 \text{ cm}$$

Distance [mm]	Concentration at 540 min. [g _B /cm ³]
-10.0000	0.0001
- 9.5000	0.0001
- 9.0000	0.0003
- 8.5000	0.0007
- 8.0000	0.0015
- 7.5000	0.0030
- 7.0000	0.0058
- 6.5000	0.0109
- 6.0000	0.0193
- 5.5000	0.0326
- 5.0000	0.0533
- 4.5000	0.0822
- 4.0000	0.1225
- 3.5000	0.1748
- 3.0000	0.2365
- 2.5000	0.3095
- 2.0000	0.3739
- 1.5000	0.4277
- 1.0000	0.4723
- 0.5000	0.5098
0.0000	0.5408
0.5000	0.5671
1.0000	0.5908
1.5000	0.6165
2.0000	0.6459
2.5000	0.6794
3.0000	0.7177
3.5000	0.7609
4.0000	0.8110
4.5000	0.8633
5.0000	0.9135
5.5000	0.9610
6.0000	0.9978

Because of the unique shape of the concentration-distance curves obtained from previous experiments, it was felt that it was important to observe the mass transfer behaviour also in a narrower concentration range. Therefore, experiments with toluene/bitumen solution and bitumen solution/bitumen systems were conducted. In this way, the concentration range was narrowed and differences in those properties which are dependent on concentration (viscosity, density, diffusivity) became less evident.

It is an interesting phenomenon that the concentration-distance curve for the toluene/bitumen solution system is similar to the curve for toluene/bitumen system in the region when the distance y is less than zero. On the other hand, the concentration distance curves for bitumen solution/bitumen system show similarity to the curve for the toluene/bitumen system in the region that y is positive (Fig. 14).

The concentration-distance curves for the toluene/bitumen solution system are typical diffusion curves (Figs. 15 and 16). The concentration differences between experiments with a gap width of 0.0086 and 0.01632 cm are negligible.

Results from all the experiments with bitumen solutions are summarized in Tables 14, 15 and 16.

$b = .012 \text{ cm}$ RUN 30

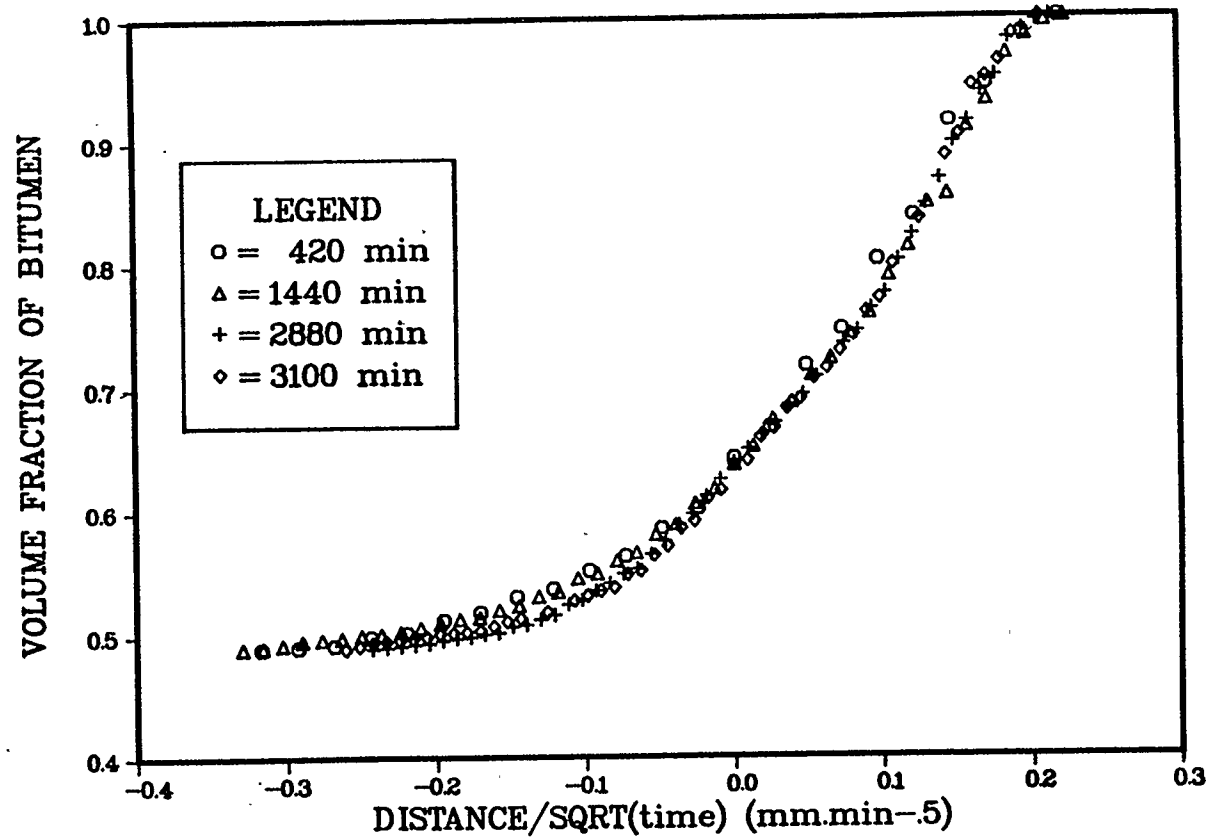


FIGURE 14: CONCENTRATION DEPENDANCE ON $y/\sqrt{t}$ RUN 30

$b = .0086 \text{ cm}$ RUN 27

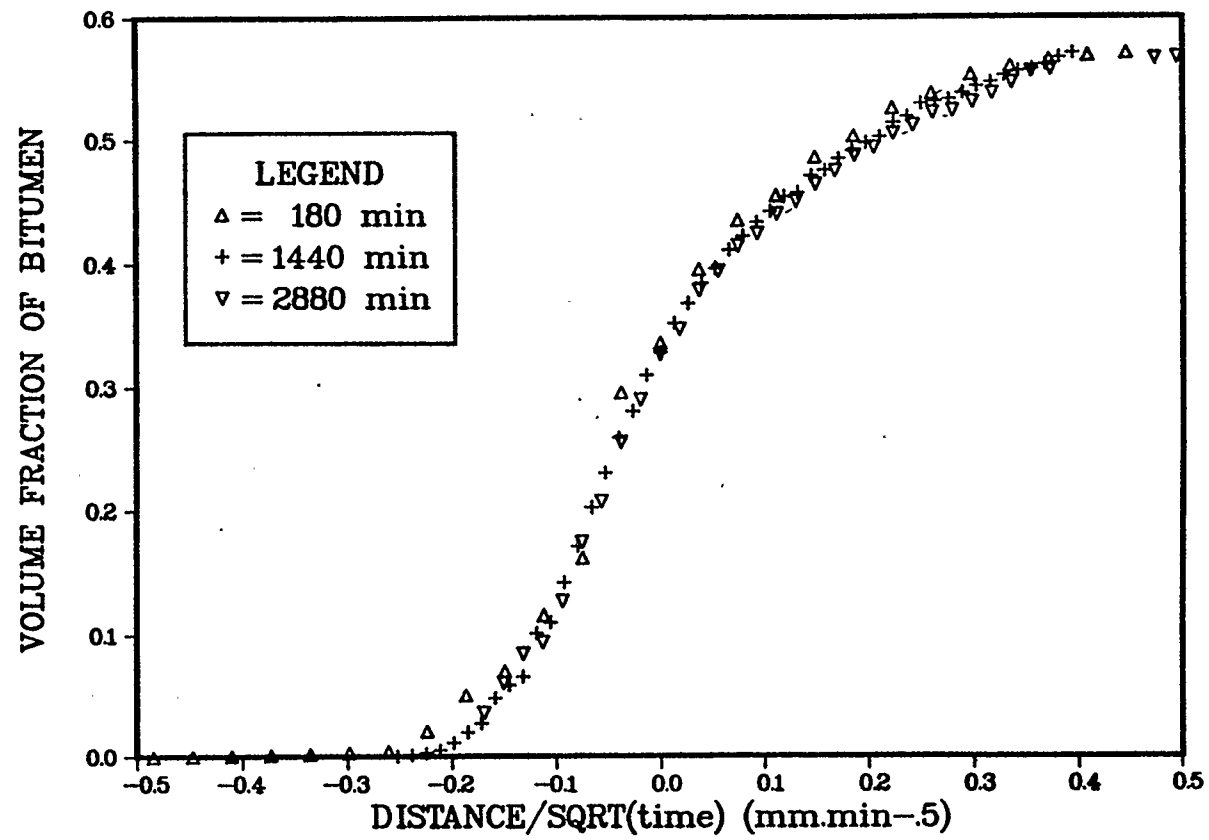


FIGURE 15: CONCENTRATION DEPENDANCE ON $y/\sqrt{t}$ RUN 27

$b = .01632 \text{ cm}$ RUN 23

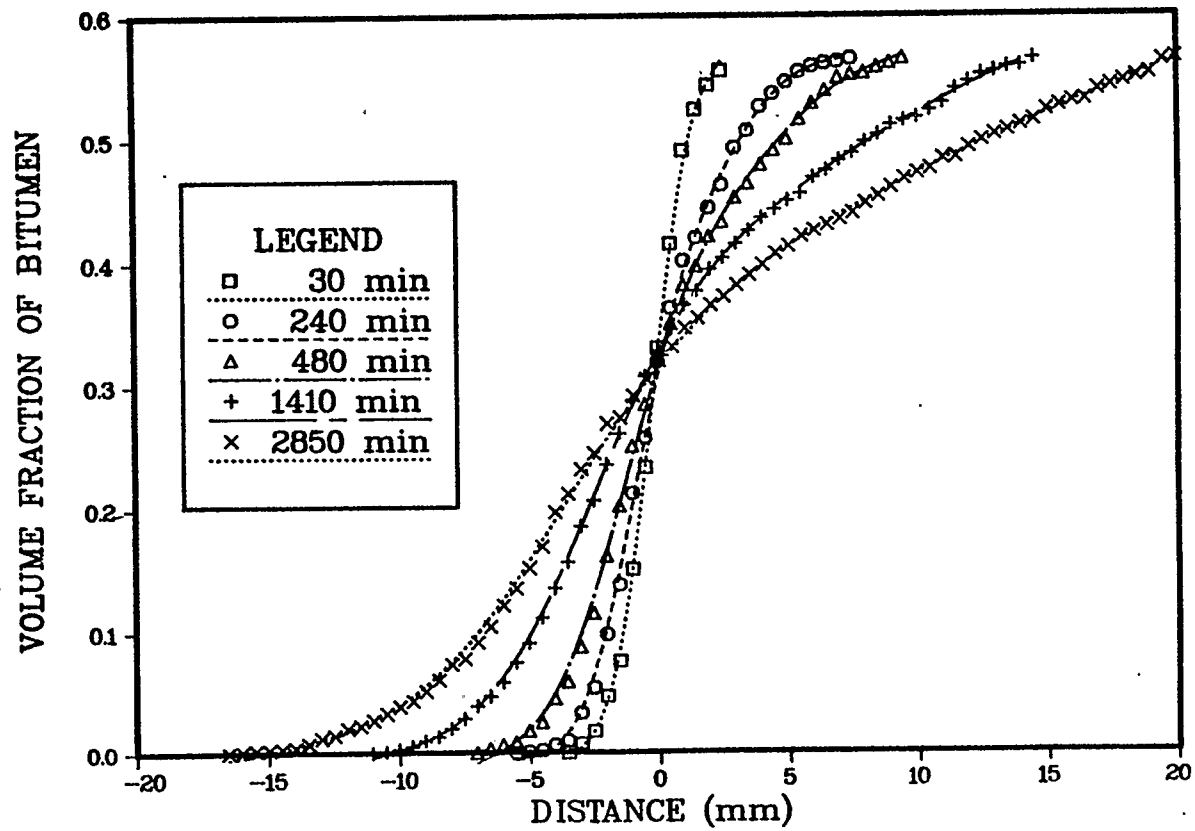


FIGURE 16: CONCENTRATION-DISTANCE CURVE RUN 23

Table 14: Smoothed Concentration values for Runs 21 and 23

$$b = .01632 \text{ cm}$$

Distance [mm]	Concentration at 540 ₃ min. [g _B /cm ³]
-10.0000	0.0000
- 9.5000	0.0001
- 9.0000	0.0001
- 8.5000	0.0003
- 8.0000	0.0006
- 7.5000	0.0012
- 7.0000	0.0023
- 6.5000	0.0043
- 6.0000	0.0074
- 5.5000	0.0125
- 5.0000	0.0202
- 4.5000	0.0315
- 4.0000	0.0470
- 3.5000	0.0679
- 3.0000	0.0948
- 2.5000	0.1278
- 2.0000	0.1665
- 1.5000	0.2101
- 1.0000	0.2569
- 0.5000	0.3059
0.0000	0.3468
0.5000	0.3717
1.0000	0.3931
1.5000	0.4124
2.0000	0.4307
2.5000	0.4467
3.0000	0.4623
3.5000	0.4767
4.0000	0.4899
4.5000	0.5020
5.0000	0.5129
5.5000	0.5227
6.0000	0.5314
6.5000	0.5388
7.0000	0.5448
7.5000	0.5507
8.0000	0.5567
8.5000	0.5626
9.0000	0.5686

Table 15: Smoothed Concentration values for Runs 27 and 29

$$b = .0086 \text{ cm}$$

Distance [mm]	Concentration at 540 min. [g _B /cm ³]
-10.0000	0.0000
- 9.5000	0.0001
- 9.0000	0.0001
- 8.5000	0.0003
- 8.0000	0.0006
- 7.5000	0.0012
- 7.0000	0.0022
- 6.5000	0.0041
- 6.0000	0.0072
- 5.5000	0.0123
- 5.0000	0.0200
- 4.5000	0.0315
- 4.0000	0.0472
- 3.5000	0.0686
- 3.0000	0.0960
- 2.5000	0.1297
- 2.0000	0.1692
- 1.5000	0.2136
- 1.0000	0.2613
- 0.5000	0.3102
0.0000	0.3453
0.5000	0.3736
1.0000	0.3975
1.5000	0.4183
2.0000	0.4368
2.5000	0.4539
3.0000	0.4696
3.5000	0.4841
4.0000	0.4974
4.5000	0.5093
5.0000	0.5200
5.5000	0.5290
6.0000	0.5369
6.5000	0.5439
7.0000	0.5503
7.5000	0.5561
8.0000	0.5616
8.5000	0.5669
9.0000	0.5722
9.5000	0.5750
10.0000	0.5780

Table 16: Smoothed Concentration values for Run 30

$$b = .012 \text{ cm}$$

Distance [mm]	Concentration at 540 min. [g _B /cm ³]
- 6.0000	0.5092
- 5.5000	0.5132
- 5.0000	0.5179
- 4.5000	0.5233
- 4.0000	0.5296
- 3.5000	0.5371
- 3.0000	0.5456
- 2.5000	0.5556
- 2.0000	0.5670
- 1.5000	0.5804
- 1.0000	0.5963
- 0.5000	0.6154
0.0000	0.6380
0.5000	0.6645
1.0000	0.6957
1.5000	0.7318
2.0000	0.7728
2.5000	0.8191
3.0000	0.8702
3.5000	0.9234
4.0000	0.9728

An overview of typical experiments is shown in Table 17.

Table 17: Summary of Experimental Conditions

Experiment	Gap Width [cm]	Initial Concentration [g/cm ³]		LV. %	
		Top	Bottom	Top	Bottom
15	0.0074	0	1.0178	0	100.0
7,14	0.0086	0	1.0178	0	100.0
13	0.0097	0	1.0178	0	100.0
17,25	0.0127	0	1.0178	0	100.0
21,23	0.0163	0	0.5802	0	57.0
27,29	0.0086	0	0.5802	0	57.0
30	0.0120	0.5034	1.0178	49.16	100.0

4.5 Calculation of an Overall Diffusion Coefficient

If the diffusion coefficient depends on concentration only, then the concentration distribution values measured at various times must lie on a single curve described by the function $C=f(y/\sqrt{t})$. It can be seen from Figures 11-15 that the diffusion coefficient in the studied system depends on concentration only.

Numerical evaluation of diffusivities from measured concentration data was very sensitive even to a small experimental error. Scatter of the experimental data caused an oscillation of the concentration gradient-distance function and, as a consequence of it, negative values of the overall diffusion coefficient at certain concentrations were obtained. Therefore,

a smoother curve was fitted through the experimental data and values read from this curve were employed for the calculation of diffusivities.

However, uncertainty arose for concentrations near the limiting values due to the infinitesimal changes in concentration and the inability of the analytical instrument to measure these changes. A method suggested by Hall [14] was used to obtain the concentrations near the extremes of the concentration range.

A variable s , that was calculated from eq. 4.9, was plotted against $y/\sqrt{t}$.

$$\frac{1}{2} (1 + \operatorname{erf} s) = C/C_{\infty} \quad 4.9$$

The curves in Fig. 17 represent the dependence of " s " on $y/\sqrt{t}$ for the toluene-bitumen system with two different cell gaps (0.0127 cm and 0.0086 cm). Bitumen concentration in 100% bitumen or in bitumen solution was considered as C_{∞} . In each case, the concentration of bitumen became zero at nearly the same value of $y/\sqrt{t}$, however, the gradients were different.

The values of k and h were calculated from the linear portion of the curve and the limiting values obtained by extrapolation.

$$s = k(y/\sqrt{t}) + h \quad 4.10$$

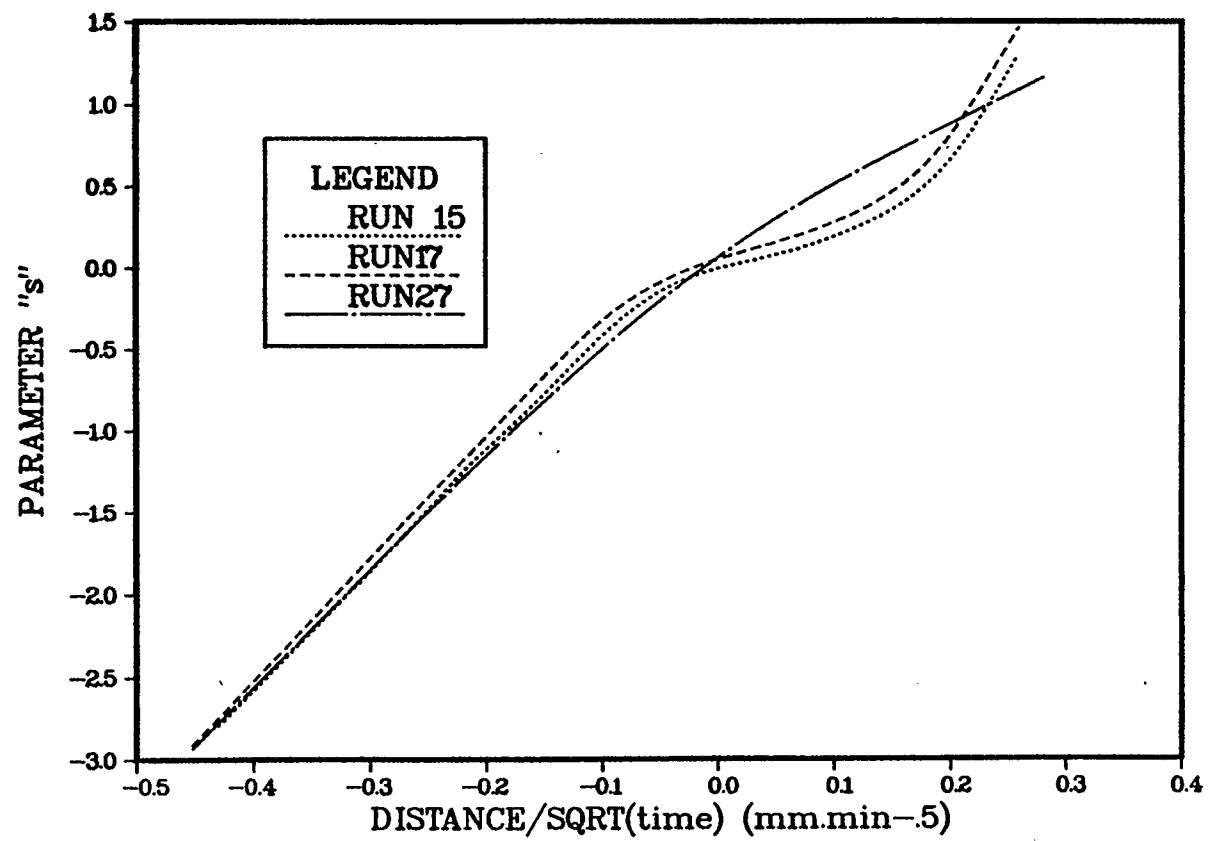


FIGURE 17: PROBABILITY CURVES

Concentration values at 540 min. were calculated from the fitted curve using a cubic spline method. This time the concentration gradient-distance curves were smooth, without any sign of oscillation. Curves of $dx_B/dy = f(y)$ for each of the three experiment types are shown on Figs. 18-20.

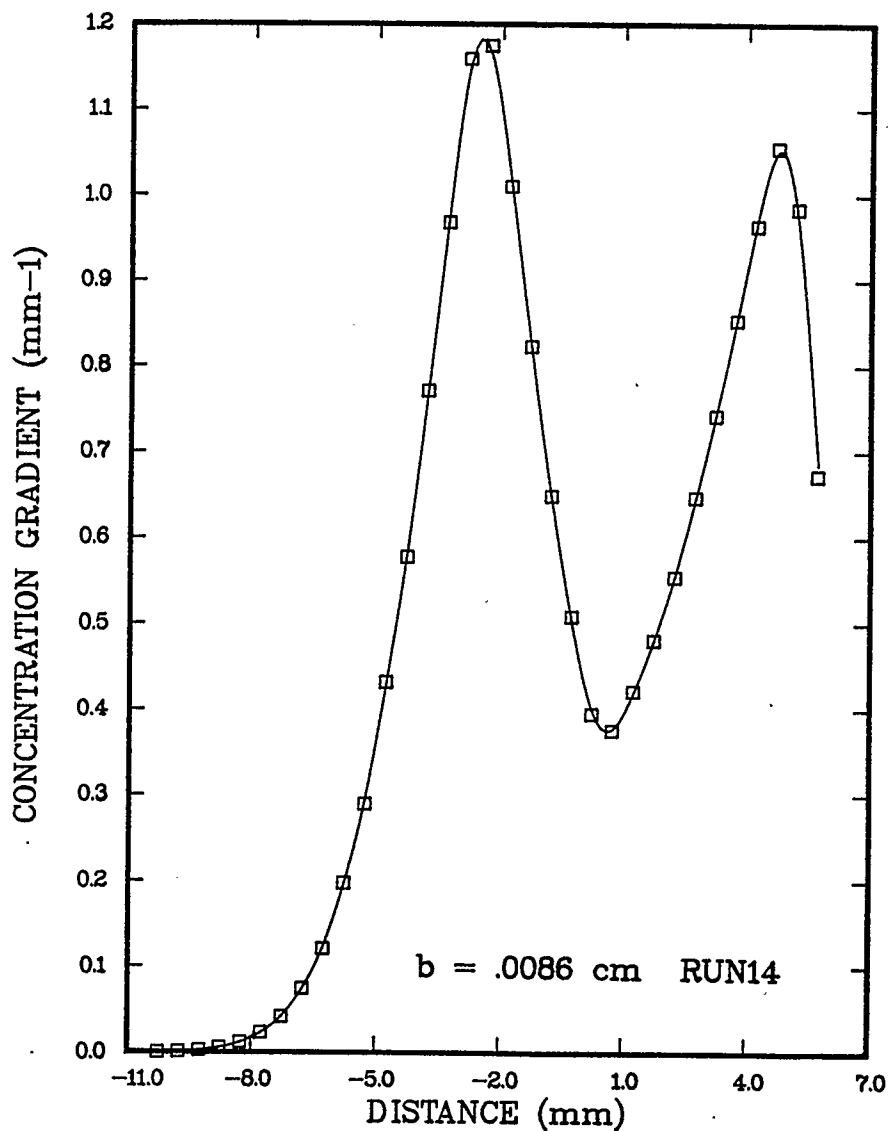


FIGURE 18: CONCENTRATION GRADIENT-DISTANCE CURVE FOR
TOLUENE-BITUMEN SYSTEM

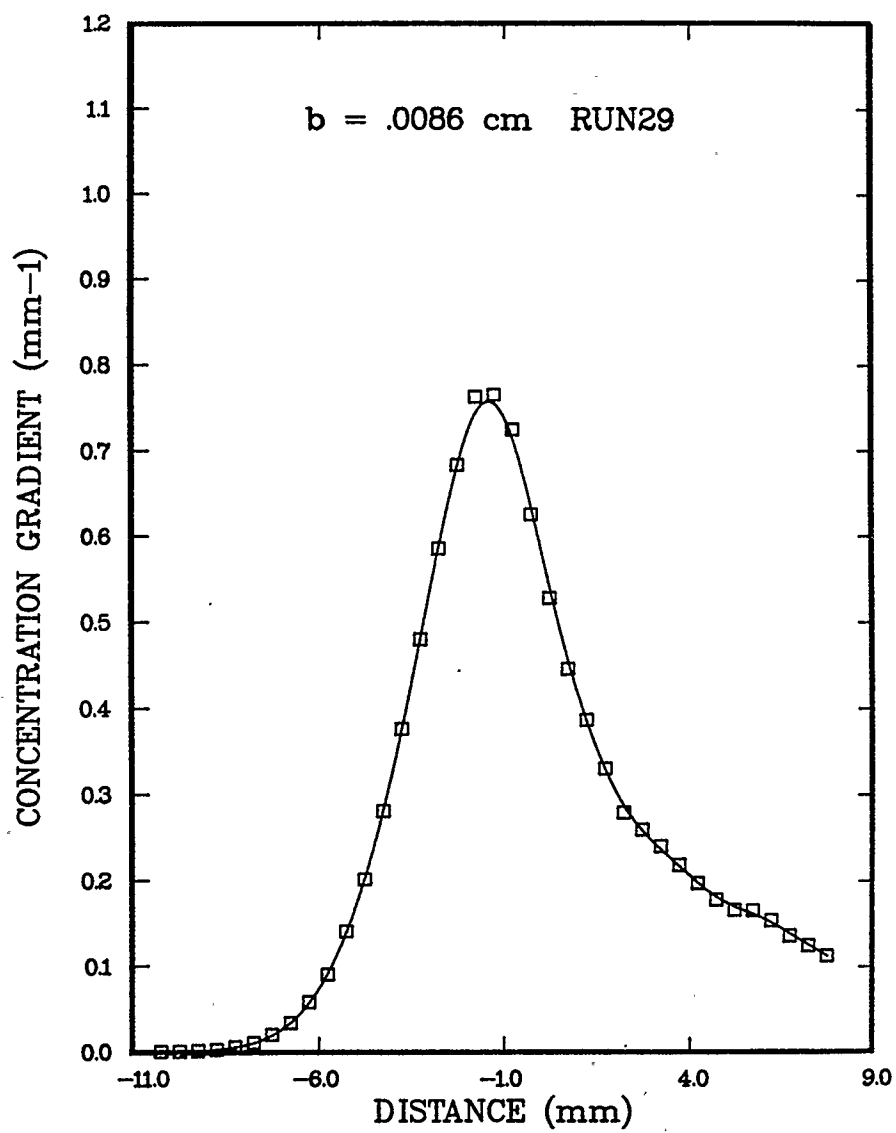


FIGURE 19: CONCENTRATION GRADIENT-DISTANCE CURVE FOR
TOLUENE-BITUMEN SOLUTION SYSTEM

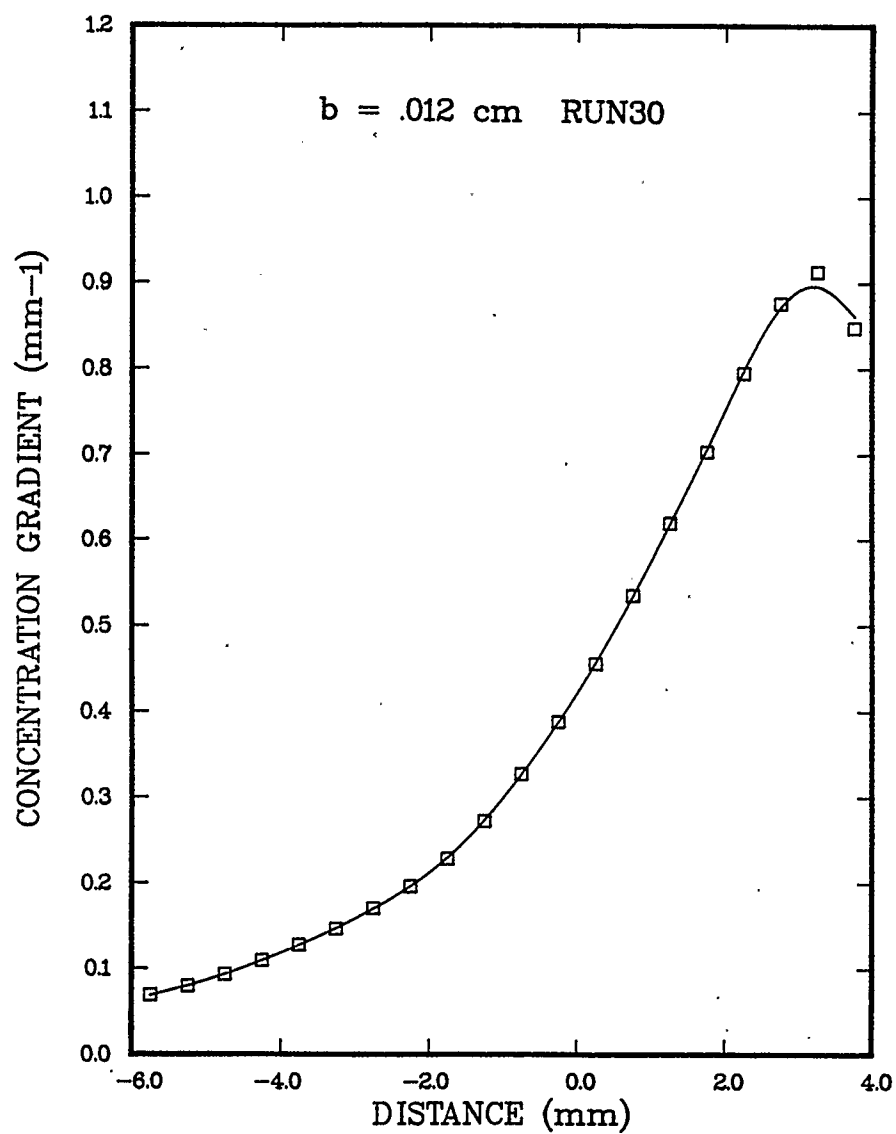


FIGURE 20: CONCENTRATION GRADIENT-DISTANCE CURVE FOR BITUMEN SOLUTION-BITUMEN SYSTEM

The smoothed concentration values were used in the evaluation of the overall diffusion coefficient from eq. 4.8. Values of the calculated overall diffusion coefficients are shown in tables 18-21.

Table 18: Overall Diffusion Coefficients - Run 13

Bitumen Concentration	Overall Diffusion Coefficient * 10^6
[vol. fraction]	[cm ² /s]
0.0000	0.9213
0.0077	0.9963
0.0616	1.0687
0.1347	1.1261
0.2533	1.2504
0.3219	1.5201
0.3824	2.0078
0.4316	2.6799
0.4704	3.5485
0.5005	4.6332
0.5244	5.5461
0.5461	5.6179
0.5691	4.9646
0.5955	4.1545
0.6265	3.4600
0.6620	2.8518
0.7028	2.2786
0.7497	1.7541
0.8028	1.3154
0.8594	0.9329
0.9165	0.6278
0.9625	0.3746
0.9925	0.1724

Table 19: Overall Diffusion Coefficients - Run 14

Bitumen Concentration [vol. fraction]	Overall Diffusion Coefficient * 10 ⁶ [cm ² /s]
0.0000	0.9399
0.0045	1.0029
0.0248	1.0599
0.1348	1.1522
0.2508	1.2745
0.3178	1.5323
0.3780	1.9828
0.4279	2.6100
0.4676	3.4208
0.4988	4.4832
0.5231	5.4874
0.5449	5.5129
0.5683	4.8587
0.5950	4.1485
0.6256	3.4546
0.6613	2.8201
0.7023	2.2514
0.7495	1.7321
0.8031	1.2613
0.8621	0.8766
0.9195	0.6141
0.9627	0.3733
0.9929	0.1784

Table 20: Overall Diffusion Coefficients - Run 15

Bitumen Concentration	Overall Diffusion Coefficient * 10 ⁶
[vol. fraction]	[cm ² /s]
0.0000	0.9295
0.0040	0.9981
0.0446	1.1612
0.1293	1.1231
0.2441	1.2524
0.3106	1.4609
0.3740	1.8539
0.4256	2.4624
0.4669	3.4736
0.4945	5.2665
0.5149	6.1650
0.5352	5.6712
0.5579	4.8936
0.5843	4.0558
0.6153	3.4335
0.6496	2.9419
0.6885	2.2703
0.7367	1.6301
0.7934	1.1397
0.8559	0.8297
0.9104	0.5364
0.9631	0.2093

Table 21: Overall Diffusion Coefficients - Run 17

Bitumen Concentration	Overall Diffusion Coefficient * 10 ⁶
[vol. fraction]	[cm ² /s]
0.0000	0.9156
0.0035	0.9465
0.0361	0.9966
0.1306	1.0833
0.2467	1.2193
0.3167	1.4568
0.3780	1.9317
0.4290	2.4822
0.4714	3.0779
0.5070	3.7526
0.5365	4.5060
0.5618	5.0721
0.5855	4.9327
0.6115	4.2515
0.6412	3.5835
0.6750	2.9822
0.7136	2.4206
0.7574	1.8814
0.8071	1.4558
0.8580	1.1416
0.9068	0.8340
0.9514	0.5413
0.9843	0.4422

The overall diffusion coefficient from the experiments with different cell spacings are plotted in Figure 21. The overall diffusion coefficient is found to be a strong function of solution concentration. The points from each of the four experiments shown all fall on the same curve. This indicates that the measurements are reproducible and that the diffusivity is independent of cell spacing, at least over the range 0.0074 - 0.012 cm.

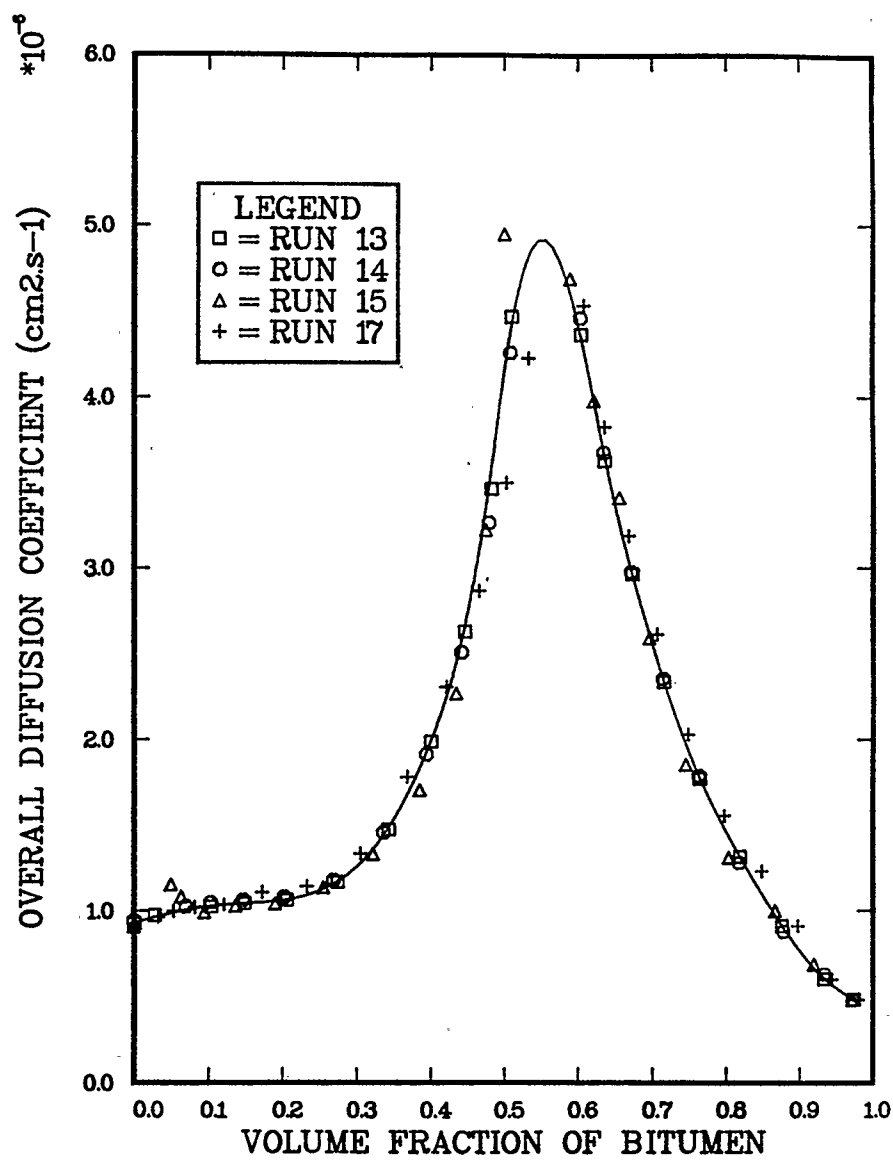


FIGURE 21: OVERALL DIFFUSIVITY DEPENDENCE ON CONCENTRATION

4.6 Intrinsic Diffusion Coefficients

"Overall diffusion coefficients" such as those shown in Figure 21 represent within them a transfer of matter which is caused by the bulk flow of solution as well as that caused by true diffusion.

Toluene molecules diffuse faster than the bitumen molecules because they are smaller. The intrusion of the smaller molecules causes pressure build up on the side containing the higher concentration of large size molecules. This results in a bulk flow of bitumen solution towards the side containing the higher concentration of smaller molecules.

The overall diffusion coefficient which was derived in the previous section represents the net result of the diffusive process and the bulk flow. These can be separated by introducing the idea of intrinsic diffusion coefficients.

The amount of toluene remaining beyond the interface ($y > 0$) is the difference between the diffusional flow of toluene $D_S \partial X_S / \partial y$ and the amount of toluene carried away in the bulk flow uX_S . To satisfy the mass balance of the system this difference must be equal to the bitumen transferred by diffusion $D_B \partial X_S / \partial y$ and in the bulk flow uX_B .

$$D_S \frac{\partial X_S}{\partial y} - uX_S = D_B \frac{\partial X_S}{\partial y} + uX_B \quad 4.11$$

u = bulk flow velocity [cm.s^{-1}]

It should be appreciated that D_S and D_B are not constants but are functions of concentration. It may be expected, and indeed it is found later, that both D_S and D_B decrease markedly as the bitumen concentration increases (i.e. as the viscosity of the solution increases).

The bulk flow velocity u is expressed as:

$$u = (D_S - D_B) \frac{\partial X_S}{\partial y} \quad 4.12$$

Equation 4.13 describes the mass conservation of toluene.

$$\frac{\partial}{\partial y} \left(D_S \frac{\partial X_S}{\partial y} - uX_S \right) = \frac{\partial X_S}{\partial t} \quad 4.13$$

The term $D_S \partial X_S / \partial y - uX_S$ represents the net flux of toluene; it was described in eq. 4.3 as $D_{BS} \partial X_S / \partial y$.

$$D_{BS} \partial X_S / \partial y = D_S \partial X_S / \partial y - uX_S \quad 4.14$$

Substituting the bulk flow velocity for u eq. 4.12) into eq. 4.14 results in the equation 4.15. This equation describes the relationship between the intrinsic diffusion coefficient of toluene (D_S) and that of bitumen (D_B) and the overall diffusion coefficient D_{BS} .

$$D_{BS} = D_S X_B + D_B X_S \quad 4.15$$

It is obvious from eq. 4.15 that the value of the overall diffusion coefficient D_{BS} is equal to the intrinsic diffusion coefficient of toluene in pure bitumen ($X_B = 1$, $X_S = 0$) and equal to the intrinsic diffusion coefficient of bitumen in pure toluene ($X_B = 0$, $X_S = 1$).

To be able to obtain individual values for D_S and for D_B from eq. 4.15, either the concentration dependence of D_S or D_B or the relationship between both intrinsic diffusion coefficients must be known. However, none of these functions is known and therefore only the range in which the values of D_S and D_B can lie will be calculated.

The toluene diffusion coefficient probably lies between the value of the overall diffusion coefficient and a maximum value equal to D_{BS}/X_B ; this is the value which would be found by setting $D_B = 0$ in equation 4.15.

The bitumen diffusion coefficient must be greater than zero; it is probably less than D_{BS} because of the larger size of the bitumen molecules.

If one assumes that the concentration dependence is the same for both intrinsic coefficients, then the ratio of D_S to D_B will be constant and can be expressed as:

$$\frac{D_S}{D_B} = \frac{D_{S0}}{D_{B0}} \quad 4.16$$

where D_{S0} is the self-diffusion coefficient of toluene ($1.75 \times 10^{-5} \text{ cm}^2/\text{s}$; literature value at 20°C [15]) and D_{B0} is the diffusion coefficient of bitumen at zero bitumen concentration which is found from the experimental data presented here.

By substituting eq. 4.16 into eq. 4.15, the bitumen coefficient can be calculated as:

$$D_B = \frac{D_{BS}}{\frac{D_{S0}}{D_{B0}} X_B + X_S} \quad 4.17$$

The dependence of D_{BS} , D_B , D_S as well as the maximum attainable values of toluene diffusion coefficient is shown in Figure 22. At very low bitumen concentration, the $D_{S\text{max}}$ values are considerably higher than the self diffusion coefficient of toluene. It means that in the diluted solutions the value of D_B is well above zero and the mass transfer is controlled by diffusion (bulk flow is relatively small). As the concentration of bitumen increases, the value of D_B is approaching zero and most of the bitumen is carried away by bulk flow.

The intrinsic diffusion coefficient of toluene decreases in the concentration range of zero to about 30 volume % of bitumen.

Then it increases and attains a maximum at a bitumen concentration of about 60 volume %. It was expected that the diffusion coefficient of toluene would decrease monotonically with concentration from a value of the self-diffusion coefficient at $X_B = 0$ to a value of the overall diffusivity at concentration $X_B = 1$. Such a variation would mirror the change in viscosity with solvent concentration.

The maximum shown by the calculated values (from experimental data) is unexpected. It is possible that the phenomenon is related to the formation of transient structures in the bitumen as it is diluted and swollen by the toluene solvent. In support of this possibility is the observation of the precipitation of a black material in a narrow concentration band - presumably this material consists of asphaltenes. This precipitate would decrease the viscosity in that region and would conceivably account for an increased toluene mobility. It will be recalled that precipitation of asphaltenes was also observed and, to a much larger extent, in the earlier diaphragm cell experiments. It is believed that such precipitate is a transient phenomenon in that, with agitation, bitumen and toluene are completely miscible.

It would be interesting to repeat the experiments described here using solvents such as CCl_4 which are known to suspend asphaltene particles more completely than aromatic solvents such as benzene and toluene. (Gulzum, Z. [21]).

It is also possible that fractionation of the bitumen during diffusional process caused by differing diffusivities of solute molecules of various types and sizes perhaps combined with transient asphaltene precipitation may have caused errors.

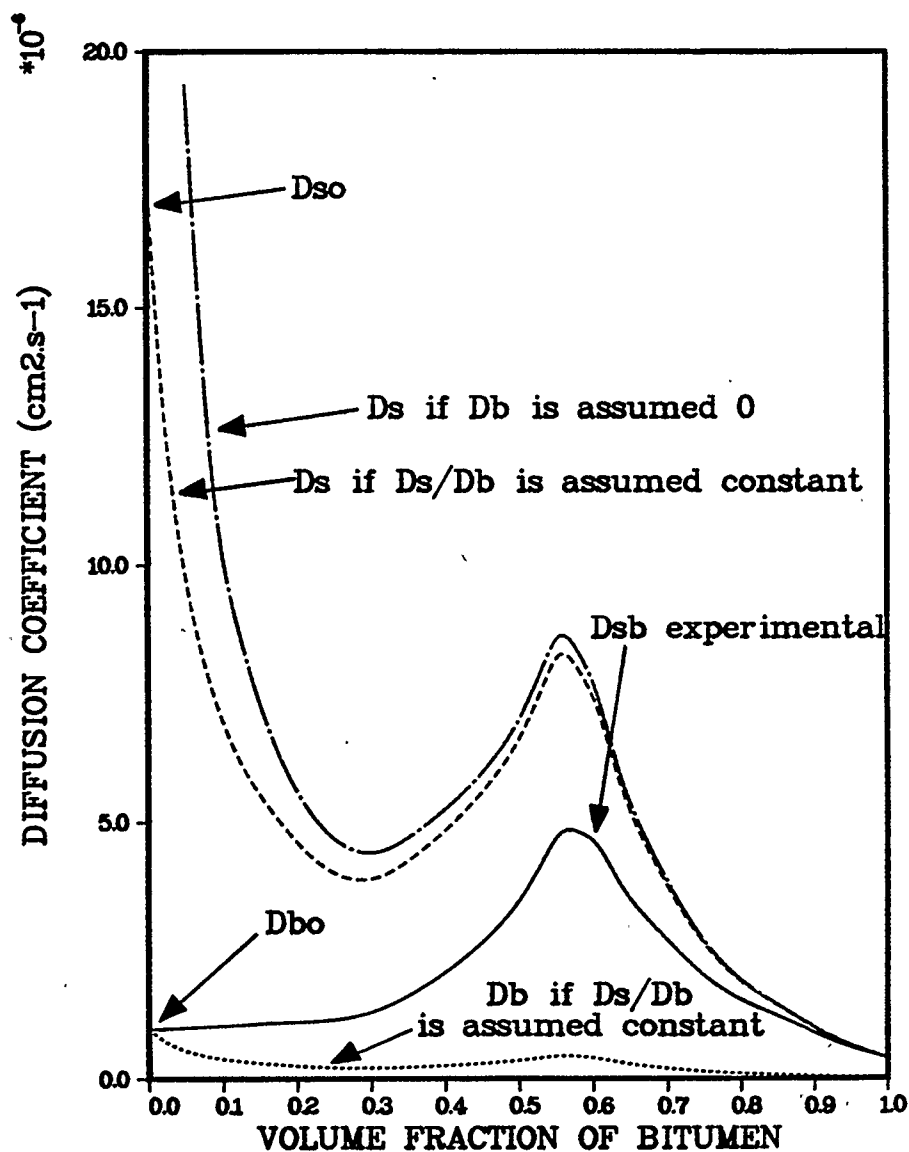


FIGURE 22: DIFFUSIVITY IN TOLUENE/BITUMEN SYSTEM

4.7 Prediction of Concentration Distribution from Measured Diffusion Coefficients

The concentration distributions for the toluene/bitumen solution and the bitumen solution/bitumen systems were predicted from eq. 4.3 using the values of the overall diffusion coefficient which were measured for the toluene/bitumen system. The initial concentration, boundary and initial conditions were chosen to correspond to experiments 21, 23, 27, 29 and 30.

The calculated and measured concentration values agree reasonably well for experiments 23 and 27 (Figures 23,24). Similar comparisons were found for experiments 21 and 29.

In the bitumen solution/bitumen system (experiment 30) the calculated values are higher than the measured concentration (Figure 25). The discrepancies might be caused by various degrees of bitumen fractionation in the bitumen solution/bitumen and the toluene/bitumen system.

The points in Figures 23-25 represent the measured concentration values. The lines show the calculated concentrations.

$b = .01632 \text{ cm}$ RUN 23

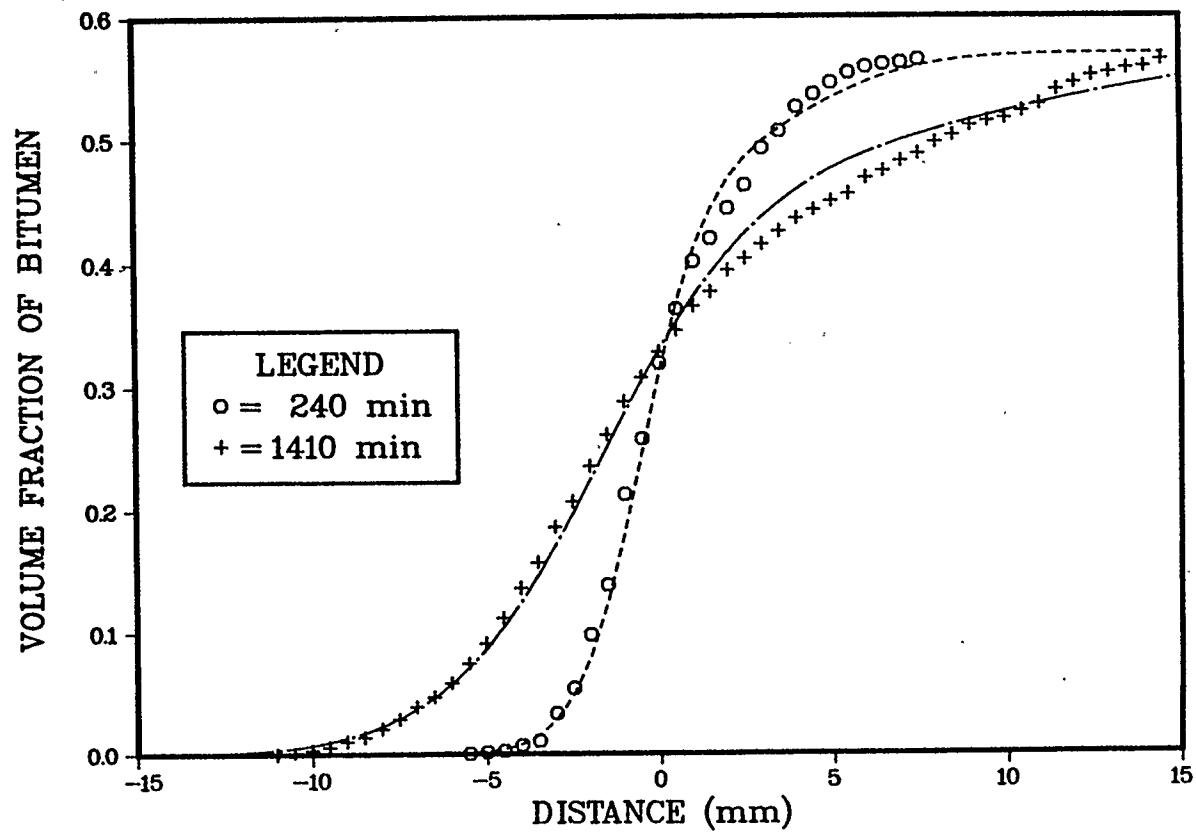


FIGURE 23: COMPARISON OF MEASURED AND CALCULATED CONCENTRATION VALUES RUN 23

$b = .0086 \text{ cm}$ RUN 27

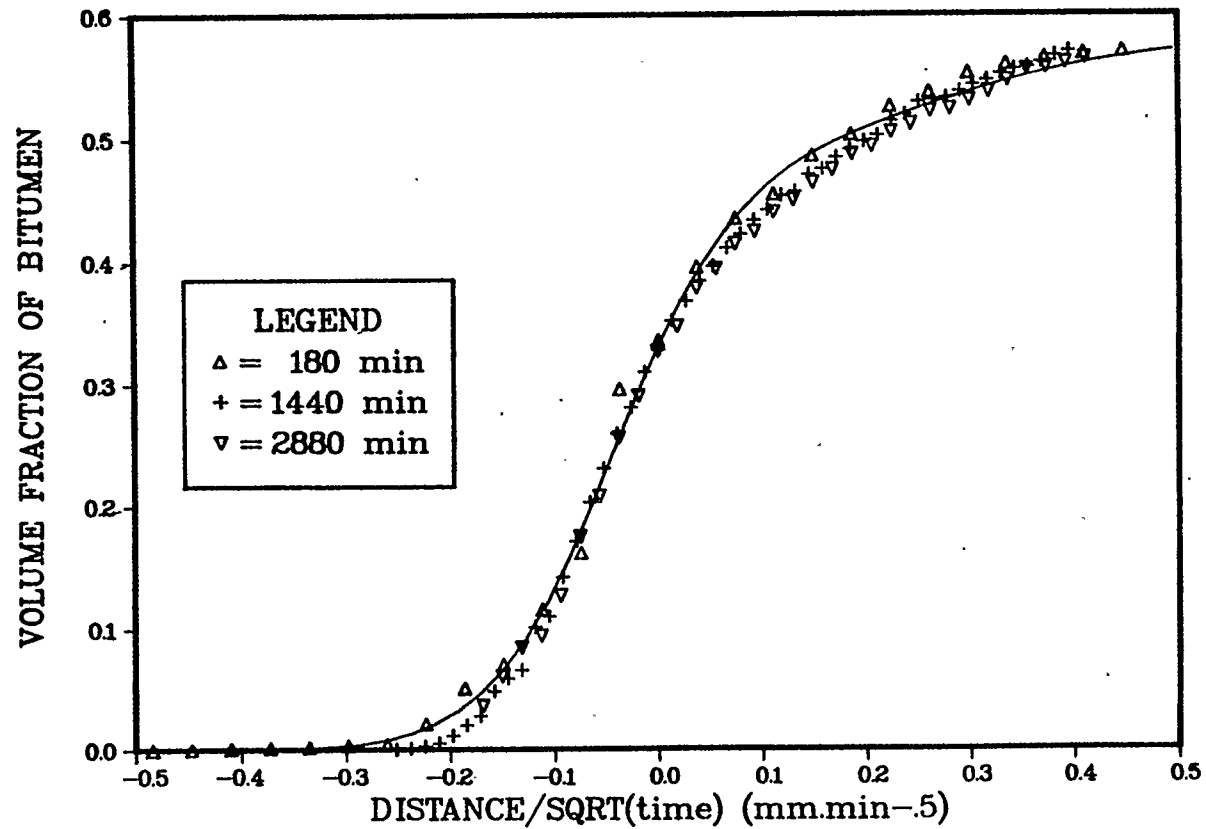


FIGURE 24: COMPARISON OF MEASURED AND CALCULATED CONCENTRATION VALUES RUN 27

$b = .012 \text{ cm}$ RUN 30

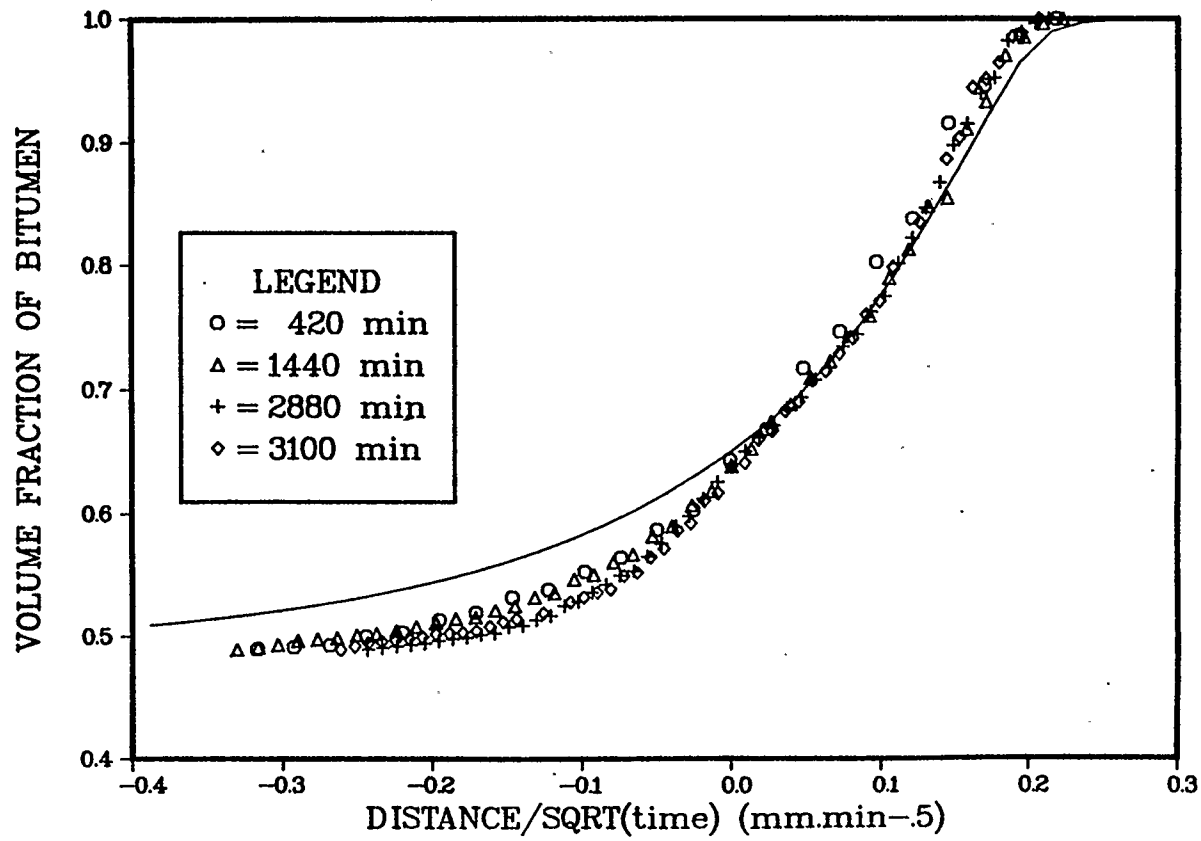


FIGURE 25: COMPARISON OF MEASURED AND CALCULATED CONCENTRATION VALUES RUN 30

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

From the results of this study it may be concluded that:

- 1) The overall diffusion coefficient D_{BS} as well as the diffusivity of bitumen and toluene are strongly dependent on concentration.
- 2) The width of the gap between the glass plates of the diffusion cell does not affect the diffusivity.
- 3) The amount of bitumen transferred in bulk decreases with decreasing initial concentration difference.
- 4) Due to the various sizes of bitumen molecules resulting in their varying mobilities, there is an indication of fractionation of the bitumen.

5.2 Recommendations

Further efforts should be directed in the following areas:

- 1) More experiments should be performed with smaller initial concentration differences. This may give more

information about the effect of bulk flow on the bitumen and toluene diffusion coefficients (especially at concentration levels between 30-70 vol.% of bitumen).

- 2) The diffusivity should be measured at elevated temperatures and pressures, using the same technique, but with a different diffusion cell.
- 3) The experiment should be repeated using solvents such as CCl_4 which is known to suspend asphaltene particles more completely than toluene.

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APPENDIX A

Lambert Beer Law

The relationship between the absorption of a light incident, concentration of an absorbing compound and the thickness of an absorbing media is expressed by the Lambert-Beer Law.

$$\log_{10}(I_0/I) = AS = \epsilon Cd \quad A.1$$

- I_0 = intensity of the emitted light
- I = intensity of the transmitted light
- ϵ = absorptivity
- C = concentration
- d = thickness of the absorbing layer
- AS = absorbance

Reflection, refraction and scatter of the light is neglected. This law is the basis for various spectrophotometric methods and is valid only for monochromatic light. Even if the condition of monochromaticity is fulfilled, it may happen that the absorbance AS is not a linear function of concentration. This may result from a chemical equilibrium reaction occurring in the observed solution e.g. dissociation, respective association of molecules, hydrolysis etc.

Viscosity Measurements

Viscosities of various bitumen solutions in toluene was measured with a UK RVB viscometer at 25°C (see Table 22 and Fig. 26)

Table 22: Viscosity of Bitumen-Toluene Mixtures

Concentration	Viscosity
[vol. %]	[m Pa.s]
0	0.77
19.74	1.6
38.93	3.8
49.66	7.7
59.40	17.0
78.25	114.0
100.00	31100.0

Density Measurements

Densities of bitumen-toluene mixtures were determined by a pycnometric method at 20°C (Table 23).

Table 23: Density of Bitumen-Toluene Mixtures

Concentration	Density
[vol. %]	[g/cm ³]
0	0.87544
19.66	0.90098
39.55	0.93058
49.34	0.94522
60.85	0.96132

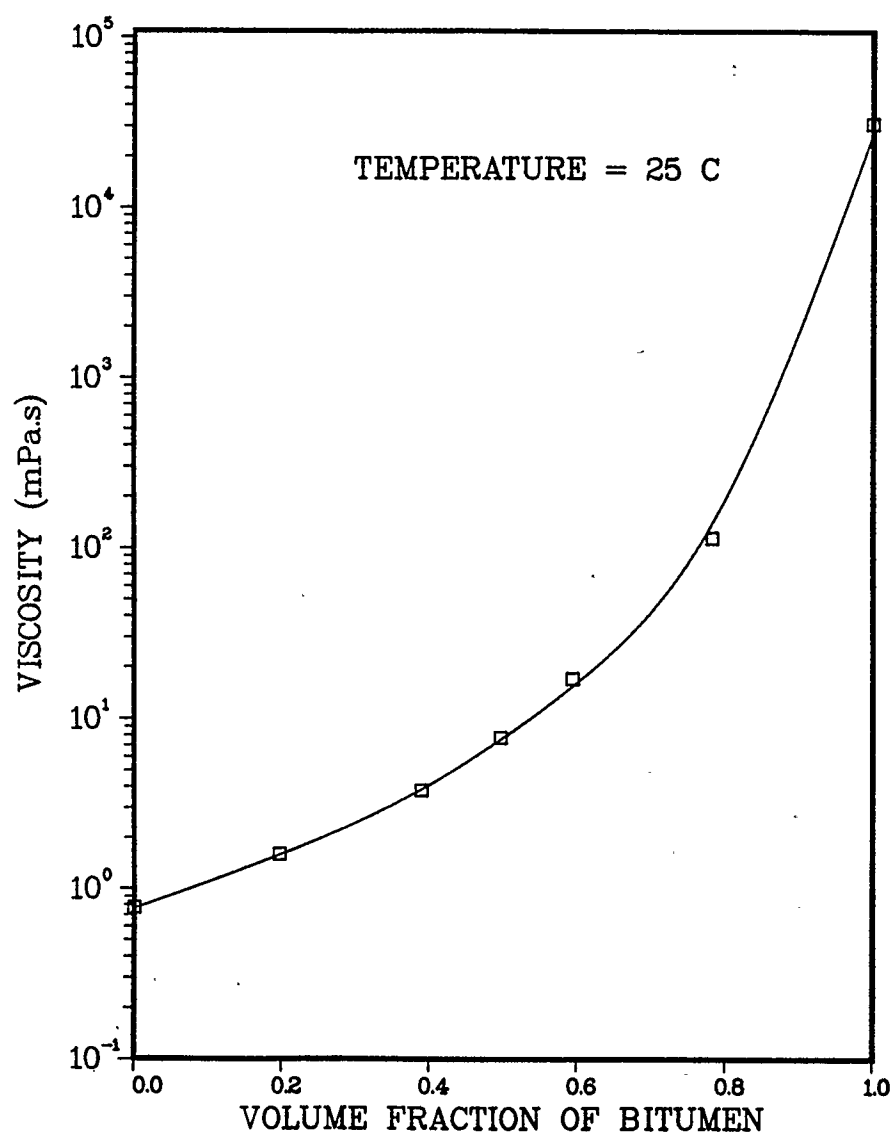


FIGURE 26: VISCOSITY OF TOLUENE-BITUMEN MIXTURES

It can be seen from Figure 27 that there is no volume change on mixing in the bitumen solutions.

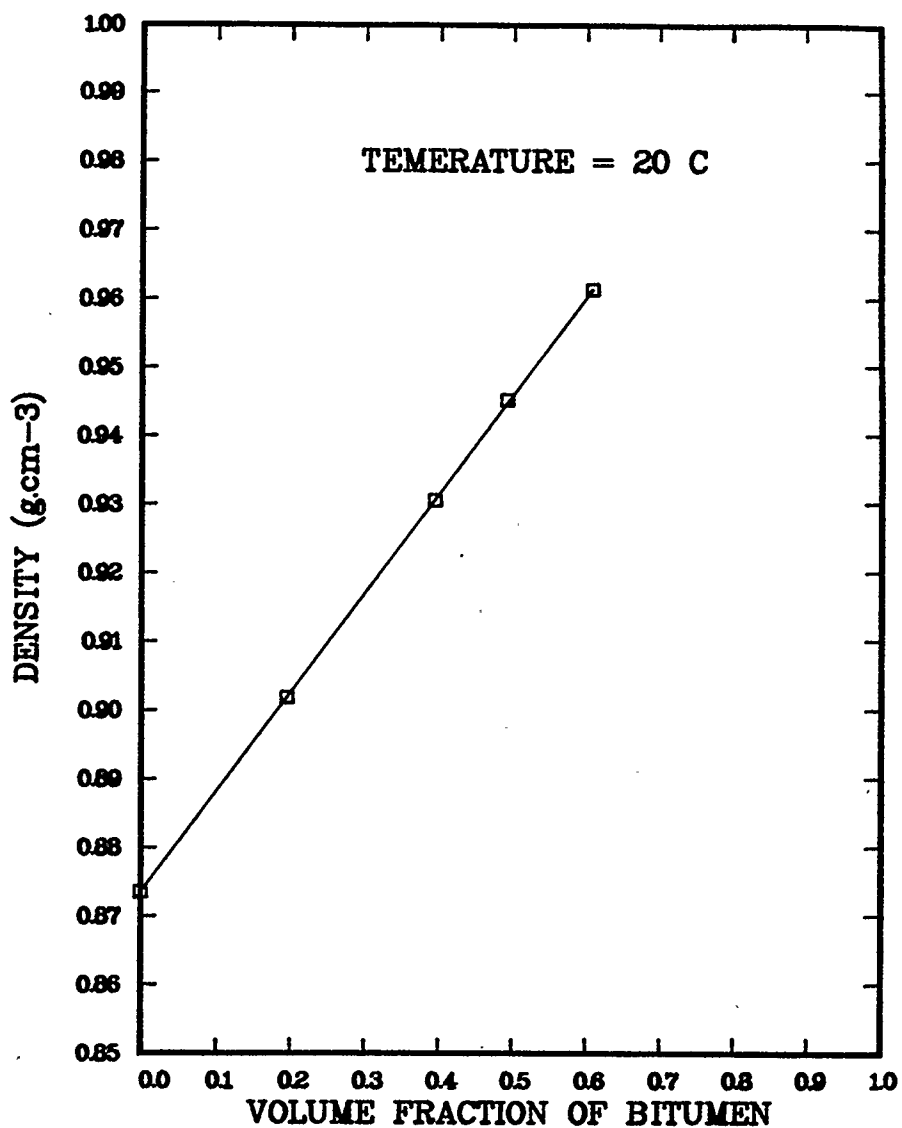


FIGURE 27: DENSITY OF TOLUENE-BITUMEN MIXTURES

APPENDIX B

Ga As Laser Diode

The Ga As laser is a compact, highly efficient semiconductor device.

A pure semiconductor must have four electrons in the atom's outer shell. It means that elements from the fourth group of the periodic table (Si, Ge) in pure state or combination of elements from other groups will fulfill the condition of a pure semiconductor. A crystalline combination of Ga (III b group) and As (V b group) results in a structure typical of a semiconductor. Introducing an impurity with more than four electrons in the outer shell into a semiconductor results in the creation of n-type material. On the other hand, impurity with less than four electrons in the outer shell creates a p-type material.

The Ga As laser consists of a flat p-n junction which is formed by contact between n-type and p-type materials. By superimposing a voltage (forward bias) across the junction, the potential of the n-type region will increase relatively to the p-type region and population inversion is created. The free electrons and holes drift towards the junction. By recombination of holes and electrons, radiation is emitted. In the Ga As laser the transition of an electron into a hole occurs directly.

Coherency of the emitted waves is achieved by polishing the

crystal faces on either side of the p-n junction which creates the Fabry-Perot cavity.

Infrared laser beams are obtained from a Ga As p-n junction because the energy gap between the valence (lower energy level) and the conduction band (higher energy level) corresponds to the electromagnetic waves in this part of the spectrum. If aluminium is used together with gallium and arsenic to form a Ga Al As semiconductor, the energy gap will increase and radiation is emitted at a lower wavelength.

Laser emission is characterized in Ga Al As diode as well as other semiconductor diodes by a change in the appearance of the light source. Below the threshold current the junction appears as a uniform horizontal line of light. As the threshold is approached, increased output from the junction is achieved and above the threshold a single laser beam with a narrow spectral width is produced.

Lasers operated in pulsed mode can produce considerably higher peak power than devices operating continuously.

The laser unit was purchased from M/A-COM Laser Diode (GaAlAs Diode Model No. LA-63; pulse generator Model No. LPA-23C; AC-DC Convertor Model No. LC-200).

The characteristics of the Ga Al As laser diode are summarized in Table 24.

Table 24: Characteristics of Ga Al As Laser Diode

Operating mode	pulsed
Total peak radiant flux at maximum forward current I_{fm}	5 W
Emitting area	$0.0152 * 0.002$ cm
Maximum peak forward current	20 A
Typical threshold current I_{th}	4 A
Typical peak forward voltage at I_{th}	6.5 V
Wave length of peak intensity	853 nm
Spectral width at 50% of peak height	3.5 nm
Rise time of radiant flux from 10%-90% of peak height	1 ns
Pulse width at 50% peak height and I_{fm}	80 ns

Silicon Detector

A silicon photodiode was used as a detector of the emitted radiation. It is a photon effect - photovoltaic type detector. In this type of detectors, the photons are absorbed in the vicinity of the p-n junction and produce free electron-hole pairs. The electrons move towards the n-type material and the holes towards the p-type material due to the internal electric field. The n-region becomes negatively charged and the p-region

positively charged. In photodiodes an external voltage and load resistance is applied in series with the photosensitive layer of the p-n junction.

A silicon photodiode has a peak response in the near infrared spectral region and therefore is very suitable as a detector of Ga Al As laser radiation.

The characteristics of the photodiode which was employed (purchased from Centronics, Model No. BPX 65) are given in Table 25.

Table 25: Characteristics of Silicon Photodiode at 23°C.

Active area	1 mm ²
Responsivity at 900 nm	.55 A/W
Rise time at 900 nm	1 ns
Noise equivalent power at 900 nm	$3.6 * 10^{-14}$ W/ $\sqrt{\text{Hz}}$
Dark current	1 nA

The signal was amplified by two cascaded ultrafast FET amplifiers, type LH 0032. The circuit diagram is shown in Fig. 28.

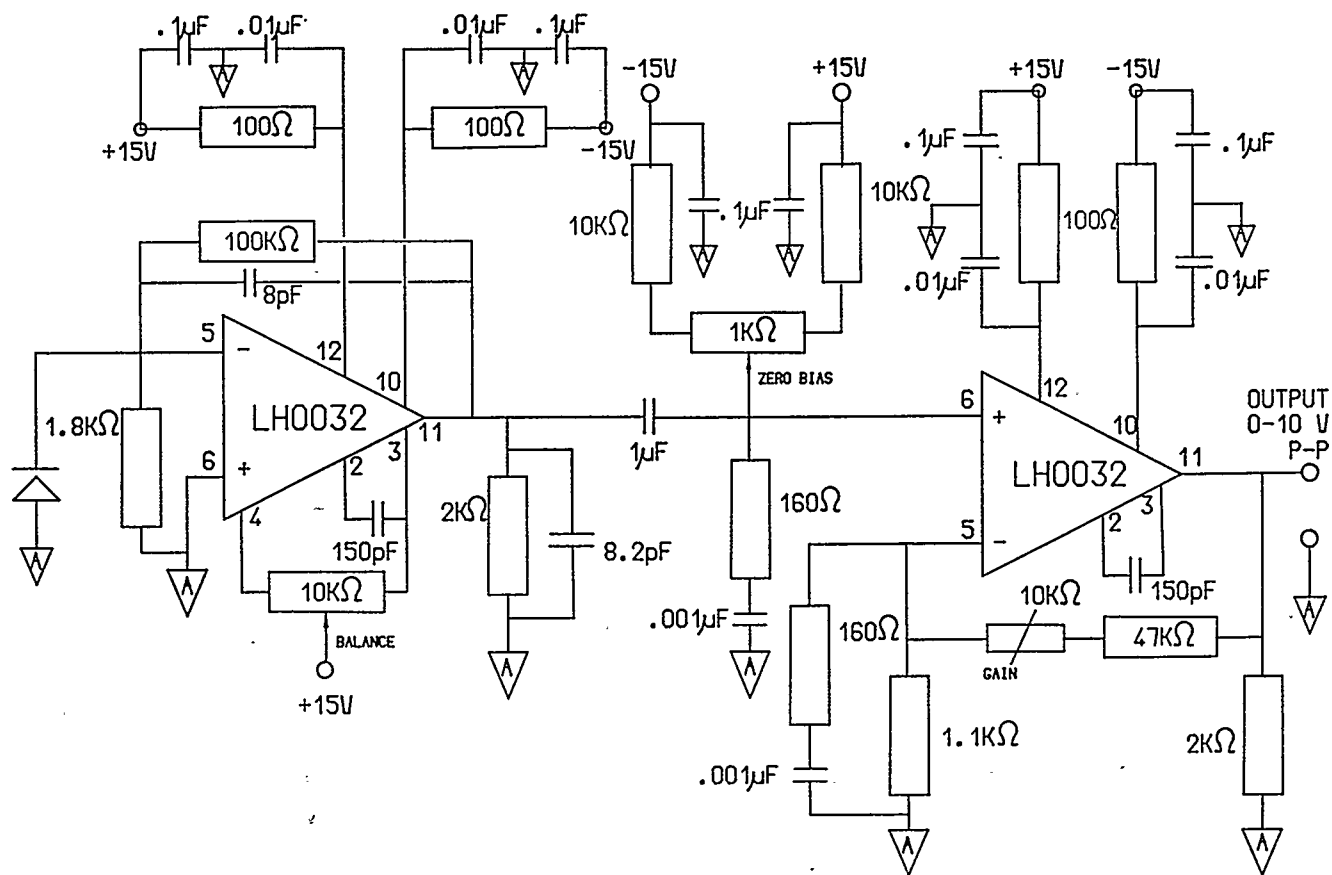


FIGURE 28: THE CIRCUIT DIAGRAM FOR SIGNAL AMPLIFIER

Figure 29 depicts the circuit diagram for the pulse peak measurement and triggering system for the laser. The ultra high speed hybrid track-and-hold amplifier HTC-0300 was used to hold the maximum value of the pulse during the fall and rise time. To synchronize the HTC-0300 and laser operation, a triggering system had to be used. It consisted of oscillator LM 555 and monostable multivibrator 74123.

The detector power supply diagram is shown on Figure 30.

References [16-20] were used.

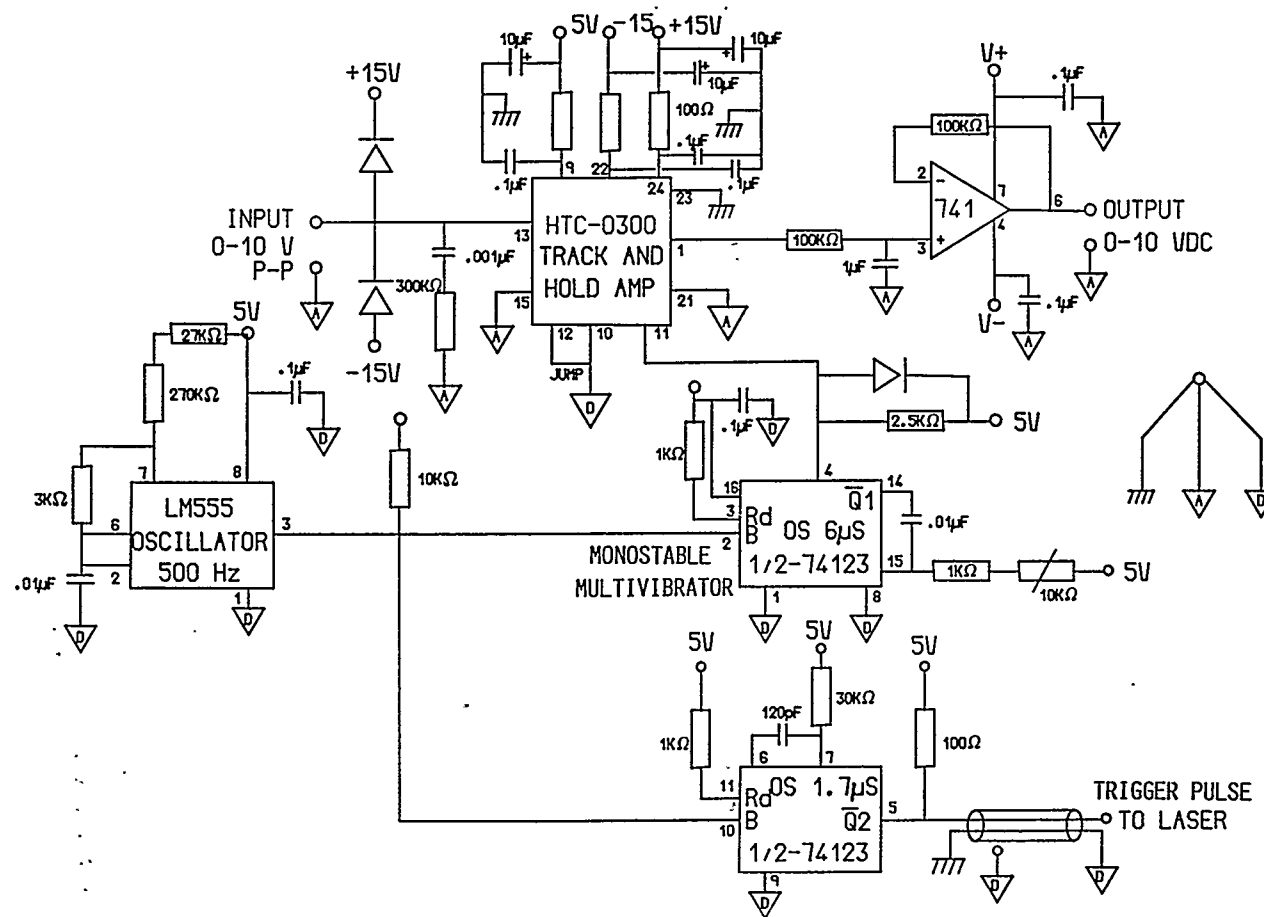


FIGURE 29: THE CIRCUIT DIAGRAM FOR THE PULSE PEAK MEASUREMENT AND TRIGGERING SYSTEM

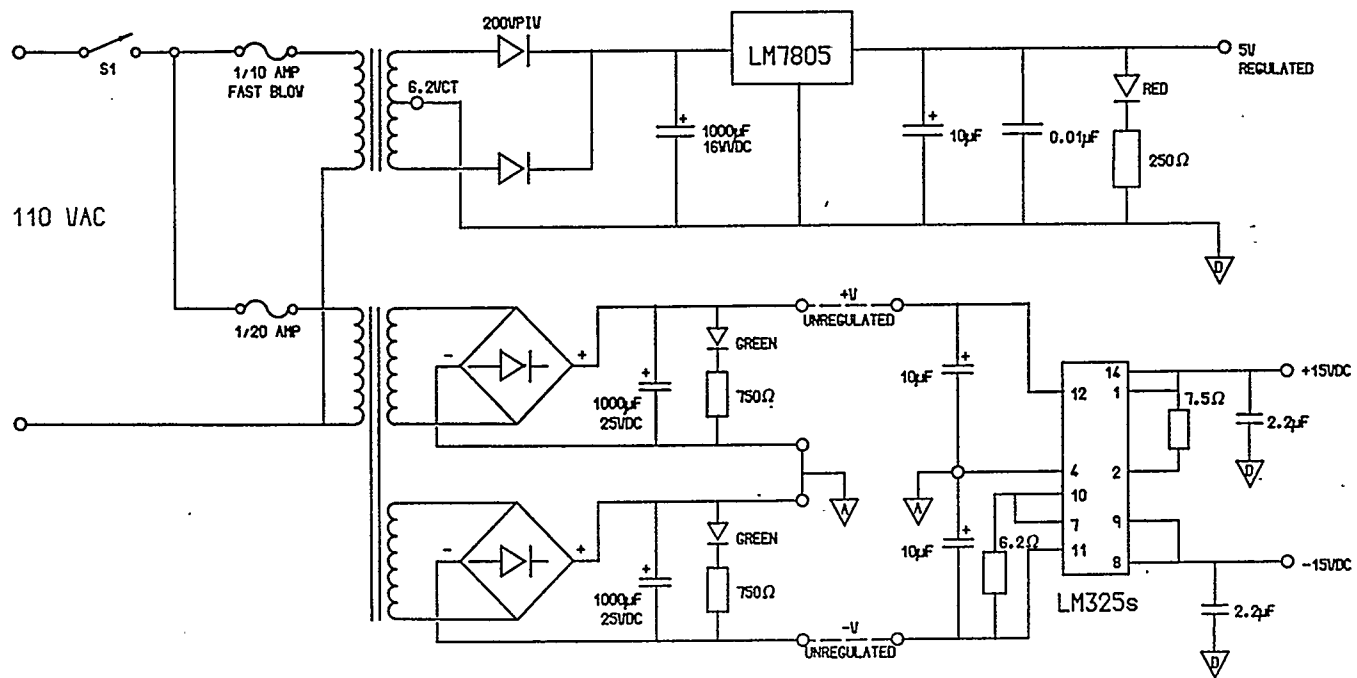


FIGURE 30: THE DETECTOR POWER SUPPLY