

THE UNIVERSITY OF CALGARY

Bitumen - Oxygenate Blends,
Viscosity Modelling and Transportation

by

Jodi L. Anhorn

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE
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DEPARTMENT OF CHEMICAL AND PETROLEUM ENGINEERING

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "Bitumen - Oxygenate Blends, Viscosity Modelling and Transportation" submitted by Jodi L. Anhorn in partial fulfilment of the requirements for the degree of Master of Science.

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ABSTRACT

The current practice of transporting bitumens by pipeline through the addition of a C_4+ liquid hydrocarbons diluent is examined. To overcome inherent drawbacks of this diluent, alternative solvents have been investigated. The oxygenates examined as alternatives were MTBE (methyl *tert*-butyl ether), TAME (*tert*-amyl methyl ether), methanol, and *iso*-propanol (2-propanol). The heavy oils used in this investigation were Cold Lake bitumen and Athabasca bitumen.

The MTBE and the TAME appeared completely soluble in the bitumens and were successful in reducing its viscosity to meet pipeline specifications. The methanol and *iso*-propanol remained insoluble in the bitumens.

The effect of the alternative solvents on the rheology of bitumens was studied along with the aspect of solvent distillation. The possibility of encountering asphaltene separation is considered. Also, a number of liquid-mixture viscosity models were evaluated.

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TABLE OF CONTENTS

	Page
APPROVAL PAGE	ii
ABSTRACT	iii
ACKNOWLEDGEMENTS	iv
TABLE OF CONTENTS	v
LIST OF TABLES	vii
LIST OF FIGURES	viii
NOMENCLATURE	x
CHAPTER 1 - INTRODUCTION	1
1.1 General Introduction	1
1.2 Research Objectives	2
CHAPTER 2 - POTENTIAL ALTERNATIVE SOLVENTS	4
2.1 Basis for Selection	4
2.2 Introduction of Oxygenates	4
2.3 Gasoline Blending	7
CHAPTER 3 - EXPERIMENTAL INVESTIGATION	9
3.1 Scope of Investigation	9
3.2 Compounds Used in Experimental Study	18
CHAPTER 4 - FLUID VISCOSITY MODELLING	22
4.1 Introduction to Previous Approaches	22
4.2 Fluid Viscosity Theories	22
4.3 Statistical Mechanical Theory of Viscosity	22
4.4 Corresponding States Theory	24
4.5 Model Theories	25

TABLE OF CONTENTS (cont.)

	Page
4.6 Empirical Correlations of Liquid Viscosity	27
4.7 Discussion of Viscosity Modelling Approaches	32
4.8 Selection of Viscosity Model	33
4.9 Prediction of Liquid-Mixture Viscosity	34
4.10 Fluid Flow in Pipelines: Effect of Pressure on Viscosity	38
CHAPTER 5 - RESULTS AND DISCUSSION	41
5.1 Solubility of Solvents	41
5.2 Viscosity Modelling	42
5.3 Rheology	88
5.4 Separation of Blended Components	89
5.5 Asphaltene Deposition	96
CHAPTER 6 - CONCLUSIONS	97
CHAPTER 7 - RECOMMENDATIONS FOR FUTURE WORK	100
REFERENCES	102

LIST OF TABLES

Table	Title	Page
2.1	Physical Properties of Solvents	6
5.1	Viscosity Correlation Results	44
5.2	Summary of Correlation Results	56
5.3	Cold Lake Bitumen Viscosity Data	59
5.4	Athabasca Bitumen Viscosity Data	59
5.5	MTBE Viscosity Data	63
5.6	TAME Viscosity Data	65
5.7	Results of Viscosity Correlations	67
5.8	Results of Method A Modelling on MTBE - Cold Lake Blend Data	73
5.9	Correlation Results For Model 1 and 2	76
5.10	Viscosity Results Cold Lake - MTBE	79
5.11	Viscosity Results Cold Lake - TAME	81
5.12	Viscosity Results Athabasca - MTBE	83
5.13	Viscosity Results Athabasca - TAME	85
5.14	Rheology of TAME-Athabasca Bitumen Blend	89

LIST OF FIGURES

Figure	Title	Page
3.1	Diagram of Rotating Spindle Viscometer	11
3.2	Photograph of Rotating Spindle Viscometer	12
3.3	Diagram of Cannon-Fenske Routine Viscometer	14
3.4	Photograph of Cannon-Fenske Routine Viscometer	15
5.1	Correlation of Sample Data Using Eq. 4.1	46
5.2	Correlation of Sample Data Using Eq. 4.2	47
5.3	Correlation of Sample Data Using Eq. 4.4	48
5.4	Correlation of Sample Data Using Eq. 4.7	49
5.5	Correlation of Sample Data Using Eq. 4.8	50
5.6	Correlation of Sample Data Using Eq. 4.9	51
5.7	Correlation of Sample Data Using Eq. 4.11	52
5.8	Correlation of Sample Data Using Eq. 4.12	53
5.9	Correlation of Sample Data Using Eq. 4.13	54
5.10	Correlation of Sample Data Using Eq. 4.14	55
5.11	Viscosity Results for Cold Lake Bitumen	60
5.12	Viscosity Results for Athabasca Bitumen	61
5.13	Viscosity Results for MTBE	64
5.14	Viscosity Results for TAME	66
5.15	Calibration Curve of Vapour Pressure Osmometer	70
5.16	Molar Mass Plot for Both Bitumens	71
5.17	Method A Modelling Results	74
5.18	Interaction Parameters From Model 1 and 2	77

LIST OF FIGURES (cont.)

Figure	Title	Page
5.19	Viscosity Results Cold Lake - MTBE	80
5.20	Viscosity Results Cold Lake - TAME	82
5.21	Viscosity Results Athabasca - MTBE	84
5.22	Viscosity Results Athabasca - TAME	86
5.23	Distillation Curve for 35.7% (mass) MTBE-Cold Lake Bitumen Blend . .	91
5.24	Distillation Curve for 30.0% (mass) MTBE-Athabasca Bitumen Blend . .	92
5.25	Distillation Curve for 30.0% (mass) TAME-Cold Lake Bitumen Blend . .	93
5.26	Distillation Curve for 30.0% (mass) TAME-Athabasca Bitumen Blend . .	94

NOMENCLATURE

a	= empirical parameter
A	= empirical parameter
b	= empirical parameter
B	= binary interaction parameter, empirical parameter
c	= empirical parameter
C	= empirical parameter
D	= diameter of pipe [m]
k	= calibration constant of VPO [$\mu\text{V}\cdot\text{g/mol}$]
K	= empirical parameter
M	= molar mass [g/mol]
n	= number of components in mixture
N	= number of sample points
P	= pressure [kPa]
Re	= Reynolds' number [dimensionless]
S	= solvent concentration [% mass]
t	= time [s]
T	= temperature [K]
v	= velocity of fluid flow [m/s]
ΔV	= depression of equilibrium temperature thermocouple voltage [μV or $\text{V}\cdot 10^{-6}$]
x	= molar fraction
y	= compositional parameter
$\partial u / \partial x$	= shear rate, or velocity gradient [s^{-1}]

NOMENCLATURE (cont.)

Greek letters

α	= empirical parameter
θ	= generalized viscosity constant
κ	= concentration term
μ	= dynamic viscosity [mPa•s or cP]; or micro [10^{-6}]
μ_0	= viscosity at standard state (adjustable parameter fit to experimental data) [mPa•s]
ρ	= density [g/cm ³]
τ	= shear stress [N m ⁻²]
ν	= kinematic viscosity [cSt]
Φ	= generalized viscosity constant

Subscripts

atm	= atmospheric pressure
B	= bitumen
cal	= calculated
exp	= experimental
g	= gauge pressure
i	= component i in mixture
j	= component j in mixture
S	= solvent
1	= component 1 in binary blend
2	= component 2 in binary blend

CHAPTER 1

INTRODUCTION

1.1 General Introduction

With the supplies of conventional Alberta crude oil gradually being depleted, a large amount of new research is focusing on alternative petroleum production. Bitumens represent the most promising alternative due to their abundance in Alberta, combined with recent, more efficient means of recovery. To fully utilize these resources however, many difficulties not associated with the recovery of conventional crude oils must now be considered.

The most detrimental factor in the production of bitumen is its excessive viscosity. As an example, Cold Lake bitumen has a viscosity of greater than 500,000 mPa•s at 4°C¹ while the viscosity of a typical conventional oil may be 3-4 orders of magnitude lower. To overcome this, bitumen is recovered using a variety of enhanced oil recovery (EOR) techniques which use heat, such as: steam stimulation, steam flooding, in-situ combustion, or steam-assisted gravity drainage². Even once the bitumen has been removed from the reservoir, problems remain in the aspects of transportation and processing.

The viscosity of the bitumen must be reduced to facilitate transportation through pipelines. The established pipeline specifications require a fluid viscosity of approximately 270 mPa•s at 4°C. The current solution to this

problem is the addition of liquid diluents to the bitumen to reduce its viscosity. The most common diluent is C_4+ paraffinic liquid hydrocarbons obtained from natural gas processing. Although successful in reducing the viscosity of the bitumen to meet specifications, the use of this solvent has a number of drawbacks.

The availability of the required liquid hydrocarbons is sometimes in question, and there may not be sufficient buyers to purchase the solvent at the end of the transportation. In fact, many suppliers of the bitumen consider the diluent to be a lost expense, and do not expect to be reimbursed. Also, the solubility of the solvent in the bitumen may pose some difficulties. The bitumen can be diluted with the solvent up to a critical dilution ratio, after which asphaltene deposition occurs³. Therefore, it can be seen that the ideal solvent choice is one which would achieve the required viscosity reduction, not cause the asphaltene fraction to precipitate, and also possess a substantial consumer market.

1.2 Research Objectives

The focus of this research is on investigating alternative solvents in diluting bitumens for the purpose of pipeline transportation. To completely research all of the issues which will determine the final success or failure of a test solvent is beyond the scope of this investigation. Therefore, identifying and examining the primary criteria by

which the alternative solvents will be tested is an important step.

A second objective of this research was to examine existing liquid-mixture viscosity models and identify the most successful one. The applicability of the identified model was then examined by comparing the predicted viscosities to those determined experimentally. Modifications to the existing model were also considered to facilitate more accurate predictions.

CHAPTER 2

POTENTIAL ALTERNATIVE SOLVENTS

2.1 Basis for Selection

The current solvent used (C_4+) involves a variety of disadvantages in the process of blending and transportation, therefore, a superior solvent must overcome these defects. The technical aspects of blending the bitumen with the C_4+ hydrocarbons are currently managed with little difficulty. In other words the viscosity reduction is achieved without reaching the critical dilution ratio, and no asphaltene precipitate is encountered. The problem which primarily needs to be addressed is the value placed on the solvent. An alternative solvent would be considered superior only if it could match the technical aspects of the C_4+ , while exhibiting a reasonable market value on its own.

2.2 Introduction of Oxygenates

The initial interest in MTBE (methyl tert-butyl ether) as the blending solvent was brought on by a number of favourable aspects. Presently, MTBE is used as the octane enhancing/anti-knock blending agent in gasoline, as tetra-ethyl lead and tetra-methyl lead are phased out as additives. The demand for MTBE is growing rapidly as clean air legislation begins to take effect and all leaded gasolines are eliminated^{4,5}. The common feedstocks of MTBE production (methanol and iso-

butylene) are produced in Alberta. As a result, a number of companies are investigating the development of MTBE plants as others are already being constructed. This is creating an environment in which Alberta stands to become a significant exporter of MTBE. Besides the reduction of the bitumen viscosity, the introduction of an ether into a heavy oil system has been noted to delay or eliminate the onset of asphaltene precipitation. These factors combined show promise for the potential use of MTBE as a liquid diluent in the pipeline transportation of bitumens.

To further this investigation, other oxygenating compounds are studied. Another ether used in smaller quantities for gasoline blending, TAME (tert-amyl methyl ether), is also examined. Alcohols constitute one of the basic feedstocks for MTBE and TAME production and therefore possess an export value. Because of this, methanol and 2-propanol (iso-propyl alcohol) are also studied as alternative solvents.

Some physical properties of the selected solvents are displayed in Table 2.1.

Table 2.1: Physical Properties of Solvents⁶

	MTBE	TAME	Methanol	<i>iso</i> -propanol
Chemical Formula	$\text{CH}_3\text{O}-\text{C}(\text{CH}_3)_3$	$\text{C}_2\text{H}_5\text{C}-\text{OCH}_3$ $(\text{CH}_3)_2$	CH_3OH	$(\text{CH}_3)_2\text{CH}-\text{OH}$
Molar Mass [g/mol]	88.15	102.18	32.04	60.10
Boiling Point [°C]	55	86	65	82
Density at 15.6°C [g/cm ³]	0.746	0.770	0.796	0.789
Reid Vapour Pressure [bars]	0.61	0.22	0.35	0.13
OCTANE NUMBERS:				
RON- determined	117	112	114	106
RON- blend	115	111	130	-
MON- determined	101	99	95	99
MON- blend	104	100	103	-

It is important to note that most of the solvents shown here have a Reid vapor pressure close to that of a typical gasoline. A further discussion of the aspects of gasoline volatility is presented in the following section.

2.3 Gasoline Blending

Today's consumer gasolines are highly developed blends which enhance the properties of the gasoline through the use of high-octane blending components and various additives. The primary requirement of a gasoline is that it should burn smoothly, without exploding, so that the maximum amount of useful energy is liberated⁶. This primary requirement is, however, offset by other properties which are essential for the suitable performance of the engine. Because many such properties exist, this discussion will limit itself to the aspects of gasoline volatility.

Volatility is a measure of the ability of a fluid to pass from the liquid to the vapour state under varying conditions of temperature and pressure⁶. Blending gasolines is not a trivial task, such as simply requiring the highest volatility attainable. On the contrary, conflicting influences demand that the gasoline volatility be closely regulated.

As an example of this, the volatility of a gasoline must be high enough that when mixed with air it readily forms a combustible mixture, even at low ambient temperatures. This consideration is not significant with temperatures above -10 °C, and is therefore termed cold starting. On the other hand, if the volatility is exceedingly high, the gasoline will not be useful due to evaporation losses. These evaporation losses can seriously affect the quality of gasoline which reaches the consumer, and can also have a detrimental effect on

atmospheric pollution and economic losses. It can be seen therefore, that the volatility of the blended gasoline must be properly maintained to take into account a number of factors, including cold starting and evaporation losses.

Due specifically to environmental concerns, legislation is calling for lower vapour pressure (ie. lower volatility) in consumer gasolines. Because C_4+ has a much higher vapour pressure than other additives, its use as a blending agent in gasoline is more limited than before.

CHAPTER 3

EXPERIMENTAL INVESTIGATION

3.1 Scope of Investigation

There are many characteristics a solvent must exhibit to establish that it may be an acceptable alternative to the use of C_4+ hydrocarbons. These characteristics include: transport properties, blending aspects, refinery limitations, economic considerations, and the broad issue of phase behaviour. To provide a concise focus for this research, the investigation must be concerned with only a select group of topics.

The principal areas of interest in this study are viscosity properties, viscosity blending, phase separation, asphaltene deposition, and rheological properties. Another important aspect of this research is the selection of a liquid-mixture viscosity model which could calculate the bitumen-solvent blend viscosities with accuracy.

3.1.1 Solubility of Solvents

The initial tests of the solvents were to determine whether they are soluble in the bitumen within a practical range of concentration. This stage involved mixing the solvents and bitumens, in all binary combinations, from a ratio of 5% - 40% mass basis, or approximately 20% - 80% mole basis solvent concentration. These samples were then mixed thoroughly and observed to suggest whether the solvent was

soluble in the bitumen. If the solvent remained insoluble, then it was not useful to consider it as a blending agent, and therefore were not examined further.

3.1.2 Viscosity Measurements

Determining the effect of the sample solvents on the viscosity of the bitumens was the predominant stage of this research. To investigate this effect, the viscosities of a number of samples were determined. These samples consisted of the pure solvents, undiluted bitumens, and bitumen-solvent blends over a range of solvent concentrations.

Because the viscosities of the pure solvents and undiluted bitumens differ by roughly six orders of magnitude^{1,2}, two viscosity measuring procedures were required. One viscosity measuring device was used for the pure solvents and the other for the bitumen and bitumen-solvent blends.

To test the samples of bitumen and bitumen-solvent blends, fluids with viscosities of 10^1 - 10^7 mPa·s, a rotating spindle viscometer is used (Model RV-8 from Viscometers UK Limited). Figure 3.1 shows a similar illustration of the viscometer, and a photograph is presented as Figure 3.2. This apparatus is comprised of two concentric cylinders separated by a thin region filled with a sample of the test fluid. The viscometer then rotates the inner cylinder and measures the torque necessary to overcome the viscous resistance to the

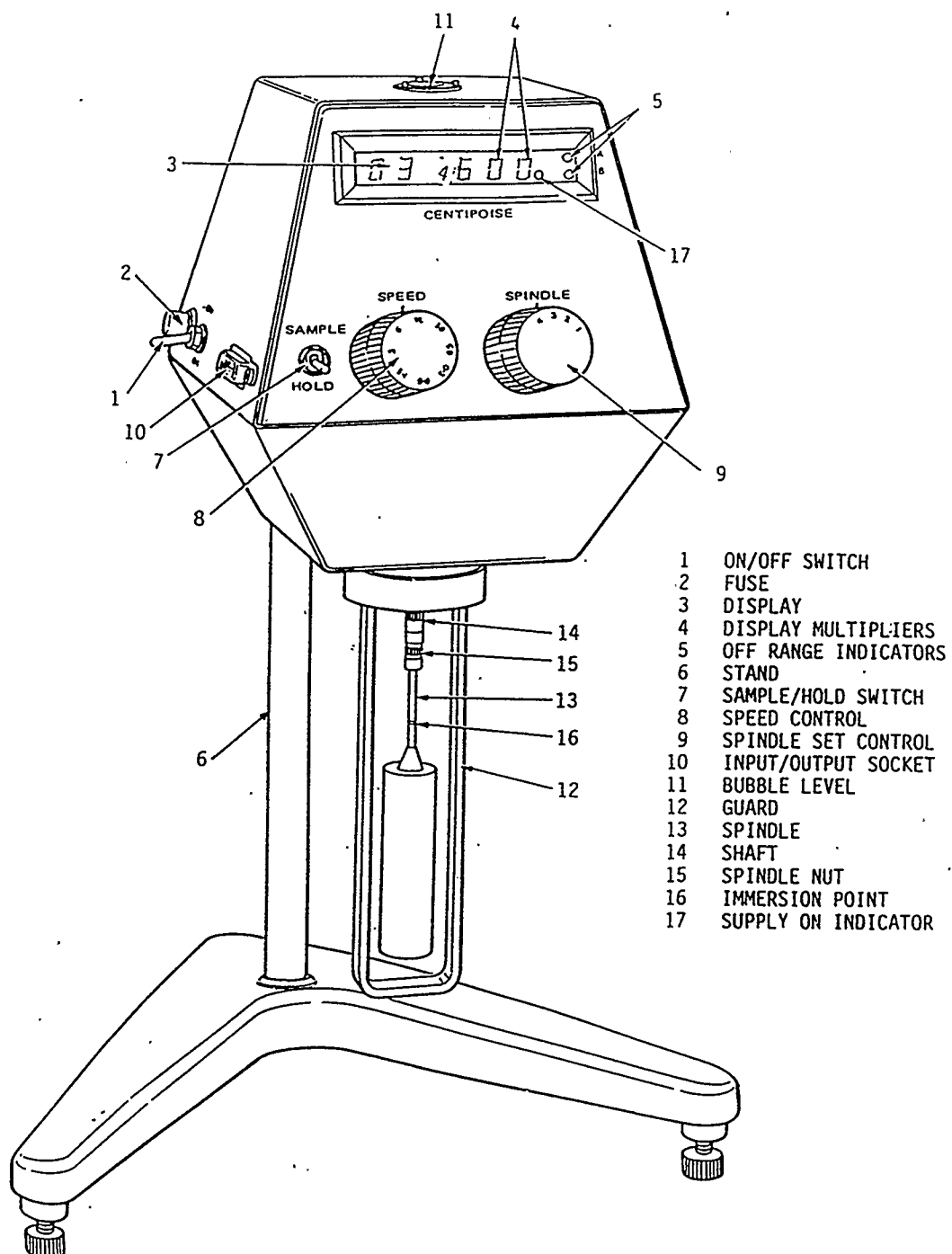


Figure 3.1: Diagram of Rotating Spindle Viscometer⁷



Figure 3.2: Photograph of Rotating Spindle Viscometer

rotation. The rotating cylinder (or spindle) is coupled via spring, to a drive shaft which is turning at a known speed. The angle through which the spindle is deflected is measured electronically, giving a measurement of torque⁷.

The relation between dynamic viscosity with known shear rate and torque is given by⁸:

$$\tau = \mu \frac{\partial u}{\partial x} \quad (3.1)$$

where:

μ = dynamic viscosity [mPa•s]

τ = shear stress, or torque [N m⁻²]

$\partial u / \partial x$ = shear rate, or velocity gradient [s⁻¹]

The equipment then automatically calculates the fluid viscosity in centipoise (mPa•s) using the known shear rate, measured torque, and spindle characteristics. This procedure was repeated at different temperatures for each of the samples to observe the effect of temperature on viscosity.

To determine the temperature-viscosity relationship for each of the pure solvents, a Cannon-Fenske routine viscometer was used. This viscometer (shown in Figure 3.3 and photographed in Figure 3.4) conforms to ASTM D 445⁹ standard test method for kinematic viscosity and calculation of dynamic viscosity. Measuring the time required for a predetermined volume of liquid to flow under gravity through a section of a glass capillary is a measure of the kinematic viscosity of the fluid. Because the dimensions of such fine glass capillary

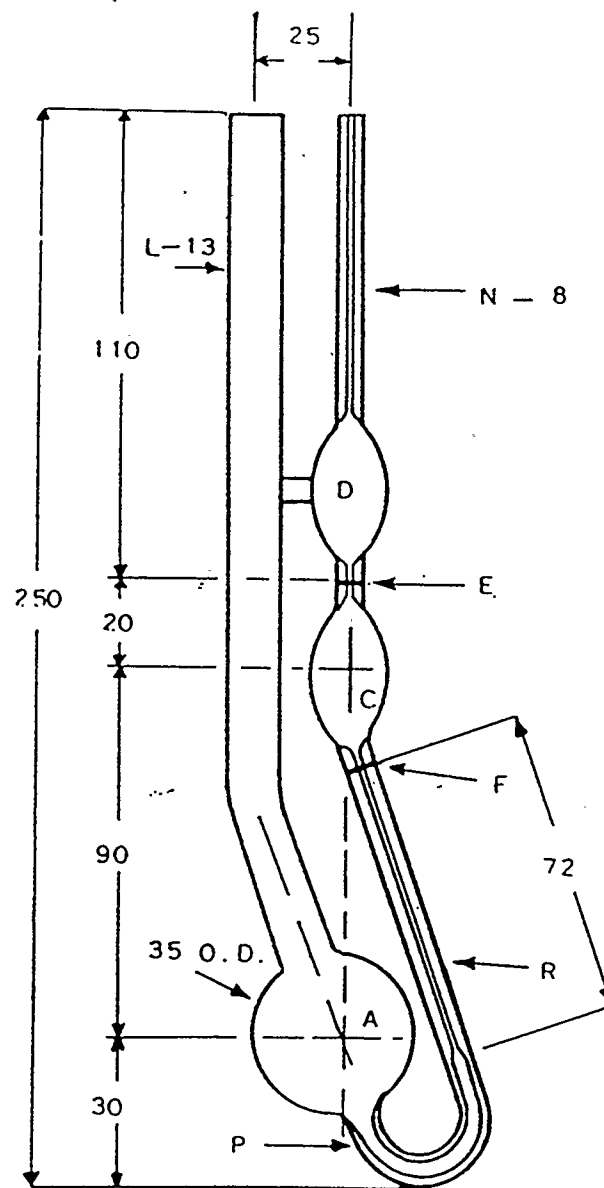


Figure 3.3: Diagram of Cannon-Fenske Routine Viscometer⁹

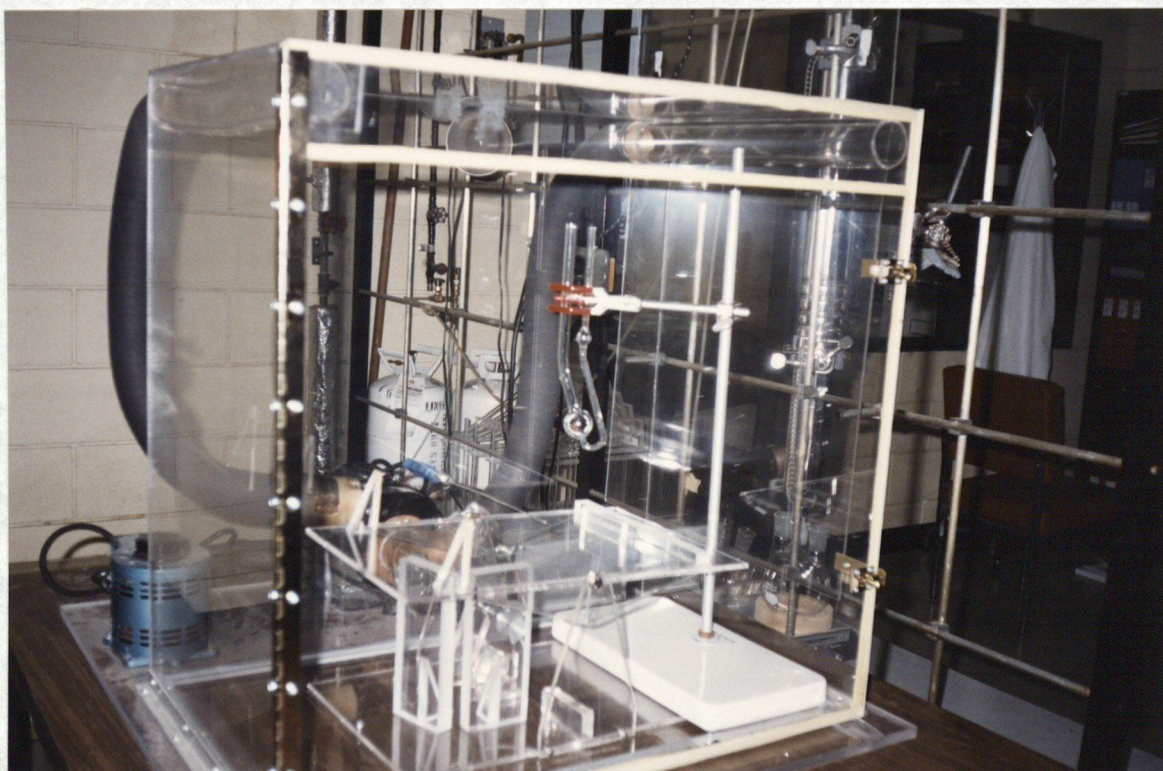


Figure 3.4: Photograph of Cannon-Fenske Routine Viscometer

tubes cannot be perfectly duplicated, each viscometer is calibrated by measuring the time for a liquid of known viscosity at a given temperature to discharge the standard volume⁸. Once the viscometer has been calibrated, the kinematic viscosity is calculating using:

$$v = C t \quad (3.2)$$

where:

v = kinematic viscosity [cSt]

C = calibration constant for viscometer at temperature of flow test [cSt/s]

t = flow time [s]

To compute the dynamic viscosity of the solvent from the determined kinematic viscosity, the following relation is used:

$$\mu = \rho v \quad (3.3)$$

where:

ρ = density of fluid at temperature of flow test [g/cm³]

To determine the density of the solvents over the temperature range required, an electronic density meter (Paar Model DMA 48) is employed. This equipment is accurate to 10⁻⁴ g/cm³, which is acceptable for the viscosity calculations.

3.1.3 Rheology

Determining whether any of the test solvents affect the rheological properties of the bitumens was also an issue of

this research. It has been demonstrated that many of the Alberta bitumens normally behave as Newtonian fluids¹⁰. However, a different bitumen under comparable conditions exhibited slightly non-Newtonian behaviour¹¹. If the addition of a solvent to these bitumens alter any rheological characteristic it may prove to be a serious concern.

To investigate the rheological properties described, the rotating spindle viscometer was employed. The viscometer, detailed in section 3.1.2, operates by measuring the apparent viscosity of a fluid at a constant spindle speed, or in other words, at a constant shear rate. Measuring the viscosity of a sample at different spindle speeds allows observation of viscosity versus changing shear rate. Performing this on the bitumens, before and after blending with the test solvents, determines if there has been any alteration in fluid behaviour.

3.1.4 Separation of Blended Components

Consideration must also be given to the aspect of separating the solvent from the bitumen upon completion of the pipeline transportation. This could be accomplished in a number of different ways however, so the intent of this research was to observe a simple distillation for potential difficulties. All of the soluble solvent-bitumen blends were distilled in the following manner.

The experimental apparatus was constructed to form a single-stage batch distillation, corresponding to ASTM D 267¹². At a set heating rate, the temperature of the distilled sample liquid and vapour is monitored while the total amount of distilled fluid is being recorded. These data can then be analyzed by producing a graph showing the temperature of the vapour versus the percent of distilled fluid. Blends which are easily separated will show a flat plateau at the boiling point temperature of the solvent.

3.1.5 Asphaltene Deposition

The possibility of encountering asphaltene deposition is taken into account during all of the phases of this research. All of the sample mixtures were examined, by means of visual inspection, to determine if any asphaltene phase is observed, either as a precipitate or remaining in suspension.

3.2 Compounds Used in Experimental Study

This section details the information regarding the compounds (ie. solvents and bitumens) used in this research. Some of the physical properties of the solvents used are detailed in Table 2.1; the purity of these solvents is now addressed.

The MTBE and methanol were obtained from BDH chemicals with minimum purities of 99.5+% and 99.8+% respectively. The TAME and iso-propanol were obtained from Aldrich chemicals

with minimum purities of 94+% and 99+% respectively. The densities of the solvents were checked experimentally using the electronic density meter introduced in section 3.1.2. These densities corresponded to those presented in Table 2.1 with less than 0.7% error for all of the solvents.

The use of oxygenating solvents were suggested as alternatives to the current use of C_4+ because of their inherent marketing advantages, along with their availability as an Alberta export. Therefore, the bitumens used to test the solvents must also be the more common Alberta bitumens used in pipeline transportations. The two chosen are the Cold Lake and Athabasca bitumens.

It is not appropriate to simply classify bitumens by the region where they were produced. There are a number of factors which affect the properties of a bitumen¹⁰. These factors include: origin, production methods, atmospheric aging, and molar mass. The available information on the bitumen samples used in this investigation are:

- 1) Esso produced Cold Lake bitumen, produced and homogenized February 1990, shipped in a metallic air-enclosed drum.

- 2) Athabasca bitumen prepared as a coker feed in 1989, shipped in metallic air-enclosed drum.

3.2.1 Determination of Bitumen Molar Mass

The molar mass of the bitumen provides the means to convert between mass and mole basis (both of which will be required later), and also serves to further identify the specifics of this bitumen.

To determine the molar mass, a Corona Wescan Molar mass Apparatus (Model 232A) using the procedure of vapour pressure osmometry is employed. It is an established principle that at constant temperature and pressure, the vapour pressure of a pure solvent is lowered by the addition of a second test solvent. At low concentrations, the magnitude of vapour pressure decrease is directly proportional to the molar concentration of the solvent being added (ie. the test solute). Consequently, measurement of vapour pressure change with weight concentration of solute can be used to determine molar mass.

For practicality, it is not convenient to measure vapour pressure decrease with enough sensitivity. Therefore, it is counteracted by a temperature increase, and this temperature increase can be measured to the desired accuracy.

The equipment provides the means for determining this change in temperature, but it requires a thorough calibration procedure to produce meaningful results. The calibration involves operating the machine with the molar mass of the second solvent already known.

Once the machine is calibrated, the molar mass relationship is established as:

$$M = k / \Delta V \quad (3.4)$$

where:

M = molar mass of sample [g/mol]

k = constant determined through calibration [$\mu V \cdot g/mol$]

ΔV = depression of equilibrium temperature thermocouple
voltage [μV]

CHAPTER 4

FLUID VISCOSITY MODELLING

4.1 Introduction to Previous Approaches

This chapter provides a brief outline to the background of viscosity modelling. The models can be classified into two distinct categories:

1. Fluid viscosity theories
2. Empirical correlations

4.2 Fluid Viscosity Theories

There exist a large number of theories developed in an attempt to understand, and predict, the complex behaviour of fluid viscosity. A further classification can then be made as follows:

1. Rigorous statistical mechanical theories
2. Corresponding states theory
3. Model theories

The following descriptions are intended to merely introduce the various fluid theories and not to provide a detailed derivation. Therefore, each of the descriptions will introduce the theories involved along with one or more references to facilitate further study.

4.3 Statistical Mechanical Theory of Viscosity¹³

By employing this theory, an expression for viscosity is

derived by equating the microscopic momentum conservation equation to one derived using continuum mechanics which contains viscosity as a transport coefficient. This theory has been utilized with the following two approaches to derive fluid viscosity models:

1. Distribution function
2. Time correlation function

4.3.1 Distribution Function Approach

The development of this approach uses non-equilibrium distribution functions to average all quantities in the microscopic momentum conservation equation to yield a macroscopic momentum conservation equation. However, the derivation of the necessary non-equilibrium distribution functions is not a trivial task. It requires kinetic equations and a number of distribution function equations to be derived, and decoupled, through the use of limiting assumptions. Dilute gases, for example, assume completely random molecular distributions. The accuracy of their predicted results depended heavily upon the coefficient values chosen in the viscosity equations. The errors versus experimentally determined viscosities ranged from one to several hundred percent.

Many variations with distinct approaches based on distribution functions have been developed¹³. However, each of these models require coefficient values, and the results

obtained have not been in good agreement with experimental data.

4.3.2 Time Correlation Function Approach¹³

Instead of using non-equilibrium distribution functions, it has been found that the viscosity of a fluid can be characterized by how spontaneous fluctuations behave in an equilibrium system. This can then be used to create an expression for fluid viscosity dependant upon a time correlation function.

A computer solution of the time correlation function by molecular dynamics has been carried out¹⁴ using the Lennard-Jones potential. The predicted viscosities deviated from the experimental values by an average of 10% without fitting of data. Due to its complexity, however, the molecular dynamics calculations are not a practical method to compute viscosity, and theoretical solutions of the time correlation function are required.

4.4 Corresponding States Theory

The principle of corresponding states, derived for the prediction of thermodynamic properties, has been extended to calculate fluid transport properties¹³. The principle simply states that at the same reduced conditions, two fluids will exhibit similar dimensionless properties. Therefore, the properties of a sample fluid may be calculated from the known

properties of a reference fluid.

The expressions utilized, however, only hold true for conformal fluids. For non-conformal fluids, the extended principle of corresponding states can be used, where shape factors are introduced to account for the non-conformality of all of the molecules¹⁵.

This method provides relatively accurate viscosity correlations, generally within 10% deviation. This procedure is only applicable to fluids whose composition is completely known. Therefore, to apply this method to prediction of bitumen viscosities requires that the overall composition be estimated.

4.5 Model Theories¹³

There exist a number of theoretical models which do not attempt to provide a rigorous physical description of the molecular interactions. Instead they simplify the procedure, and attempt to model while complying with one or more specific conditions. These semi-theoretical approaches can be very useful in correlating the viscosity data of complex mixtures.

Some of the more significant types of model theories are:

1. Activated state theories
2. Free-volume theories
3. Combined model theories

4.5.1 Activated State Theory of Liquid Viscosity

Eyring¹⁶ applied his reaction rate theory for chemical reactions to formulate a model theory for liquid viscosity. This theory states that the molecules of a liquid in viscous flow move in parallel layers. By overcoming an energy barrier, a given liquid molecule in a layer can change its site. This energy barrier is called the activation energy. This model was utilized by Gold and Ogle who found deviations of 50 - 100%¹⁷.

4.5.2 Free Volume Theories

It has been speculated^{18,19} that molecular flow is proportional to the excess volume in a liquid; excess volume being defined as the difference between the volume of the liquid and the volume of the solid-like structure at which flow stops. This model has been shown to be valid only for pure and non-associated liquids.

4.5.3 Combined Model Theories

This classification of theories generally refers to any model theory which has borrowed elements of separate model theories. Their intent is to preserve the successful features

of previous models while incorporating new aspects. An example of this type was derived by Macedo and Litovitz²⁰. They utilized the activation energy as well as that of the redistribution of the free volume. The resulting model requires three empirical parameters, and represents the data reasonably well.

4.6 Empirical Correlations of Liquid Viscosity

Correlations are used primarily due to their convenience and accuracy in representing experimental results. Furthermore, due to the complex nature of bitumens, even the best physical models will require some type of oil characterization, therefore introducing empirical parameters. All of the following correlations are tested and evaluated in section 5.2.1 to determine the most reliable model.

4.6.1 Andrade Equation

The following equation was derived for liquid viscosity correlations, and has been used previously for heavy hydrocarbons²¹:

$$\mu = A e^{B/T} \quad (4.1)$$

where:

A, B = empirical parameters

4.6.2 Gross and Zimmerman²¹

This model was proposed for the viscosity of liquids based upon their liquid cluster research:

$$\ln \mu = \frac{1}{1 - (1 - e^{-C/T})^{1/3}} + \ln \mu_0 \quad (4.2)$$

where:

μ_0 = viscosity at standard state (adjustable parameter
fit to experimental data) [mPa•s]

C = empirical parameter

4.6.3 ASTM Model

A prominent model used to correlate the viscosities of lubricating oils in the ASTM charts²¹ can be generalized as:

$$\ln(\ln(v + K)) = A - B \ln T \quad (4.3)$$

where:

K, A, B = empirical parameters

Actually, the ASTM model is derived from the Walther²² correlation, written here in a modified form as:

$$\log(\log(\mu + 0.8)) = b_1 + b_2 \log T \quad (4.4)$$

where:

b_1, b_2 = empirical parameters

Equation 4.4 has been previously used^{23,24,25} with slight modifications, to model the fluid viscosities of bitumens and solvents.

It has been identified²⁶ that a cross-correlation exists between parameters b_1 and b_2 . The cross-correlation can be represented by a linear relationship:

$$b_1 = \log \theta + (\log \Phi) b_2 \quad (4.5)$$

where:

θ = generalized parameter

Φ = generalized parameter

Inserting equation 4.5 into equation 4.4 yields the following one-parameter viscosity-temperature correlation:

$$\log(\mu + 0.8) = \theta(\Phi T)^{b_2} \equiv \theta(\Phi T)^b \quad (4.6)$$

where:

b = empirical parameter (single parameter required)

The values of θ and Φ have been regressed for a large set of experimental viscosity data²⁶. The "best" values of the constants were selected as $\log \theta = 2.0$ and $\log \Phi = -2.0$. Using these numerical values, equation 4.6 becomes:

$$\log(\mu + 0.8) = 100(0.01 T)^b \quad (4.7)$$

4.6.4 Vogel-Fulcher Equation²⁷

The following equation was also derived for liquid viscosity correlations, and not specifically heavier hydrocarbons:

$$\ln \mu = \frac{B}{T - T_B} + \ln A \quad (4.8)$$

where:

A, B, T_B = empirical parameters

4.6.5 Double Exponential Viscosity Equation²⁷

The following equation was developed to account for deficiencies in the Andrade equation:

$$\mu = A e^{Be^{C/T}} \quad (4.9)$$

where:

A, B, C = empirical parameters

4.6.6 Mehrotra and Svrcek Model²⁷

The earliest empirical correlation of the viscosity of gas saturated bitumens is shown here:

$$\log(\log(\mu)) = a_1 + a_2 T + a_3 P + a_4 \frac{P}{T} \quad (4.10)$$

where:

a_1, a_2, a_3, a_4 = empirical parameters

Equation 4.10 is modified in this study to eliminate the effect of gas solution pressure on viscosity because all of the experimental samples contain no gas in solution of the bitumens (the effect of pressure on the viscosity of fluids is discussed in section 4.10). The modified equation then becomes:

$$\log(\log(\mu)) = a_1 + a_2 T + \frac{a_3}{T} \quad (4.11)$$

4.6.7 Double Log Expression

The following equation was used²⁸ to represent the viscosity of gas-free bitumen at atmospheric pressure:

$$\ln(\ln(\mu)) = e^{-b_1 T} [1 + b_1 T + b_2 (b_1 T)^2] \quad (4.12)$$

where:

b_1, b_2 = empirical parameters

4.6.8 Comparative Equations

The following equations are utilized here to display the relative accuracy of the previous correlations versus two non-unique curve fitting approaches.

The first equation is a simple polynomial:

$$\mu = a + bT + cT^2 \quad (4.13)$$

The second equation employs a double-log term:

$$\ln(\ln(\mu)) = a + b/T \quad (4.14)$$

where:

a, b, c = empirical parameters

4.7 Discussion of Viscosity Modelling Approaches

It can be seen that a variety of methods have been developed to help calculate the viscosity of fluids. The rigorous statistical mechanical models require no experimental viscosity data to correlate. However, without proper coefficient values for the non-equilibrium distribution functions, the predictions of the viscosity model can be highly inaccurate. The time correlation function method provides a means of side-stepping the need for coefficient values, but it comes at some cost. The actual solution to performing the molecular dynamics simulation is difficult, and not practical for viscosity calculations. The theoretical solutions to this molecular dynamics problem will again introduce assumptions and estimations.

The corresponding states theory provides an accurate and reliable method of predicting viscosities of fluids whose composition is known. However, the use of this theory in predicting the viscosity of bitumens introduces additional errors in identifying the bitumen composition accurately.

The model theories discussed in section 4.5 are generally empirical equations which arose from observations of fluid

behaviour. This behaviour was then modelled in an equation, along with adjustable parameters, to predict the viscosity of fluids. These equations, although loosely based on fluid behaviour, generally are not as accurate as the equations derived empirically.

The empirical equations discussed here are used as a simple tool to correlate the experimental viscosity data of fluids. These equations are typically the most accurate means of calculating fluid viscosities of complex mixtures. To use these equations a set of temperature-viscosity data must be determined experimentally.

4.8 Selection of Viscosity Model

For the purposes of this research, the most acceptable means of calculating fluid viscosity is through empirical correlations. Accuracy and ease of implementation are foremost to this study, and correlations provide the best means of achieving these requirements. The correlations introduced in section 4.6 are further addressed in chapter 5, where each of the equations are employed to correlate the experimental viscosity data. The performance of each of these correlations are then compared, with the most accurate model being used to complete the viscosity modelling section.

4.9 Prediction of Liquid-Mixture Viscosity

The viscosity models discussed in this chapter are generally used to calculate the viscosity of pure fluids or pseudo-components. To calculate blend viscosity, consisting of a mixture of liquids, mixing rules must be established. Two such mixing rules will be evaluated in this research.

4.9.1 Simple (Additive) Mixing Rules

Many of the liquid-mixture viscosity formulae which have been established can simply be described as a weighted average of component viscosities, shown here as:

$$f(\bar{\mu}) = \sum_{i=1}^n \kappa_i f(\mu_i) \quad (4.15)$$

Equation 4.15 is shown in general terms, where the functional form of $f(\mu)$ could be any of the viscosity models or correlations described in this chapter. The choice for the concentration term κ could be the mole, volume, or mass fraction, or possibly a combination of these factors. A number of the possible combinations have been discussed in the literature^{23,29}.

Many other liquid-mixture viscosity formulae exist which employ a viscous interaction parameter³⁰. This parameter could be binary or higher order, and is often made a function of temperature to better represent the experimental data.

If we introduce a binary interaction parameter term to equation 4.15, it can then be expressed as²³:

$$f(\bar{\mu}) = \sum_{i=1}^n \kappa_i f(\mu_i) + 2 \sum_{i=1}^{n-1} \sum_{j=i+1}^n \kappa_i \kappa_j B_{ij} \quad (4.16)$$

The binary interaction term in equation 4.16 observes that the interaction between two identical components is zero ($B_{ii} = B_{jj} = 0$), and also that the interaction between two components is identical regardless of orientation ($B_{ij} = B_{ji}$).

A choice for the concentration term κ which has been detailed in the literature is shown here³¹:

$$\kappa_i = x_i \left(\frac{M_i}{\bar{M}} \right)^{0.5} \quad (4.17)$$

where:

M = molar mass [g/mol]

x = molar fraction

The average molar mass is calculated using:

$$\bar{M} = \sum_{i=1}^n x_i M_i \quad (4.18)$$

The concentration term described by equation 4.17 is actually the geometric mean of mass and mole fractions, and has been successfully used in modelling bitumen-blend viscosities^{23,24,25}.

Equation 4.16 with the concentration term described in equation 4.17, will be employed along with the viscosity correlations described in section 4.6 to correlate the experimental viscosity data. The model which gives the most accurate results over a select portion of the experimental results, will then be utilized to correlate all of the remaining data. Any possible modifications or improvements to the existing models will then be considered.

4.9.2 Shu Liquid-Mixture Viscosity Correlation

A procedure for determining the viscosity of a liquid-mixture has also been proposed by Shu³². This procedure requires the component viscosities to be previously determined. Using the viscosity data, the Lederer³³ equation is now used as the basic mixing rule:

$$\ln \bar{\mu} = y_B \ln \mu_B + (1-y_B) \ln \mu_S \quad (4.19)$$

where:

y_B = compositional parameter; defined by equation 4.20

$$y_B = \frac{\alpha V_B}{\alpha V_B + V_S} \quad (4.20)$$

where:

V_B, V_S = volume fractions of bitumen and solvent

The volume fractions can be calculated from the experimentally measured mass fractions using the following:

$$V_i = \frac{w_i / \rho_i}{\sum_{j=1}^n w_j / \rho_j} \quad (4.21)$$

where:

ρ_i = density of component i

w_i = mass fraction of component i

Shu utilized these equations by generalizing α as a function of bitumen and solvent densities. The viscosity data was comprised of binary systems where the ratio of heavy oil viscosity to solvent viscosity was greater than 20. This data was then regressed using a power-law relationship to determine a "best-fit" correlation of α . An adequate representation of the data was found with:

$$\alpha = \frac{17.04 (\rho_B - \rho_S)^{0.5237} \rho_B^{3.2745} \rho_S^{1.6316}}{\ln \left(\frac{\mu_B}{\mu_S} \right)} \quad (4.22)$$

In this investigation, the component viscosity data will be calculated using the most accurate correlation presented in section 4.6 (the accuracy will be determined in section 5.2.1).

The Shu mixing rules will be investigated using two approaches, with the results compared to the blend viscosity data determined experimentally. The first approach, as detailed by Shu, assumes that the temperature affects α by changing the component viscosities only, and not by changing the component densities. In this case a single density value near 25 °C is required for the bitumens and the solvents.

The second approach also takes into account the variation in α due to a change in the fluid densities. This change in fluid densities will also have a corresponding affect on the relative volume fractions. This approach requires that density-temperature data is available for the bitumens and the solvents.

4.10 Fluid Flow in Pipelines: Effect of Pressure on Viscosity

Until this point, the discussion of fluid viscosity has dealt only with viscosities measured at atmospheric pressure. When considering fluid flow in pipeline transportation however, the effect of pressure on viscosity must be considered. This is due to the fact that any real fluid flowing in a pipe will gradually undergo a pressure loss (ie. head loss) due to friction. This fact dictates that the fluid entering the pipeline will be maintained at a pressure greater than that at the exit of the pipeline to overcome the loss due friction. The pressure drop attributed to friction depends upon the characteristics of the fluid flow.

Fluid flows can be categorized into two distinct patterns of motion: when fluids flow in parallel straight lines, it is referred to as laminar flow; and fluid flow which is erratic with eddies superimposed on the bulk flow is called turbulent flow³⁴. The criterion including all of the factors which determine whether the flow is laminar or turbulent, can be represented by Reynolds number⁸:

$$Re = \frac{D \rho v}{\mu} \quad (4.23)$$

where:

Re = Reynolds number [dimensionless]

v = average velocity of fluid [m/s]

In pipeline flow, laminar conditions prevail as long as Reynolds number is less than approximately 2100. Turbulent conditions prevail when Reynolds number is greater than 4000. In between the two values, there is a transition region where flow is neither fully turbulent nor entirely laminar³⁴.

Although a detailed pressure drop calculation requiring pipeline and flow characteristics is beyond the scope of this investigation, a simple estimation will allow for discussion of the effect of pressure on viscosity.

Previous experimental work^{35,36} has shown that increased pressure has the effect of increasing the viscosity of bitumens.

The effect of pressure on viscosity can be represented by the following equation:

$$\ln(\ln\mu) = [b_1 + b_2 T] + P_g K \quad (4.24)$$

where:

P_g = gauge pressure [MPa]

b_1, b_2, K = empirical parameters

It can be seen that equation 4.24 is very similar to equation 4.4, used previously to model the temperature-viscosity data. The value of K for Cold Lake bitumen has been shown to be 4.288; and K for Athabasca bitumen to be 5.119^{35,36}.

The effect of pressure on viscosity for a fluid in a pipeline is an important consideration. This research however, determined bitumen viscosities at atmospheric pressure only. Therefore, the modelling results discussed in chapter 5 will only examine viscosities at atmospheric pressure.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Solubility of Solvents

The first test of the proposed solvents was to determine whether they are soluble in the bitumens. To help facilitate mixing of the two components, vigorous shaking and a magnetic stirrer were required. There exist eight binary combinations of the two bitumens and the four solvents. The bitumen-solvent blends tested were:

1. Cold Lake - MTBE (methyl tert-butyl ether)
2. Athabasca - MTBE (methyl tert-butyl ether)
3. Cold Lake - TAME (tert-amyl methyl ether)
4. Athabasca - TAME (tert-amyl methyl ether)
5. Cold Lake - methanol
6. Athabasca - methanol
7. Cold Lake - 2-propanol
8. Athabasca - 2-propanol

The MTBE was blended with the Cold Lake bitumen in mass fractions of 5% up to 40% and appeared completely soluble. The MTBE was also soluble in the Athabasca bitumen, with test samples consisting of 15% up to 40% mass fraction MTBE.

The TAME - Cold Lake bitumen blends were mixed with 15% up to 35% mass fraction TAME with all of the mixtures showing complete solubility. The TAME was also soluble in the

Athabasca bitumen, with test samples of 15% up to 35% mass fraction TAME.

All of the bitumen-alcohol blends remained insoluble. The blends tested (all in mass fraction of solvent) were: 20%, 30% Cold Lake - methanol; 10%, 25% Athabasca - methanol; 15%, 25% Cold Lake - 2-propanol; 20%, 35% Athabasca - 2-propanol. To further assist the mixing of the two phases, the insoluble samples were heated to 50°C for 24 hours and then shaken as before. However, this did not alter the observed result.

The alcohol in the sample mixtures took on a slightly murky blue colour when shaken with the bitumens. This suggests that a small amount of the bitumen components had been dissolved in the alcohol.

As mentioned previously, only the soluble solvents (ie. ethers) were examined in the following experiments. The insoluble solvents (ie. alcohols) are no longer discussed as possible alternatives.

5.2 Viscosity Modelling

With the experimental viscosity results available, the comparison between the various empirical correlations and their relevant mixing rules are discussed here.

5.2.1 Viscosity Correlations

The first consideration was to determine which correlation best represents the experimental temperature-

viscosity data. To determine this, all of the correlations were employed to correlate a select portion of the experimental data. The sample data were chosen to represent the major segments of the whole experimental results, and the viscosities range from 50 - 40,000 mPa•s. The sample data consisted of the following:

- Sample #1: Unblended Cold Lake bitumen
- Sample #2: Unblended Athabasca bitumen
- Sample #3: MTBE - Cold Lake blend (30% mass MTBE)
- Sample #4: TAME - Athabasca blend (15% mass TAME)

The correlated viscosities versus the experimental viscosities for each of the correlative equations are presented in Table 5.1 and summarized in Table 5.2 with Figures 5.1 - 5.10 displaying the results.

The results show that the majority of the equations can correlate the temperature-viscosity data within 5% AAD (absolute average deviation), where %AAD is defined by:

$$\% AAD = \frac{1}{N} \sum_{i=1}^N \left| \frac{\mu_{cal} - \mu_{exp}}{\mu_{exp}} \right| \times 100 \quad (5.1)$$

where:

N = number of sample points in calculation

The most accurate correlations are provided by equations 4.4, 4.11, and 4.14 with the AAD of all four near 1.5%.

Table 5.1: Viscosity Correlation Results

Sample	Temp. [°C]	Exper. Visc. [cP]	Calculated Viscosities				
			Eq. 4.1 [cP]	Eq. 4.2 [cP]	Eq. 4.4 [cP]	Eq. 4.7 [cP]	Eq. 4.8 [cP]
1	30	24600	24579	24001	24402	17652	24803
1	40	7740	7958	8133	8026	7444	7848
1	50	3140	2763	3117	3072	3468	3054
1	65	910	635	895	917	1291	982
2	25	39990	40082	39434	39791	29122	40242
2	30	22560	22448	22372	21662	18107	22139
2	40	7100	7443	7962	7298	7623	7544
2	50	2810	2642	3184	2849	3547	2938
2	60	1290	998	1405	1258	1798	1277
3	4	205	205	207	207	180	207
3	10	124	125	125	123	120	125
3	15	85.8	85	84	83	89	85
3	20	57.6	58	58	58	67	60
4	4	4439	4439	4413	4440	4219	4442
4	10	2413	2472	2417	2411	2405	2400
4	20	983	983	977	983	1047	996

Table 5.1: Viscosity Correlation Results (cont.)

Sample	Temp. [°C]	Exper. Visc. [cP]	Calculated Viscosities				
			Eq. 4.9 [cP]	Eq. 4.11 [cP]	Eq. 4.12 [cP]	Eq. 4.13 [cP]	Eq. 4.14 [cP]
1	30	24600	24663	24362	24224	24397	24409
1	40	7740	7955	8013	8111	10097	7738
1	50	3140	2930	3068	3068	2067	2967
1	65	910	804	916	916	1778	927
2	25	39990	39760	41112	39225	38005	40066
2	30	22560	21940	21808	21681	25526	21219
2	40	7100	7450	7201	7368	7980	7015
2	50	2810	2869	2837	2854	316	2778
2	60	1290	1229	1287	1244	2534	1271
3	4	205	206	205	211	204	209
3	10	124	125	126	123	126	124
3	15	85.8	85	85	84	83	84
3	20	57.6	59	58	59	58	60
4	4	4439	4424	4436	4430	4425	4450
4	10	2413	2412	2412	2415	2408	2391
4	20	983	974	983	982	994	985

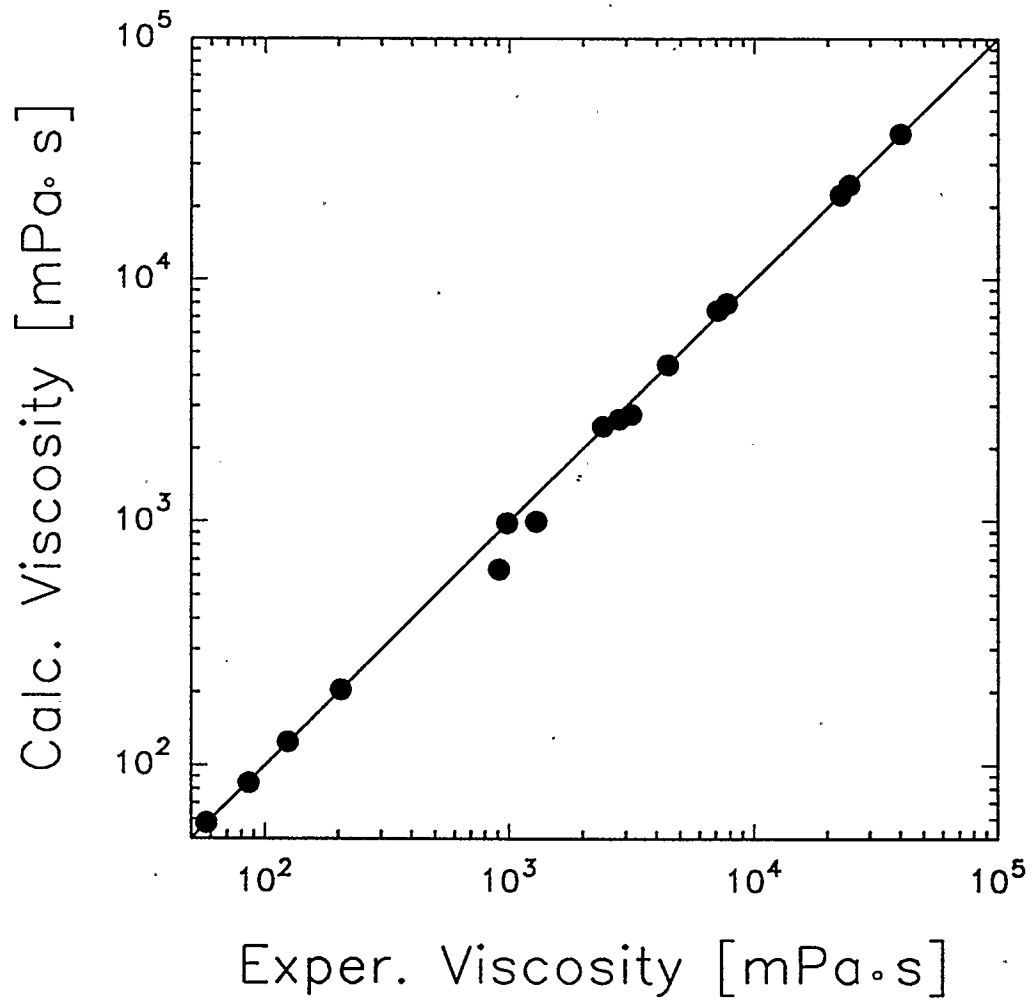


Figure 5.1: Correlation of Sample Data Using Eq. 4.1

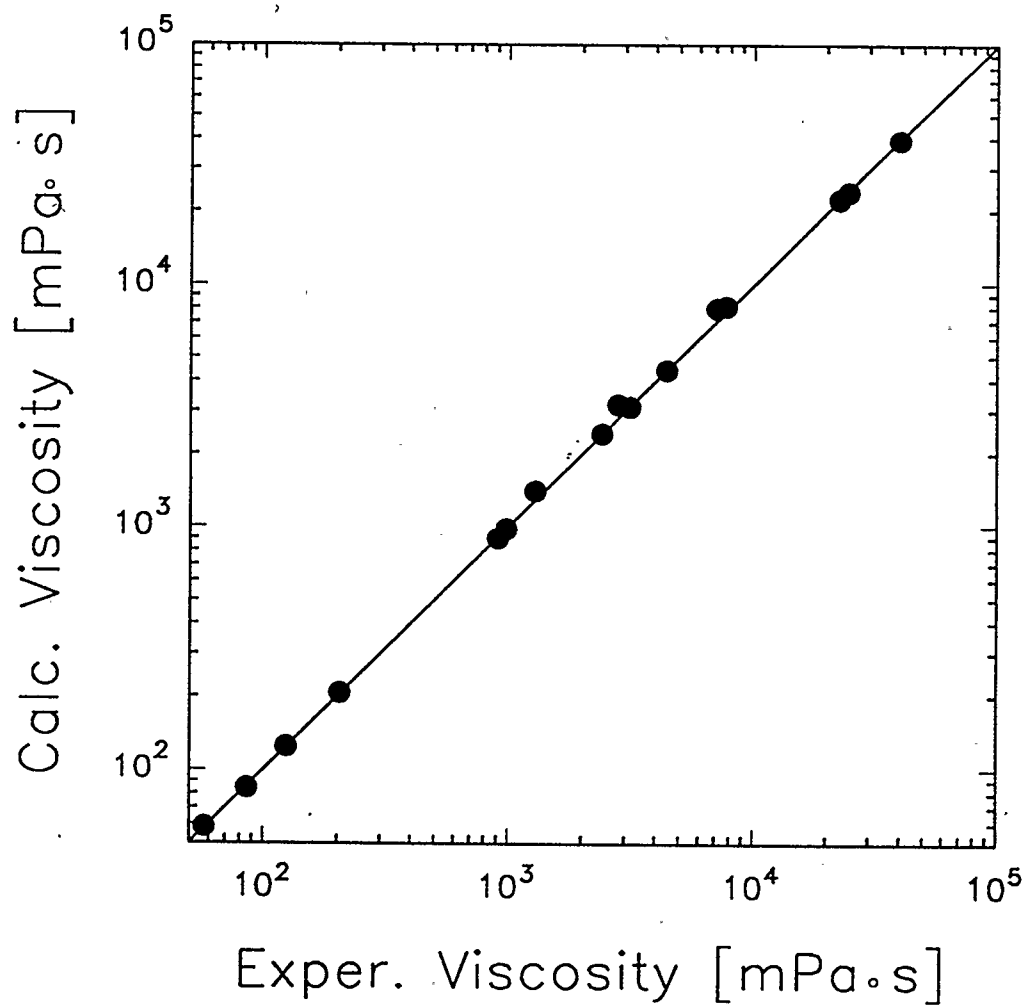


Figure 5.2: Correlation of Sample Data Using Eq. 4.2

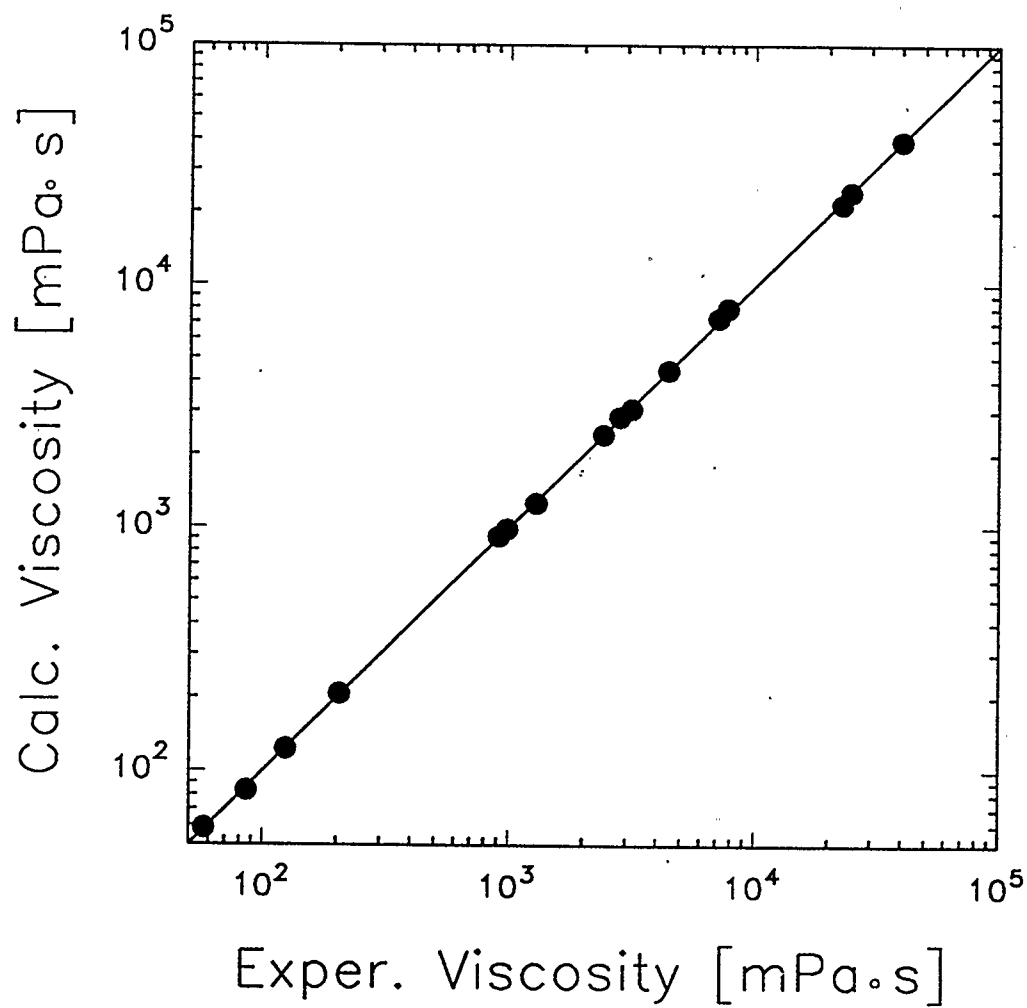


Figure 5.3: Correlation of Sample Data Using Eq. 4.4

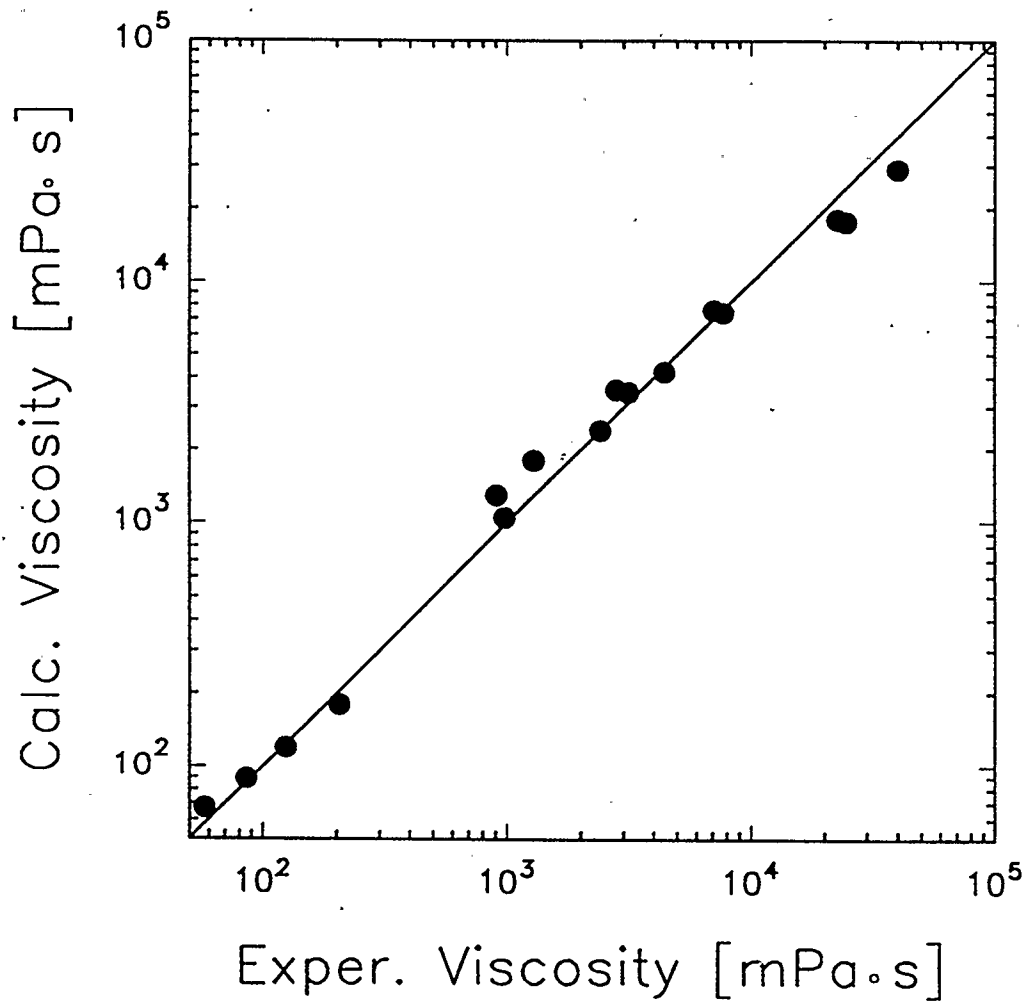


Figure 5.4: Correlation of Sample Data Using Eq. 4.7

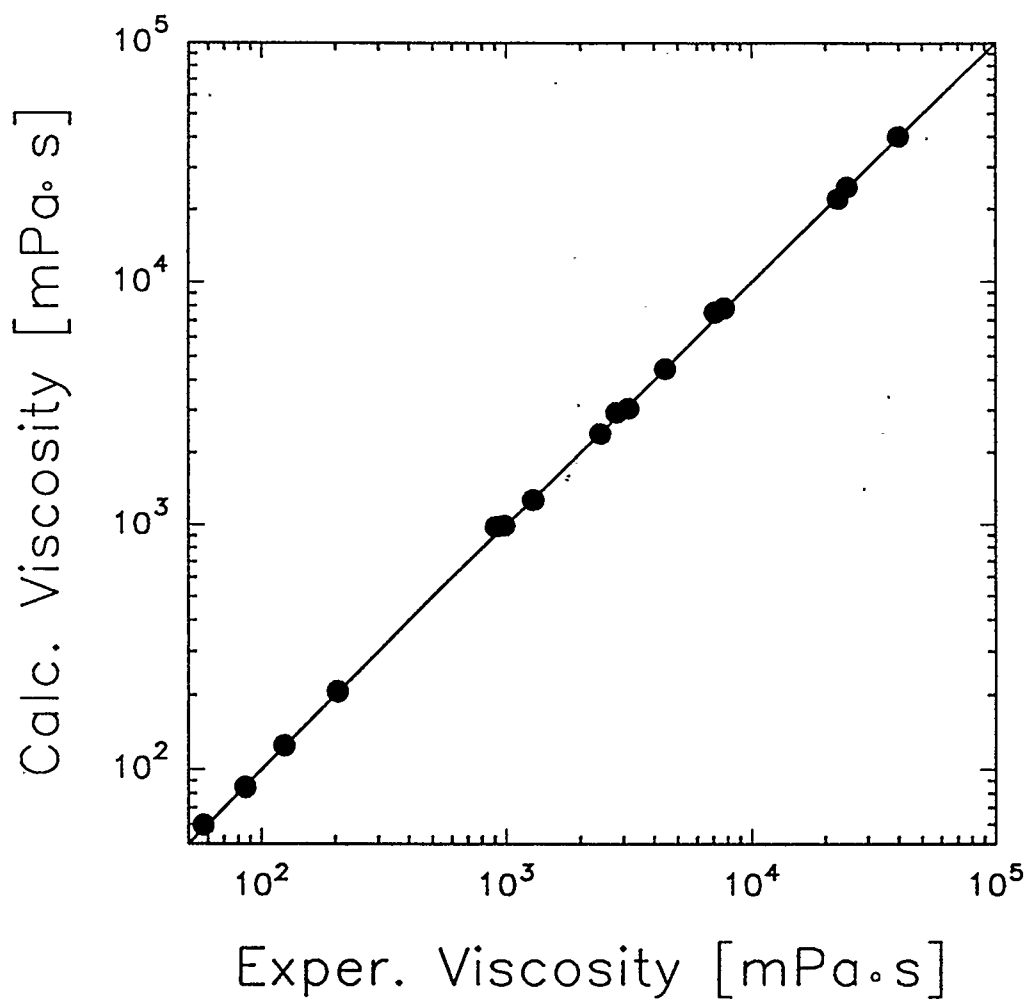


Figure 5.5: Correlation of Sample Data Using Eq. 4.8

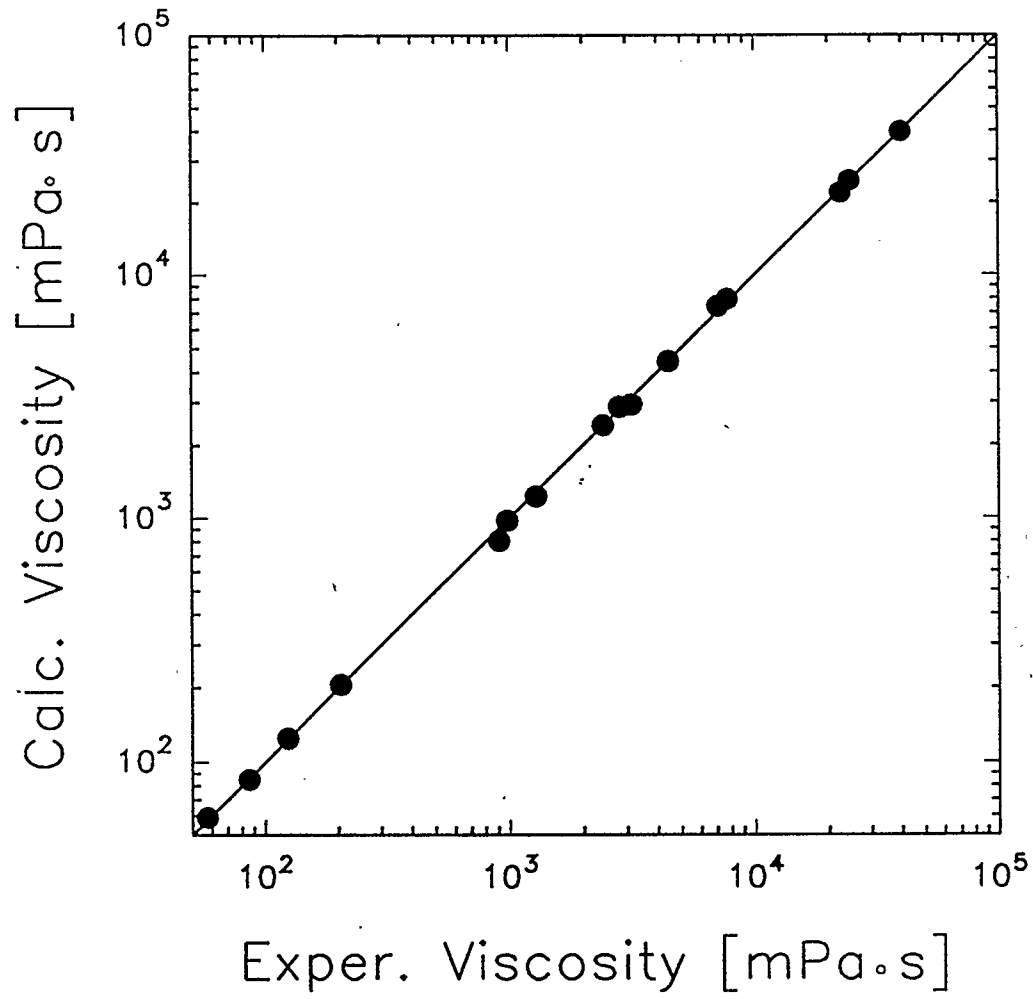


Figure 5.6: Correlation of Sample Data Using Eq. 4.9

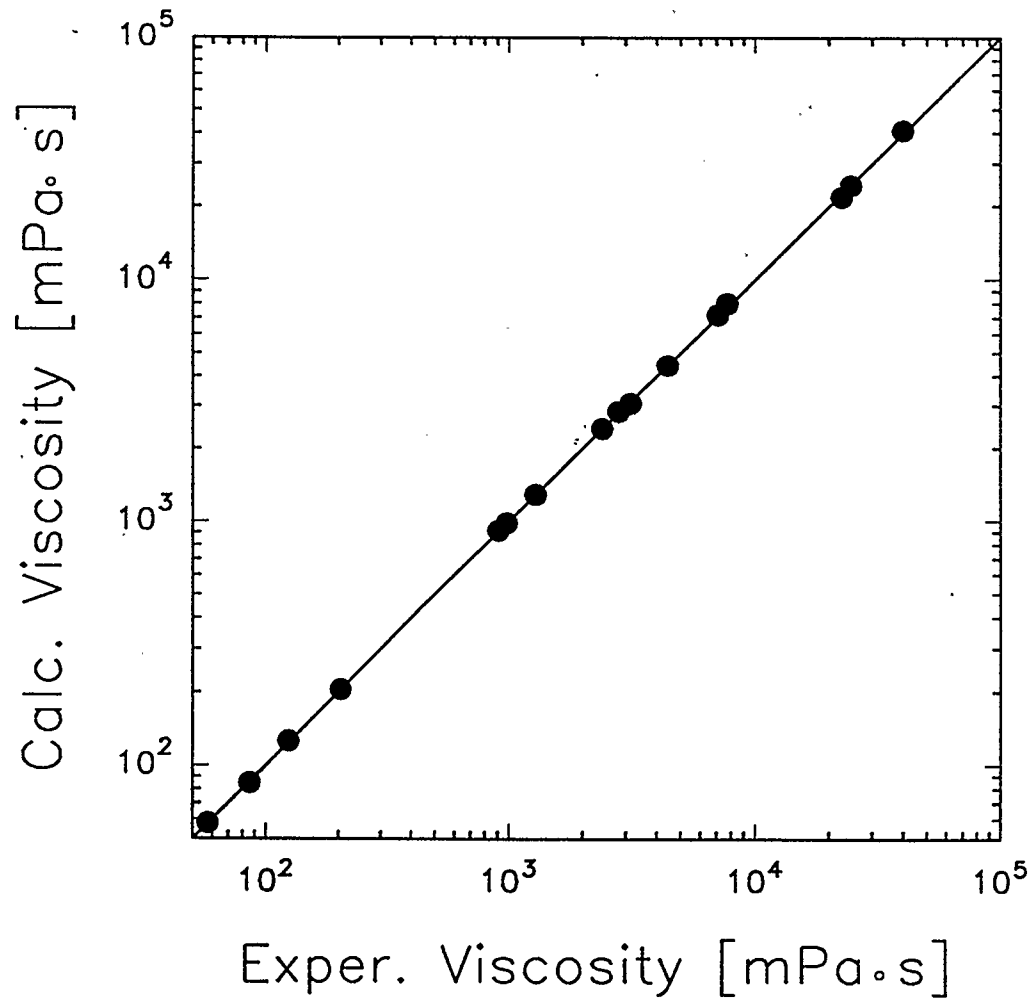


Figure 5.7: Correlation of Sample Data Using Eq. 4.11

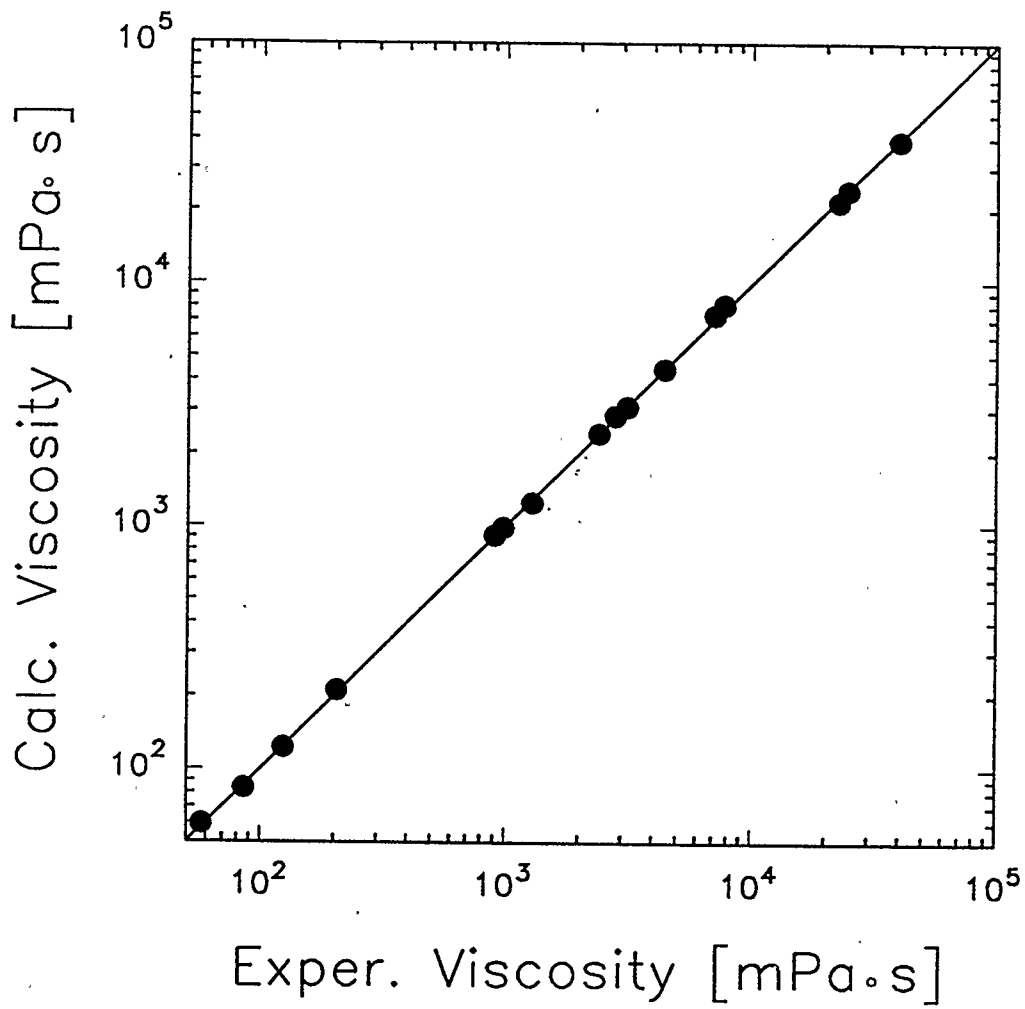


Figure 5.8: Correlation of Sample Data Using Eq. 4.12

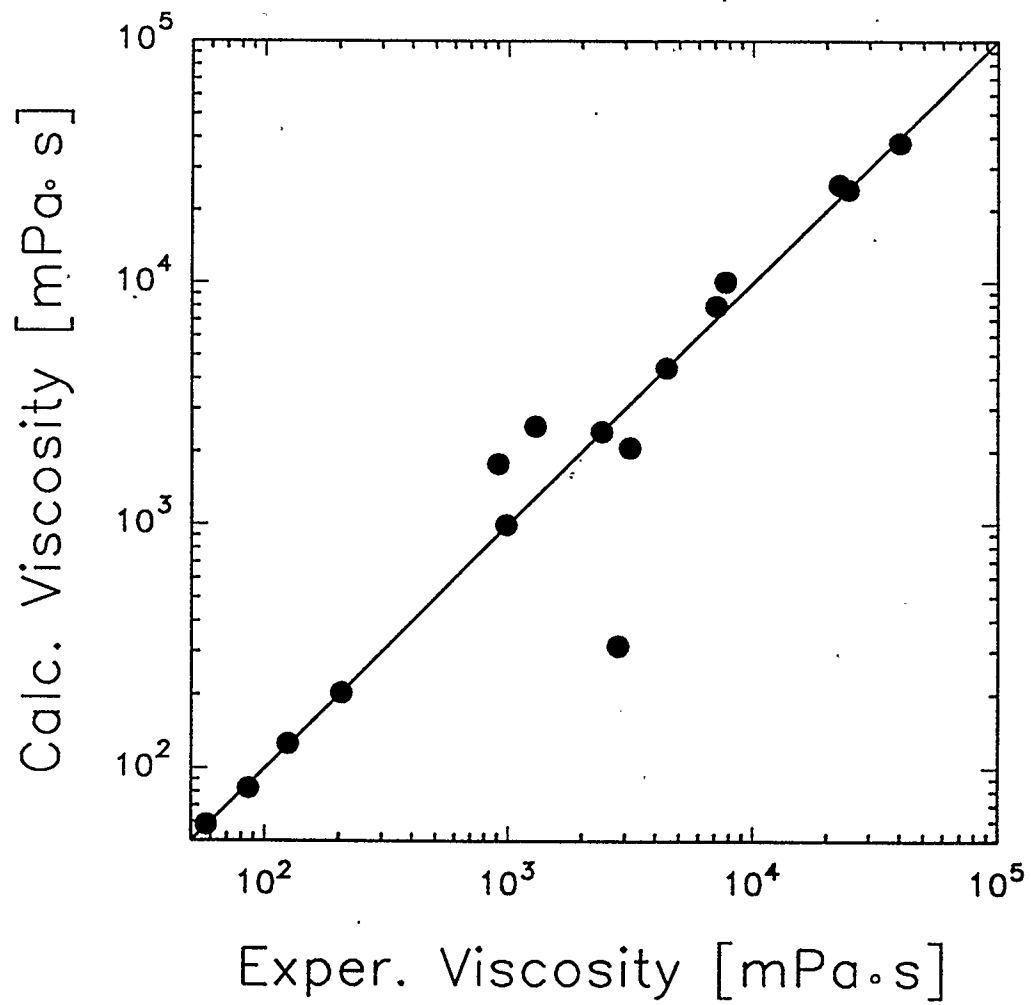


Figure 5.9: Correlation of Sample Data Using Eq. 4.13

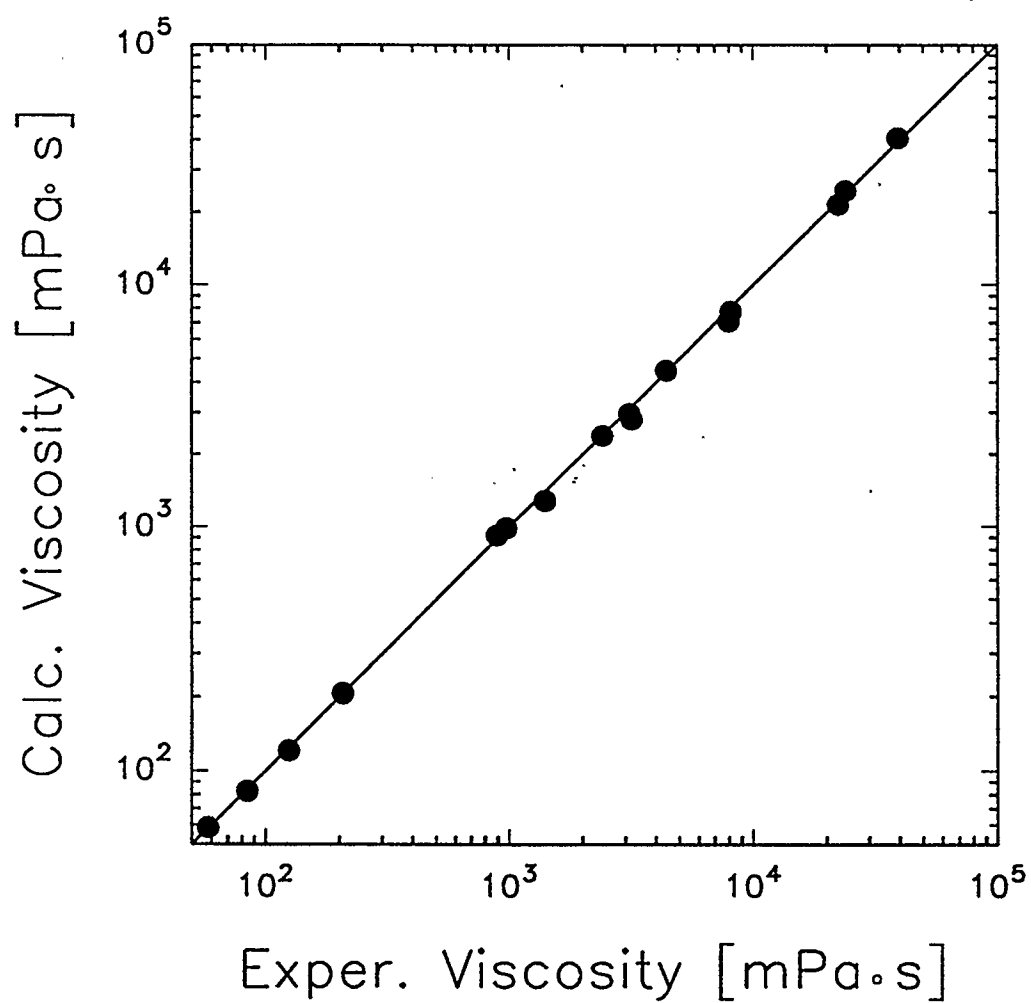


Figure 5.10: Correlation of Sample Data Using Eq. 4.14

Table 5.2: Summary of Correlation Results

Equation	Maximum Deviation [%]	AAD [%]
4.1	30.2	5.3
4.2	13.3	3.3
4.4	4.0	1.6
4.7	41.8	15.7
4.8	7.9	2.5
4.9	11.6	3.2
4.11	3.5	1.5
4.12	4.8	2.0
4.13	96.4	29.5
4.14	5.5	1.5

Any of the correlations evaluated here with errors less than 5% AAD could be used to model the viscosity-temperature data. This is due to the fact that the majority of liquid-viscosity measurements have an accuracy near ± 10 –15%. This does not, however, preclude the use of the correlation which seemingly best fits the data of this investigation. The error in the experimental viscosities results will be discussed in section 5.2.2.

Apparently, the most accurate overall correlation is obtained from equation 4.11 because it yields the lowest maximum deviation and the lowest AAD. Equation 4.11 requires three correlated parameters however, and equation 4.4 (with two parameters) is almost equally as accurate. Also, as mentioned, equation 4.4 has been used previously^{23,24,25} to model the temperature-viscosity data of bitumens and solvents. Therefore, this study will employ equation 4.4 to correlate the effect of temperature on the viscosity of the mixture components (ie. the pure solvents and the undiluted bitumens).

5.2.2 Correlation of Component Viscosities

The experimental viscosity data of the pure solvents and the unblended bitumens can now be presented along side the correlation results provided using equation 4.4.

The definition of "selected viscosity" is used here to provide the best representative experimental results. For the viscosity results where a large scattering of data exists, the average viscosity will be used as the selected viscosity. In the case where the results of different experimental runs are similar, the results of a single run which best represents the group of data is termed the selected viscosity.

The temperature-viscosity data obtained experimentally for the Cold Lake bitumen is presented in Table 5.3 and displayed in Figure 5.11. The data selected to best represent the sample is shown in the final column of Table 5.3, and the correlation results of the selected data are presented in Table 5.7.

The temperature-viscosity data obtained experimentally for the Athabasca bitumen is presented in Table 5.4 and displayed in Figure 5.12. The data selected to best represent the sample is shown in the final column of Table 5.4, and the results of correlating the selected data are presented in Table 5.7.

The viscosity results for the two bitumens (Tables 5.3 and 5.4) show a relatively small scattering of the experimental data. By comparing the "selected" viscosity to the results of the individual test runs yields the following: the Cold Lake bitumen data exhibits an average error of 5.5%, with a maximum error of 8.8%; the Athabasca bitumen data exhibits an average error of 1.8%, with a maximum error of 6.8%.

It is interesting to note that the experimental results indicate that the viscosity of the Athabasca bitumen is lower than that of the Cold Lake bitumen. This is opposite to what has generally been observed². One factor which may have contributed to this reversal, is the amount of solvent remaining in the "pure" bitumen. A solvent has been used in

Table 5.3: Cold Lake Bitumen Viscosity Data

Temperature [°C]	Experimental Viscosity			Selected* Viscosity [cP]
	Test 1 [cP]	Test 2 [cP]	Test 3 [cP]	
20	94400	—	—	—
30	25590	22820	25400	24600
40	8190	7320	8300	7740
50	3140	2880	3400	3140
60	1370	—	—	—
65	990	890	860	910

Table 5.4: Athabasca Bitumen Viscosity Data

Temperature [°C]	Experimental Viscosity			Selected* Viscosity [cP]
	Test 1 [cP]	Test 2 [cP]	Test 3 [cP]	
25	39990	42100	38970	39990
30	22560	22100	22600	22560
40	7100	7500	7100	7100
50	2810	3000	2900	2810
60	1290	—	1300	1290

* "Selected Viscosity" described in section 5.2.2

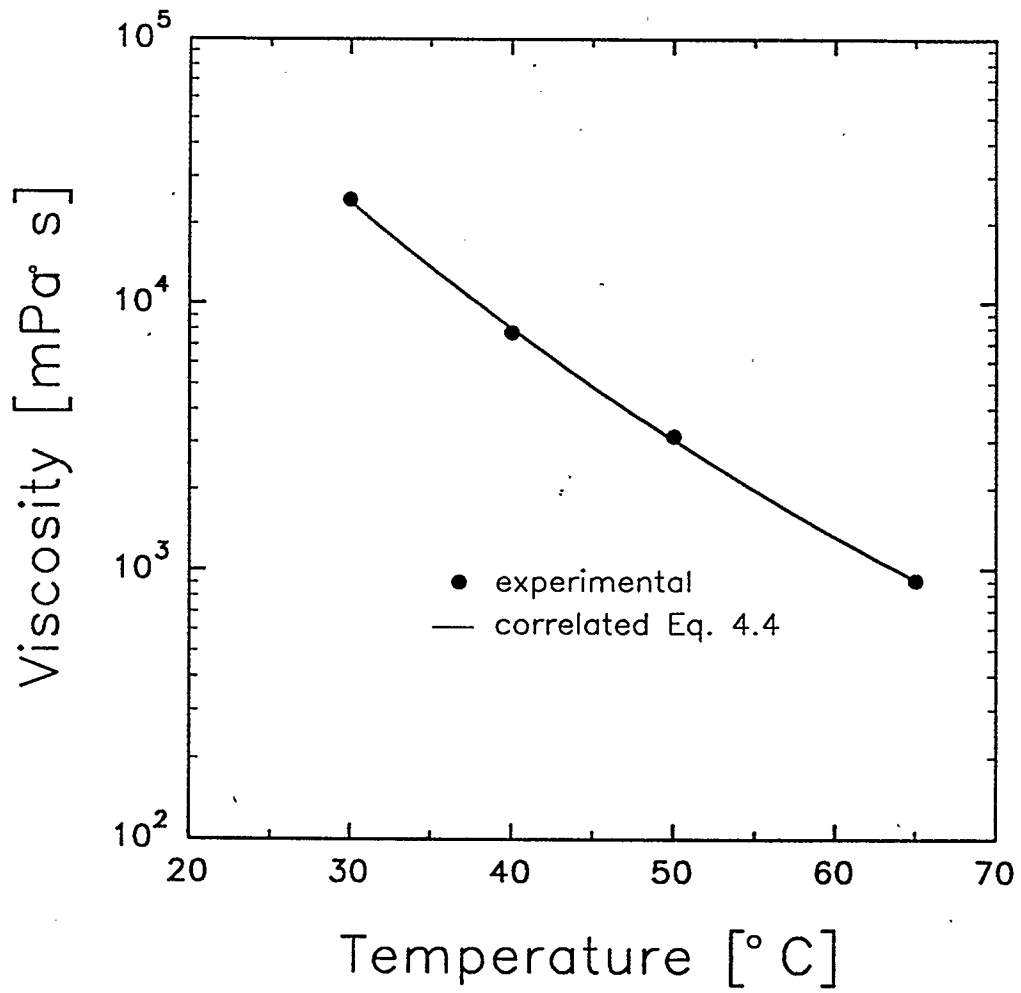


Figure 5.11: Viscosity Results for Cold Lake Bitumen

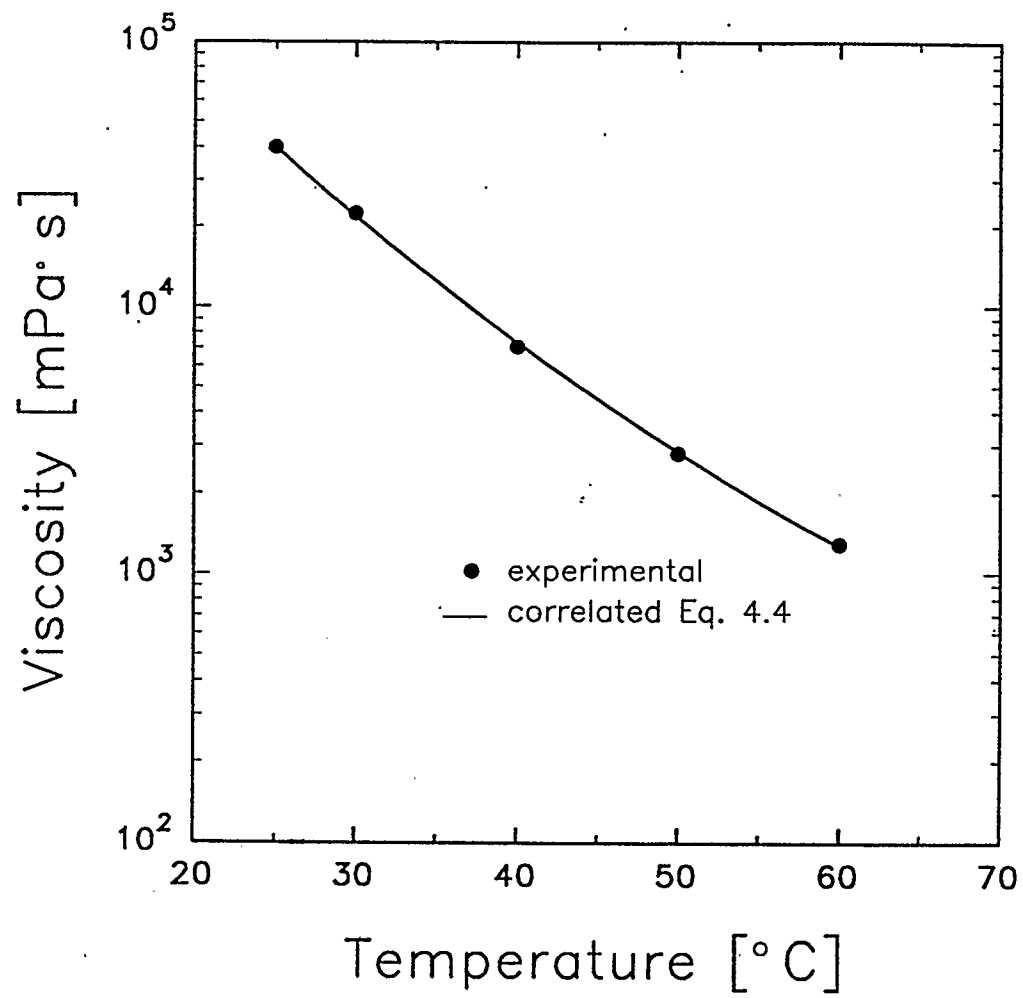


Figure 5.12: Viscosity Results for Athabasca Bitumen

the production and processing of both the Cold Lake and Athabasca bitumens, with the majority of the solvent subsequently removed. Even a small amount of residual solvent, however, would have a serious impact on the experimentally determined viscosities.

The experimental viscosity data of the sample ethers are presented in a slightly different manner. This is due to the fact that for low viscosity samples, the Cannon-Fenske viscometer was required. Thus, the data are presented in terms of kinematic viscosity, as read out of the Cannon-Fenske viscometer. The density data of the solvents was determined, and are provided along with the kinematic viscosities. The dynamic viscosities are then calculated and presented.

The temperature-viscosity data of the MTBE solvent are presented in Table 5.5 and displayed in Figure 5.13. The data selected to represent the samples are shown in the final column of Table 5.5, and the correlation results of the selected data are presented in Table 5.7.

The temperature-viscosity data of the TAME solvent are presented in Table 5.6 and displayed in Figure 5.14. The data selected to represent the samples are shown in the final column of Table 5.6, and the results of correlating the selected data are presented in Table 5.7.

Table 5.5: MTBE Viscosity Data

Temperature [°C]	Kinematic Viscosity [cSt]	Density [g/cm ³]	Selected* Viscosity [cP]
22.2	0.4620	0.7384	0.3411
22.2	0.4620	0.7384	
26.3	0.4384	0.7341	0.3218
26.3	0.4384	0.7341	
26.3	0.4406	0.7341	
30.0	0.4213	0.7301	0.3010
30.0	0.4213	0.7301	
30.0	0.4042	0.7301	
35.0	0.3913	0.7250	0.2837
35.0	0.3913	0.7250	
40.0	0.3763	0.7198	0.2709
40.0	0.3763	0.7198	
43.0	0.3719	0.7166	0.2623
43.0	0.3634	0.7166	
43.0	0.3655	0.7166	

* "Selected Viscosity" described in section 5.2.2

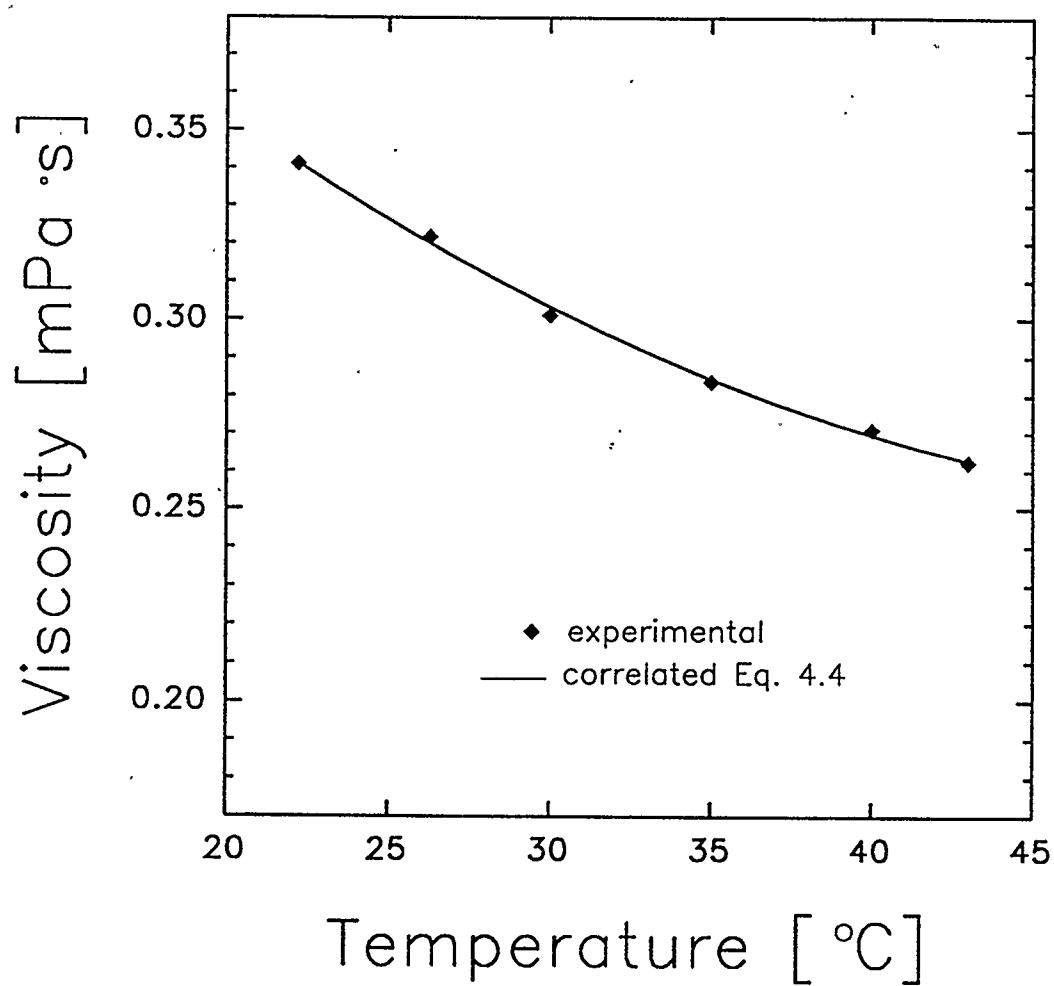


Figure 5.13: Viscosity Results for MTBE

Table 5.6: TAME Viscosity Data

Temperature [°C]	Kinematic Viscosity [cSt]	Density [g/cm ³]	Selected* Viscosity [cP]
24	0.5684	0.7686	0.4385
24	0.5705	0.7686	
24	0.5705	0.7686	
30	0.5340	0.7629	0.4058
30	0.5319	0.7629	
30	0.5319	0.7629	
35	0.5083	0.7581	0.3854
35	0.5062	0.7581	
35	0.5083	0.7581	
40	0.4890	0.7534	0.3668
40	0.4869	0.7534	
40	0.4847	0.7534	
45	0.4675	0.7487	0.3500
45	0.4675	0.7487	
45	0.4675	0.7487	

* "Selected Viscosity" described in section 5.2.2

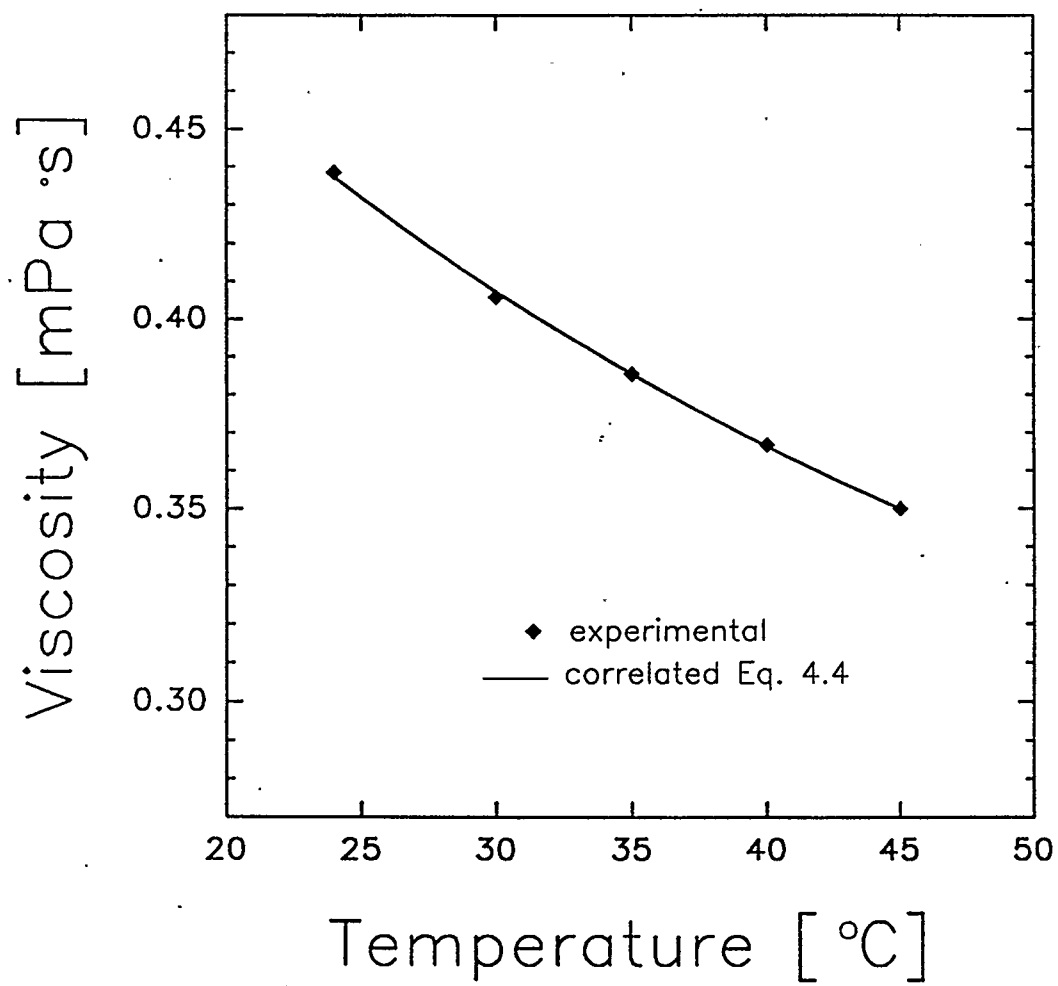


Figure 5.14: Viscosity Results for TAME

Table 5.7: Results of Viscosity Correlations

Component	Equation 4.4 Correlation		Maximum Deviation [%]	AAD [%]
	b_1	b_2		
Cold Lake	9.5580	-3.5928	3.0	1.9
Athabasca	9.4567	-3.5538	3.5	2.2
MTBE	27.1854	-11.5068	0.7	0.4
TAME	14.2598	-6.1843	0.4	0.1

The viscosity results for the two ethers (Tables 5.5 and 5.6) show much less scattering of the experimental data than did the bitumens. By comparing the "selected" viscosity to the results of the individual test runs yields the following: the MTBE data exhibits an average error of 0.4%, with a maximum error of 4.1%; the TAME data exhibits an average error of 0.5%, with a maximum error of 0.1%.

The summary of results provided in Table 5.7 show that equation 4.4 accurately represents the experimental data. With all of the correlated results showing maximum errors and average errors of 3.5% and 2.2% respectively, the component viscosities are suitably correlated.

It can be seen that there exists a wide range of values for the parameters b_1 and b_2 . The cross-correlation of these

parameters suggested²⁶ by equation 4.7 yields a single parameter whose range of values is smaller. Correlating the temperature-viscosity data with equation 4.7 yields the following:

Cold Lake bitumen:	$b = -2.8483$; AAD = 21.1%
Athabasca bitumen:	$b = -2.8460$; AAD = 24.0%
MTBE:	$b = -6.9989$; AAD = 3.3%
TAME:	$b = -6.4082$; AAD = 0.3%

Although more convenient to use, equation 4.7 cannot correlate the current temperature-viscosity data within the accuracy of the experimental results.

Table 5.7 does show that a distinct cross-correlation between b_1 and b_2 exists for the bitumens and ethers investigated, regardless that the generalized equation 4.7 yielded poor results.

By using the following "best-fit" equations, the cross-correlation is less generalized, but more accurate: for the bitumens: $b_1 = -2.6606 \cdot b_2$, and for the ethers: $b_1 = -2.3342 \cdot b_2$. These cross-correlations used in conjunction with equation 4.4, and then fit to the experimental data yield the following:

Cold Lake bitumen:	$b_2 = -3.5943$; AAD = 3.4%
Athabasca bitumen:	$b_2 = -3.5622$; AAD = 2.2%
MTBE:	$b_2 = -9.3617$; AAD = 1.5%
TAME:	$b_2 = -7.3178$; AAD = 1.2%

5.2.3 Bitumen Molar Mass Results

The experimental procedure detailed in section 3.2.1 to determine the molar mass of the sample bitumens was followed, with the results presented here. Figure 5.15 displays the results of the calibration of the vapour pressure osmometry equipment. The data is plotted as change in thermocouple voltage versus concentration of the Benzil solution (the calibrating solvent). This is then extrapolated to the y-axis which yields the voltage shift corresponding to the zero concentration limit (calibrated to be $184.3 \mu\text{V}$). This voltage shift multiplied by the known molar mass of the calibrating solvent (ie. molar mass of Benzil = 210.2 g/mol) yields the equipment calibration constant. The constant is calculated to be $38740 \mu\text{V}\cdot\text{g/mol}$.

With the machine calibrated, the same procedure is followed for the two bitumen samples. Figure 5.16 displays the extrapolation of the data for the bitumens. The resulting molar masses are calculated using equation 3.4: Cold Lake bitumen = 559 g/mol , and Athabasca bitumen = 602 g/mol .

The samples were prepared on a concentration, or mass/volume, basis. The error involved in measuring the mass of the samples, due to systematic errors in the weighing apparatus, was slightly under $\pm 10\%$. The error involved in measuring the volume of the samples was approximately $\pm 0.5\%$. Therefore, the molar weights determined in this investigation should be considered to have an experimental accuracy of $\pm 10\%$.

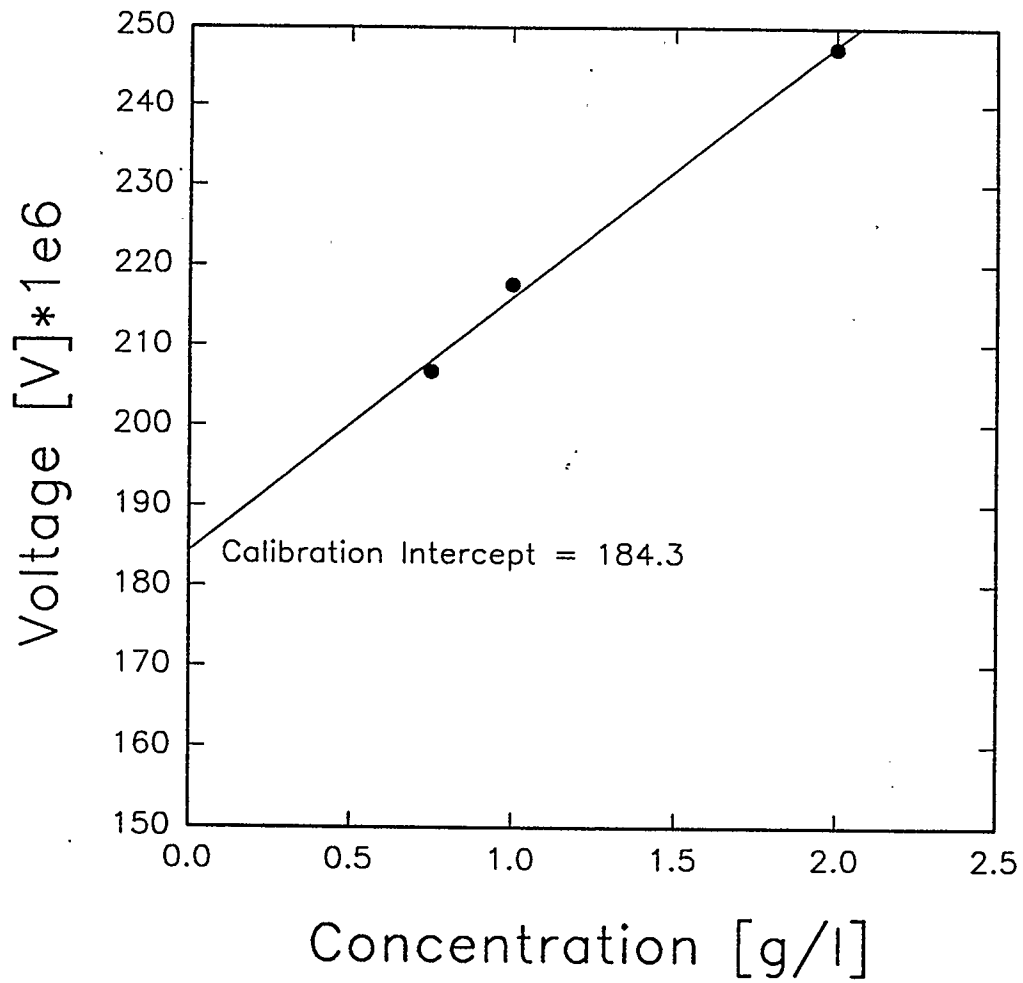


Figure 5.15: Calibration Curve of Vapour Pressure Osmometer

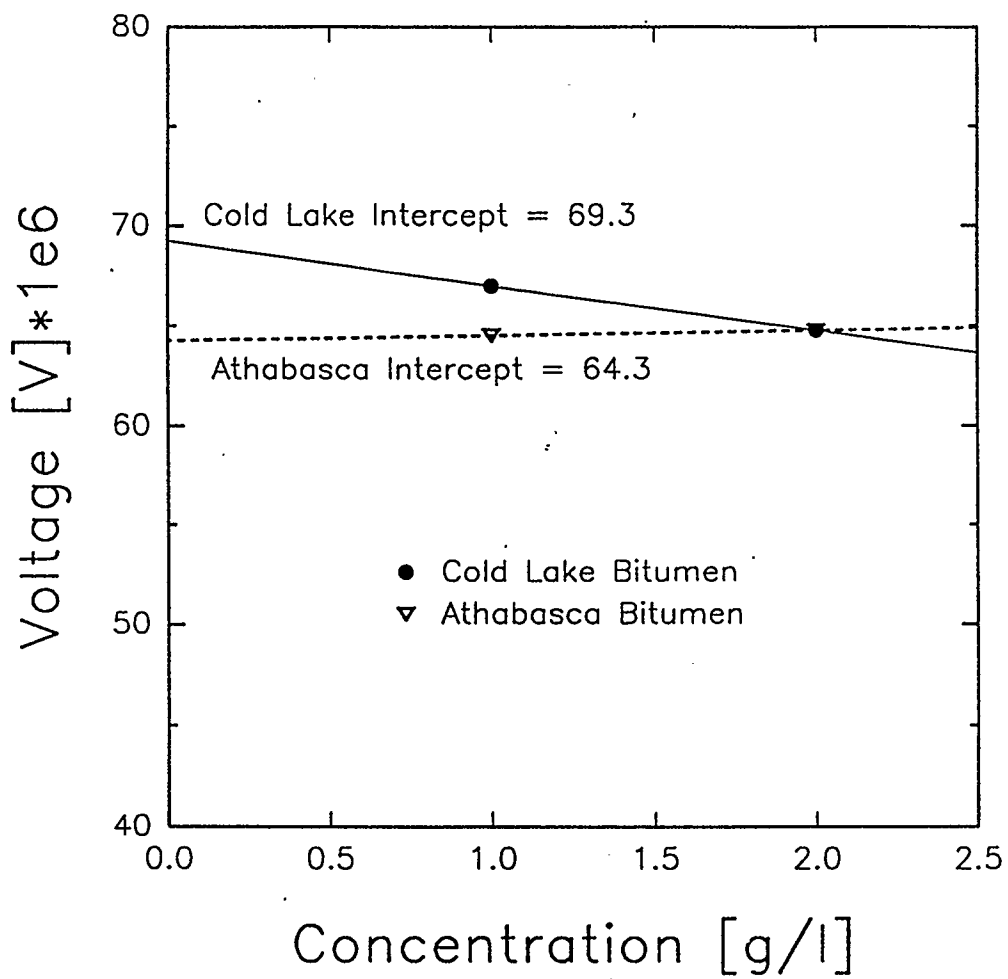


Figure 5.16: Molar Mass Plot For Both Bitumens

5.2.4 Calculation of Liquid-Mixture Viscosities

Section 4.9.1 details the general approach taken to calculate the viscosity of a liquid-mixture, using additive mixing rules and known component viscosities. Those principles are applied here to predict the blend viscosities when the component viscosities are correlated using equation 4.4 (with no cross-correlation of b_1 and b_2).

Three different attempts were made to model the viscosity data for all of the bitumen-solvent blends. The first effort is labelled as Method A, and it is comprised of equation 4.13 using the concentration term described by equation 4.15.

The results of Method A, without consideration of an interaction parameter, are presented for the case of the MTBE-Cold Lake blends in Table 5.8 and the accuracy of these calculations are displayed in Figure 5.17.

The results show that Method A is capable of providing order-of-magnitude results only; consequently, accurate viscosity predictions by this method are not possible. All the viscosity results calculated are near twice the experimental viscosity.

To predict the viscosities of the blends accurately, it was then apparent that an interaction parameter must be taken into account in subsequent models. Equation 4.14 with the concentration term described by equation 4.15 can be re-written for the case of the pseudo-binary system which is currently being considered (ie. bitumen-solvent).

Table 5.8: Results of Method A Modelling
on MTBE - Cold Lake Blend Data

Solvent Fraction [mass]	Temp. [°C]	Exper. Viscosity [cP]	Method A Viscosity [cP]	Error [%]
5	20	11930	14916	25.0
10	20	2521	3943	56.4
15	20	785	1374	75.0
20	4	1014	2472	143.8
20	10	603	1366	126.5
20	20	288	576	100.0
25	4	421	1010	139.9
25	10	266	595	123.7
25	20	124	276	122.6
30	4	205	465	126.8
30	10	124	289	133.1
30	15	85.8	202	135.4
30	20	57.6	145	151.7
			AAD = 112.3%	

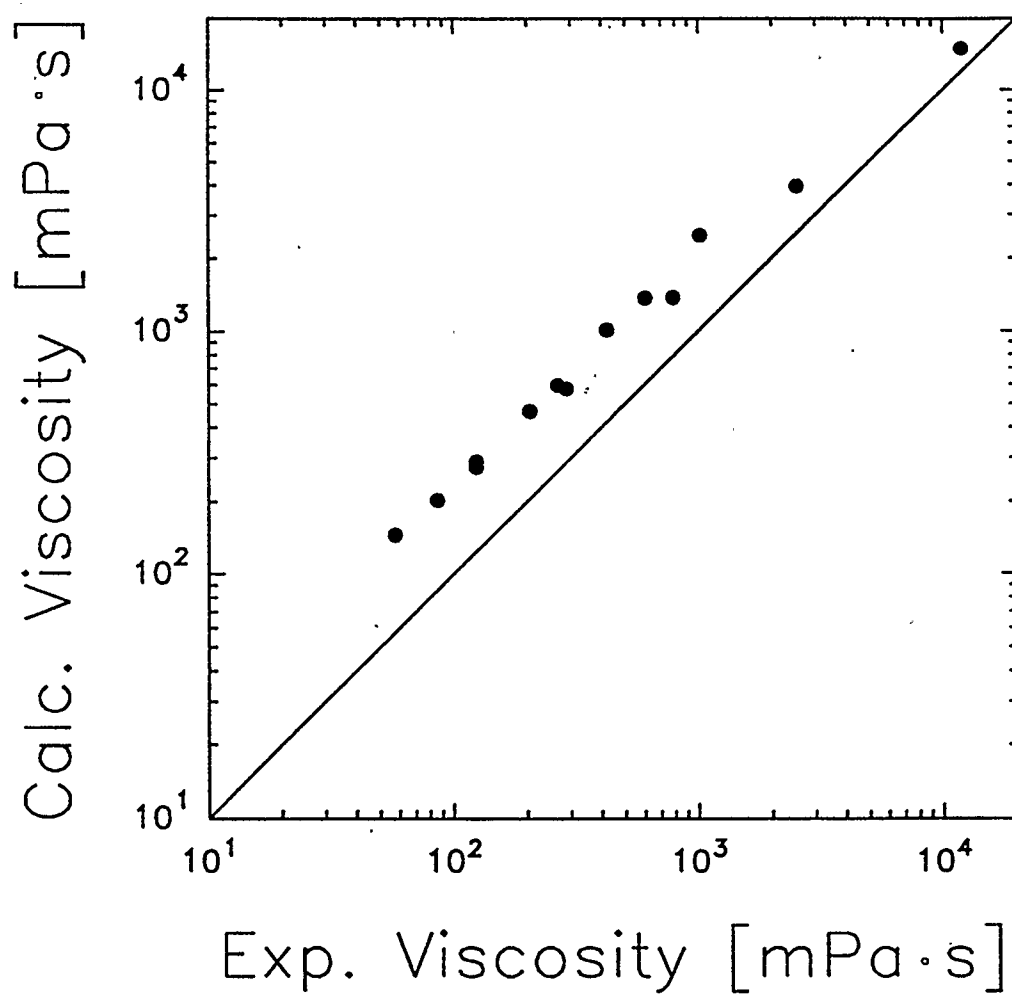


Figure 5.17: Method A Modelling Results

The resulting equation is written as:

$$\begin{aligned} \log(\bar{\mu} + 0.8) = & x_S \left(\frac{M_S}{\bar{M}} \right)^{0.5} \log(\mu_S + 0.8) \\ & + (1 - x_S) \left(\frac{M_B}{\bar{M}} \right)^{0.5} \log(\mu_B + 0.8) \\ & + 2 x_S x_B \left(\frac{M_S M_B}{\bar{M}^2} \right)^{0.5} B_{SB} \end{aligned} \quad (5.2)$$

where:

B_{SB} = interaction between solvent and bitumen phase

The next two modelling efforts are labelled as Model 1 and Model 2. Both begin with equation 5.2; however, it is employed using two different methods of correlating the interaction parameter to the experimental viscosity data. Model 1 correlates B_{SB} as a function of temperature, and Model 2 correlates it as a function of temperature and composition. The following relationships demonstrate the interaction correlations of Model 1 and 2:

$$\begin{aligned} \text{Model 1: } B_{SB} &= a_1 + a_2 T \\ \text{Model 2: } B_{SB} &= c_1 + c_2 T + c_3 S \end{aligned} \quad (5.3)$$

where:

T = temperature [K]

S = solvent concentration [% mass]

a_1, a_2, c_1, c_2, c_3 = empirical parameters

Table 5.9 shows the results of correlation for all of the binary blends using both models. Figure 5.18 shows the two different model predictions versus the actual interaction parameters which were calculated.

Figure 5.18 shows that the addition of the concentration term to the correlation of the interaction parameter greatly improves the representation of the experimental data. This in turn will provide much more accurate viscosity predictions. The accuracies in calculating interactions provided by models 1 and 2, are $\pm 6.9\%$ and $\pm 2.6\%$ respectively.

Table 5.9: Correlation Results For Model 1 and 2

System	Model 1 Parameters		Model 2 Parameters		
	a_1	a_2	c_1	c_2	c_3
Cold Lake- MTBE	-.958	4.59e-3	-.643	6.09e-3	-1.25e-2
Cold Lake- Tame	-1.114	9.59e-3	-.654	1.12e-2	-1.94e-2
Athabasca- MTBE	-1.277	1.73e-2	-.339	1.24e-2	-2.81e-2
Athabasca- TAME	-1.134	1.41e-2	-.318	1.27e-2	-3.05e-2

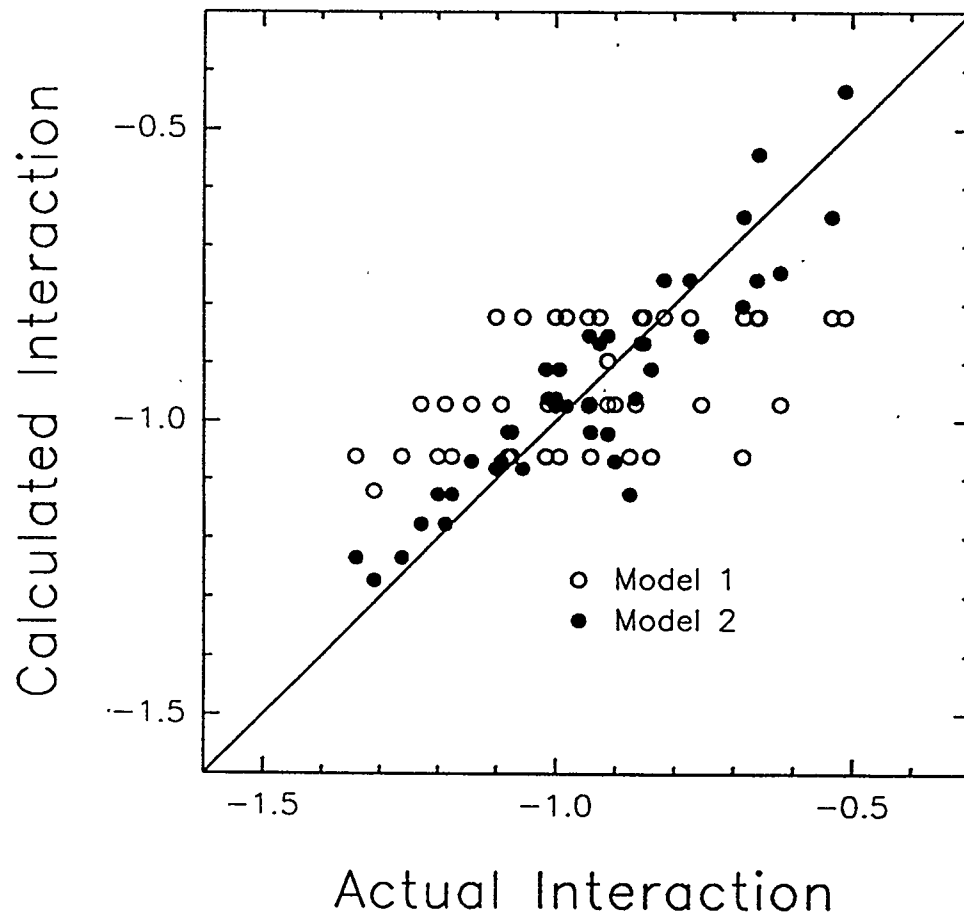


Figure 5.18: Interaction Parameters From Model 1 and 2

The viscosity predictions calculated using equation 5.2 and the two interaction models are presented alongside the experimental viscosity data in Tables 5.10 - 5.13; these data are also displayed in Figures 5.19 - 5.22.

As expected, the viscosity calculations using Model 2 were more accurate than those calculated using Model 1 (compare overall accuracies of 10.4% and 2.4%). However, this accuracy comes at the cost of requiring one extra correlation parameter. When you consider that the liquid mixture is compromised of components whose viscosities are 5-6 orders of magnitude apart, being able to correlate the blend viscosities with less than 5% deviation is exceptional.

Now that an accurate means of calculating blend viscosities is available, the actual amount of solvent needed to reduce the bitumen viscosity to meet the pipeline specifications can be calculated. The specifications call for the blend to have a viscosity of 250 cSt at 4°C with an API gravity of 21°; this works out to be a fluid viscosity of 269 mPa•s at the same temperature. The calculations yield that (all in mass fractions): 27.6% MTBE - Cold Lake blend and 25.9% MTBE - Athabasca blend meet the pipeline specifications. Also, 28.5% TAME - Cold Lake blend and 27.5% TAME - Athabasca blend meet the pipeline specifications.

Table 5.10: Viscosity Results Cold Lake - MTBE

Solvent Conc. [mass%]	Temp. [°C]	Exper. Visc. [cP]	Model 1		Model 2	
			Visc. [cP]	Error [%]	Visc. [cP]	Error [%]
5	20	11930	10222	14.3	11565	3.1
10	20	2521	2186	13.3	2537	0.6
15	20	785	675	14.0	766	2.4
20	4	1014	1065	5.0	1135	11.9
20	10	603	603	0.0	647	7.3
20	20	288	265	8.0	287	0.2
25	4	421	422	0.1	424	0.7
25	10	266	255	4.3	258	3.0
25	20	124	123	0.9	126	1.6
30	4	205	193	5.8	183	10.8
30	10	124	123	0.8	117	5.3
30	15	86	88	2.2	84	1.9
30	20	58	64	11.6	62	7.8
			AAD = 5.8%		AAD = 4.0%	

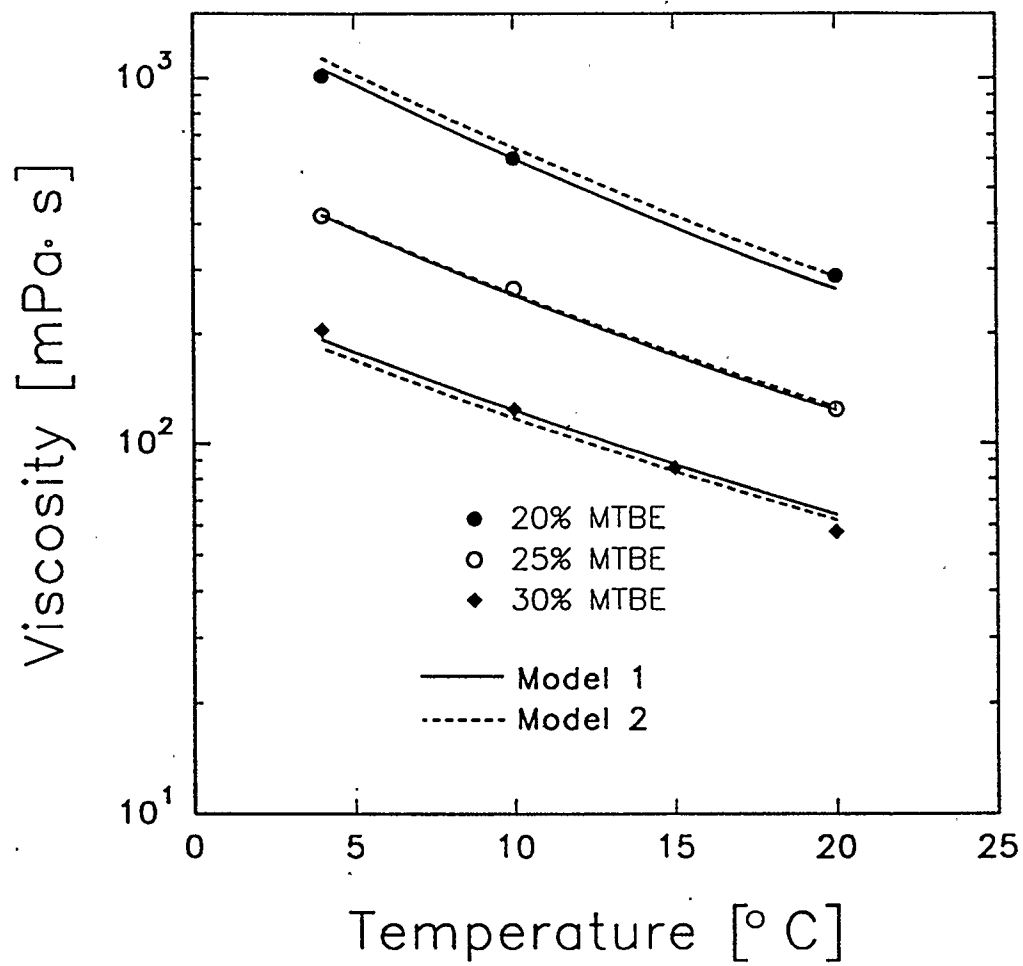


Figure 5.19: Viscosity Results Cold Lake - MTBE

Table 5.11: Viscosity Results Cold Lake - TAME

Solvent Conc. [mass%]	Temp. [°C]	Exper. Visc. [cP]	Model 1		Model 2	
			Visc. [cP]	Error [%]	Visc. [cP]	Error [%]
20	4	1412	1343	4.9	1437	1.8
20	10	819	767	6.3	829	1.2
20	20	375	341	8.9	375	0.1
25	4	518	523	0.9	511	1.3
25	10	320	319	0.2	315	1.4
25	20	156	157	0.5	158	1.0
30	4	207	235	13.3	209	0.9
30	10	134	152	13.2	136	1.8
30	20	72	81	12.0	74	2.4
			AAD = 6.7%		AAD = 1.3%	

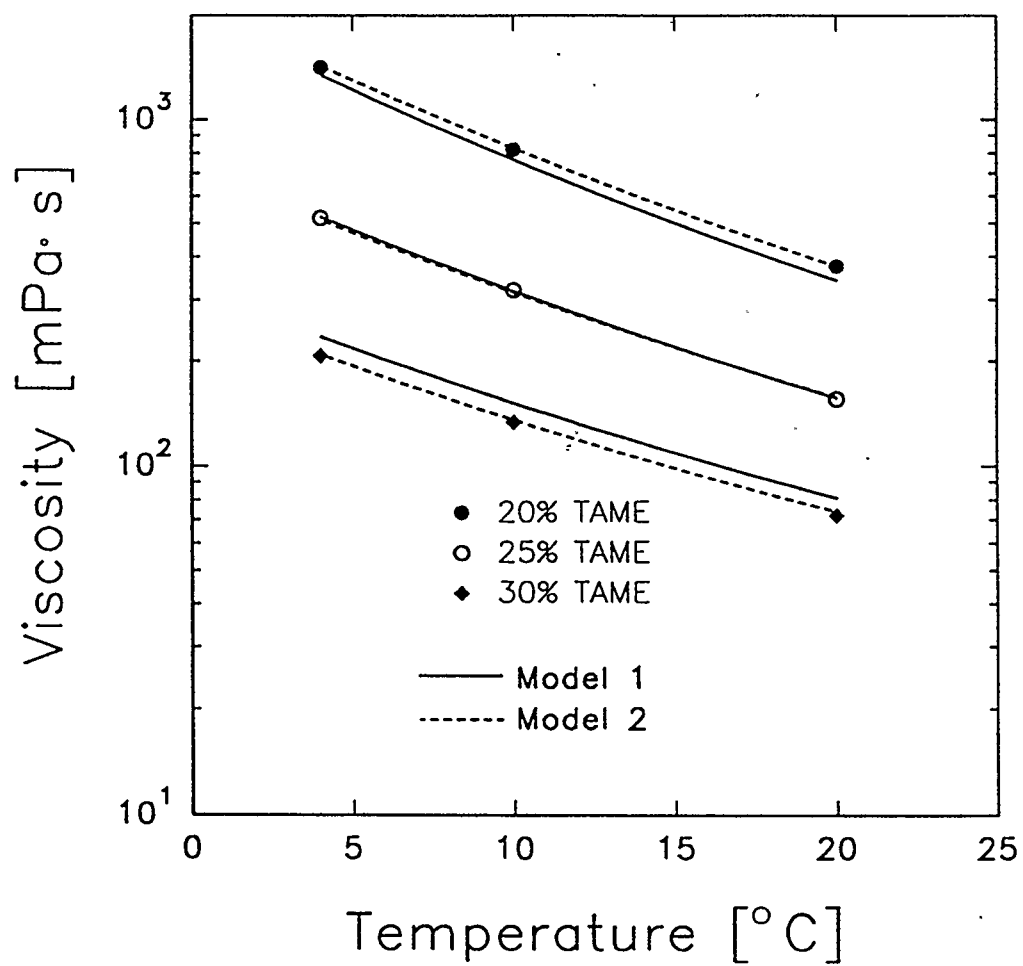


Figure 5.20: Viscosity Results Cold Lake - TAME

Table 5.12: Viscosity Results Athabasca - MTBE

Solvent Conc. [mass%]	Temp. [°C]	Exper. Visc. [cP]	Model 1		Model 2	
			Visc. [cP]	Error [%]	Visc. [cP]	Error [%]
20	4	916	660	28.0	906	1.1
20	10	559	409	26.8	548	2.0
20	20	265	208	21.5	267	0.7
30	4	127	123	2.9	132	4.0
30	10	87	86	1.2	90	3.0
30	20	51	52	1.4	52	1.0
35	0	79	82	3.1	78	1.2
35	4	61	64	5.0	61	1.1
35	10	44	47	7.9	43	1.1
35	20	26	30	16.5	26	2.0
			AAD = 11.4%		AAD = 1.7%	

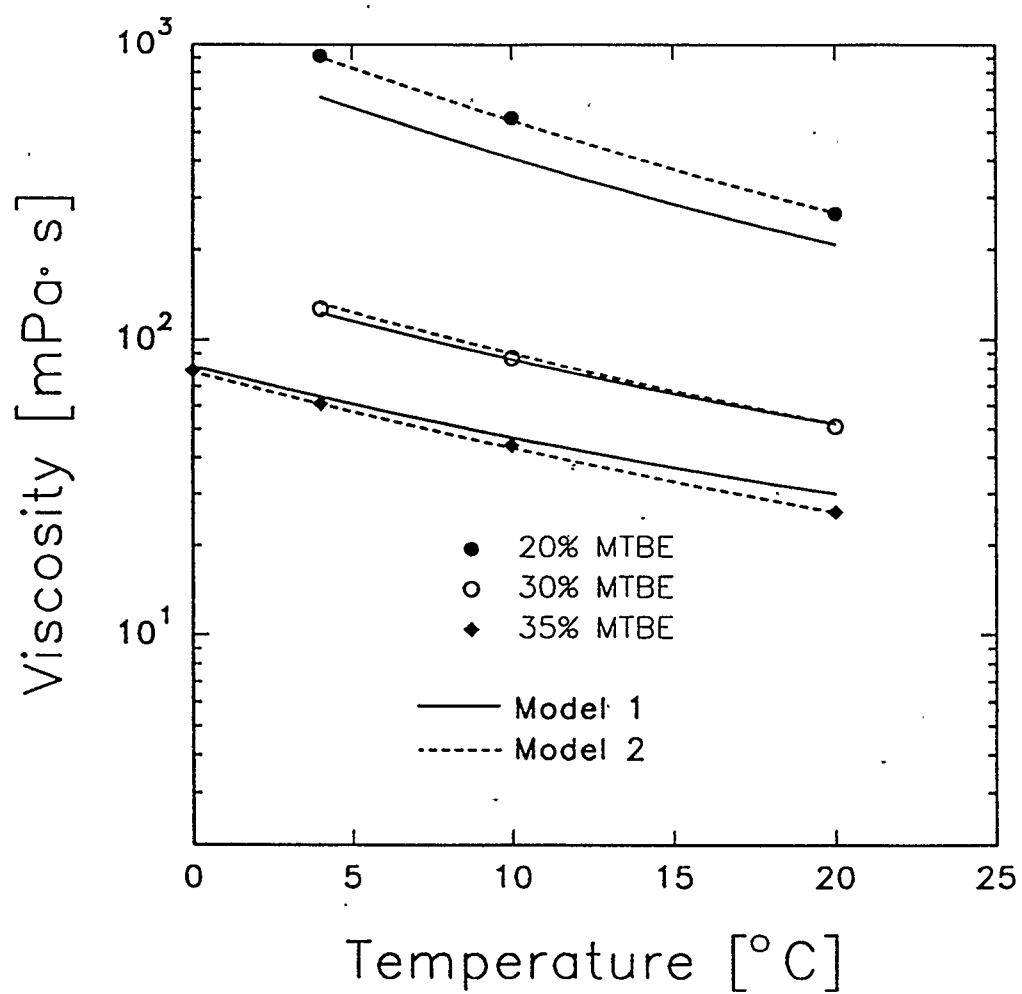


Figure 5.21: Viscosity Results Athabasca - MTBE

Table 5.13: Viscosity Results Athabasca - TAME

Solvent Conc. [mass%]	Temp. [°C]	Exper. Visc. [cP]	Model 1		Model 2	
			Visc. [cP]	Error [%]	Visc. [cP]	Error [%]
15	4	4439	3212	27.6	4291	3.3
15	10	2413	1777	26.4	2358	2.3
15	20	983	756	23.0	993	1.0
25	4	416	415	0.3	433	4.2
25	10	270	266	1.5	276	2.2
25	20	141	141	0.1	144	2.3
35	4	76	97	28.3	76	0.5
35	10	55	69	25.1	53	2.9
35	20	33	42	27.0	32	2.9
			AAD = 17.7%		AAD = 2.4%	

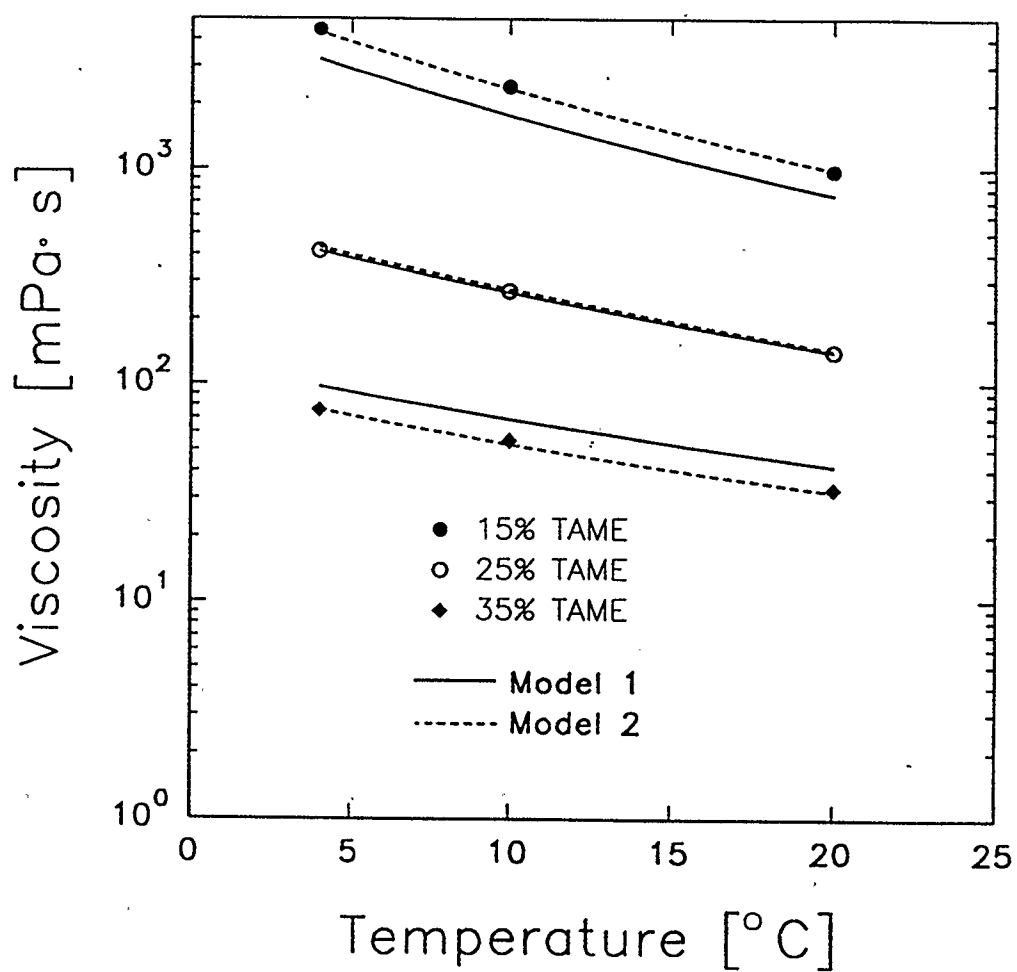


Figure 5.22: Viscosity Results Athabasca - TAME

5.2.5 Calculation of Blend Viscosity Using Shu Correlation

The general viscosity mixing model detailed in section 4.9.2 as introduced by Shu³², will be evaluated versus the experimental results. The Shu model requires that the viscosities of the components in the mixture be known. To achieve this, equation 4.4 is used. The Shu model also requires the density at 25 °C for the components in the mixture. The following data is used:

Cold Lake bitumen: $\rho = 0.995$ (from reference 23)

Athabasca bitumen: $\rho = 0.997$ (experimental)

MTBE: $\rho = 0.7355$ (experimental)

TAME: $\rho = 0.7676$ (experimental)

By using equation 4.4 and the density data presented above, the Shu model is able to predict blend viscosities as a function of temperature and composition. The Shu model predicts the blend viscosities with the following accuracies:

Cold Lake-MTBE = 16.3% AAD Cold Lake-TAME = 14.2% AAD

Athabasca-MTBE = 9.6% AAD Athabasca-TAME = 10.9% AAD

The overall accuracy of the Shu model in predicting the blend viscosities of this investigation was determined to be 12.8% AAD. It is evident that the Shu model is more accurate than Model A in the prediction of blend viscosities in the absence of experimentally determined interaction parameters.

5.3 Rheology

As previously mentioned, the procedure to examine the rheology of the bitumens and bitumen-solvent blends involved measuring fluid viscosity while varying the rotational speed (ie. shear rate) of the spindle immersed in the test sample. From these results, a plot of viscosity versus changing shear rate could be depicted, and its rheological properties determined.

The accuracy of this viscometer is, however, dependant upon the spindle speed. Therefore, changing the shear rate will affect the accuracy of the machine as well as the observed fluid properties. Consequently, any small changes in viscosity may be caused by experimental error, and not by the actual rheological properties of the sample mixture.

This decrease of accuracy reduces the usefulness of the results. For example, when the shear rate is halved, the new viscosity which is determined has twice the experimental error.

The procedure described was followed for a number of bitumen-solvent mixtures at various temperatures. Similar results were found for all of the samples examined, with Table 5.14 presented as an example. Table 5.14 shows the results of a 35% mass TAME - Athabasca blend at 20°C.

It can be seen in Table 5.14 that the small shift in fluid viscosity as the shear rate changes, can more than be accounted for by the experimental error. If the change in

Table 5.14: Rheology of TAME - Athabasca Bitumen Blend

Spindle Speed [rpm]	Shear Rate [s ⁻¹]	Experimental Viscosity [cP]
100	122.4	33.3 ± 0.6
50	61.18	34.6 ± 1.3
20	24.47	34.6 ± 3.2
10	12.24	35.8 ± 6.4

viscosity was greater than what could be attributed to the inaccuracy of the equipment, then it could be determined to behave non-Newtonian. Therefore, the only conclusion that can be made from these results are that the mixture behaves as a Newtonian fluid within the experimental uncertainty; similar results have also been found for Athabasca bitumen³⁷.

5.4 Separation of Blended Components

The batch distillation detailed in section 3.1.4 was carried out for the four soluble bitumen-solvent blends and the two pure solvents in this investigation. The distillation of the solvents was performed to determine its boiling point at atmospheric pressure, and to observe if any possible impurities would alter the expected results.

The bitumen-solvent blends chosen to perform the distillation experiments were mixed in concentrations similar to those required to meet the pipeline specifications, namely near 30% (mass) solvent. The experimental distillation curves for all four blends are displayed in Figures 5.23-5.26. The figures show the temperature of the vapour in the distillation head and the temperature of the liquid-mixture in the flask. These temperatures were plotted versus the amount of distillate recovered.

Small boiling point ranges (ie. vapour temperature at plateau) were observed for the TAME blends, but not as much for the MTBE blends. However, this may be caused by the increased impurity in the TAME sample (compare purities of 94% TAME to 99.5% MTBE; section 3.2).

It should be noted that the drop off of vapour temperature when nearing the ultimate recovery of distillate is atypical. The expected result would have the vapour temperature remain nearly constant (as the liquid temperature continues to rise) until the heating apparatus is turned off. In this experimental set-up, however, the thermometer resting in the distillation head is very near the condenser. This was obviously cooling the air near the thermometer used to measure the vapour temperature. Therefore, when no vapour was passing through the distillation head, the air would cool off to room

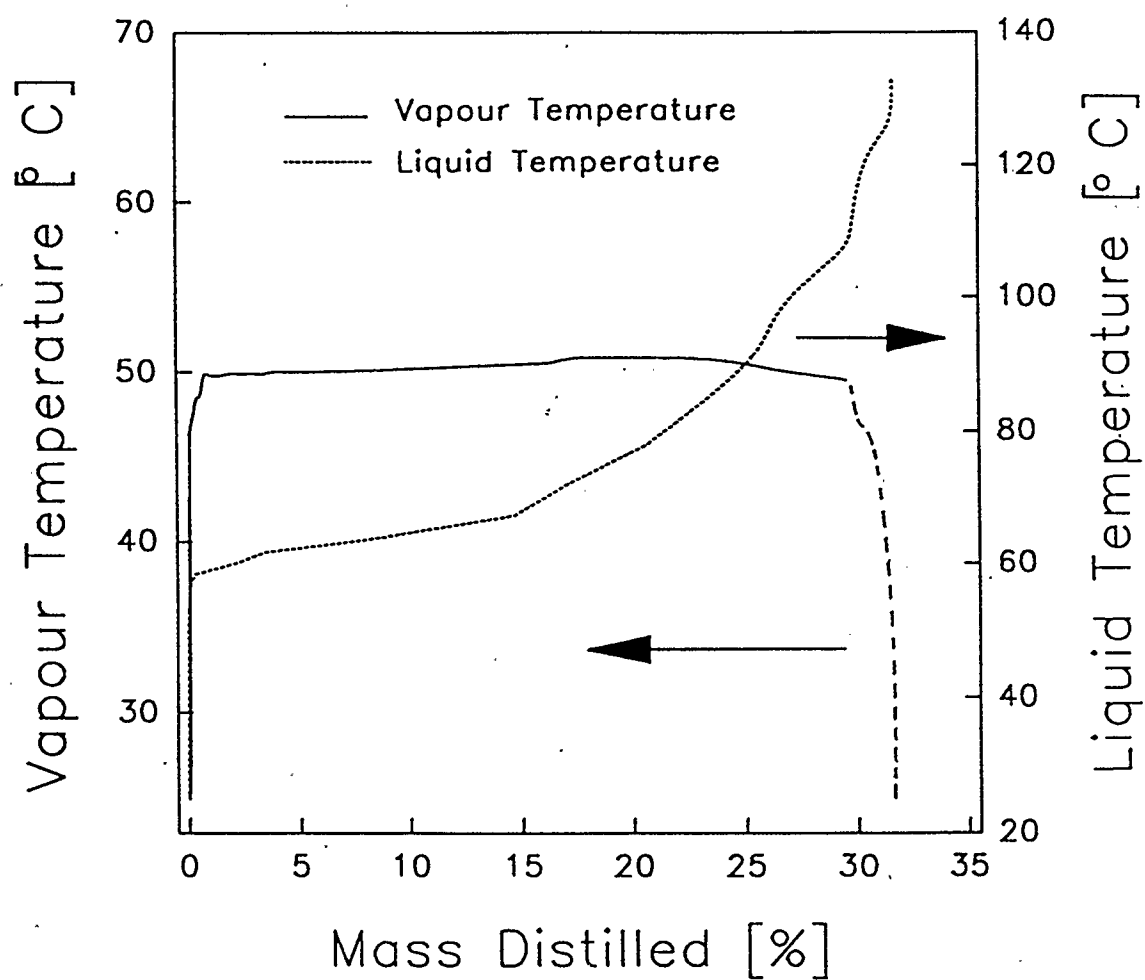


Figure 5.23: Distillation Curve for
35.7% (mass) MTBE-Cold Lake Bitumen Blend

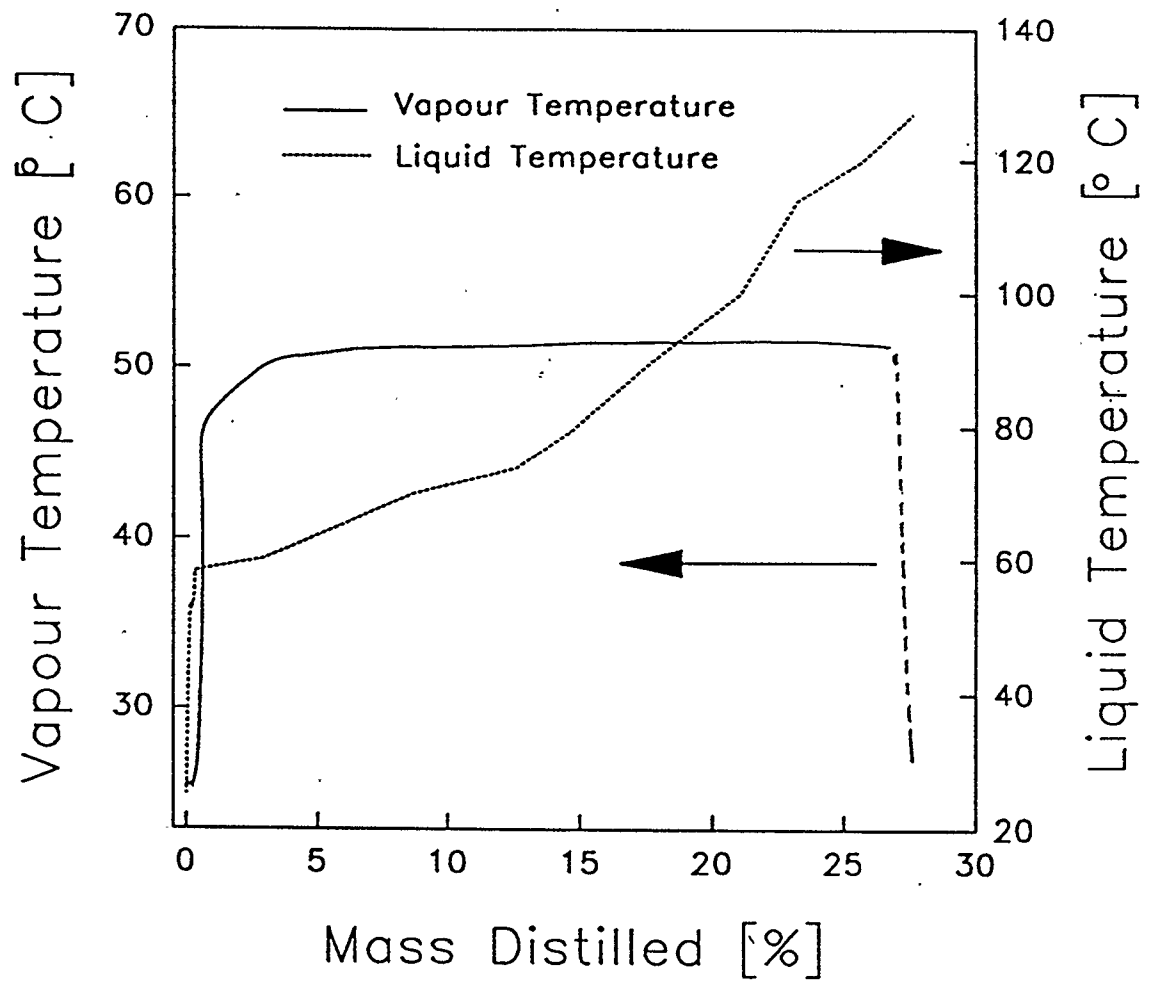


Figure 5.24: Distillation Curve for
30.0% (mass) MTBE-Athabasca Bitumen Blend

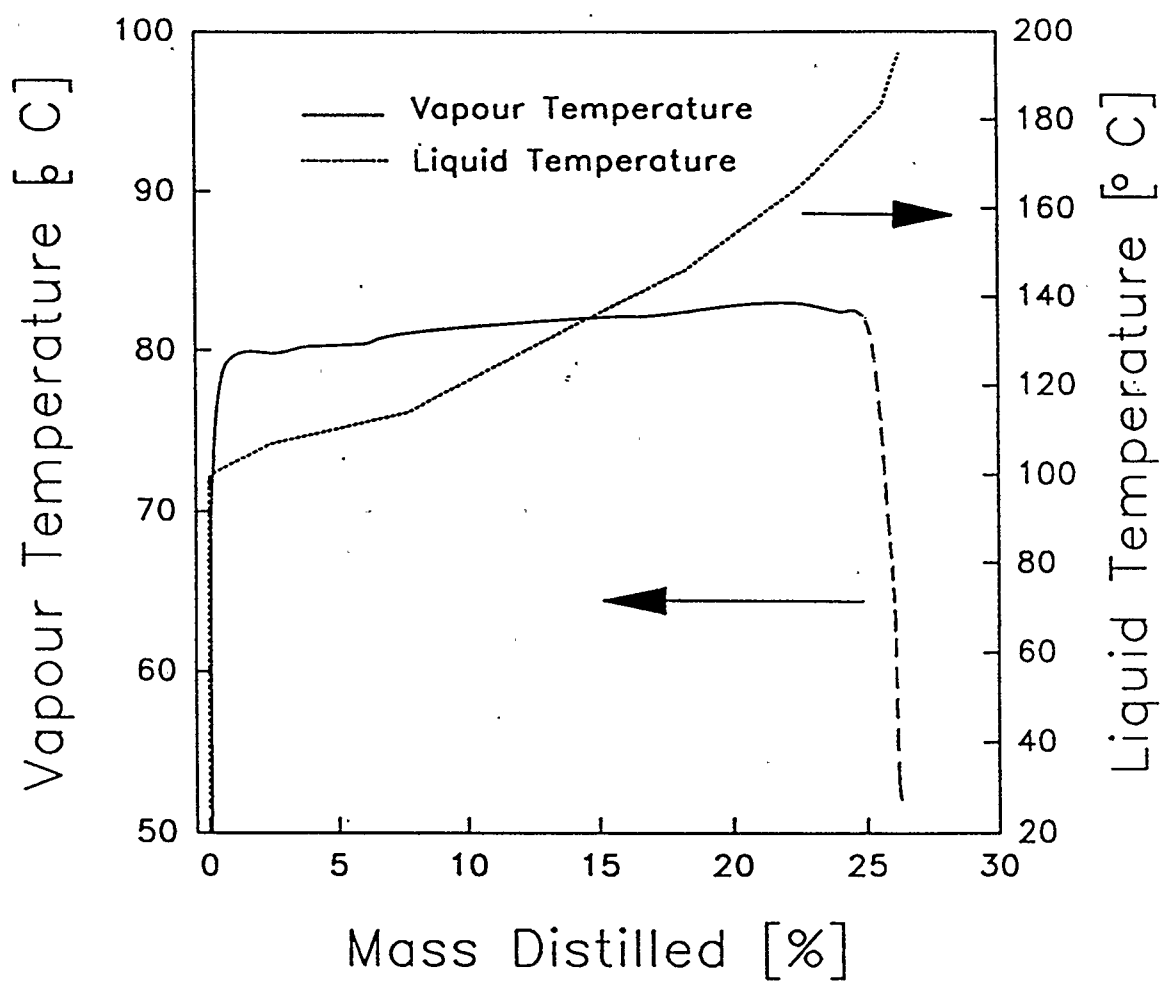


Figure 5.25: Distillation Curve for
30.0% (mass) TAME-Cold Lake Bitumen Blend

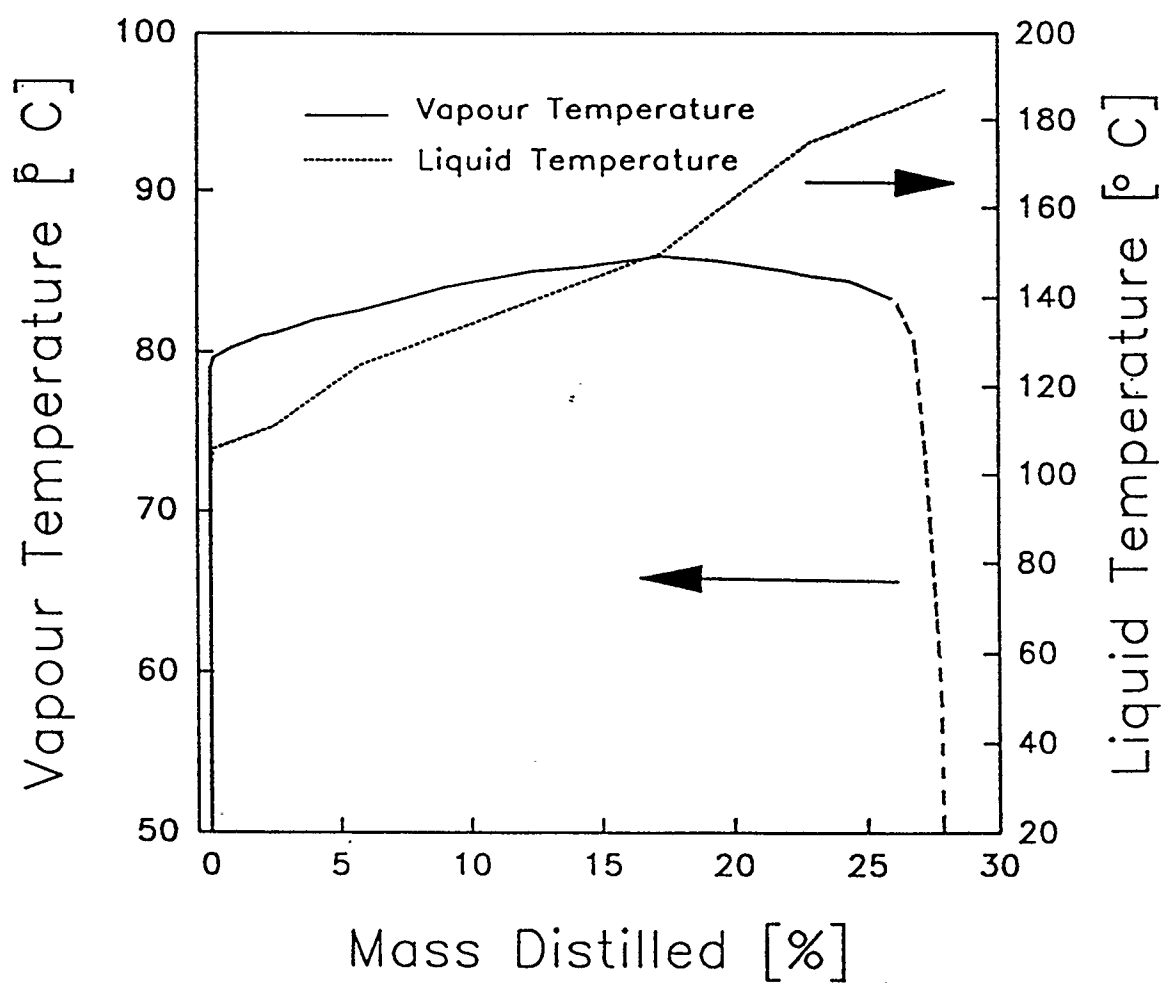


Figure 5.26: Distillation Curve for
30.0% (mass) TAME-Athabasca Bitumen Blend

temperature. This is shown in Figures 5.23 - 5.26 as the broken line which extends down from the vapour temperature curve.

The boiling point of the pure MTBE was found to be near 50.7°C at the atmospheric pressure of 88.0 kPa (660 mmHg). The boiling point of the pure TAME was found to be near 81.5°C at the atmospheric pressure of 90.5 kPa (679 mmHg). No large deviations were observed during the distillation of the pure ethers.

The amount of solvent ultimately recovered for each of the distillations were (all on mass basis): 89.0% MTBE & 87.5% MTBE for Cold Lake bitumen and Athabasca bitumen respectively; 87.5% TAME & 93.2% TAME for Cold Lake bitumen and Athabasca bitumen respectively. Recoveries of approximately 90% can be expected for a distillation apparatus which is open to the atmosphere at the solvent discharge end.

The density of the recovered solvents were determined for all four distillation experiments. All of the resulting ether samples had no change in density from before the distillation. This indicates that no impurities (eg. light ends of the bitumen) had boiled off with the solvents.

Although the experimental set-up was a simple batch distillation, the results show that much of the solvent can be removed from the blend without any noticeable difficulties.

5.5 Asphaltene Deposition

Throughout the course of this research, close attention was paid to all of the bitumens and bitumen-solvent blends to observe the possibility of encountering asphaltene precipitation. By means of visual inspection it can be stated that no such separation of a solid phase was observed, either as a precipitate or in suspension. This observation is relevant over the range of solvent/bitumen concentrations which were investigated.

CHAPTER 6

CONCLUSIONS

The following conclusions were reached during the investigation to identify alternate solvents used in bitumen-solvent blending and liquid-mixture viscosity modelling:

- (1) Of the four alternative solvents suggested, the ethers, MTBE (methyl *tert*-butyl ether) and TAME (*tert*-amyl methyl ether), appeared completely soluble in the bitumens (ie. Cold Lake bitumen and Athabasca bitumen), up to the solvent concentrations investigated.
- (2) The alcohols, methanol and 2-propanol (*iso*-propyl alcohol), remained insoluble in the bitumens.
- (3) The pipeline specifications requiring a blend viscosity of 269 cP at 4°C were achieved by the average addition of 27% (mass) solvents to the Cold Lake and Athabasca bitumens.
- (4) The application of Method A (liquid-mixture viscosity model without interaction) provides only order-of-magnitude viscosity results, and reliable viscosity predictions are not generated.

- (5) Two models for correlating interaction parameters were examined. Model 1 correlates the parameter as a function of temperature, and Model 2 was proposed to correlate the parameter as a function of temperature and composition.
- (6) Model 2 achieves more accurate viscosity calculations compared to the experimental data than does Model 1, however it requires an additional correlation parameter.
- (7) Model 1 was shown to deviate from the experimental viscosities by an overall AAD of 10.4% and Model 2 was shown to deviate from the experimental viscosities by an overall AAD of 2.4%, incorporating the data from all of the blends at the temperatures examined.
- (8) The Shu³² model was also used to predict the viscosity of the bitumen/solvent blends as a function of temperature and composition. The calculated viscosities deviated from the experimental results by 12.8% AAD.
- (9) In the absence of experimentally determined binary interaction parameters, the Shu model provides much more accurate results than does Model A.

- (10) The rheological properties of the bitumens were not altered; the resulting bitumen-solvent blends remained Newtonian in behaviour within the experimental uncertainty of the apparatus.
- (11) The construction of a simple distillation apparatus displayed that the light solvent phase can be easily separated from the bitumen-solvent mixture with little, or no difficulties.
- (12) By visual means of inspection, the bitumen-solvent blends of this investigation showed no asphaltene precipitation over the practical range of solvent concentrations investigated.

CHAPTER 7
RECOMMENDATIONS FOR FUTURE WORK

- (1) The investigation of alternative solvents could continue with a variety of other diluents available.
- (2) A number of other bitumens could be utilized to expand the total number of bitumen-solvent systems investigated.
- (3) A more appropriate means of determining the rheological properties of the bitumens and bitumen-solvent systems could be employed.
- (4) An accurate procedure for monitoring the precipitation of asphaltenes, such as a laser particle analyzer, could be used to verify the visual observations.
- (5) Ensuring that subsequent batches in the pipeline transportation process will not be contaminated by the alternative solvents.
- (6) The possibility of the solvents deteriorating the elastomer seals could be investigated.

- (7) The investigation into any possible adverse impacts that the alternative solvents may have on refinery processes such as reforming and isomerization.
- (8) Investigate the possible handling of water contaminated with solvents in refineries and/or intermediate tank locations.
- (9) A more sophisticated distillation apparatus could be employed to allow for more analysis into the separation of the solvent phase.

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