

## INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

**The quality of this reproduction is dependent upon the quality of the copy submitted.** Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

ProQuest Information and Learning  
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA  
800-521-0600

UMI<sup>®</sup>



Surfactant Enhanced Mobilisation of  
Non-Aqueous Phase Liquids

Andrew Duffield

A Thesis

in

The Department

of

Building, Civil, and Environmental Engineering

Presented in Partial Fulfilment of the Requirements  
for the Degree of Master of Applied Science at  
Concordia University  
Montreal, Quebec, Canada

April 2001

© Andrew Duffield, 2001



National Library  
of Canada

Acquisitions and  
Bibliographic Services

395 Wellington Street  
Ottawa ON K1A 0N4  
Canada

Bibliothèque nationale  
du Canada

Acquisitions et  
services bibliographiques

395, rue Wellington  
Ottawa ON K1A 0N4  
Canada

*Your file Votre référence*

*Our file Notre référence*

The author has granted a non-exclusive licence allowing the National Library of Canada to reproduce, loan, distribute or sell copies of this thesis in microform, paper or electronic formats.

The author retains ownership of the copyright in this thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without the author's permission.

L'auteur a accordé une licence non exclusive permettant à la Bibliothèque nationale du Canada de reproduire, prêter, distribuer ou vendre des copies de cette thèse sous la forme de microfiche/film, de reproduction sur papier ou sur format électronique.

L'auteur conserve la propriété du droit d'auteur qui protège cette thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

0-612-59302-9

Canada

## ABSTRACT

### Surfactant Enhanced Mobilisation of Non-Aqueous Phase Liquids

Andrew Duffield

The remediation of non-aqueous phase liquid (NAPL) using conventional aquifer treatment technologies is limited by the low solubility of NAPLs. Surfactants can promote the enhanced removal of NAPL through mobilisation, a mechanism that relies on the reduction of interfacial tension (IFT) at the flushing solution / NAPL interface. The conditions governing mobilisation can be represented by the total trapping number ( $N_T$ ), a dimensionless quantity relating viscous and buoyancy forces to the capillary forces trapping the NAPL residual.

A highly reliable experimental apparatus and procedure were developed to study the effect of flow rate and surfactant concentration on the removal of a residual NAPL. Column studies were conducted to investigate the relative flushing efficiencies of very dilute Triton X-100 solutions delivered through Ottawa sand spiked with light white mineral oil. At the higher flow rate, the surfactant solutions yielded  $N_T$  values greater than the critical  $N_T$ , promoting greater NAPL recovery as IFT dropped. While NAPL removal at the lower flow rate should not be enhanced because the critical  $N_T$  was not surpassed, variations in mineral oil recovery during flushing clearly indicate a surfactant effect. At the lower flow rate, the surfactant-induced enhancement and retardation of NAPL removal both highlight the limitations of the  $N_T$  approach. For more realistic systems where free product NAPL is present, the total trapping number approach requires further study to define its applicability as an indicator for NAPL mobilisation.

## Acknowledgements

I would like to thank both my current and past supervisors, Dr. A. S. Ramamurthy and Dr. J. R. Campanelli, for their learned guidance and continued support towards the culmination of this research. Dr. Campanelli, through his encouragement, provided an unexpected opportunity and convinced both this student and the university that the potential justified the investment. Dr. Ramamurthy, through his interest and co-operation, offered the support to ensure the realisation of this study.

I would also like to acknowledge the contribution of the following:

- Ron Parisella, Environmental engineering lab instructor, for his guidance with effluent analysis, and sage counsel;
- Miguel Artola, Mechanical engineering technician, for the assembly of the soil compaction apparatus;
- Michelle and my family for their perseverance with a smile.

## TABLE OF CONTENTS

LIST OF FIGURES.....	viii
LIST OF TABLES.....	ix
LIST OF ABBREVIATIONS.....	x
LIST OF SYMBOLS.....	xi
<b>1 INTRODUCTION &amp; BACKGROUND .....</b>	<b>1</b>
1.1 SOURCES AND NATURE OF CONTAMINATION .....	1
1.1.1 NAPL contamination.....	1
1.2 DEVELOPMENT OF NAPL REMEDIATION.....	1
1.2.1 Enhanced oil recovery .....	1
1.2.2 Remediation mechanisms.....	2
<b>2 THEORETICAL CONSIDERATIONS.....</b>	<b>3</b>
2.1 POROUS MEDIA PROPERTIES .....	3
2.1.1 Trapping mechanisms.....	3
2.1.2 Forces on NAPL residual.....	6
2.1.3 Mobilisation expressions .....	7
2.2 FLUSHING SOLUTION PROPERTIES.....	8
2.2.1 Surfactants .....	8
2.2.2 Emulsion formation.....	10
2.3 MOBILISATION.....	11
2.3.1 Surfactant induction.....	11
2.3.2 Co-surfactant induction.....	12
2.4 SYSTEM OPTIMISATION .....	13
2.4.1 Total trapping number .....	13
2.4.2 Hydrophilic / Lipophilic balance.....	15
2.4.3 Winsor systems .....	17
<b>3 RESEARCH FOCUS.....</b>	<b>19</b>
3.1 CONTEMPORARY RESEARCH.....	19
3.2 THESIS OBJECTIVES.....	20
<b>4 EXPERIMENTAL DESIGN .....</b>	<b>22</b>
4.1 MEDIA CHARACTERISTICS .....	22
4.2 CONTAMINANT CHARACTERISTICS .....	22
4.3 SURFACTANT CHARACTERISTICS.....	23

## TABLE OF CONTENTS

4.4	COLUMN DESIGN CRITERIA .....	24
4.4.1	Column diameter.....	24
4.4.2	Column length.....	24
4.4.3	Column filters .....	24
4.5	PACKING CRITERIA .....	25
4.5.1	Compaction studies .....	25
4.5.2	Packing procedure.....	25
4.6	EXPERIMENTAL CONTROL .....	26
4.6.1	Flow rate.....	26
4.6.2	Pressure drop .....	27
4.6.3	Sample collection.....	27
4.7	FLOW CONDITIONS.....	28
4.7.1	Water saturation.....	28
4.7.2	Residual LNAPL saturation.....	28
4.7.3	Surfactant delivery.....	29
4.8	EXPERIMENTAL PARAMETERS.....	29
4.8.1	Fixed variables.....	30
4.8.2	Manipulated variables.....	31
5	DATA COLLECTION .....	32
5.1	PORE VOLUME .....	32
5.1.1	Column determination .....	32
5.1.2	Cumulative volume .....	32
5.2	CONTAMINANT RECOVERY.....	33
5.2.1	Extraction procedure.....	33
5.2.2	NAPL mass determination .....	34
5.3	SURFACE TENSION .....	35
5.3.1	Measurement.....	35
5.3.2	Surfactant concentration .....	35
6	RESULTS .....	36
6.1	SURFACTANT FRONT .....	36
6.1.1	Low flow rate .....	36
6.1.2	High flow rate .....	37
6.2	PRESSURE VARIATION.....	37
6.2.1	Initial pressure drop.....	37
6.2.2	Breakthrough point.....	38
6.2.3	Final pressure drop .....	38



## TABLE OF CONTENTS

6.3	CONTAMINANT RECOVERY.....	39
6.3.1	Replicate trials.....	39
6.3.2	Low flow rate .....	40
6.3.3	High flow rate .....	40
7	ANALYSIS OF RESULTS .....	51
7.1	PARAMETER RELATIONSHIPS .....	51
7.1.1	Reynolds number .....	52
7.1.2	Peclet number.....	52
7.1.3	Capillary number .....	54
7.1.4	Bond number.....	54
7.1.5	Total trapping number ( $N_T$ ).....	56
7.1.6	Critical $N_T$ .....	56
7.2	ERROR ANALYSIS .....	58
7.2.1	Interfacial tension.....	58
7.2.2	Capillary number .....	58
7.2.3	Intrinsic permeability.....	59
7.2.4	Effective permeability .....	59
7.2.5	Total trapping number .....	60
7.3	FLOW RATE.....	61
7.3.1	Low flow rate .....	61
7.3.2	High flow rate .....	62
7.4	PRESSURE DROP.....	63
7.5	SURFACTANT CONCENTRATION.....	64
7.5.1	Surfactant breakthrough.....	64
7.5.2	Contaminant removal .....	65
8	SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS.....	68
8.1	SUMMARY & CONCLUSIONS.....	68
8.2	RECOMMENDATIONS.....	70
	REFERENCES.....	71
	APPENDIX A: Column data sheets for mobilisation trials .....	76
	APPENDIX B: Hexane extraction trials .....	89
	APPENDIX C: Sample calculations .....	94

## LIST OF FIGURES

Figure 1: Schematic of an aquifer with residual DNAPL .....	4
Figure 2: Capillary-trapping mechanisms in water saturated soil .....	5
Figure 3: Schematic of the pore entrapment model .....	6
Figure 4: Schematic of the surfactant adsorption process .....	9
Figure 5: Correlation of residual NAPL saturation with $N_T$ .....	14
Figure 6: Relationship between phase behaviour and IFT .....	18
Figure 7: Parameter relationships in surfactant systems .....	19
Figure 8: Schematic of the experimental apparatus .....	26
Figure 9: Solution Surface Tension @ $5 \text{ mL} \cdot \text{min}^{-1}$ .....	42
Figure 10: Solution Surface Tension @ $50 \text{ mL} \cdot \text{min}^{-1}$ .....	43
Figure 11: Column Pressure Drop @ $50 \text{ mL} \cdot \text{min}^{-1}$ .....	44
Figure 12: Replicate for 0 CMC @ $5 \text{ mL} \cdot \text{min}^{-1}$ .....	45
Figure 13: Replicate for 0 CMC @ $50 \text{ mL} \cdot \text{min}^{-1}$ .....	46
Figure 14: Replicate for 1 CMC @ $5 \text{ mL} \cdot \text{min}^{-1}$ .....	47
Figure 15: Replicate for 1 CMC @ $50 \text{ mL} \cdot \text{min}^{-1}$ .....	48
Figure 16: Mineral Oil Recovered @ $5 \text{ mL} \cdot \text{min}^{-1}$ .....	49
Figure 17: Mineral Oil Recovered @ $50 \text{ mL} \cdot \text{min}^{-1}$ .....	50

## LIST OF TABLES

Table 1: Comparison of immiscible and miscible flow properties .....	11
Table 2: Experimental soil column parameters .....	30
Table 3: Parameters for the analysis of mobilisation conditions.....	51
Table 4: Dimensionless quantities characterising column experiments .....	56

## LIST OF ABBREVIATIONS

A	Aqueous phase
CMC	Critical Micelle Concentration
HLB	Hydrophilic-Lipophilic Balance
IFT	Interfacial Tension
(L/D)NAPL	(Light/Dense) Non-Aqueous Phase Liquid
N	Non-aqueous phase
PCE	Tetrachloroethylene
SDS	Sodium Dodecyl Sulphate
Span 80	Sorbitan monooleate

## LIST OF SYMBOLS

$A_C$	Column cross sectional Area, $m^2$
$d_p$	mean particle diameter, m
$D_d$	molecular Diffusion coefficient, $m^2 \cdot s^{-1}$
$D_L$	Longitudinal hydrodynamic Dispersion coefficient, $m^2 \cdot s^{-1}$
$g$	acceleration of gravity, $m \cdot s^{-2}$
$k$	intrinsic permeability, $m^2$
$k_e$	effective permeability, $m^2$
$k_{rA}$	relative permeability to the Aqueous phase, dimensionless
$L$	column Length, m
$M_{O,e}$	Mass of mineral Oil extracted, g
$M_{O+pan}$	Mass of mineral Oil and weighing pan after evaporation, g
$M_{O,t}$	Mass of mineral Oil in test tube, g
$M_{pan}$	Mass of weighing pan, g
$M_S$	Mass of Sand in column, g
$n$	porosity, dimensionless
$n_e$	effective porosity, dimensionless
$N_B$	Bond Number, dimensionless
$N_C$	Capillary Number, dimensionless
$N_P$	Peclet Number, dimensionless
$N_R$	Reynolds Number, dimensionless
$N_T$	total Trapping Number, dimensionless

## LIST OF SYMBOLS

$N_T^*$	Critical total Trapping Number, dimensionless
$\Delta P$	column Pressure drop, mm Hg
$q_A$	Darcy velocity of the Aqueous phase, $m \cdot s^{-1}$
$Q$	flow rate, $mL \cdot min^{-1}$
$S_A$	Aqueous phase Saturation, dimensionless
$S_{A,r}$	residual Aqueous phase Saturation, dimensionless
$S_e$	effective Saturation, dimensionless
$S_N$	Non-aqueous phase Saturation, dimensionless
$S_{N,r}$	residual Non-aqueous phase Saturation, dimensionless
$v_A$	average linear Aqueous phase velocity, $m \cdot s^{-1}$
$V_b$	breakthrough Volume, fractional $V_p$
$V_C$	total Column Volume, mL
$V_{hex,e}$	Volume of hexane extracted, mL
$V_{hex,t}$	Volume of hexane added to test tube, mL
$V_{mix,e}$	Volume of hexane/oil mixture extracted, mL
$V_{O,d}$	Volume of Oil discharged, mL
$V_{O,e}$	Volume of mineral Oil extracted, mL
$V_{O,i}$	Volume of Oil initially injected, mL
$V_{O,r}$	Volume of Oil residual, mL
$V_p$	column Pore Volume, mL

## LIST OF SYMBOLS

$\alpha$	flow angle with respect to the horizontal axis, radians
$\varepsilon$	empirical exponent, dimensionless
$\gamma_{AN}$	interfacial tension at the Aqueous / Non-aqueous interface, $\text{mN} \cdot \text{m}^{-1}$
$\lambda$	empirical index of pore size distribution, dimensionless
$\mu_A$	dynamic viscosity of the Aqueous phase, $\text{mN s} \cdot \text{m}^{-2}$
$\theta_r$	minimum volumetric water content, dimensionless
$\sigma$	surface tension of aqueous phase in test tube, $\text{mN} \cdot \text{m}^{-1}$
$\sigma_i$	surface tension of aqueous phase injected, $\text{mN} \cdot \text{m}^{-1}$
$\Delta\rho$	density difference of aqueous and non-aqueous phases, $\text{kg} \cdot \text{m}^{-3}$
$\rho_A$	density of the Aqueous phase, $\text{kg} \cdot \text{m}^{-3}$
$\rho_N$	density of the Non-aqueous phase, $\text{kg} \cdot \text{m}^{-3}$
$\rho_O$	density of mineral Oil, $\text{kg} \cdot \text{m}^{-3}$
$\rho_S$	density of the Sand particles, $\text{kg} \cdot \text{m}^{-3}$

# 1 INTRODUCTION & BACKGROUND

## 1.1 SOURCES AND NATURE OF CONTAMINATION

The widespread contamination of the subsurface by non-aqueous phase liquid (NAPL), such as organic solvents and other hydrocarbons, presents a significant health risk due to the potential exposure to contaminated ground water. Conventional pump and treat technologies have proven to be an ineffective and costly means of aquifer restoration. To overcome these limitations, mobilisation of residual NAPL has been proposed as both a promising and cost effective alternative.

### 1.1.1 *NAPL contamination*

NAPL in the subsurface presents a potential long-term source of contamination. Despite the low solubility of NAPL, contaminants such as chlorinated solvents will often be present at levels exceeding the specified maximum for potable water, which are usually in the low parts per billion range (Brandes & Farley 1993). Small amounts of NAPL are therefore capable of contaminating large aquifer volumes. The low solubility of NAPL, however, requires large volumes of water for removal by conventional means. Even with the highest practical hydraulic gradients, the large capillary forces found in the subsurface immobilise the majority of the NAPL trapped in porous media.

## 1.2 DEVELOPMENT OF NAPL REMEDIATION

### 1.2.1 *Enhanced oil recovery*

Research on enhanced oil recovery has provided the basis for NAPL remediation through the introduction of surface-active agents (surfactants). The study of petroleum recovery in porous media indicates that dilute stable emulsions, formed through the use of



surfactants, can be employed as mobility control agents (Ouyang *et al.* 1995a). The principles involved in enhanced oil recovery can be applied to aquifer remediation. There are significant differences, however, in the conditions, criteria for success, and costs between these applications.

### 1.2.2 Remediation mechanisms

Surfactant enhanced remediation has been proposed as an alternative method for recovering contaminants such as residual NAPL from contaminated aquifers. A dramatic improvement in NAPL recovery can be realised through the use of aqueous surfactant solutions in a conventional pump and treat remediation framework. The enhanced removal of residual NAPL is recognised to occur via two general mechanisms: solubilisation and mobilisation. Solubilisation improves NAPL recovery by increasing the aqueous solubility of NAPL, which relies on high surfactant concentrations to provide adequate contaminant recovery. Mobilisation can significantly enhance NAPL removal by reducing the interfacial tension (IFT) at the flushing solution / NAPL interface. Because minimum IFT occurs at very low surfactant concentrations, mobilisation offers a means to promote NAPL removal with low resource requirements. Given the ability to provide mass displacement of residual NAPL when the required remediation conditions are met, mobilisation offers greater potential than solubilisation as a more cost-effective removal mechanism.

## 2 THEORETICAL CONSIDERATIONS

To design a system to provide effective NAPL recovery by mobilisation, the trapping mechanisms and forces acting on NAPL trapped within porous media must be examined. The fundamental parameters affecting the mobilisation of residual NAPL can then be incorporated into working models to aid practical application.

### 2.1 POROUS MEDIA PROPERTIES

#### 2.1.1 *Trapping mechanisms*

Due to spills or releases from disposal sites, NAPL can enter the subsurface and become subject to the forces associated with a specific subsurface environment. NAPLs that have densities greater than that of water are termed dense non-aqueous phase liquids (DNAPLs). In the saturated zone below the water table, capillary forces will oppose DNAPL migration. Globules of residual DNAPL, known as ganglia, will then become trapped in the interstitial pore space, as represented in Figure 1 (Brandes & Farley 1993).

When two immiscible phases such as oil and water flow through a soil system, two major mechanisms result in the entrapment of oil within the soil pores: snap-off, and bypassing (Ouyang *et al.* 1995b). The snap-off mechanism, shown in Figure 2A, demonstrates that initially some NAPL, represented by the black body, will be displaced as water flows into the pores. At the pore throats, represented by the pore constrictions, capillary pressure will be highest. If the capillary pressure becomes high enough, the NAPL will be snapped off leaving behind disconnected globules within the pores of the flow path, as illustrated in Figure 2A.

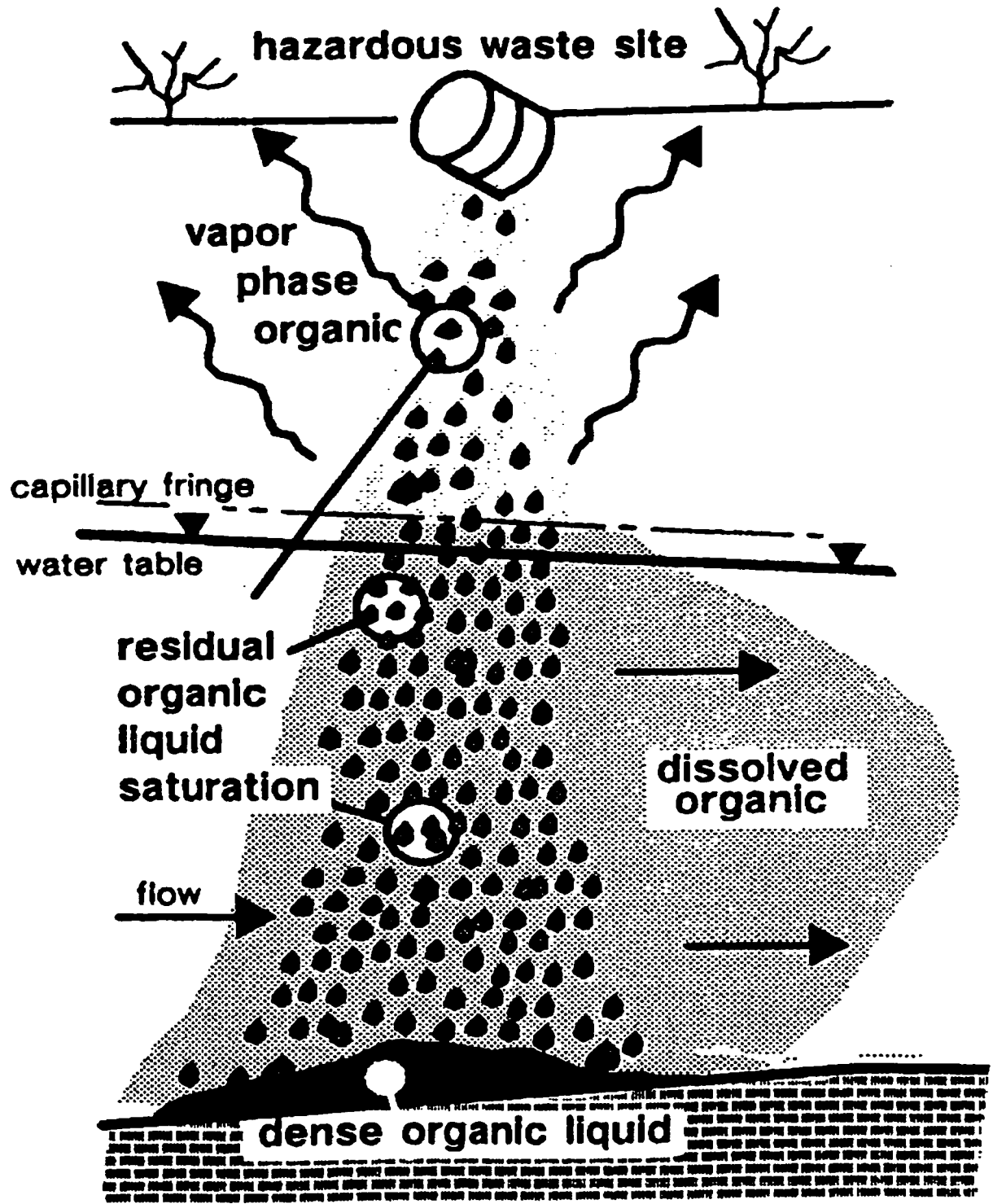


Figure 1: Schematic of an aquifer with residual DNAPL (Brandes & Farley 1993)

The entrapment mechanism termed bypassing is illustrated on a microscopic scale by a model consisting of a tube that splits into two pores of different diameter, as depicted in Figure 2B. The capillary pressure is considerably greater in the smaller diameter pore causing the water to move more rapidly, as shown in the upper branch of step 2 (Ouyang *et al.* 1995b). The NAPL in the larger diameter pore is thus trapped and isolated from potential displacement as illustrated in step 3. Both models illustrate the entrapment of NAPL, which can be mobilised only by overcoming the forces retaining the residual within the pore.

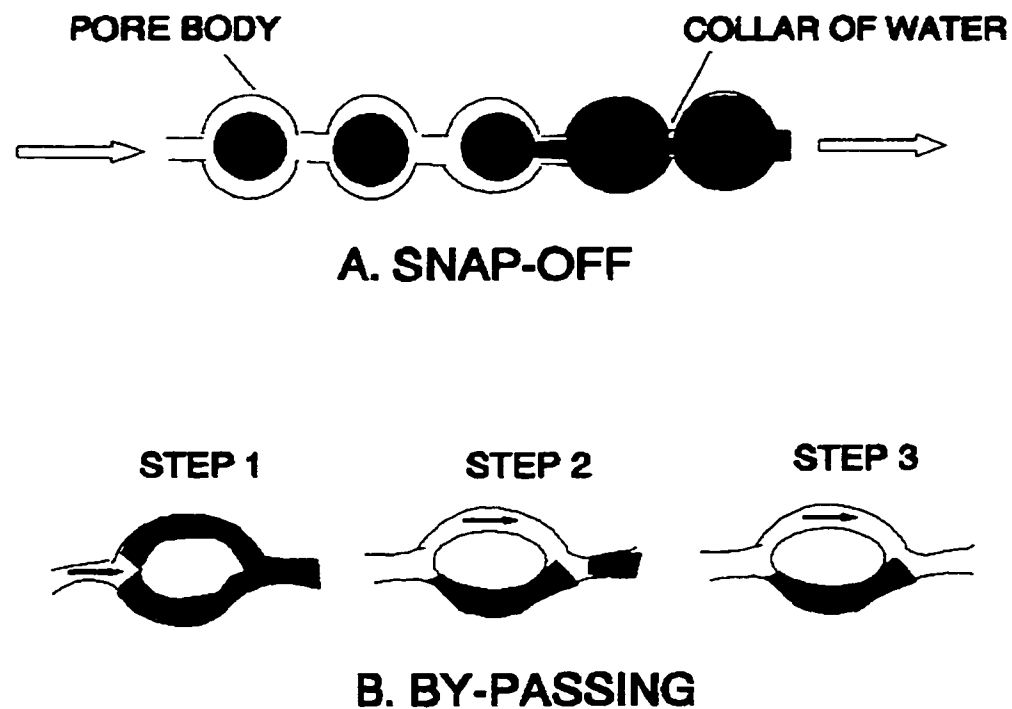


Figure 2: Capillary-trapping mechanisms in water saturated soil (Ouyang *et al.* 1995b)

### 2.1.2 Forces on NAPL residual

An examination of the forces acting on a single NAPL globule will permit a better understanding of the factors governing NAPL mobilisation. The globule, as illustrated in Figure 2A of the snap-off model, is depicted in Figure 3 within a single pore under water wet conditions. The trapped residual is subject to a gravity force component and the applied pressure gradient, acting to mobilise the globule, whereas capillary forces act to retain the NAPL globule. If the NAPL of Figure 3 is lighter than water (LNAPL), the capillary forces retaining the globule must oppose both viscous pressure and buoyancy forces to prevent mobilisation, given the pore flow direction. The conditions for which mobilisation and retention forces are in equilibrium are designated as the critical conditions for mobilisation (Pennel *et al.* 1996).

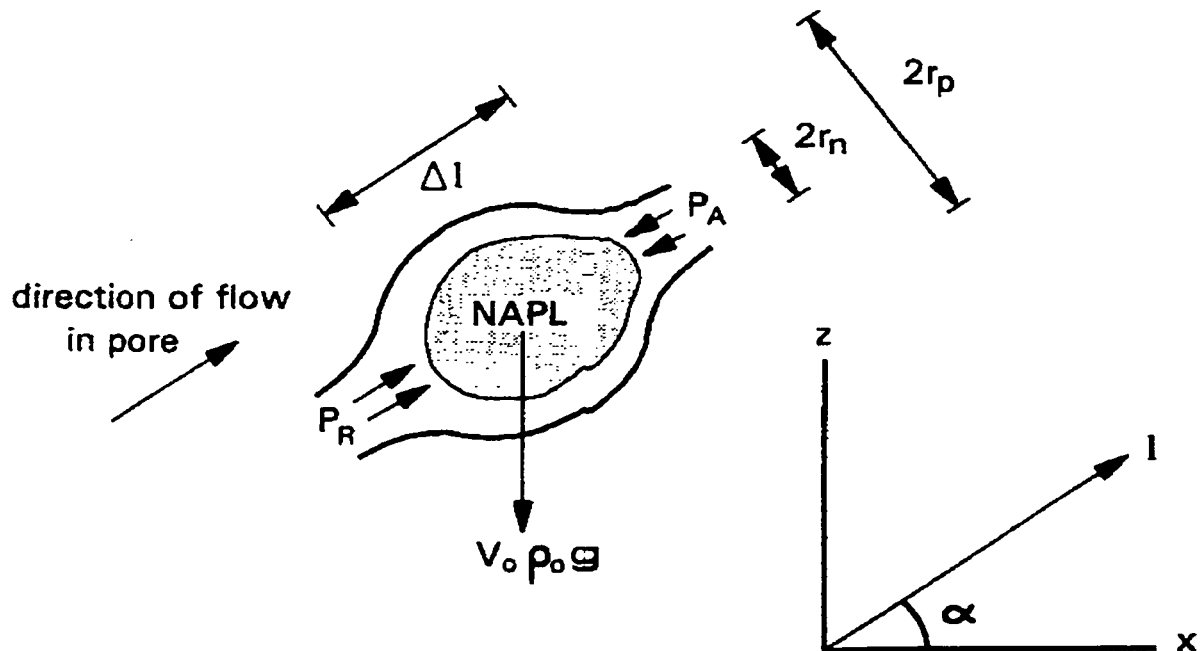


Figure 3: Schematic of the pore entrapment model (Pennel *et al.* 1996)

### 2.1.3 Mobilisation expressions

The relative importance of viscous and buoyancy forces acting to mobilise NAPL can be represented by the capillary and Bond numbers. Using the terms viscosity of the aqueous phase ( $\mu_A$ ), Darcy velocity of the aqueous phase ( $q_A$ ), interfacial tension between the aqueous and non-aqueous phases ( $\gamma_{AN}$ ), the capillary number ( $N_C$ ), a dimensionless quantity representing the ratio of viscous to capillary forces, can be expressed as (Morrow *et al.* 1988):

$$N_C = \frac{\mu_A q_A}{\gamma_{AN}}. \quad [1]$$

In a system where both aqueous and non-aqueous liquids are present, the effective aqueous permeability is defined in terms of the intrinsic permeability of the porous medium ( $k$ ), as well as the relative permeability to the aqueous phase ( $k_{rA}$ ), or  $k_e = k \cdot k_{rA}$ . An equivalent expression for  $N_C$ , in column experiments for example, is defined in terms of  $k_e$ , the pressure change across the column ( $\Delta P$ ), the column length ( $L$ ), and  $\gamma_{AN}$  (Morrow *et al.* 1988):

$$N_C = \frac{k_e \Delta P}{\gamma_{AN} L}. \quad [2]$$

Using the terms difference in phase densities ( $\Delta\rho$ ), acceleration due to gravity ( $g$ ),  $k_e$ , and  $\gamma_{AN}$ , the Bond number ( $N_B$ ), another dimensionless quantity representing the ratio of buoyancy to capillary forces, can be defined as (Pennel *et al.* 1996):

$$N_B = \frac{\Delta\rho g k_e}{\gamma_{AN}}. \quad [3]$$

As demonstrated by experimental trials, both viscous and buoyancy forces must be considered to evaluate the potential of NAPL mobilisation for a given system (Pennel *et al.* 1996). The Bond and capillary numbers can be incorporated to establish an integral means to evaluate mobilisation potential. When  $N_C$  and  $N_B$  are defined as above, the dimensionless total trapping number ( $N_T$ ) can be expressed as (Pennel *et al.* 1996):

$$N_T = \sqrt{N_C^2 + 2 N_C N_B \sin \alpha + N_B^2} . \quad [4]$$

For one dimensional column experiments and ideal conditions in the field, when flow is vertical ( $\alpha = 90^\circ$ ) in the direction of the buoyancy force, equation [4] reduces to the following expression:

$$N_T = | N_C + N_B | . \quad [5]$$

Column experiments have demonstrated that a critical value of  $N_T$ , symbolised as  $N_T^*$ , signals the onset of NAPL mobilisation. Where the pore velocity is limited by the fluid and pore media interaction and where the fluid density difference is fixed, attempts to promote mobilisation must therefore concentrate on reducing the interfacial tension to permit the system specific  $N_T^*$  to be attained.

## 2.2 FLUSHING SOLUTION PROPERTIES

### 2.2.1 Surfactants

The critical conditions for mobilisation can be achieved through the introduction of surfactants to conventional pump and treat remediation systems. Surfactants, or surface-active agents, function as wetting, cleaning, and emulsifying agents. The formation of stable solid-liquid suspensions or liquid-liquid emulsions is facilitated by the unique qualities of a surfactant molecule. Surfactants are strongly amphiphilic molecules with a

polar (hydrophilic) head and non-polar (hydrophobic or lipophilic) tail. For systems containing an aqueous surfactant solution and NAPL, as depicted in Figure 4, the amphiphilic surfactant molecules (monomers) will diffuse from the bulk solution to the interface between the aqueous (A) and non-aqueous (N) phases. The adsorption of a surfactant at the interface is achieved through a diffusion step followed by a transfer step (Wang 1997). As new interface is formed, surfactant molecules in the bulk phase will first diffuse to the subsurface layer. The surfactant monomers will then undergo a transfer step from a dissolved to an adsorbed state at the A/N interface, with the hydrophobic tails oriented towards the NAPL. At bulk solution concentrations greater than a specific threshold value, defined as the critical micelle concentration (CMC), surfactant molecules aggregate together as micelles with hydrophobic interiors.

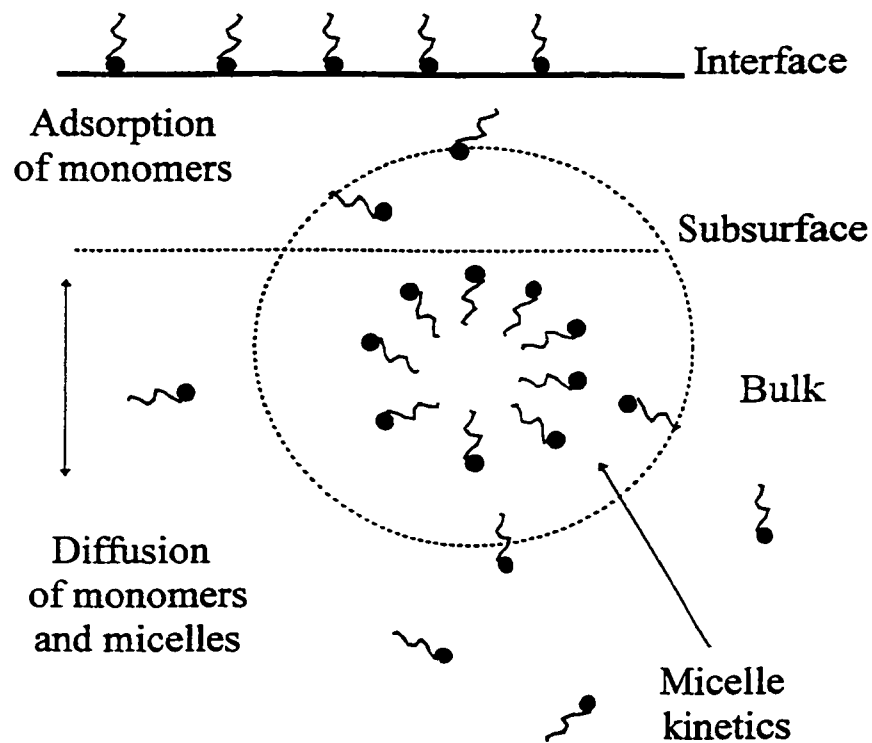


Figure 4: Schematic of the surfactant adsorption process (Wang 1997)



### 2.2.2 Emulsion formation

Surfactant monomers adsorbed at an A/N interface lower the energy of a two-phase system. The work required to generate new interfacial area is thus reduced, which in turn facilitates the preparation of emulsified systems (Myers 1988). Within a flow field, the mixing of the constituents, such as the surfactant solution and NAPL, causes one of the liquids to be dispersed as droplets in the other, which produces an emulsion. Emulsions for the purposes of aquifer remediation fall into two groups: macro-emulsions and micro-emulsions (Ouyang *et al.* 1995b). A macro-emulsion behaves more like a dispersion, with droplet sizes ranging from 1 to 10  $\mu\text{m}$ , which can be unstable. A micro-emulsion is more like a molecular solution with droplet size ranges between 0.01 and 0.1  $\mu\text{m}$  and is more thermodynamically stable. In comparison, porous media such as soil has pore sizes ranging from macro-pores with a diameter greater than 100  $\mu\text{m}$ , to micro-pores that can have a diameter less than that of macro-emulsion droplets. Droplet size depends on a number of factors such as the NAPL type, interfacial properties of the A/N system, flow velocity, and the nature of porous materials of the contaminated aquifer (Ouyang *et al.* 1995a).

The nature of the emulsion produced will thus have a bearing on the removal efficiency of residual NAPL. The formation of macro-emulsions may cause pore clogging and promote the entrapment of NAPL due to the mechanisms of snap-off and bypassing. The major differences between immiscible flow as separate phases and miscible flow as an emulsion are illustrated in Table 1:

**Table 1: Comparison of immiscible and miscible flow properties (Ouyang *et al.* 1995a).**

Immiscible flow: A & N as separate phases	Miscible flow: N emulsified within A phase
<ul style="list-style-type: none"> <li>• A and N compete for flow path</li> <li>• Low N flow velocity</li> <li>• Droplets trapped by snap-off</li> </ul>	<ul style="list-style-type: none"> <li>• A and N in same flow channel</li> <li>• Similar flow velocity for A and N</li> <li>• Droplets trapped by filtration</li> </ul>

Disadvantages such as pore clogging and non-uniform flow for a given aquifer system demonstrate that macro-emulsions, formed with the aid of surfactants, must be avoided for NAPL remediation strategies relying on mobilisation.

## 2.3 MOBILISATION

### 2.3.1 Surfactant induction

Mobilisation occurs when viscous and gravitational forces acting on the NAPL exceed the capillary forces responsible for immobilising the residual (Okuda *et al.* 1996). Where the interfacial tension (IFT) between the aqueous and non-aqueous phases is high, as encountered in a contaminated aquifer, a correspondingly high hydraulic gradient is required to push residual NAPL droplet from its confining pore space. Surfactants can promote the enhanced mobilisation of NAPL by preferentially adsorbing at the A/N interface, which causes a corresponding reduction the interfacial tension (IFT). This reduction in IFT causes the trapped oil globules to become elongated, thus making them easier to be displaced through pore constrictions under normal flow regimes. Where surfactant properties are carefully matched to the target NAPL, ultra low IFT can be achieved through the formation of a middle phase micro-emulsion between the aqueous and non-aqueous phases. The ability to attain ultra-low IFT facilitating the induction of mobilisation is greatly enhanced by the incorporation of co-surfactants.

### 2.3.2 Co-surfactant induction

The addition of co-solvents, such as alcohols, and brine to promote the formation of the middle phase micro-emulsion has been investigated by the petroleum industry (Pope & Wade 1995). Subsequent research in aquifer remediation has shown that the combination of a surfactant and a co-surfactant is more effective in recovery of NAPL than the use of alcohols or surfactants separately (Ouyang *et al.* 1995a). The addition of co-surfactants will reduce the potential formation of macro-emulsions which could lead to pore clogging and consequently low remedial efficiencies.

Alcohols enhance DNAPL mobility through both IFT reductions and DNAPL swelling. Alcohols preferentially partition into the DNAPL phase and cause swelling of the trapped DNAPL globules (Brandes & Farley 1993). Swollen, mobilised droplets may form a region of continuous DNAPL, which more readily displaces residual droplets than aqueous phase flow alone (Imhoff *et al.* 1995). In addition, gravity forces that cause downward mobilisation of DNAPL droplets may be decreased because the partitioning of alcohol into the DNAPL reduces the density difference between the DNAPL and the aqueous phase (Imhoff *et al.* 1995). The risk of uncontrolled downward migration of mobilised DNAPL can thus be minimised to an extent.

The condition of the contaminated aquifer will have a bearing on the choice of surfactant and co-surfactant, and will influence ultimate removal efficiencies. System conditions such as lower temperatures and the presence of metallic ions, as found with ground water, will require additional co-surfactant to maintain the surfactant balance and micro-emulsion stability (Ouyang *et al.* 1995a). The design of a surfactant system must therefore account for surfactant structure, the nature of residual NAPL, the composition of

ground water, and the temperature of the aquifer to permit the significant IFT reductions required to induce mobilisation.

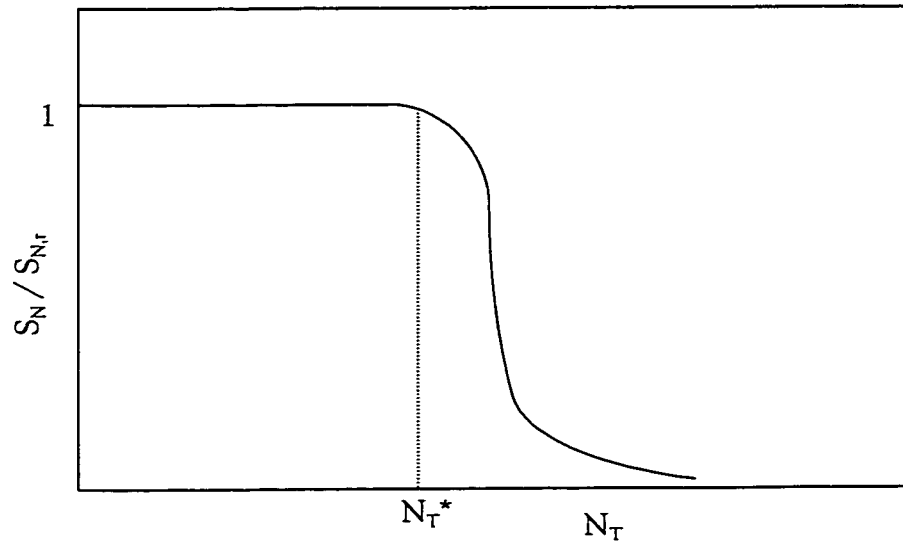
## 2.4 SYSTEM OPTIMISATION

The stability and efficiency of the system chosen to remediate residual NAPL hinges on several parameters to attain the required IFT reductions. To help determine the suitable types, concentrations, and mixtures of surfactants and co-surfactants for a given aquifer, three methods exist to aid in the design: the total trapping number, the hydrophilic / lipophilic balance, and Winsor systems.

### 2.4.1 *Total trapping number*

The total trapping number provides a useful measure to describe the onset and extent of NAPL mobilisation. As described in section 2.1.3, the capillary and Bond numbers offer a quantitative means to evaluate the effects of viscous and buoyancy forces, respectively, on the residual saturation of NAPL in porous media. Previous studies have neglected the effect of buoyancy forces on mobilisation (Pennel *et al.* 1996). Where the density difference between the aqueous and non-aqueous phases is appreciable, the Bond number ( $N_B$ ) will have a significant effect on the total trapping number. Column studies on PCE, conducted at relatively low flow rates, have generated correspondingly low values of the system capillary number ( $N_C$ ). The complete displacement of residual PCE observed in these experiments indicates that the increase in  $N_B$  due to buoyancy forces provided the necessary conditions for mobilisation. The capillary number approach cannot therefore be used alone to predict NAPL mobilisation when buoyancy forces are significant.

The relationship between residual NAPL saturation and the total trapping number ( $N_T$ ) can provide an indication of the critical  $N_T$  value required to induce mobilisation. The correlation between residual NAPL saturation and the total trapping number, depicted in Figure 5, illustrates the concept of the critical trapping number ( $N_T^*$ ). The vertical axis represents the ratio of NAPL saturation after flushing ( $S_N$ ) to NAPL residual saturation present before flushing ( $S_{N,r}$ ). With increasing  $N_T$ , reduction in the NAPL saturation ratio ( $S_N / S_{N,r}$ ) begins only when a critical value of  $N_T$  (or  $N_T^*$ ) is reached, signalling the onset of mobilisation. A subsequent increase in  $N_T$  results in a drastic reduction of the NAPL saturation.



**Figure 5: Correlation of residual NAPL saturation with  $N_T$  (West & Harwell 1992)**

The value of  $N_T^*$  appears, however, to be constant for a given system, irrespective of whether the critical value is attained by increasing  $N_C$  and  $N_B$  individually, or through a combined increase of these dimensionless numbers (West & Harwell 1992). The total trapping number thus illustrates the importance of considering the contribution of both viscous and buoyancy forces when assessing the potential for NAPL mobilisation.

The parameters affecting the capillary and Bond numbers determine the remediation conditions required to induce mobilisation. By inspection of the capillary number expression, an increase in the flushing solution's Darcy velocity or a decrease in the IFT at the A/N interface will both help to increase the capillary number. Similarly, a reduction in interfacial tension will result in an increase in Bond number. Where the relevant mobilisation parameters can be obtained from previous research, or can be established from experiments on the specific system, the remediation design can be tailored to foster mobilisation. Once the required hydraulic gradient for remediation of a given soil-contaminant system is established, the critical trapping number can be attained by selecting a surfactant that achieves the required IFT reduction for the target NAPL. The following sections present methods to select a surfactant with the necessary interfacial properties to promote mobilisation.

#### 2.4.2 *Hydrophilic / Lipophilic balance*

As illustrated previously, surfactants possess hydrophilic and lipophilic regions. The balance of the head (hydrophilic) group and carbon (lipophilic) tail, termed the hydrophilic / lipophilic balance (HLB), determines the phase that the surfactant molecule will dissolve into more easily (Ouyang *et al.* 1995a). The surfactants chosen for aquifer remediation possess a HLB number that promotes the formation of NAPL emulsions. Under these conditions, the NAPL will be pulled into solution as droplets encased in a shell of surfactant molecules (Ouyang *et al.* 1995a).

Each surfactant has a HLB number indicative of the types of NAPL it can emulsify. The HLB requirements of an organic chemical are directly related to its hydrophobicity.

More water-soluble chemicals, such as alcohols, have higher HLB requirements. The surfactant chosen must therefore possess a HLB number that reflects the HLB requirements of the target contaminant (West & Harwell 1992). Efforts to produce minimum IFT must concentrate on the surfactant-NAPL system design that maximises the interfacial concentration of adsorbed surfactant molecules. Maximum adsorption at the interface is seen to occur when the surfactant is equally soluble in the NAPL and aqueous phases (Ouyang *et al.* 1995a).

The surfactant structure will determine the HLB at the interface, and influence the degree of IFT reduction possible. Unlike solubilisation which depends only the concentration and stability of surfactant micelles in the aqueous phase, mobilisation relies on specific interfacial requirements (West & Harwell 1992). Solubilisation can only occur, however, within a small range of HLB values from 15 to 18, whereas NAPL emulsions are possible within a broader HLB range from 8 to 18 (Myers 1988). Emulsion mediated remediation therefore can be applied to a wider group of contaminated aquifer systems. The HLB method, however, does not incorporate the effects of temperature and electrolyte concentration, which are important considerations for field scale applications.

The HLB method provides a quantitative means of correlating the chemical structure of surfactant molecules to surface activity, thereby facilitating the choice of a surfactant or surfactant mixture for a given system. By selecting a surfactant with a HLB number meeting the minimum HLB requirement of the target contaminant, an initial choice for surfactant type can be made (Myers 1988).

Blends of anionic and non-ionic surfactants have been used successfully to enhance petroleum production. The HLB of a mixture is assumed to be an algebraic mean of the respective HLB values for each of the components:  $HLB_{mix} = f_A \cdot HLB_A + (1 - f_A) \cdot HLB_B$ , where  $f_A$  is the weight fraction of surfactant “A” in the mixture (Myers 1988). If, for example, the surfactants chosen for the mixture are sorbitan monooleate (Span 80) and sodium dodecyl sulphate (SDS), their corresponding values are  $HLB_A = 4.3$  and  $HLB_B = 38.7$ , respectively (Myers 1988). By substituting in the above formula the HLB requirement for benzene as  $HLB_{mix} = 15$ , the mixture will require 69% Span 80 and 31% SDS. The simple relation described above, however, assumes a linear relationship where each surfactant is able to act independently of the other.

In mixtures of aqueous and non-aqueous soluble surfactants, the possibility of the formation of co-operative complexes at the A/N interface may also result in a net synergistic effect exceeding the weighted, linear relationship described above (Myers 1988). Due to the absence of considerations for a surfactant's effects on the interfacial properties of the continuous phase, the HLB method can only provide a simple technique for the initial choice of a suitable surfactant type.

#### 2.4.3 Winsor systems

The Winsor method involves choosing and altering the system parameters to promote the formation of a middle phase micro-emulsion between the aqueous surfactant and non-aqueous phases. Figure 6 illustrates the relationship between IFT (symbolised by  $\gamma$  on the y-axis) and phase behaviour. The surfactant in a Winsor Type I system is too water soluble, whereas in a Winsor Type II system the surfactant is too oil soluble. Both systems



provide less than optimum IFT. The Winsor Type III system, where the phases are delicately balanced by a surfactant that is partly soluble in both phases, produces the lowest IFT (West & Harwell 1992). As indicated on the x-axis of the figure, the formation of the desired middle phase micro-emulsion, exhibiting low interfacial tension, is influenced by effects that depend on the surfactant type. Non-ionic surfactants are subject to the effects of temperature, anionic surfactants are subject to the effects of salinity, and all surfactants subject to the effects related to water solubility. When temperature and salinity requirements are met, surfactants that have equal affinity for both the aqueous and non-aqueous phases will provide the lowest IFT (West & Harwell 1992).

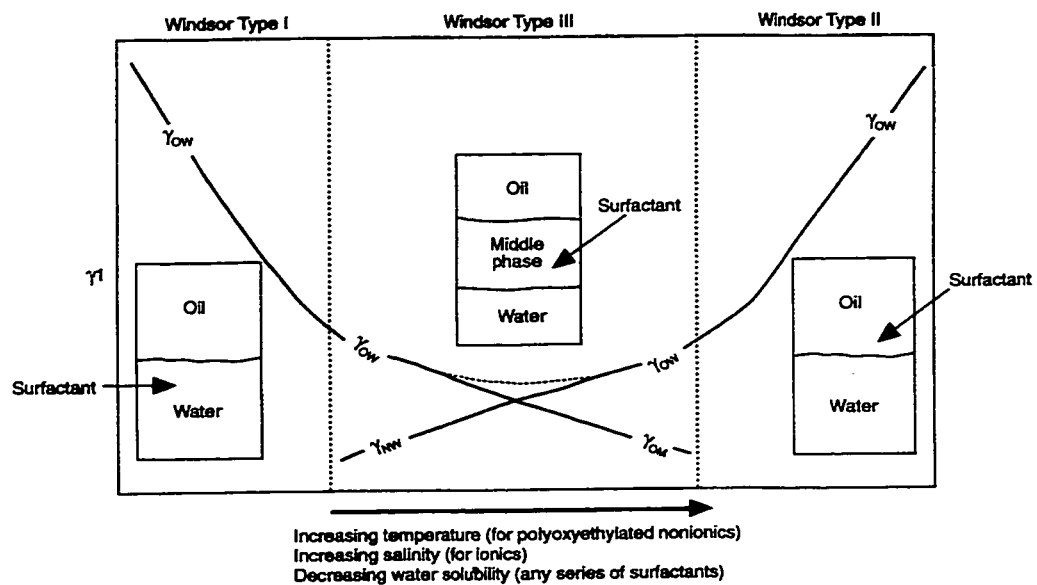


Figure 6: Relationship between phase behaviour and IFT (West & Harwell 1992)

The formation of middle phase micro-emulsions within a Winsor Type III system will ensure that removal efficiencies are not lowered due to possible pore clogging by NAPL droplets. By ensuring that the head measured across the columns remains at levels consistent with micro-emulsion transport, favourable flow characteristics can be maintained.

### 3 RESEARCH FOCUS

#### 3.1 CONTEMPORARY RESEARCH

The formation of micro-emulsions, observed in Winsor Type III systems, can provide significantly greater NAPL removal rates than those produced using solubilisation (Shiau *et al.* 1995). The high surfactant doses required for remediation by solubilisation can also have inhibitory effects on biodegradation due to the preferential use of surfactant molecules as a substrate or due to interference with microbial metabolic activity (Longino & Kueper 1995). The influence of surfactant concentration on IFT and NAPL solubility is illustrated in Figure 7. Increasing surfactant concentrations, and thus costs, are required to promote higher degrees of NAPL solubility above the CMC. For NAPL mobilisation, however, the minimum IFT is achieved at the surfactant CMC, typically at only 0.5% to 1% solutions. Systems that rely on mobilisation induction alone therefore require far lower surfactant doses.

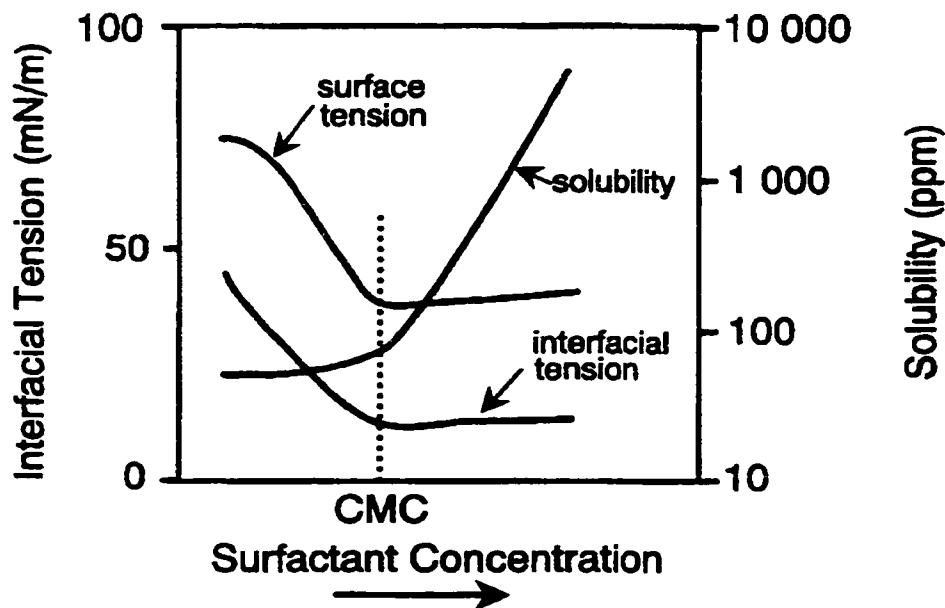


Figure 7: Parameter relationships in surfactant systems (Longino & Kueper 1995)

In experiments designed to study mobilisation, less than two pore volumes of aqueous surfactant were flushed through soil columns to minimise the removal of residual NAPL by micellar solubilisation. Column studies performed on tetrachloroethylene (PCE) produced a  $N_T^*$  falling in the range from  $2 \times 10^{-5}$  to  $5 \times 10^{-5}$ , corresponding to an IFT range from 4.3 to 1.7  $\text{mN} \cdot \text{m}^{-1}$  (Pennel *et al.* 1996). The PCE trials succeeded in displacing 95% of the residual DNAPL as a separate phase. Experiments with dodecane entrapped in a soil column provided an estimate for  $N_T^*$  varying between  $4.5 \times 10^{-5}$  and  $4.7 \times 10^{-5}$  to induce mobilisation (Pennell *et al.* 1993).

These experiments with PCE demonstrated that the formation of middle phase micro-emulsions, exhibiting ultralow IFT ( $< 0.001 \text{ mN} \cdot \text{m}^{-1}$ ), was not required to induce mobilisation. The column studies also revealed that with only 1.5 pore volumes of injected surfactant solution, mobilisation proved far more efficient than solubilisation which required 10 to 20 pore volumes of flushing solution to achieve similar removal levels (Pennell *et al.* 1993). Another column experiment with Ottawa sand succeeded in mobilising most of the residual PCE even though the phase behaviour was Winsor Type I and the IFT was  $0.09 \text{ mN} \cdot \text{m}^{-1}$ , a value clearly in excess of the IFT associated with Winsor Type III systems (Pope & Wade 1995).

### 3.2 THESIS OBJECTIVES

As a removal mechanism, mobilisation offers distinct advantages for the implementation of remediation systems for light NAPL (LNAPL). Within contaminated porous media, the seasonal fluctuation of the water table can produce zones of residual LNAPL under saturated aquifer conditions. Under such circumstances, the displacement

of residual LNAPL through surfactant enhanced mobilisation would enable the trapped globules to rise to the top of the water table where removal would be further simplified.

The experimental conditions for this thesis were designed to investigate the potential that mobilisation offers for improved contaminant recovery with lower resource requirements. Prior column studies have focused either on solubilisation using high surfactant concentrations (Martel & G  linas 1996), or on flushing with low flow rates (Pennel *et al.* 1996). To minimise recovery through solubilisation in the present study, flushing solutions were prepared with very low concentrations about the surfactant's CMC. Flow rates for the flushing solutions were chosen to compare remediation efficiency under different flow regimes with respect to LNAPL mobilisation. The research objectives of this thesis can be summarised as follows:

- to design a soil flushing apparatus and procedure capable of ensuring a high degree reproducibility across trials as well as providing a quality assessment of the experimental data;
- to examine the effects of surfactant concentration and flow rate on the mobilisation of a LNAPL;
- to evaluate the total trapping number approach as a means to characterise the critical conditions required to induce NAPL mobilisation in a soil-surfactant system.

## 4 EXPERIMENTAL DESIGN

The system design for the experimental apparatus must consider the following factors: initial NAPL residual concentration, potential surfactant loss mechanisms and sites, volume and flow direction of surfactant solution, injection and pumping systems, as well as a means to monitor and control the system accurately.

### 4.1 MEDIA CHARACTERISTICS

Ottawa sand was selected as the porous media based on its uniform mineral composition, low particle porosity, and its extremely low content of fractional organic carbon (Pennell *et al.* 1993, Martel & Gélinas 1996). The sand was supplied by Geneq of Montréal with a particle size from 0.55 mm (mesh no. 20) to 0.85 mm (mesh no. 30). Prior to use, the sand was further sieved using mesh sizes 20 to 30. The sand was then thoroughly washed five times to remove colloidal material, and oven dried at 105 °C for 24 hrs, and finally allowed to cool to room temperature prior to packing. Previous column studies investigating the removal of NAPL from porous media have demonstrated that Ottawa sand permits uniform column packs and good experimental reproducibility (Pennell *et al.* 1993, Martel & Gélinas 1996, Oliveira *et al.* 1996).

### 4.2 CONTAMINANT CHARACTERISTICS

The model NAPL chosen for the trials was light white mineral oil, the primary component of some common aquifer pollutants (Abdul *et al.* 1990). The oil was employed as received from Sigma Chemical. The density and dynamic viscosity of the mineral oil was determined to be, respectively, 862 kg · m<sup>-3</sup> and 22.7 mN s · m<sup>-2</sup> at 21 ± 1 °C (Wang 1997). The HLB requirement reported for light white mineral oil has a value of 12 (Myers 1988).

Mineral oil was selected because it was expected to exhibit low sorption to the porous medium chosen. The low water solubility, low volatility, and low toxicity of this colourless fluid permitted safe laboratory work without the need for a fume hood or a respirator during the column experiments (Mace & Wilson 1992).

#### 4.3 SURFACTANT CHARACTERISTICS

The surfactant Triton X-100 was selected due to the low observed sorption to the sand medium used, and because of the extensive research conducted with this non-ionic surfactant (Okuda *et al.* 1996, Adeel & Luthy 1995, Sun *et al.* 1995, Yeom *et al.* 1996). The surfactant was employed as received from Sigma Chemical. The critical micelle concentration (CMC) of the Triton X-100, used to prepare the flushing solutions, was determined by a previous study to be 0.165 mM (Wang 1997). This value for CMC agrees very closely with the values determined by previous studies with Triton X-100 (Adel & Luthy 1995, Yeom *et al.* 1996). The calculated HLB value for Triton X-100 is 13.5 (Sigma 1999). Batch studies with the chosen media, conducted using the range of surfactant solutions employed in the column studies, indicate that little surfactant is lost due to adsorption to Ottawa sand (Wang 1997). Given that the adsorption of non-ionic surfactants on silicon oxide surfaces decreases with increasing surfactant water solubility (West & Harwell 1992), the highly water-soluble nature of Triton X-100 supports the results of the batch trials.

## 4.4 COLUMN DESIGN CRITERIA

### 4.4.1 Column diameter

To ensure uniform fluid flow, the column diameter was chosen to limit channelling along the column wall. The term “wall effect” refers to a sharp rise in voids observed along the walls of packed columns. Preferential channelling due to the wall effect has for some studies been ignored for experimental designs exhibiting aspect ratios (column diameter to particle diameter) greater than 20. The influence of channelling, however, has been observed for columns with aspect ratios up to 40 (Niu *et al* 1996). To ensure statistical uniformity of porosity, the aspect ratio must exceed 50 (Martel & Gélinas 1996). For the Ottawa sand particles used, ranging in diameter from 0.55 to 0.85 mm, the mean particle diameter ( $d_p$ ) is 0.70 mm. With an internal diameter of 3.90 cm, the experimental column yields an aspect ratio of 56.

### 4.4.2 Column length

The wall effect can also be reduced by increasing the ratio of column length to column diameter. Previous studies, however, have indicated that it is difficult to produce uniform and reproducible packing densities between trials for columns that exceed 36 cm in length (Oliviera *et al.* 1996). A column length twice the diameter was judged sufficient to minimise wall effects (Martel & Gélinas 1996). With a packed bed length of 25.3 cm and diameter of 3.90 cm, the column apparatus provides a length to diameter ratio of 6.5.

### 4.4.3 Column filters

The column was also equipped at either end with porous stone discs to contain the porous media. With a pore size of 2  $\mu\text{m}$ , the porous stones filtered out any residual fines

that may remain after the media washing technique described in section 4.1. The porous stones also allow injected fluid to spread radially and evenly before entering the column, thereby promoting uniform fluid delivery.

#### 4.5 PACKING CRITERIA

##### 4.5.1 *Compaction studies*

For packed column beds, non-uniform lateral porosity, due to particle segregation, can seriously effect transport properties such as hydrodynamic dispersion and moisture content relationships (Oliviera *et al.* 1996). Studies on the packing of homogeneous porous media indicate that a standardised packing procedure, with sand compacted in thin layers by a metal pestle, is recommended for trials calling for an initially dry column (Oliviera *et al.* 1996). This procedure produces the best reproducibility in packing characteristics for dry sand columns, without the lateral segregation that is observed for packing using vibration.

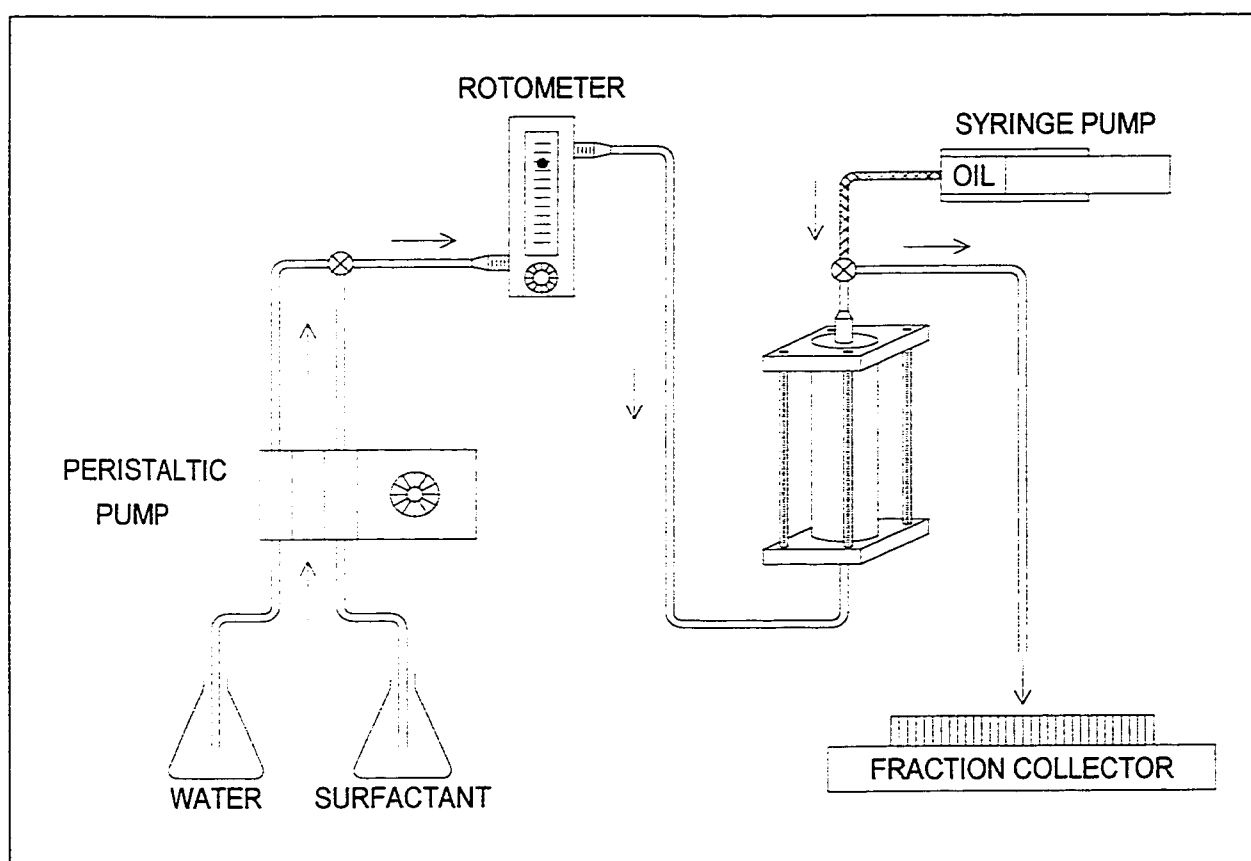
##### 4.5.2 *Packing procedure*

The column was packed using a standardised procedure by dropping a metal weight 10 times, from a controlled height of 10 cm, onto a metal plunger positioned on the sand. Because the packing uniformity increases with layer thinness and pestle weight, thin 5mm layers and a relatively heavy 600 g compaction weight were employed. Packing uniformity was also verified with visual tests using UV sensitive rhodamine dye to eliminate the possibility of fingering along the column wall. The bulk density, porosity ( $n$ ), and pore volume ( $V_p$ ) produced using this procedure are presented for each trial in Table 2 and discussed in section 4.8.1.



## 4.6 EXPERIMENTAL CONTROL

To limit the investigation to NAPL removal by mobilisation, flushing solutions with low surfactant concentrations were delivered over few pore volumes to discourage micellar solubilisation. Water and surfactant solutions were injected from separate reservoirs with a peristaltic pump, as used for previous studies of this nature (Martel & G  linas 1996). A schematic of the experimental apparatus is provided in Figure 8.



**Figure 8: Schematic of the experimental apparatus**

### 4.6.1 Flow rate

Constant flow rates for fluid delivery, from the reservoirs, were established and maintained by means of a Gilmont rotometer (flow meter), with an accuracy of  $\pm 5\%$ , equipped with a needle valve. In this manner, the initial column water saturation could be

maintained at a constant low flow rate. A Harvard Apparatus syringe pump provided uniform delivery of mineral oil into the column, prior to the introduction of the surfactant solutions. The valve-controlled rotometer also permitted the flushing solutions to be delivered from the surfactant reservoir at a constant flow rate during the course of each trial.

#### 4.6.2 *Pressure drop*

The pressure drop across the column ( $\Delta P$ ) during operation was monitored with the aid of pressure gauges, measuring mm of mercury, fitted to the column inlet and outlet. The pressure drop across the column at a given instance was determined by subtracting the pressure measured at the inlet from that measured at the outlet. Readings were taken at 15-second intervals to track the formation of obstructions in the flow field of the soil pack. The effectiveness of surfactant enhanced mobilisation of the LNAPL could thus be observed throughout the entirety of the flushing cycle.

#### 4.6.3 *Sample collection*

Column effluent samples were collected into test tubes with a Spectrum fraction collector at constant time intervals. The constant flow rate, maintained by the rotometer needle valve, permitted a near uniform volume collection by each successive test tube. Immediately following collection, each test tube was sealed with a threaded cap fitted with a Teflon liner to ensure that no NAPL was lost due to evaporation.

## 4.7 FLOW CONDITIONS

### 4.7.1 *Water saturation*

The column was initially saturated with 10 pore volumes of distilled water, in an upward flow. This quantity of water was injected at the low flow rate of  $2.5 \text{ mL} \cdot \text{min}^{-1}$  to provide complete saturation and to ensure the thorough removal of air from the column (Pennell *et al.* 1993).

### 4.7.2 *Residual LNAPL saturation*

Mineral oil was injected in a downward flow, against buoyancy forces, to promote uniform LNAPL delivery and to achieve a stable displacement of water from the saturated column. A flow rate of  $2.5 \text{ mL} \cdot \text{min}^{-1}$  was selected for oil delivery by the syringe pump (Dawson & Roberts 1997). Oil injection continued at this constant flow rate until 75 % of the column pore volume was occupied, similar to that used for previous studies (Pennell *et al.* 1996). Attempts to inject oil to a saturation greater than 75 % resulted in the appearance of oil at the column end before the entire target volume was injected. The value achieved for initial oil saturation is consistent with the range in saturation values observed for continuous, free product NAPL in water saturated systems (Bedient *et al.* 1994).

The digital volume meter of the syringe pump, precise to 0.1 mL, enabled the accurate determination of oil volume injected. Distilled water was then reintroduced in a upflow mode from the column base, at  $2.5 \text{ mL} \cdot \text{min}^{-1}$  over 1 pore volume, to displace the free product mineral oil. The oil discharged by the water was collected in a graduated cylinder. The volume discharged ( $V_{O,d}$ ) was measured and subtracted from the volume

initially injected ( $V_{O,i}$ ) to determine the volume of residual oil remaining ( $V_{O,r}$ ). This procedure was employed as a reproducible means to establish the residual LNAPL saturation prior to introduction of the flushing solutions (Pennel *et al.* 1996). The residual LNAPL saturation established for each trial using this procedure is presented in Table 2, displayed as a percentage of pore volume, and discussed in section 4.8.1.

#### 4.7.3 Surfactant delivery

Aqueous surfactant solutions were introduced over two pore volumes in an upward flow. As demonstrated in the literature, 1.5 pore volumes of the flushing solutions were sufficient to induce NAPL removal by mobilisation, while limiting the removal of residual NAPL due to micellar solubilisation (Pennel *et al.* 1996). Because flow of the low concentration surfactant solutions is in the same direction as buoyancy and the imposed viscous forces, mobilisation is expected to govern mineral oil recovery.

### 4.8 EXPERIMENTAL PARAMETERS

The uniform material characteristics, apparatus design, and experimental procedure ensure a high degree of reproducibility across the trials conducted, thereby permitting a meaningful comparison of the data results. From the data tables found in Appendix A, a summary of the column parameters for each of the final trials is provided in Table 2.

**Table 2: Experimental soil column parameters**

Trial No.	$C_{\text{Triton}}$ (CMC)	Flow Rate ( $\text{mL} \cdot \text{min}^{-1}$ )	Bulk density ( $\text{kg} \cdot \text{m}^{-3}$ )	Porosity	$V_p$ (mL)	Residual oil (% $V_p$ )
1	0	5.0	1749	0.340	102.7	25.8
2	0	5.0	1752	0.339	102.3	24.4
3	0	50.0	1743	0.342	103.3	25.2
4	0	50.0	1754	0.338	102.0	24.3
5	1	5.0	1750	0.340	102.5	24.5
6	1	5.0	1748	0.340	102.8	25.3
7	1	50.0	1751	0.339	102.4	25.0
8	1	50.0	1752	0.339	102.3	25.7
9	0.5	5.0	1760	0.336	101.4	24.6
10	0.5	50.0	1753	0.339	102.2	25.9
11	2	5.0	1755	0.338	102.0	25.5
12	2	50.0	1752	0.339	102.3	25.2

#### 4.8.1 Fixed variables

The bulk soil density, porosity ( $n$ ), and pore volume ( $V_p$ ) were established and accurately reproduced with the packing procedure described in section 4.5. The compaction technique described in section 4.5 produced a pore volume of  $102.4 \pm 0.9$  mL, and a porosity of  $0.339 \pm 0.003$ , determined as described in section 5.1.1. It has been previously determined that a pack density of  $1700 \text{ kg} \cdot \text{m}^{-3}$  prevents fluid short circuiting and fingering (Martel & G  linas 1996). The experimentally determined dry density of  $1751 \pm 8 \text{ kg} \cdot \text{m}^{-3}$  thus indicates that uniformity is likely to have been achieved both longitudinally and laterally.

The flow conditions detailed in section 4.7.2 were chosen to ensure that residual LNAPL saturation was equivalent across all trials. All trials were conducted at  $21 \pm 1^\circ\text{C}$ . The non-aqueous phase residual saturation ( $S_{N,r}$ ) was determined as  $25.1 \pm 0.8$  % of the column pore volume. A residual NAPL saturation representing 25% of the column pore

volume falls within the range observed for saturated media (Bedient *et al.* 1994). Residual saturation is also very sensitive to soil properties and heterogeneities (Bedient *et al.* 1994). The level of reproducibility achieved for the experimental values of residual saturation attests to the uniformity of the media characteristics over the trials conducted. The system design and experimental parameters were selected to provide reproducible column porosity, residual oil saturation, and total flushing volumes across all trials, as well as uniform flow rates during trials.

#### 4.8.2 *Manipulated variables*

To examine the onset of LNAPL remediation due to mobilisation, surfactant solution concentrations were chosen close to the CMC of Triton X-100. By limiting the effects of solubilisation, removal efficiencies can thus be related to the mechanism of mobilisation alone. The flushing solutions were prepared with distilled water and surfactant to provide aqueous Triton X-100 concentrations ( $C_{\text{Triton}}$ ) of 0, 0.5, 1, and 2 times the CMC. The preparation of surfactant solutions below, at, and above the CMC will permit an investigation of mobilisation at the onset of micelle formation.

To study the effect of surfactant delivery on LNAPL remediation, trials were also conducted at different flow rates. The flow rates ( $Q$ ) employed for each of the surfactant solutions were 5 and 50 mL·min<sup>-1</sup>. By imposing flow rates that differ by an order of magnitude, remediation efficiency under different flow regimes can thus be evaluated with respect to LNAPL mobilisation.

## 5 DATA COLLECTION

### 5.1 PORE VOLUME

#### 5.1.1 *Column determination*

The dimensions of the column provide the necessary values to calculate the total sealed volume of the column apparatus ( $V_C$ ). Given the density of the Ottawa sand particles ( $\rho_s$ ) and the sand mass ( $M_s$ ) packed into the column, the volume occupied by only the sand particles ( $V_s = M_s / \rho_s$ ) within the column can be calculated. The net difference between  $V_C$  and  $V_s$  represents the total pore volume ( $V_p$ ) occupied by the voids in the packed column (Corey 1990). The porosity ( $n$ ) of the media packed within the experimental column is the ratio of  $V_p$  to  $V_C$ . All fluid delivery to the soil column and effluent collection is expressed in units of  $V_p$ .

#### 5.1.2 *Cumulative volume*

To evaluate the phenomena influencing LNAPL recovery, total pore volume serves as a common variable for comparison of the trials at differing surfactant concentrations over the imposed flow rates. While the total volume of effluent collected (flushing solution and mineral oil) can vary slightly with each trial and even with each test tube within a trial, the total pore volume provides a means to standardise dependent variables against a common independent variable. Effective comparison of parameters such as surface tension, column pressure drop, and contaminant recovery will offer insight to the conditions affecting NAPL mobilisation.

## 5.2 CONTAMINANT RECOVERY

Similar column experiments, performing effluent collection using a fraction collector, determined NAPL recovery volumetrically using test tubes graduated to 0.1 mL (Pennel *et al.* 1996). For the present study, the quantity of mineral oil collected with the flushing solution in each of the test tubes was far from sufficient to permit an accurate volume reading of NAPL eluted. A liquid-liquid extraction technique was therefore developed to determine the mass of mineral oil collected per pore volume fraction of effluent collected with each test tube.

### 5.2.1 Extraction procedure

The solvent chosen for the mineral oil extraction was HPLC grade hexane. Hexane is a commonly used solvent for liquid-liquid extractions of organic liquids that exhibit a low volatility, such as mineral oil (Wilson & Clarke 1994). Given its high volatility, hexane will completely evaporate over a 48 hours period. The following procedure describes the mineral oil extraction method in detail:

- i. Effluent samples are collected into test tubes by a Spectrum fraction collector.
- ii. To each numbered test tube, 2 mL of HPLC grade hexane ( $V_{\text{hex},t}$ ) is added using a digital micro pipette ("Nichipet" manufactured by Nichiryo), whereupon the tube is immediately sealed by a cap faced with inert Teflon lining.
- iii. The contents of each test tube are then thoroughly mixed by a vortexometer ("Vortex Genie" manufactured by Scientific Industries) for one minute at high speed, thereby dissolving the collected mineral oil completely within the hexane.



- iv. To break the emulsion formed between the surfactant and lipophilic mixture (hexane and mineral oil), the test tubes are placed in a centrifuge ("HN-SII" manufactured by Damon / IEC) for 30 minutes at 4000 rpm.
- v. Once the emulsion is broken, 1 mL of the lipophilic mixture is extracted ( $V_{\text{mix,e}} = V_{\text{hex,e}} + V_{\text{O,e}}$ ) from each test tube with the digital micro pipette.
- vi. The extracted fluid is then deposited on pre-weighed aluminium pans ( $M_{\text{pan}}$ ), numbered to reflect the test tube order. Stored within a fume hood, the hexane is allowed to evaporate at room temperature.
- vii. After 48 hours of evaporation, each pan is weighed ( $M_{\text{O+pan}}$ ) by means of an analytical balance, precise to  $1 \times 10^{-4}$  g. The mass of mineral oil extracted ( $M_{\text{O,e}}$ ) within the 1 mL lipophilic mixture can then be calculated by net difference, expressed as follows:  $M_{\text{O,e}} = M_{\text{O+pan}} - M_{\text{pan}}$ .

### 5.2.2 NAPL mass determination

The mass of mineral oil within the original test tube ( $M_{\text{O,t}}$ ) is determined using the following relationships:

$$M_{\text{O,t}} = M_{\text{O,e}} \cdot V_{\text{hex,t}} / (V_{\text{hex,e}})$$

$$V_{\text{hex,e}} = V_{\text{mix,e}} - V_{\text{O,e}} = 1 \text{ mL} - M_{\text{O,e}} / \rho_{\text{O}}$$

$$M_{\text{O,t}} = (M_{\text{O,e}}) \cdot (2 \text{ mL hexane}) / (1 - M_{\text{O,e}} / 0.862)$$

$$M_{\text{O,t}} = 2 \cdot M_{\text{O,e}} / (1 - 1.16 \cdot M_{\text{O,e}})$$

The details of the hexane extraction trials for this procedure, demonstrating an accuracy of 2.4%, are presented in Appendix B.

### 5.3 SURFACE TENSION

The rate of NAPL removal from the column is governed by the concentration of surfactant present at the interface between the trapped residual and the flushing solution. For the different experimental parameters manipulated, surface tension measurement provides a means to measure the effect of surfactant delivery on remediation efficiency.

#### 5.3.1 Measurement

A DuNuoy ring apparatus has been used by previous studies to measure the surface tension of bulk non-ionic surfactant solutions for both aqueous and soil/aqueous solutions (Edwards *et al.* 1992). To monitor surfactant delivery, the flushing solution surface tension was measured in each test tube, for each pore volume fraction of effluent collected. Approximately 5 mL of aqueous solution was extracted with a syringe from each test tube and placed one at a time into a cleaned sampling reservoir. The reservoir was then placed in a calibrated DuNuoy ring apparatus to determine the sample's surface tension ( $\sigma$ ), recorded in units of  $\text{mN} \cdot \text{m}^{-1}$ . In the data tables of Appendix A, the surface tension of the influent flushing solution is represented by the symbol  $\sigma_i$ .

#### 5.3.2 Surfactant concentration

The surface tension of the surfactant solution is inversely related to the surfactant concentration of the aqueous solution. By measuring the change in effluent surface tension over the course of a flushing trial, the behaviour of the leading surfactant front within the aqueous flushing solution can be monitored. The effect of surfactant flushing on NAPL recovery can then be examined under different flow regimes.

## 6 RESULTS

The data tables compiled for the mobilisation trials are located in Appendix A. The figures referred to below are found at the end of this section. Replicate trials were conducted for aqueous flushing solutions with surfactant concentrations of 0 CMC and 1 CMC. The curves representing the average plots of the replicate trials, with the error bars displayed, serve as the reference for the comparative evaluation of flushing over the range of surfactant concentrations examined.

### 6.1 SURFACTANT FRONT

For each of the flow rates considered, Figure 9 and Figure 10 depict the change in surface tension of the flushing solution over the course of each trial. Breakthrough ( $V_b$ ) is defined as the pore volume at which the surface tension of the flushing solution, collected at the column outlet, begins to drop. The values of  $V_b$ , as determined for each of the trials, are in turn indicated for each of the corresponding curves for contaminant recovery, as well as that for column pressure drop. For both of the flow rates examined, the surface tension for each trial approaches a constant value, once two pore volumes of the flushing solution have passed through the column.

#### 6.1.1 *Low flow rate*

For each of the flushing solutions delivered at  $5 \text{ mL} \cdot \text{min}^{-1}$ , breakthrough occurs after 1 pore volume of flushing solution has passed through the column. For the solution concentrations of 0.5, 1(avg.), and 2 CMC, breakthrough occurs at 1.36, 1.18, and 1.06, respectively. Breakthrough therefore approaches 1 pore volume with increasing surfactant concentration of the solutions employed. At trial termination, the apparent surface

tension for the 0.5, 1(avg.), and 2 CMC solutions is 47.5, 43.5, and 40.8 mN · m<sup>-1</sup>, respectively.

#### 6.1.2 *High flow rate*

For each of the flushing solutions delivered at 50 mL · min<sup>-1</sup>, breakthrough occurs before 1 pore volume of flushing solution has passed through the column. For the solution concentrations of 0.5, 1(avg.), and 2 CMC, breakthrough occurs at 0.95, 0.88, and 0.80, respectively. Higher surfactant concentrations therefore permit breakthrough to occur increasingly before 1 pore volume has passed through the column. At trial termination, the apparent surface tension for the 0.5, 1(avg.), and 2 CMC solutions is 47.5, 43.3, and 40.6 mN · m<sup>-1</sup>, respectively. While the higher flow rate causes breakthrough for a given solution concentration to occur sooner, the apparent surface tension at trial termination for each of the solutions is virtually the same for both flow rates investigated.

### 6.2 PRESSURE VARIATION

Pressure drop across the column during the course of each trial was determined using the procedure described in section 4.6.2. The pressure gauges were not sensitive enough to record the pressure drop for experiments conducted at 5 mL · min<sup>-1</sup>. Pressure drop across the column during flushing at 50 mL · min<sup>-1</sup> is depicted in Figure 11. Solution breakthrough is again depicted to permit an analysis of changes in flow continuity at the onset of mobilisation.

#### 6.2.1 *Initial pressure drop*

The initial pressure observed across the column varied noticeably for the different flushing solutions. Solutions with a concentration at or above the CMC produced

markedly higher initial pressure drop than that produced by solutions with a concentration below the CMC. For the 2 CMC and 1(avg.) CMC solutions, the pressure drop observed at 0.12 pore volumes was 50.0 and 48.5 mm Hg, respectively. Conversely, the initial pressure drop for the 0 CMC (avg.) solution was 42.5 mm Hg, and that for the 0.5 CMC solution was lower still at 40.0 mm Hg.

For the solutions at and above the CMC, pressure drop fell abruptly over 0.73 pore volumes to about 41 mm Hg, the same value as that for water alone at the same pore volume. The 0.5 CMC solution produced a more gradual change over the same wash volume, exhibiting a pressure drop of 38.0 mm Hg at over 0.73 pore volumes. For the 0(avg.), 0.5, 1(avg.), and 2 CMC solutions, the change in pressure drop over the initial 0.73 pore volumes was 2.3, 2.0, 7.3, and 9.0 mm Hg, respectively.

#### 6.2.2 *Breakthrough point*

Breakthrough for each of the surfactant solutions preceded a second abrupt change in column pressure drop. Immediately after breakthrough for each case, the change pressure drop between readings was 2, 3, and 4.5 mm Hg for the 0.5, 1(avg.), and 2 CMC solutions, respectively. From each of their respective breakthrough points to trial termination, the change in pressure drop for the 0.5, 1(avg.), and 2 CMC solutions was 5.7, 10.3, and 10.8 mm Hg, respectively. Conversely, from 1 to 2 pore volumes, the change in pressure drop for the water alone was only 3.1 mm Hg.

#### 6.2.3 *Final pressure drop*

At trial termination, the final pressure drop observed was similar for the three surfactant solutions, with an average value of 31.4 mm Hg. For water alone, the final

pressure drop of 36.6 mm Hg was significantly more elevated. For the 0(avg.), 0.5, 1, and 2 CMC solutions, the change in pressure drop over the entirety of each trial was 5.9, 8.5, 18.5, and 20.5 mm Hg, respectively.

### 6.3 CONTAMINANT RECOVERY

The technique employed to establish a reproducible, residual non-aqueous saturation ( $S_m$ ), described in section 4.7.2, was not designed to produce a reduced residual value. Residual saturation established for the present trials, and observed for other studies (Morrow *et al.* 1988, Corey 1990, Wardlaw & McKellar 1985), reflects the saturation present after a normal waterflood. As evident from the curves depicted in Figure 16 and Figure 17, contaminant recovery will therefore be possible even for the 0 CMC case, where no surfactant is present.

#### 6.3.1 Replicate trials

Mobilisation experiments were first conducted with flushing solutions consisting only of distilled water to establish a baseline. Trials were conducted for Triton concentrations of 0 CMC at both flow rates investigated. The replicate runs depicted in Figure 12 and Figure 13 served to illustrate the experimental reproducibility and establish an average baseline curve. Replicate trials were also conducted with 1 CMC flushing solution, at both flow rates, as depicted in Figure 14 and Figure 15, to provide a reference for contaminant recovery when surfactant is present. The replicate curves were then used to establish average curves, and the corresponding error bars, to compare oil recovery over the range of surfactant concentrations examined.

### 6.3.2 *Low flow rate*

The graph illustrated in Figure 16 depicts cumulative contaminant recovery at a flow rate of  $5 \text{ mL} \cdot \text{min}^{-1}$ , with average curves and error bars for the 0 and 1 CMC cases. Prior to breakthrough, surfactant flushing solutions demonstrate a greater rate of oil recovery than that for the water solution, with the 1 CMC case only marginally exceeding the 0 CMC case.

After breakthrough, the rate of oil recovery falls off noticeably for each of the 0.5, 1, and 2 CMC cases. In fact for the 0.5 and 1 CMC cases, cumulative oil recovery approaches or is even surpassed by the 0 CMC case at breakthrough. Beyond breakthrough, the 1 CMC solution is markedly less efficient for oil recovery than the other solutions. At trial termination, the error bars of the 0 CMC case indicate that there is little difference in the total oil recovery between the 0, 0.5, and 2 CMC cases. For these cases, the cumulative mass recovered approaches 6 g of mineral oil, for two pore volumes of solution pumped at  $5 \text{ mL} \cdot \text{min}^{-1}$ .

### 6.3.3 *High flow rate*

Similarly, Figure 17 shows contaminant recovery at  $50 \text{ mL} \cdot \text{min}^{-1}$ , with average curves and error bars displayed for the 0 and 1 CMC cases. Prior to and after breakthrough, the flushing solutions with surfactant all clearly exhibit a rate of oil recovery that is greater than that for the water solution.

The error bars displayed for the 1 CMC case indicate that there is no meaningful difference in oil recovery between 0.5 and 1 CMC solutions throughout the trial duration. For each of the surfactant solutions employed, the rate of oil recovery tails off slightly after

breakthrough, with respect to the 0 CMC case. While the surfactant solutions demonstrate a greater total oil recovery than the 0 CMC case at trial termination, the margin of recovery is less evident than that observed at breakthrough. For the surfactant solutions, the cumulative mass recovered approaches 4 g of mineral oil, for two pore volumes of solution pumped at  $50 \text{ mL} \cdot \text{min}^{-1}$ .



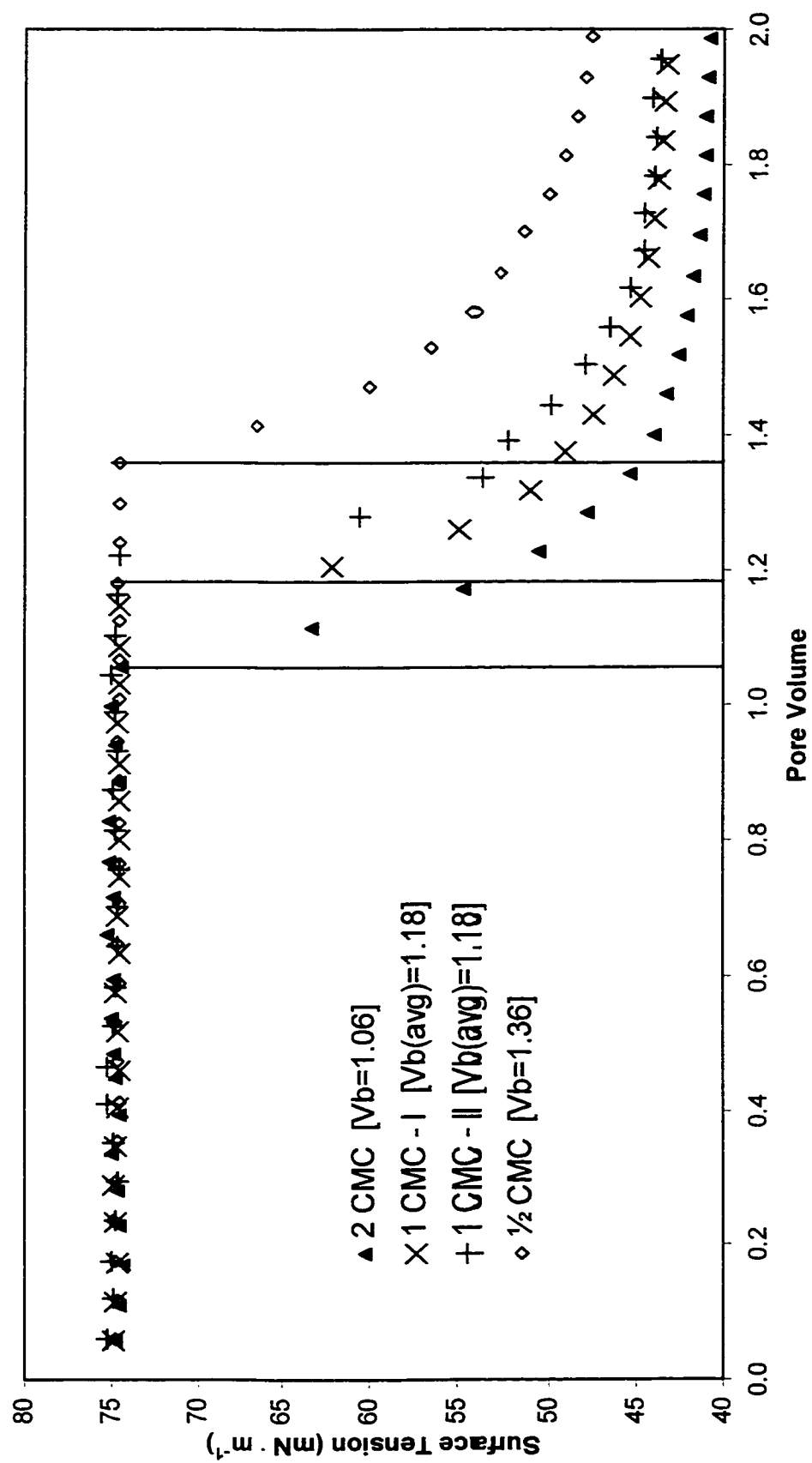


Figure 9: Solution Surface Tension @  $5 \text{ mL} \cdot \text{min}^{-1}$

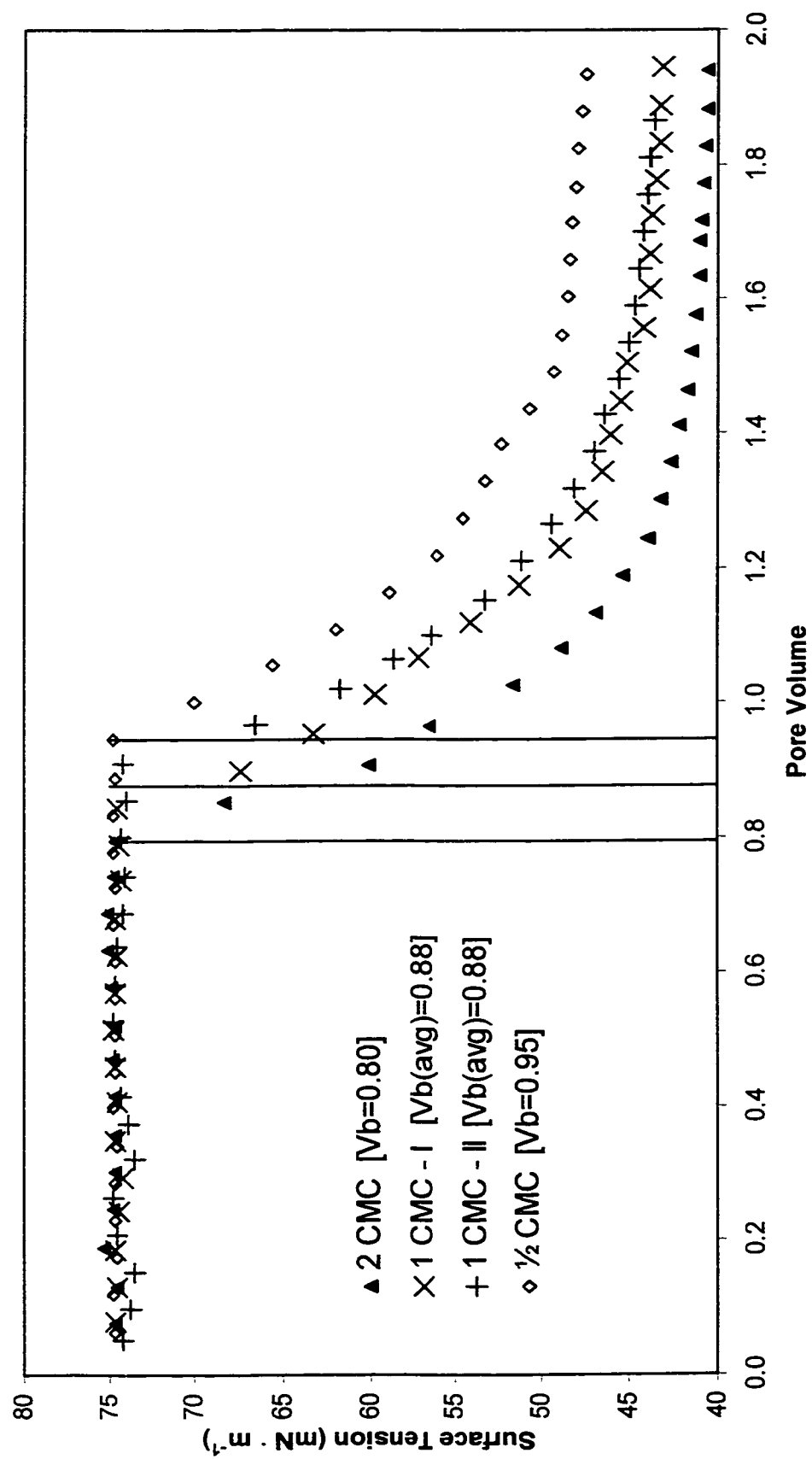


Figure 10: Solution Surface Tension @  $50 \text{ mL} \cdot \text{min}^{-1}$

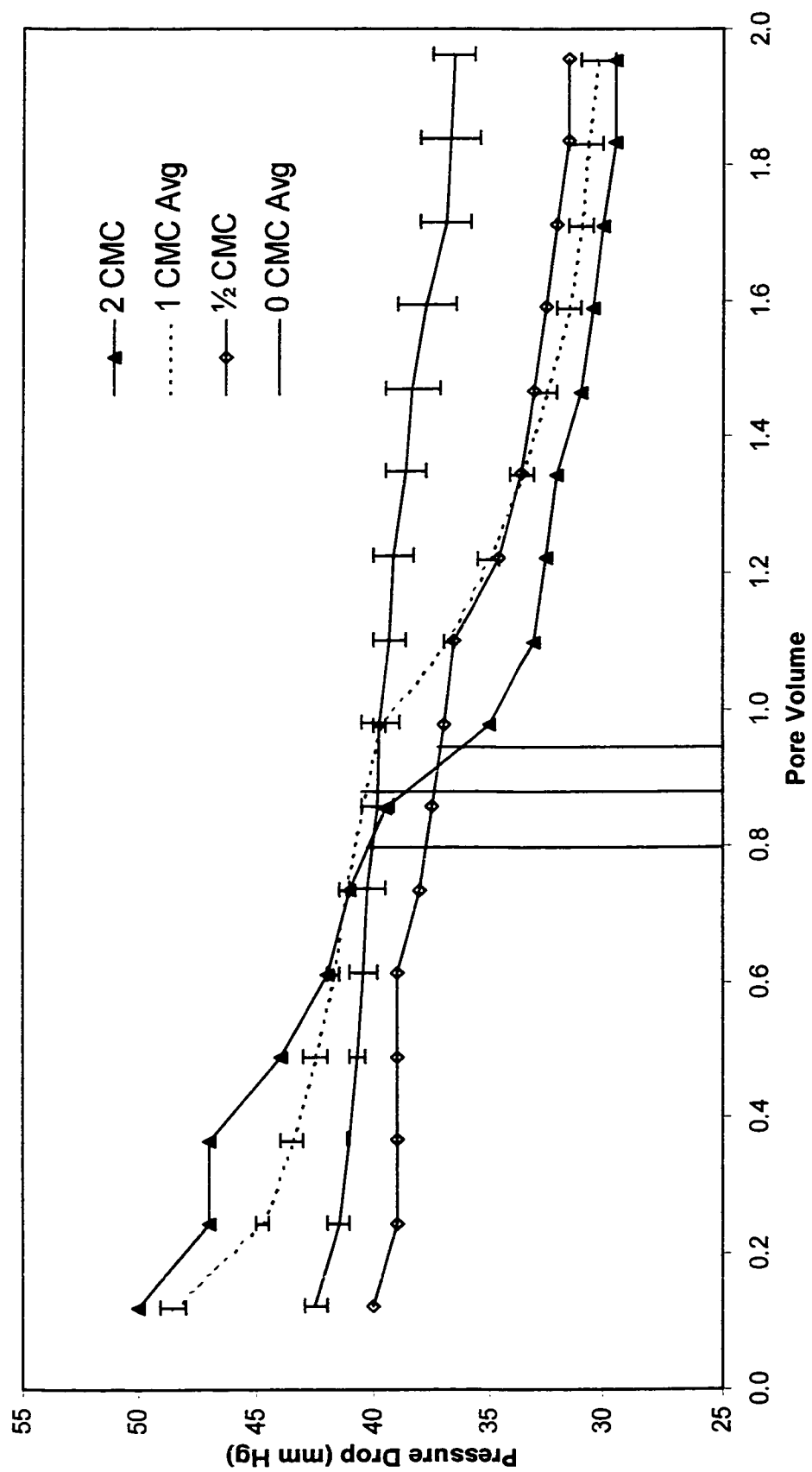


Figure 11: Column Pressure Drop @ 50 mL · min<sup>-1</sup>

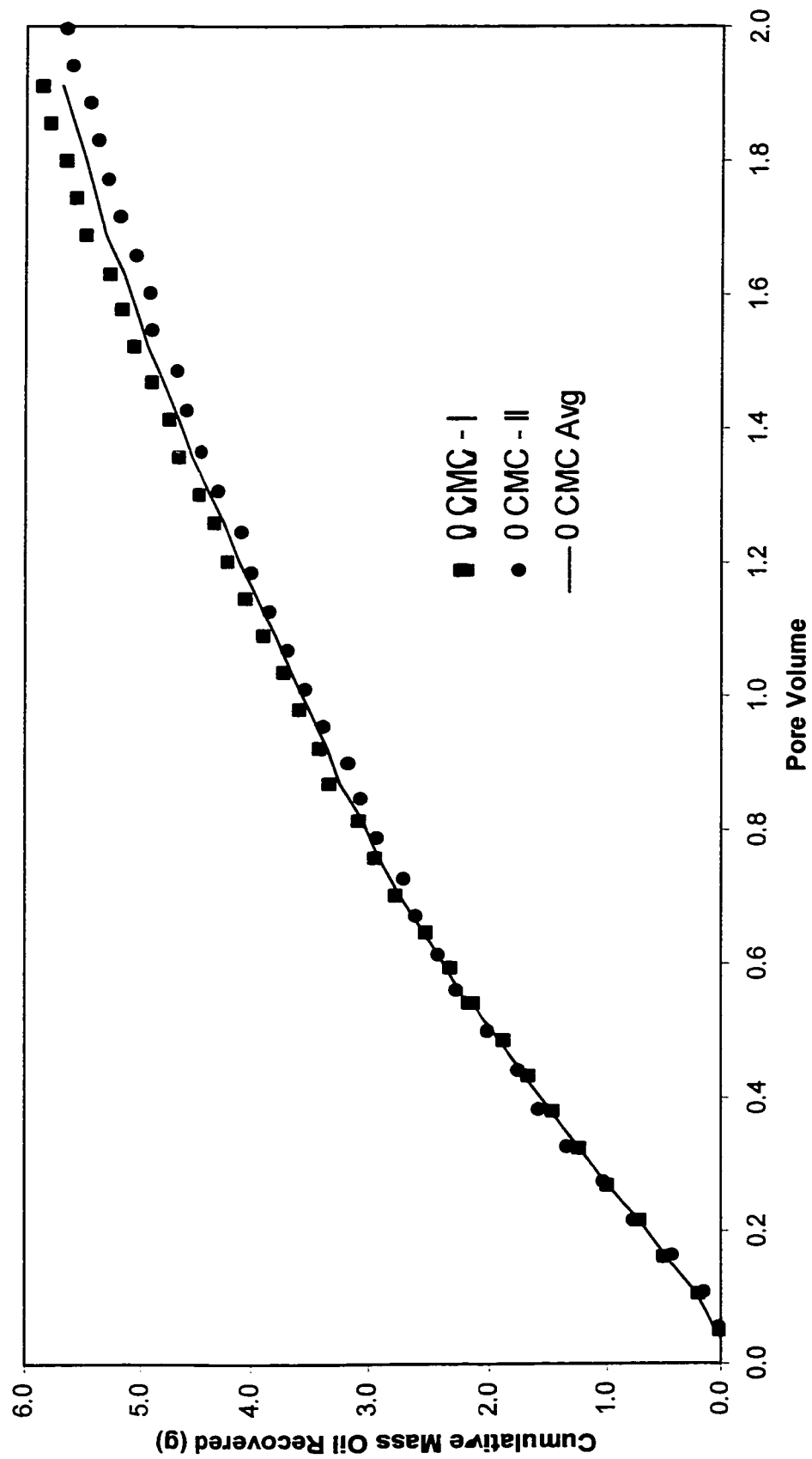


Figure 12: Replicate for 0 CMC @ 5 mL · min<sup>-1</sup>

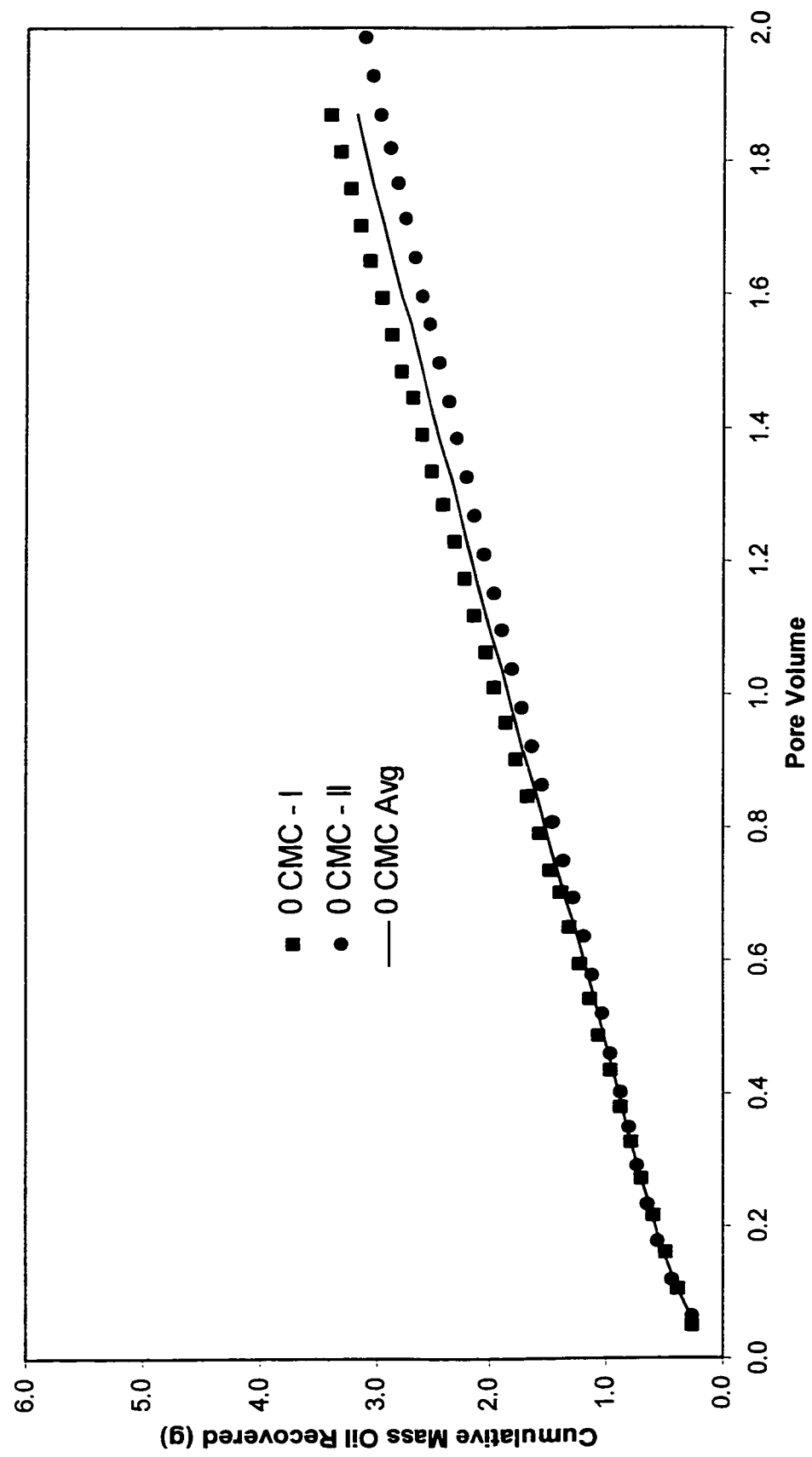


Figure 13: Replicate for 0 CMC @ 50 mL · min<sup>-1</sup>

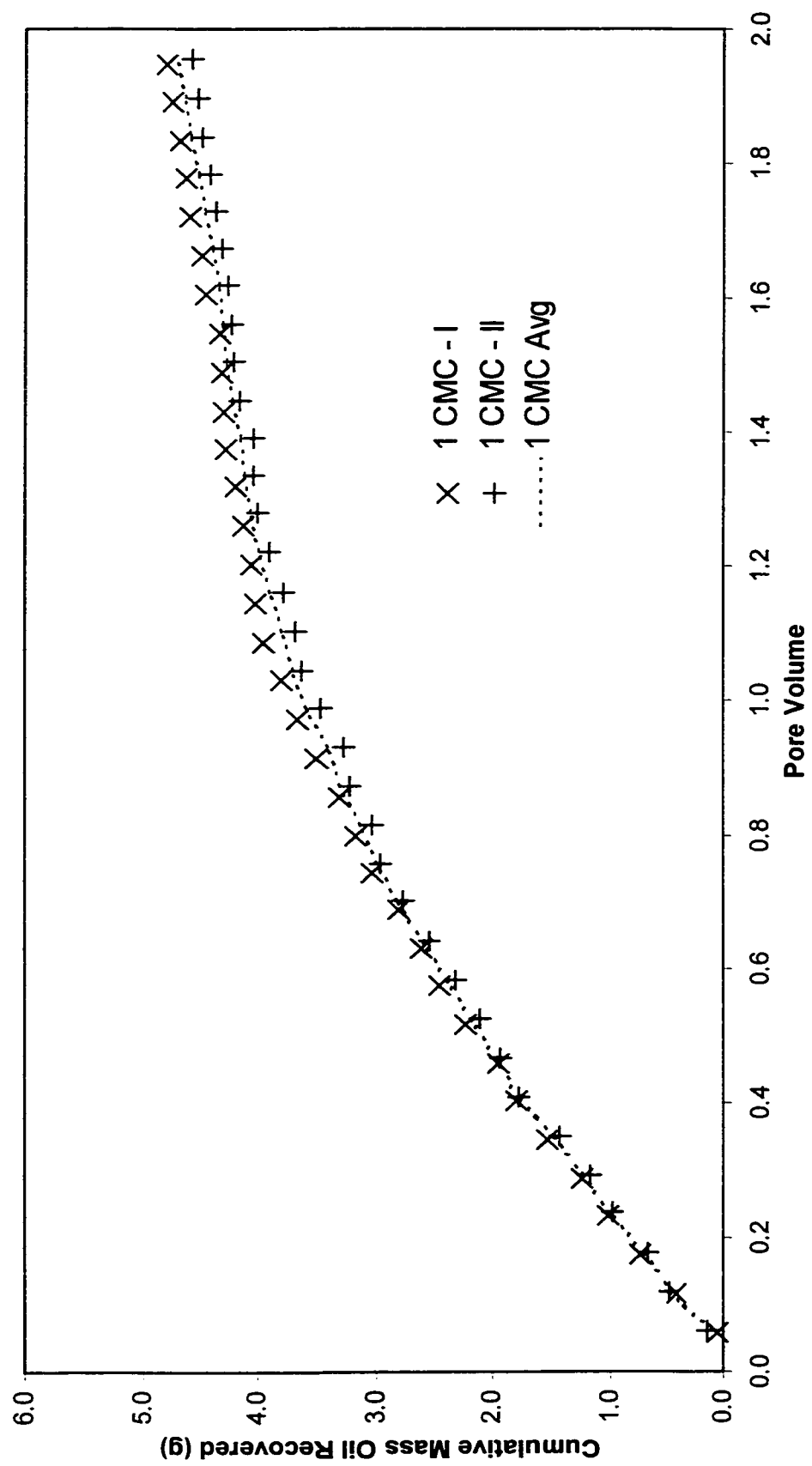


Figure 14: Replicate for 1 CMC @ 5 mL · min<sup>-1</sup>

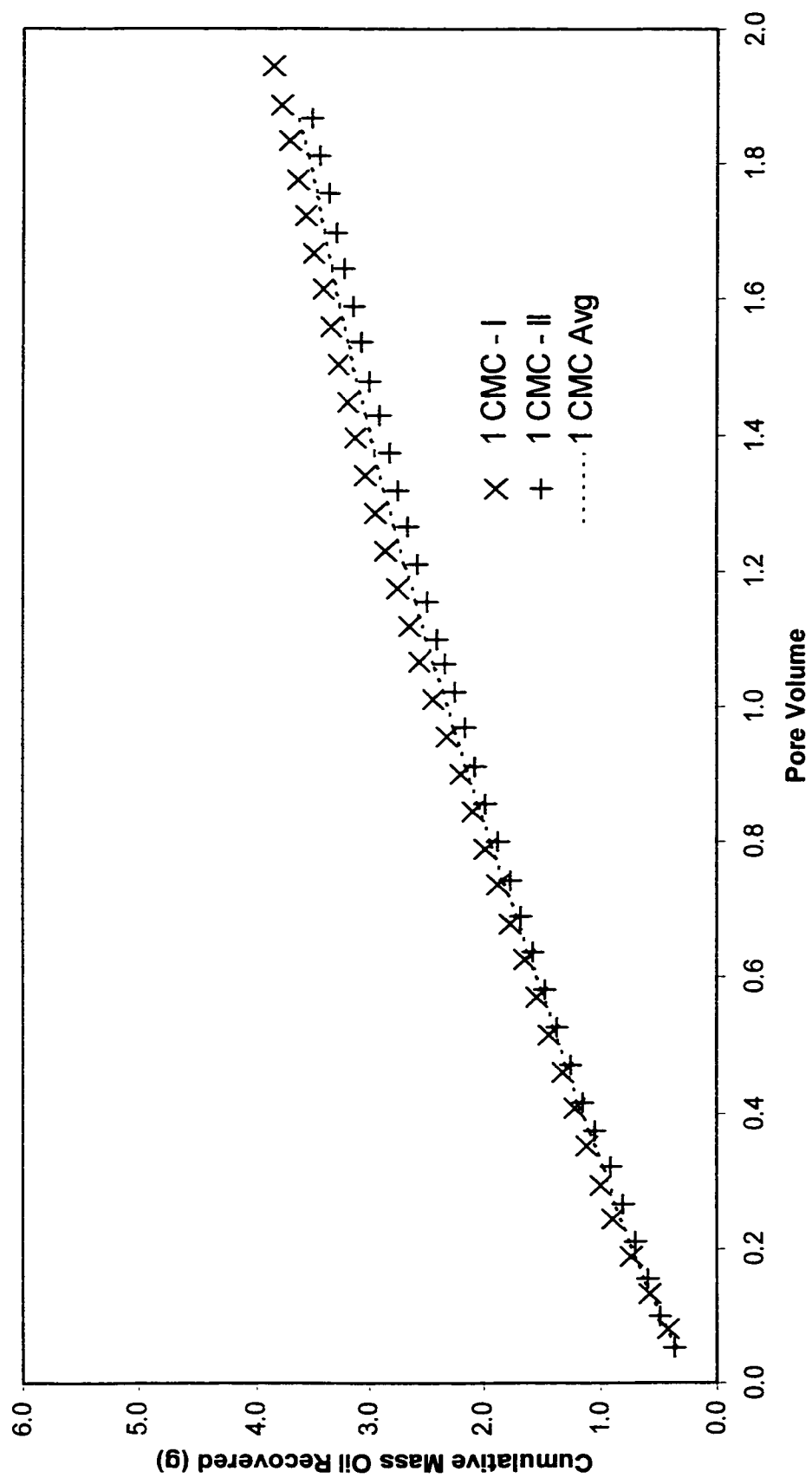


Figure 15: Replicate for 1 CMC @ 50 mL · min<sup>-1</sup>

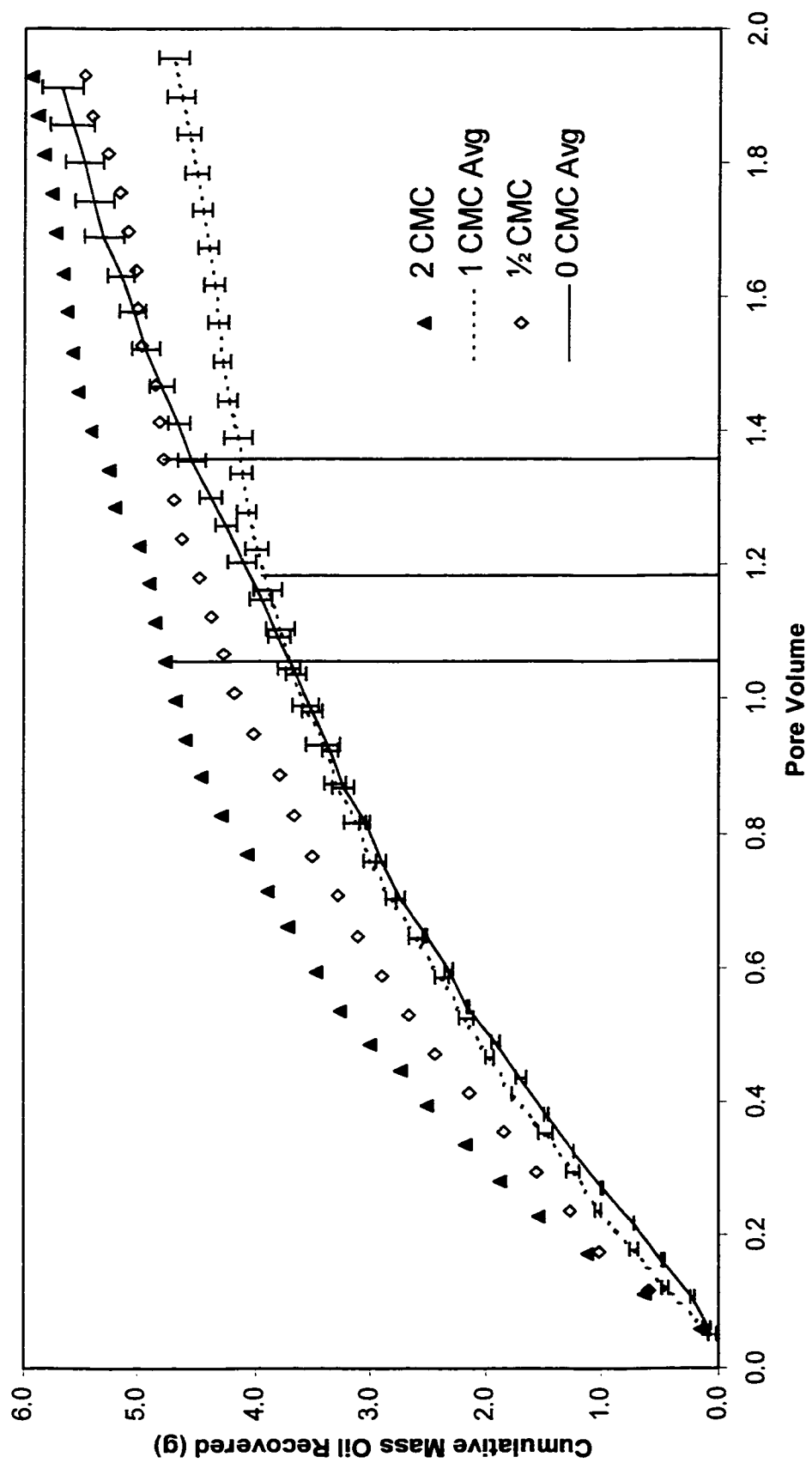


Figure 16: Mineral Oil Recovered @ 5 mL · min<sup>-1</sup>



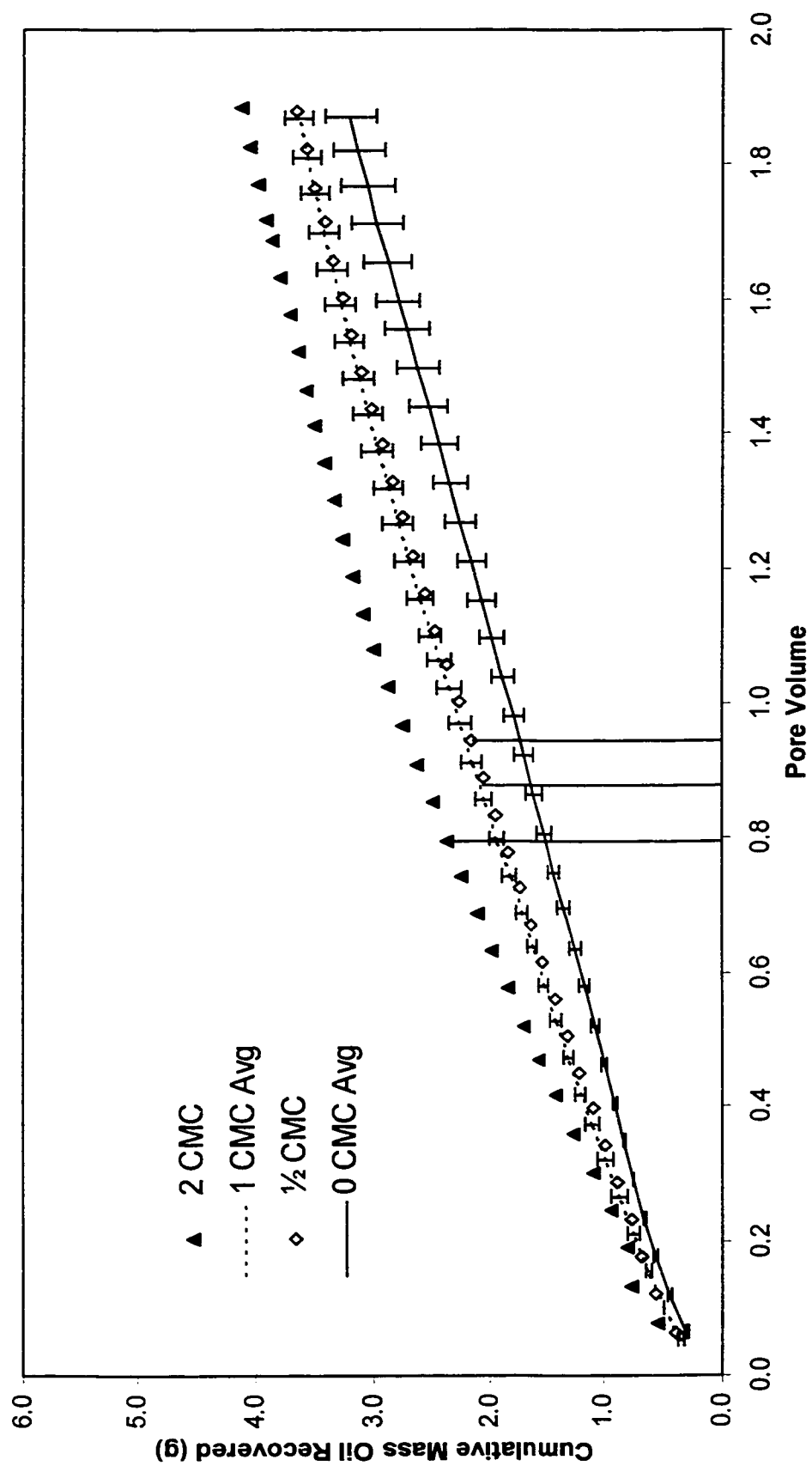


Figure 17: Mineral Oil Recovered @ 50 mL · min<sup>-1</sup>

## 7 ANALYSIS OF RESULTS

### 7.1 PARAMETER RELATIONSHIPS

An analysis of the relationships between the fixed and manipulated parameters provides insight into the factors governing the mobilisation of entrapped NAPL. The fixed experimental parameters relevant to the following analysis are summarised in Table 3. Given the very weak surfactant solution concentrations employed (0.005 to 0.02 % v/v), as well as the low aqueous solubility of mineral oil, the presence of the surfactant and non-aqueous species will have a negligible effect on the density and viscosity of the aqueous phase (Pennell *et al.* 1993). The aqueous density and viscosity are reported for the trial mean temperature (Reynolds & Richards 1996). The values provided in Table 3 are for 21°C.

Table 3: Parameters for the analysis of mobilisation conditions

Parameter	Symbol	Value	Units	Section
Non-aqueous phase density	$\rho_N$	862	$\text{kg} \cdot \text{m}^{-3}$	4.2
Aqueous phase density	$\rho_A$	998	$\text{kg} \cdot \text{m}^{-3}$	
Aqueous dynamic viscosity	$\mu_A$	0.984	$\text{mN s} \cdot \text{m}^{-2}$	
Acceleration of gravity	$g$	9.806	$\text{m} \cdot \text{s}^{-2}$	
Column cross sectional area	$A_C$	$1.20 \times 10^{-3}$	$\text{m}^2$	4.4.1
Column length	$L$	0.253	$\text{m}$	4.4.2
Mean particle diameter	$d_p$	$7.0 \times 10^{-4}$	$\text{m}$	4.4.1
Mean Porosity	$n$	0.339		4.8.1
Mean residual NAPL saturation	$S_{N,r}$	0.251		4.8.1

The following dimensionless quantities derived from these parameters offer a means to characterise the experimental conditions affecting the observed removal rates. Samples of the calculations performed in this section are provided in Appendix C.

### 7.1.1 Reynolds number

The expressions developed in the following sections are valid only for laminar flow. Darcy's law and calculations using Darcy velocity are valid for Reynolds numbers ( $N_R$ ) less than 1 (Bedient *et al.* 1994). Darcy velocity ( $q_A$ ) is defined here as the flow rate through the column cross section, which is expressed as:  $q_A = Q / A_C$ . For flow in porous media, the dimensionless Reynolds number can be expressed as follows (Weber & DiGiano 1996):

$$N_R = \frac{\rho_A q_A d_p}{\mu_A} . \quad [6]$$

Darcy's law is valid for most ground water systems. However, the Reynolds number should be calculated for at least the highest flow rate ( $Q$ ) of  $50 \text{ mL} \cdot \text{min}^{-1}$  used to deliver some of the aqueous flushing solutions. Using the information provided in Table 3,  $N_R$  at  $50 \text{ mL} \cdot \text{min}^{-1}$  is equal to 0.50. Laminar flow must therefore prevail across all flushing trials, and dimensionless quantities expressed in terms of Darcy velocity can be considered valid.

### 7.1.2 Peclet number

Mass transport in porous media is governed by hydrodynamic dispersion, comprised of both mechanical dispersion and diffusion. The Peclet number provides a means to evaluate the relative contribution of mechanical dispersion and diffusion to the mass transport of surfactant flushing solutions. Where some of the pore fraction is occupied by NAPL residual ( $S_{N,r}$ ), the effective porosity ( $n_e$ ) can be expressed as follows (Pennell *et al.* 1993):  $n_e = n (1 - S_{N,r})$ . The average Linear aqueous phase velocity ( $v_A$ ) is a function of Darcy velocity and the effective porosity available to the flushing solution, which is determined as follows (Fetter 1993):  $v_A = q_A / n_e$ . Using  $v_A$ , mean particle diameter ( $d_p$ ),

and the molecular diffusion coefficient of the surfactant in solution ( $D_d$ ), the dimensionless Peclet number ( $N_p$ ) in column studies can be defined as the transport ratio of advection to molecular diffusion (Fetter 1993):

$$N_p = \frac{v_A d_p}{D_d}. \quad [7]$$

Under most aquifer conditions diffusion is insignificant, and bulk phase transport due to molecular diffusion is often neglected (Pennell *et al.* 1993, Fetter 1993). To illustrate the use of empirical correlations, the Peclet number for surfactant delivery will be calculated for the lower flow rate of  $5 \text{ mL} \cdot \text{min}^{-1}$ . Values for  $D_d$  for the 0.5 and 1 CMC Triton X-100 solutions were determined by a previous study to be  $2.24 \times 10^{-10}$  and  $2.02 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ , respectively (Wang 1997). Using the information provided in Table 3,  $N_p$  equals 860 for the conditions of  $5 \text{ mL} \cdot \text{min}^{-1}$  and 0.5 CMC, the lowest value of  $N_p$  for the trials performed.

Tracer experiments for sand columns have produced curves plotting the ratio of the longitudinal hydrodynamic dispersion coefficient ( $D_L$ ) to  $D_d$  versus  $N_p$  as defined above (Logan 1999). For  $N_p$  values greater than 6, advection dispersion controls (Fetter 1993). While the Peclet number determination comes to the anticipated conclusion that surfactant transport is dominated by mechanical dispersion, these dispersion curves offer an empirical means to determine  $D_L$ . For  $N_p$  values approaching  $10^3$  and above, the ratio of  $D_L$  to  $D_d$  equals  $1.8 N_p$ . Using this empirical relationship with the  $N_p$  value calculated above, the hydrodynamic dispersion coefficient ( $D_L = 1.8 N_p D_d$ ) for transport of the 0.5 CMC solution at  $5 \text{ mL} \cdot \text{min}^{-1}$  can be estimated as  $3.5 \times 10^{-7} \text{ m}^2 \cdot \text{s}^{-1}$ .

### 7.1.3 Capillary number

The capillary number ( $N_C$ ), as defined by equation [1] of section 2.1.3, can be readily determined using the information provided in Table 3. For the mineral oil and the surfactant solutions employed, the equilibrium IFT values for the 0, 0.5, and 1 CMC solutions were determined by a previous study to be 47.7, 13.0, and 9.5 mN · m<sup>-1</sup>, respectively (Wang 1997). While an IFT value for the 2 CMC solution was not determined, Figure 7 of section 3.1 clearly illustrates that IFT remains essentially constant for solution concentrations greater than CMC. The dimensionless quantities  $N_C$ ,  $N_B$ , and  $N_T$ , as shown in Table 4, will therefore be determined only for the 0, 0.5, and 1 CMC cases.

### 7.1.4 Bond number

To calculate the Bond number ( $N_B$ ) as defined by equation [3] of section 2.1.3 the effective permeability ( $k_e$ ) must be determined. For well-sorted packings of uniform sand, the intrinsic permeability ( $k$ ) is related to the soil porosity ( $n$ ) and particle diameter ( $d_p$ ) by the semi-empirical Kozeny-Carmen equation (Logan 1999):

$$k = \frac{d_p^2 n^3}{180(1-n)^2} \cdot \quad [8]$$

Using the values provided in Table 3,  $k$  for all the column trials is estimated as  $2.4 \times 10^{-10}$  m<sup>2</sup>.

Given that relative permeability relationships are rarely developed from individual field studies (Bedient *et al.* 1994), the relative permeability to the aqueous phase ( $k_{rA}$ ) can be determined from empirical relationships. In two-phase flow, relative permeability is dependent in part on the effective aqueous saturation of the porous media. For purposes

of the present study, the effective saturation ( $S_e$ ) is defined in terms of the residual aqueous saturation ( $S_{A,r}$ ) at maximum NAPL saturation, as well as the aqueous saturation ( $S_A$ ) at residual NAPL saturation, prior to the introduction of the flushing solution. Using these terms, effective saturation can be expressed as the following (Corey 1990):

$$S_e = \frac{S_A - S_{A,r}}{1 - S_{A,r}}. \quad [9]$$

Using the value of  $S_{N,r}$  from Table 3, the value of  $S_A$  is determined as 0.749, given that the  $S_{N,r} + S_A = 1$ . Because NAPL saturation reached a maximum at 75 % of the pore volume, as explained in section 4.7.2, the value of  $S_{A,r}$  can be taken as 0.25. The residual aqueous saturation can be related to the minimum volumetric water content ( $\theta_r$ ) using the following expression (Corey 1990):  $\theta_r = n S_{A,r}$ . The value determined for  $S_{A,r}$  corresponds to a  $\theta_r$  value of 0.09, which agrees reasonably with a  $\theta_r$  value of 0.1 reported for well sorted soil (Fetter 1993).

The relative permeability to the aqueous phase is related to effective saturation by the following semi-empirical expression, where  $\epsilon$  and  $\lambda$  are empirical indices of the pore size distribution (Corey 1990):

$$k_{rA} = S_e^\epsilon, \text{ where } \epsilon = (2 + 3\lambda) / \lambda. \quad [10]$$

For experiments conducted with sands of uniform grain size,  $\lambda$  approaches  $\infty$ , which reduces the exponent,  $\epsilon$ , to 3 (Corey 1990). Using the information provided in Table 3,  $k_{rA}$  is estimated as 0.295. This value compares favourably with a  $k_{rA}$  of 0.3 at a  $S_A$  of 0.75 determined from relative permeability curves for a very similar uniform sand, possessing a 20-30 mesh size and a  $k$  of  $2.47 \times 10^{-10} \text{ m}^2$  (Demond & Roberts 1987). The effective

permeability ( $k_e$ ) is simply the quotient of the intrinsic and relative permeabilities, as discussed in section 2.1.3, and here  $k_e$  is estimated as  $7.1 \times 10^{-11} \text{ m}^2$ . Using the values of IFT given in section 7.1.3 as well as those from Table 3, the values of Bond number ( $N_B$ ), calculated from equation [3] for the different experimental conditions, are presented in Table 4.

#### 7.1.5 Total trapping number ( $N_T$ )

The aqueous surfactant solutions were pumped upwards through the column spiked with a light NAPL. The flushing trials were therefore conducted in the direction of the buoyancy force acting on the trapped residual. For this flushing orientation, the total trapping number ( $N_T$ ) as defined by equation [5] of section 2.1.3 is simply the arithmetic sum of  $N_C$  and  $N_B$ . Samples of the calculations employed to determine  $N_C$ ,  $N_B$ , and  $N_T$  are provided in Appendix C. The values determined for these dimensionless quantities, offering an evaluation of the potential for NAPL mobilisation, are summarised in Table 4.

**Table 4: Dimensionless quantities characterising column experiments**

Triton Conc. (CMC)	Flow Rate ( $\text{mL} \cdot \text{min}^{-1}$ )	$q_A$ ( $\text{cm} \cdot \text{h}^{-1}$ )	$\gamma_{AN}$ ( $\text{mN} \cdot \text{m}^{-1}$ )	$N_C$ ( $\times 10^{-5}$ )	$N_B$ ( $\times 10^{-5}$ )	$N_T$ ( $\times 10^{-5}$ )
0	5.0	25.1	47.7	0.14	0.20	0.34
0.5	5.0	25.1	13.0	0.53	0.73	1.3
1	5.0	25.1	9.5	0.72	1.0	1.7
0	50.0	251	47.7	1.4	0.20	1.6
0.5	50.0	251	13.0	5.3	0.73	6.0
1	50.0	251	9.5	7.2	1.0	8.2

#### 7.1.6 Critical $N_T$

In previous studies, the conditions required to induce mobilisation were represented by a critical value of capillary number alone (Ouyang *et al.* 1995b, West & Harwell 1992,

Wardlaw & McKellar 1985, Patel & Greaves 1987). Where the density difference between the aqueous and non-aqueous phases is appreciable, as observed in aquifer remediation, buoyancy forces may significantly affect flushing conditions. In flushing experiments conducted at low flow rates, yielding low values of  $N_C$ , mobilisation occurred at  $N_B$  values significantly greater than the corresponding  $N_C$  values (Pennel *et al.* 1996, Morrow & Songkran 1981). Efforts to quantify the onset of mobilisation must therefore consider the relative contribution of both viscous and buoyancy forces in overcoming the capillary forces that retain the trapped residual.

Different mobilisation expressions have been developed to incorporate the effects of both viscous and buoyancy forces (Pennel *et al.* 1996, Dawson & Roberts 1997, Morrow & Songkran 1981). When flushing conditions are represented by  $N_T$  as defined by equation [5], the onset of mobilisation can be described by a critical value ( $N_T^*$ ), determined by experiments designed to produce a range of  $N_T$  values. Column experiments with uniform glass beads and a LNAPL revealed that residual saturation remained constant when the sum of  $N_C$  and  $N_B$  was approximately  $2 \times 10^{-5}$  (Morrow & Songkran 1981). For experiments using the same media and particle size fraction as that for the present study,  $N_T^*$  was estimated between  $4.5 \times 10^{-5}$  and  $4.7 \times 10^{-5}$  for a LNAPL (Pennell *et al.* 1993), and observed within the range of  $2 \times 10^{-5}$  to  $5 \times 10^{-5}$  for a DNAPL (Pennel *et al.* 1996). Given that the model contaminant for the present study is an LNAPL, the value of  $N_T^*$  used for the following comparative analysis will be taken as  $5 \times 10^{-5}$ .



## 7.2 ERROR ANALYSIS

### 7.2.1 *Interfacial tension*

The IFT values used were determined in the absence of solid substrate. Given that the surfactant used exhibits high water solubility, the adsorption onto silicon oxide surfaces should be low (West & Harwell 1992). The sorption of Triton X-100, however, onto Lincoln fine sand, with a fractional organic carbon content of 0.05%, was observed to be dependent on the influent surfactant concentration (Adeel & Luthy 1995). In the present column trials, solutions with low surfactant concentrations were flushed through Ottawa sand exhibiting little or no fractional organic carbon. While some surfactant monomers and micelles will be adsorbed to the porous media, the bulk aqueous surfactant concentration, and thus the IFT, will be only marginally affected, especially given the short residence times observed for the column trials.

### 7.2.2 *Capillary number*

Aqueous phase viscosity and the IFT are both established by the physical and chemical properties of the two fluids present in the soil matrix. Errors in the determination of capillary number will most likely stem from the Darcy velocity term. While constant flow rate was controlled by the needle valve of the rotometer, the peristaltic pump causes small fluctuations in fluid delivery rates. Variations in flow rate were slightly more pronounced at the higher flow rate. Given that the small fluctuations were similar across all trials at a given flow rate, little systematic error should be introduced to the determination of capillary number values.

### 7.2.3 Intrinsic permeability

Direct measurement of  $k$  provides the most accurate means to determine the column permeability. The estimated  $k$  value of  $2.4 \times 10^{-10} \text{ m}^2$ , however, compares reasonably with a value of  $1.86 \times 10^{-10} \text{ m}^2$ , determined experimentally (Pennell *et al.* 1993) from columns packed with the same sand and size fraction, with a similar porosity (Ottawa sand,  $d_p = 0.71 \text{ mm}$ ,  $n = 0.326$ ). Given that the porosity indicated in Table 3 ( $n = 0.339$ ) is slightly higher, one should expect a slightly higher intrinsic permeability.

Using the values of  $n$  and  $d_p$  given for the column study referred to above (Pennell *et al.* 1993), equation [8] yields a  $k$  value of  $2.1 \times 10^{-10} \text{ m}^2$ , compared to the experimental value  $1.86 \times 10^{-10} \text{ m}^2$ . This value suggests that, for well-sorted uniform sands, the Kozeny-Carmen equation slightly overestimates intrinsic permeability.

### 7.2.4 Effective permeability

Like intrinsic permeability, once residual NAPL saturation is established in the column, effective permeability is most accurately determined from direct measurement. Relative permeability is dependent on several factors: intrinsic permeability, pore-size distribution, ratio of fluid viscosities, interfacial tension, and wettability (Domenico & Schwartz 1990). Any estimation using empirical expressions for relative permeability is therefore limited by their inability to incorporate these system specific parameters.

For the column study used for comparison in section 7.2.3 (Pennell *et al.* 1993), injection of an LNAPL, dodecane, was stopped at an initial NAPL saturation of 0.7. Given that the porous medium and particle size is the same, with a similar porosity, the maximum saturation for this LNAPL will likely be similar to that used in the present research. Using

the reported aqueous saturation ( $S_A$ ) value of 0.842, as well as the same assumptions stated in section 7.1.4, equation [10] yields a relative permeability of 0.49. This estimated value compares well with the reported value of 0.5 for the relative permeability to the aqueous phase ( $k_{rA}$ ). For these imposed conditions of these studies, good experimental agreement for  $k_{rA}$  is achieved with equation [10]. Given that  $k$  is overestimated by equation [8] for well-sorted uniform sands, the value for effective permeability determined in section 7.1.4 is likely overestimated.

#### 7.2.5 Total trapping number

The use of equilibrium values of IFT determined in the absence of a soil matrix is likely to yield underestimates of IFT (Wang, 1997). Given that IFT figures in the denominator of the expressions for both  $N_C$  and  $N_B$ , use of equilibrium IFT values yields a slight overestimation of the capillary and Bond numbers. Given that  $k_c$  appears in the numerator of the expression for  $N_B$ , the empirical determination of effective permeability is liable to produce an overestimate of the Bond number. The values of total trapping number presented in Table 4 therefore represent a small overestimation of the actual mobilisation conditions characterising the experimental trials.

The value for the critical trapping number, presented in section 7.1.6, was not determined specifically for the present trial conditions. The critical  $N_T$  is system specific and depends upon the experimental design as well as the properties of the NAPL and porous medium (Abriola *et al.* 1995). While the adopted critical value was established from studies with different target NAPLs, the studies employed nearly identical flushing procedures for the same media with a similar permeability. Mobilisation experiments with

Ottawa sand yielded a range of critical  $N_T$  from  $2 \times 10^5$  to  $5 \times 10^5$  that remained the same regardless of grain size, permeability, or residual non-aqueous saturation (Pennel *et al.* 1996). This observation provides further support for the critical  $N_T$  value of  $5 \times 10^5$  adopted in the present study.

### 7.3 FLOW RATE

#### 7.3.1 Low flow rate

With reference to Table 4 at the lower flow rate, the values determined for  $N_B$  are not only on the same order but exceed the corresponding values for  $N_C$ . Where there is an appreciable density difference between the aqueous and non-aqueous phases, the contribution of buoyancy forces to NAPL mobilisation must therefore be considered, as observed by previous studies (Pennel *et al.* 1996, Dawson & Roberts 1997, Morrow & Songkran 1981). The greatest value of  $N_T$  determined at the lower flow rate is  $1.7 \times 10^5$ , compared with a  $N_T^*$  value of  $5 \times 10^5$ . For the 2 CMC case to achieve this value of  $N_T^*$ , the IFT value would have to be less than  $3.3 \text{ mN} \cdot \text{m}^{-1}$ , which is not possible for this surfactant concentration. The error analysis of total trapping number in section 7.2.5 indicates that the  $N_T$  values of Table 4 are if anything slightly overestimated. Using the  $N_T$  approach alone, the trial conditions at  $5 \text{ mL} \cdot \text{min}^{-1}$  would not be adequate to induce mobilisation. Given that contaminant recovery after two pore volumes of flushing is similar for the 0, 0.5, and 2 CMC solutions, failure to reach the critical  $N_T^*$  would support the conclusion that NAPL removal by mobilisation does not occur. The inability to account for the variations in recovery rate observed during the course of the trial, however, highlights the limitations of the  $N_T$  approach, which is further elaborated in section 7.5.2.

### 7.3.2 High flow rate

In contrast to the low flow rate trials, flushing solutions delivered at  $50 \text{ mL} \cdot \text{min}^{-1}$  yield  $N_T$  values that exceed  $5 \times 10^5$  for all but the 0 CMC case. The curves for contaminant recovery demonstrate that, at the higher flow rate, NAPL removal improves as the concentration of the surfactant solution increases. As demonstrated by previous studies (Pennel *et al.* 1996, Wardlaw & McKellar 1985, Patel & Greaves 1987), contaminant recovery is enhanced by higher values of  $N_T$  or  $N_C$ .

As explained in section 6.3, the total mass of mineral collected at  $50 \text{ mL} \cdot \text{min}^{-1}$  approaches 4 g versus a cumulative mass of 6 g for trials at  $5 \text{ mL} \cdot \text{min}^{-1}$ . This finding demonstrates that while the critical conditions for mobilisation were not achieved at the lower flow rate, total contaminant removal was poorer at  $50 \text{ mL} \cdot \text{min}^{-1}$ . This result is due to flushing inefficiencies caused in part by viscous fingering, which is amplified by the higher flow rate.

High mobility fluids, such as flushing solutions, move at a greater pore velocity than displaced fluids, such as a viscous NAPL. Instabilities can arise when a less viscous fluid displaces a more viscous fluid, which can lead to viscous fingering (Morrow & Hornof 1987). Given that the aqueous to non-aqueous viscosity is greater than 20 for the present study, viscous fingering may significantly reduce the flushing efficiency. Aqueous channels can then form within the porous media that, once established between the column inlet and outlet, provide the primary flow paths for the flushing solutions.

Given that the flushing solution will not pass through a portion of the column pore volume, the surfactant will not reach all of the residual mineral oil. The remediation inefficiencies caused by flushing at the higher flow rate will therefore limit the ability of the

surfactant to reduce IFT over the entirety of the trapped NAPL. Flow bypassing causing the development of preferential flow paths was observed for column experiments with a DNAPL (Imhoff *et al.* 1995). Because IFT is seen to increase as the pressure increases (Ouyang *et al.* 1995a), the higher pressure gradient imposed at  $50 \text{ mL} \cdot \text{min}^{-1}$  will also limit contaminant recovery that relies on IFT reduction. Coupled with the reduction in column residence time, overall removal efficiency is thus reduced at the higher flow rate.

#### 7.4 PRESSURE DROP

Pressure drop across the column can be used as a means to track the possibility of pore clogging by NAPL ganglia (Ouyang *et al.* 1995b). The curves depicted in Figure 11 demonstrate that surfactant solution concentrations at or above CMC produce a high column pressure drop at the start of flushing. Previous column studies also demonstrated that pressure increased with an increase in surfactant concentration (Roy *et al.* 1997). At the start of solution flushing, the applied energy is driven not towards fluid flow but towards the formation of the emulsion. Consequently, mineral oil droplets of a sufficient size will block some soil pores, resulting in the development of a high column pressure. The solubilisation of NAPL within the micelles present in solutions above the CMC will quickly reach a maximum given the low surfactant concentrations. The pressure drop then begins to fall rapidly as the IFT at the A/N interface reduces and the applied pressure gradient displaces the trapped NAPL.

With few micelles present in the 0.5 CMC solution, the applied energy is directed primarily towards displacement of the NAPL, increasingly liberated from the pores as IFT is reduced. Flushing with the 0.5 CMC solution therefore causes the fewest pore

blockages, which in turn produces the lowest initial pressure drop. From each of their respective breakthrough points to trial termination, the 2 CMC solution achieves the greatest change in pressure drop and the lowest final value as more NAPL is displaced. The corresponding reduction in IFT for the 2 CMC case therefore results in the greatest NAPL displacement at  $50 \text{ mL} \cdot \text{min}^{-1}$ , as confirmed by the recovery curves of Figure 17.

## 7.5 SURFACTANT CONCENTRATION

### 7.5.1 *Surfactant breakthrough*

As shown in Figure 9 and Figure 10, increasing surfactant concentration results in breakthrough occurring at a lower pore volume. This shift in breakthrough volume ( $V_b$ ) with increasing surfactant concentration is due to a corresponding decrease in apparent surfactant retardation (Pennell *et al.* 1993, Adeel & Luthy 1995). Where retardation is due to surfactant sorption, the quantity sorbed for higher concentrations constitutes a smaller fraction of the total resident surfactant mass, therefore permitting breakthrough to occur earlier.

At the lower flow rate,  $V_b$  is seen to approach one pore volume with increasing surfactant concentration. For a Lincoln fine sand at an equivalent porosity ( $n = 0.34$ ), surfactant breakthrough was observed at slightly more than one pore volume for surfactant solutions delivered at a Darcy velocity of  $0.47 \text{ cm} \cdot \text{h}^{-1}$  (Adeel & Luthy 1995). At the higher flow rate for the present study, a similar shift in  $V_b$  occurs but at values all below one pore volume. The solution channelling and fracturing at  $50 \text{ mL} \cdot \text{min}^{-1}$ , described in section 7.3.2, causes the surfactant solutions to bypass a portion of the total pore volume, and therefore allows breakthrough to occur well before one pore volume. This early

breakthrough is further evidence of the flushing inefficiencies responsible for the lower NAPL removal rates observed at the higher flow rate.

#### 7.5.2 Contaminant removal

As depicted by Figure 16, the total mineral oil collected at  $5 \text{ mL} \cdot \text{min}^{-1}$  differs little between the 0, 0.5, and 2 CMC cases, despite the reductions in IFT achieved by the surfactant solutions. Similar column flushing experiments (Pennel *et al.* 1996), conducted at  $N_T$  values less than  $2 \times 10^{-5}$ , demonstrated that surfactant solutions producing an IFT as low as  $5 \text{ mN} \cdot \text{m}^{-1}$  also yielded NAPL removal that was equivalent to those for water alone. Unlike trials for the present study, Pennel *et al.* and other researchers flushed surfactant solutions through a soil column prepared with a reduced residual, where little or no free product NAPL is present, which does not reflect NAPL saturation for typical field conditions (Bedient *et al.* 1994). Pennel *et al.* employed the  $N_T$  approach to compare only the total NAPL recovery at trial end. No comparison was offered between the different trials for contaminant removal during the course of flushing.

While  $N_T^*$  was not attained at  $5 \text{ mL} \cdot \text{min}^{-1}$ , contaminant removal by the 0.5 and 2 CMC solutions was clearly superior, and marginally so for the 1 CMC solution, to that achieved by the 0 CMC solution over the first pore volume of flushing solution. At 0.5 CMC, NAPL removal by solubilisation is not possible, therefore the enhanced mineral oil recovery observed must be due to mobilisation. The presence of surfactant in the flushing solutions therefore provides some degree of enhancement in NAPL recovery, through IFT reduction, contrary to the conclusions offered by the  $N_T$  approach.



For flushing volumes greater than one pore volume, the rate of mineral oil removal by the surfactant solutions is reduced relative to the removal rate for water alone. This retardation effect observed at higher flushing volumes suggests that the surfactant solutions can induce flushing inefficiencies, even at low flow rates, as more surfactant enters the flow field. A third mechanism of surfactant enhanced removal of NAPL has been proposed that involves the transport of macro-emulsions, where small droplets of the NAPL are suspended in the aqueous phase (Okuda *et al.* 1996). As opposed to carefully designed mixtures, single surfactant solutions can produce unfavourable phase behaviour, such as the formation of macro-emulsions, that can result in pore clogging and significantly reduce removal efficiency (Ouyang *et al.* 1995b).

Contaminant recovery for all the surfactant solutions flushed at  $5 \text{ mL} \cdot \text{min}^{-1}$  dips perceptibly at their respective breakthrough points. Most notably, the mineral oil removal after breakthrough for 1 CMC solution is more significantly retarded with respect to the other solutions. For solutions at and below the CMC, the 1 CMC solution likely produces more stable macro-emulsions capable of clogging more pores, thereby causing a more pronounced retardation. For solutions above the CMC, the formation of macro-emulsions reduces with increasing surfactant concentration (Okuda *et al.* 1996). Coupled with the possibility that some the mineral oil is removed by solubilisation, the retardation observed for the 2 CMC solution is less pronounced. The enhancement and retardation effects induced by the surfactant solutions clearly highlight the limitations of the  $N_T$  approach when applied to systems where free product NAPL is present.

As shown in Figure 17 for the higher flow rate, no reduction in removal efficiency was observed for the 1 CMC case, relative to the other solutions. The higher pressure gradient imposed at  $50 \text{ mL} \cdot \text{min}^{-1}$  is likely capable of flushing any possible macro-emulsions that could further limit the available flow paths. While the pressure drop profiles described for the 0.5 and 1 CMC solutions at  $50 \text{ mL} \cdot \text{min}^{-1}$  are not similar, there is little difference between their respective recovery curves.

Under the dynamic conditions present at the higher flow rate, the surfactant concentration at the A/N interface will be governed by the interfacial adsorption kinetics of the surfactant. A previous study of the adsorption kinetics at the interface between aqueous Triton X-100 and light white mineral oil has demonstrated that the interfacial surfactant concentration is diffusion limited (Wang 1997). The IFT reduction possible in a system where new interface is continually being formed, such as flushing experiments, will therefore be controlled by diffusion of the surfactant. Because the diffusion coefficients of Triton X-100, reported in section 7.1.2, are very close in value for the 0.5 and 1 CMC solutions, recovery based on IFT reduction will be very similar.

Previous studies have demonstrated that, at the onset of mobilisation, capillary forces are more important than viscous forces in determining the extent of NAPL mobilisation (Patel & Greaves 1987). This conclusion is especially pertinent given the remediation inefficiencies observed in the present study for flushing at a high flow rate. The design of remediation systems relying on mobilisation as a NAPL removal mechanism should therefore concentrate on achieving the critical total trapping number through IFT reduction rather than through increase in flushing rate.

## 8 SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

### 8.1 SUMMARY & CONCLUSIONS

The column studies conducted to examine the phenomena influencing surfactant enhanced NAPL mobilisation demanded highly reproducible experimental conditions. The experimental design developed for the present study represented an integral part of this thesis, providing the necessary conditions for a comparative analysis of surfactant enhanced remediation. The conclusions of the present study with respect to the research objectives can be summarised as follows:

- the experimental apparatus and design procedures achieved reproducible residual NAPL saturations, as well as provided a means to assess the quality of the data;
- the solution concentrations and flow rates chosen for the experiments produced results that permitted a meaningful examination of the effects of surfactants on the mobilisation of a LNAPL;
- the total trapping number approach demonstrated limitations as a means to evaluate the potential for NAPL mobilisation when free product residual is present.

The significance of these findings with respect to surfactant enhanced mobilisation of NAPL are elaborated in greater detail below.

The similar porosity and bulk density achieved across all trials validates the packing procedure as a design providing both uniform and reproducible soil properties. Given that residual saturation is very sensitive to soil heterogeneity, the level of reproducibility attests to the uniformity of the media characteristics achieved over the trials conducted.

The trapping number provided a means to quantify the relative contribution of both viscous and buoyancy forces in overcoming the capillary forces that retain the trapped NAPL residual. At the higher flow rate, the critical trapping number approach effectively characterised the mineral oil recovery that increased with higher surfactant concentration. Surfactant breakthrough curves, however, demonstrated that flushing inefficiencies were induced by delivery at the higher flow rate. The total mineral oil removal was as a consequence lower than that observed at the lower flow rate, highlighting the importance of ensuring uniform flushing solution delivery.

When applied to flushing conditions at the lower flow rate, the trapping number approach indicates that mobilisation will not enhance NAPL recovery. Variations in contaminant recovery observed during flushing, however, indicate that NAPL removal was influenced by the presence of surfactants. The enhancement and retardation effects induced by the surfactant solutions clearly highlight the limitations of the  $N_T$  approach. The present research also reveals the shortcoming of previous studies that employ reduced residual saturations of NAPL. For real systems containing free product NAPL, the formation and transport of macro-emulsions will hinder the ability of a surfactant - soil system to promote NAPL recovery through mobilisation.

## 8.2 RECOMMENDATIONS

The success of surfactant enhanced remediation of NAPL at the field scale will be largely dependent on the ability to provide a cost-effective alternative to conventional technologies. Whether systems rely on the mechanisms of solubilisation or mobilisation, non-uniform delivery and flushing inefficiencies will have a profound effect on remediation efficiency. Given the uncertainties associated with heterogeneous media properties and surfactant-NAPL interactions in the subsurface, future research should concentrate on remediation technologies with lower resource requirements. Because the minimum IFT is achieved at the surfactant CMC, mobilisation offers greater promise as a remediation mechanism with far lower resource costs than solubilisation.

Where flushing rates are limited by aquifer conditions, the design of remediation systems relying on mobilisation must provide surfactant solutions capable of producing the required reduction in IFT. For design purposes, the total trapping number approach has demonstrated some limitations, especially for systems where free product NAPL is present. This rule of thumb approach should therefore be further investigated for more realistic systems to determine its applicability as an indicator for NAPL mobilisation. The apparatus and procedure developed for the present research offer an experimental framework for future study of the mobilisation potential for various surfactant /soil/NAPL systems.

## REFERENCES

- Abdul, A. S. *et al.* (1990) "Selection of Surfactants for the Removal of Petroleum Products from Shallow Sandy Aquifers," *Ground Water*, vol. 28, no. 6, pp. 920-926.
- Abriola, L. M. *et al.* (1995) "Impact of Surfactant Flushing on the Solubilization and Mobilization of Dense Nonaqueous-Phase Liquids" in Surfactant-Enhanced Subsurface Remediation, edited by D. A. Sabatini, *et al.*, Washington D. C.: American Chemical Society, pp. 10-23.
- Adeel, Z. & R. G. Luthy (1995) "Sorption and Transport Kinetics of a Nonionic Surfactant through an Aquifer Sediment," *Environmental Science and Technology*, vol. 29, no. 4, pp. 1032-1042.
- Bedient, P. B. *et al.* (1994) Ground water contamination: transport and remediation, New Jersey: PTR Prentice-Hall, Inc.
- Brandes, D. & K. J. Farley (1993) "Importance of phase behaviour on the removal of residual DNAPLs from porous media by alcohol flooding," *Water Environment Research*, vol. 65, no. 7, pp. 869-78.
- Corey, A. T. (1990) Mechanics of Immiscible Fluids in Porous Media, Chelsea (Michigan): Water Resources Publications.
- Dawson, H. E. & P. V. Roberts (1997) "Influence of Viscous, Gravitational, and Capillary Forces on DNAPL Saturation," *Ground Water*, vol. 35, no. 3, pp. 261-270.

Demond, A. H. & P. V. Roberts (1987) "An Examination of Relative Permeability Relations for Two-phase Flow in Porous Media," *Water Resources Bulletin*, vol. 23, no. 4, pp. 616-628.

Domenico, P. A. & F. W. Schwartz (1990) Physical and Chemical Hydrogeology, Toronto: John Wiley & Sons, Inc.

Edwards, D. A. *et al.* (1992) "Solubilization and Biodegradation of Hydrophobic Organic Compounds in Soil-Aqueous Systems with Nonionic Surfactants" in Transport and Remediation of Subsurface Contaminants, edited by D. A. Sabatini *et al.*, Washington D. C.: American Chemical Society, pp. 159-168.

Fetter, C. W. (1993) Contaminant Hydrology, New York: Macmillan Publishing Company.

Imhoff, P. T. *et al.* (1995) "Cosolvent-Enhanced Remediation of Residual Dense Nonaqueous Phase Liquids: Experimental Investigation," *Environmental Science and Technology*, vol. 29, no. 8, pp. 1966-76.

Logan, B. E. (1999) Environmental Transport Processes, Toronto: John Wiley & Sons, Inc.

Longino, B. L. & B. H. Kueper (1995) "The use of upward gradients to arrest downward dense, nonaqueous phase liquid (DNAPL) migration in the presence of solubilizing surfactants," *Canadian Geotechnical Journal*, vol. 32, pp. 296-308.

Mace, R. E. & J. L. Wilson (1992) "Clay and Immiscible organic liquids" in Transport and Remediation of Subsurface Contaminants, edited by D. A. Sabatini *et al.*, Washington D. C.: American Chemical Society, pp. 205-216.

- Martel, R. & P. J. Gélinais (1996) "Surfactant Solutions Developed for NAPL Recovery in Contaminated Aquifers," *Ground Water*, vol. 34, no. 1, pp. 143-154.
- Morrow, N. R. *et al.* (1988) "Entrapment and Mobilization of Residual Oil in Bead Packs," *Society of Petroleum Engineers Reservoir Engineering*, pp. 927-934.
- Morrow, N. R. & V. Hornof (1987) "Gravity Effects in the Displacement of Oil by Surfactant Solutions," *Society of Petroleum Engineers Reservoir Engineering*, pp. 627-638.
- Morrow, N. R. & B. Songkran (1981) "Effect of Viscous and Buoyancy forces on Nonwetting Phase Trapping in Porous Media" in Surface Phenomena in Enhanced Oil Recovery, edited by D. O. Shah, New York: Plenum Press, pp. 387-411.
- Myers, D. (1988) Surfactant science and technology, New York: VCH Publishers, Inc., pp. 209-53.
- Niu, M. *et al.* (1996) "Reduction of the Wall Effect in a Packed Bed by a Hemispherical Lining," *AIChE Journal*, vol. 42, no. 4, pp. 1181-1186.
- Okuda, I. *et al.* (1996) "Physicochemical Transport Processes Affecting the Removal of Residual DNAPL by Nonionic Surfactant Solutions," *Environmental Science and Technology*, vol. 30, no. 6, pp. 1852-1860.
- Oliviera, I. B. *et al.* (1996) "Packing of Sands for the Production of Homogeneous Porous Media," *Journal of Soil Science Society of American*, vol. 60, pp. 49-53.
- Ouyang, Y. *et al.* (1995a) "Emulsion-Mediated Transport of Non-aqueous Phase Liquid in Porous Media: A Review," *Critical Reviews in Environmental Science and Technology*, vol. 25, no. 3, pp. 269-90.



- Ouyang, Y. *et al.* (1995b) "Flow of Gasoline-in Water Microemulsion Through Water-Saturated Soil Columns," *Ground Water*, vol. 33, no. 3, pp. 399-406.
- Patel, K. & M. Greaves (1987) "Role of Capillary and Viscous Forces in Mobilization of Residual Oil," *The Canadian Journal of Chemical Engineering*, vol. 65, pp. 676-679.
- Pennel, K. D. *et al.* (1996) "Influence of Viscous and Buoyancy Forces on the Mobilization of Residual Tetrachloroethylene during Surfactant Flushing," *Environmental Science and Technology*, vol. 30, no. 4, pp. 1328-35.
- Pennell, K. D. *et al.* (1993) "Surfactant-Enhanced Solubilization of Residual Dodecane in Soil Columns," *Environmental Science and Technology*, vol. 27, no. 12, pp. 2332-2351.
- Pope, G. A. & W. H. Wade (1995) "Lessons from Enhanced Oil Recovery Research for Surfactant-Enhanced Aquifer Remediation," in Surfactant-Enhanced Subsurface Remediation, edited by D. A. Sabatini, *et al.*, Washington D. C.: American Chemical Society, pp. 142-60.
- Reynolds, T. D. & P. A. Richards (1996) Unit operations and processes in environmental engineering, 2<sup>nd</sup> edition, Toronto: PWS Publishing Company.
- Roy, D. *et al.* (1997) "Soil Washing Potential of a Natural Surfactant," *Environmental Science and Technology*, vol. 31, no. 3, pp. 670-675.
- Shiau, B.-J. *et al.* (1995) "Surfactant Selection for Optimizing Surfactant-Enhanced Subsurface Remediation," in Surfactant-Enhanced Subsurface Remediation, edited by D. A. Sabatini, *et al.*, Washington D. C.: American Chemical Society, pp. 65-79.

Sigma (1999) Triton X-100 Product Information, St-Louis (MO): Sigma-Aldrich Publications.

Sun, S. *et al.* (1995) "Sorption of Nonionic Organic Compounds in Soil-Water Systems Containing a Micelle-Forming Surfactant," *Environmental Science and Technology*, vol. 29, no. 4, pp. 903-913.

Wang, X. (1997) Characterization of Surfactant Adsorption at a Liquid-Liquid Interface by Drop Volume Tensiometry, Montreal: Concordia University.

Wardlaw, N. C. & M. McKellar (1985) "Oil Blob Populations and Mobilization of Trapped Oil in Unconsolidated Packs," *The Canadian Journal of Chemical Engineering*, vol. 63, pp. 525-532.

Weber, W. J. Jr. & F. A. DiGiano (1996) Process dynamics in environmental systems, New York: John Wiley & Sons, Inc.

West, C. C. & J. H. Harwell (1992) "Surfactants and Subsurface Remediation," *Environmental Science and Technology*, vol. 26, no. 12, pp. 2324-30.

Wilson, D. J. & A. N. Clarke (1994) "Soil Surfactant Flushing/Washing" in Hazardous waste site soil remediation: theory and application of innovative technologies, edited by D. J. Wilson & A. N. Clarke, New York: Marcel Dekker Inc., pp. 493-549.

Yeom, I. T. *et al.* (1996) "Kinetic Aspects of Surfactant Solubilization of Soil-Bound Polycyclic Aromatic Hydrocarbons," *Environmental Science and Technology*, vol. 30, no. 5, pp. 1589-1595.

## **APPENDIX A:**

Column data sheets for mobilisation trials

**COLUMN DATA SHEET** (abbreviations as defined by sections 4.7 & 5)

Trial No.: 1      Rate(ml/min)= 5.0      T(°C) = 21.0

Surfactant      C<sub>Triton</sub> (CMC) = 0.00       $\sigma_i$  (mN/m) = N/APore Volume      M<sub>i</sub> (g)= 886.66      M<sub>f</sub> (g)= 358.83      M<sub>S</sub> (g)= 527.83 $V_P$  (ml) =  $V_C - [M_S/\rho_S]$  = 102.7       $V_{O,i}$  (ml) = 0.75( $V_P$ ) = 77.0 $V_{O,r}$  (ml) =  $V_{O,i} - V_{O,d}$  = 26.5       $V_{O,d}$  (ml) = 50.5Oil Recovery       $M_{O,e} = M_{O+pan} - M_{pan}$        $M_{O,t} = 2M_{O,e}/[1 - 1.16M_{O,e}]$ 

No.	V(ml)	$\sigma$	$\sigma_i / \sigma$	$M_{pan}$	$M_{O+pan}$	$M_{O,t}$ (g)	$\Sigma V_P$	$\Sigma M_{O,t}$
1	5.2	n/a	n/a	1.3412	1.3530	0.0239	0.05	0.0239
2	5.6	n/a	n/a	1.3417	1.4257	0.1861	0.11	0.2101
3	5.7	n/a	n/a	1.3521	1.4751	0.2869	0.16	0.4970
4	5.8	n/a	n/a	1.3457	1.4436	0.2209	0.22	0.7179
5	5.4	n/a	n/a	1.3152	1.4336	0.2745	0.27	0.9924
6	5.6	n/a	n/a	1.3453	1.4501	0.2386	0.32	1.2310
7	5.7	n/a	n/a	1.3423	1.4433	0.2288	0.38	1.4598
8	5.6	n/a	n/a	1.3456	1.4365	0.2032	0.43	1.6631
9	5.4	n/a	n/a	1.3448	1.4412	0.2171	0.49	1.8801
10	5.6	n/a	n/a	1.3123	1.4268	0.2641	0.54	2.1442
11	5.5	n/a	n/a	1.3474	1.4147	0.1460	0.60	2.2902
12	5.4	n/a	n/a	1.3228	1.4198	0.2186	0.65	2.5088
13	5.7	n/a	n/a	1.3216	1.4349	0.2609	0.70	2.7697
14	5.7	n/a	n/a	1.3279	1.4076	0.1756	0.76	2.9453
15	5.7	n/a	n/a	1.3214	1.3867	0.1413	0.81	3.0866
16	5.6	n/a	n/a	1.3231	1.4277	0.2381	0.87	3.3247
17	5.6	n/a	n/a	1.3233	1.3669	0.0918	0.92	3.4166
18	5.9	n/a	n/a	1.3243	1.4013	0.1691	0.98	3.5857
19	5.8	n/a	n/a	1.3351	1.4018	0.1446	1.04	3.7303
20	5.6	n/a	n/a	1.3180	1.3910	0.1595	1.09	3.8898
21	5.8	n/a	n/a	1.3385	1.4092	0.1540	1.15	4.0438
22	5.6	n/a	n/a	1.3375	1.4157	0.1720	1.20	4.2158
23	5.9	n/a	n/a	1.3426	1.3977	0.1177	1.26	4.3335
24	4.3	n/a	n/a	1.3416	1.4037	0.1338	1.30	4.4674
25	5.7	n/a	n/a	1.3152	1.3994	0.1866	1.36	4.6540
26	5.7	n/a	n/a	1.3360	1.3813	0.0956	1.41	4.7496
27	5.7	n/a	n/a	1.3375	1.4090	0.1559	1.47	4.9056
28	5.6	n/a	n/a	1.3129	1.3843	0.1557	1.52	5.0613
29	5.7	n/a	n/a	1.3241	1.3709	0.0990	1.58	5.1602
30	5.4	n/a	n/a	1.3233	1.3716	0.1023	1.63	5.2626
31	5.9	n/a	n/a	1.3291	1.4236	0.2123	1.69	5.4748
32	5.6	n/a	n/a	1.3154	1.3610	0.0963	1.74	5.5711
33	5.8	n/a	n/a	1.3417	1.3816	0.0837	1.80	5.6548
34	5.7	n/a	n/a	1.3399	1.4017	0.1331	1.86	5.7880
35	5.8	n/a	n/a	1.3423	1.3807	0.0804	1.91	5.8683

**COLUMN DATA SHEET** (abbreviations as defined by sections 4.7 & 5)**Trial No.:** 2      **Rate**(ml/min)= 5.0      **T**(°C) = 20.5**Surfactant**       $C_{\text{Triton}}$  (CMC) = 0.00       $\sigma_i$  (mN/m) = N/A**Pore Volume**       $M_i$  (g)= 883.20       $M_f$  (g)= 354.46       $M_S$  (g)= 528.74 $V_P$  (ml) =  $V_C - [M_S/\rho_S]$  = 102.3       $V_{O,i}$  (ml) = 0.75( $V_P$ ) = 76.8 $V_{O,r}$  (ml) =  $V_{O,i} - V_{O,d}$  = 25.0       $V_{O,d}$  (ml) = 51.8**Oil Recovery**       $M_{O,e} = M_{O+pan} - M_{pan}$        $M_{O,t} = 2M_{O,e}/[1 - 1.16M_{O,e}]$ 

No.	V(ml)	$\sigma$	$\sigma_i / \sigma$	$M_{pan}$	$M_{O+pan}$	$M_{O,t}$ (g)	$\Sigma V_P$	$\Sigma M_{O,t}$
1	5.8	n/a	n/a	1.0100	1.0208	0.0219	0.06	0.0219
2	5.3	n/a	n/a	1.0080	1.0705	0.1348	0.11	0.1566
3	5.7	n/a	n/a	1.0113	1.1342	0.2867	0.16	0.4433
4	5.3	n/a	n/a	1.0098	1.1432	0.3156	0.22	0.7590
5	6.1	n/a	n/a	1.0084	1.1237	0.2662	0.28	1.0252
6	5.4	n/a	n/a	1.0163	1.1477	0.3101	0.33	1.3352
7	5.7	n/a	n/a	0.9918	1.0967	0.2389	0.38	1.5741
8	5.9	n/a	n/a	0.9936	1.0773	0.1854	0.44	1.7595
9	6.0	n/a	n/a	0.9960	1.1073	0.2556	0.50	2.0151
10	6.1	n/a	n/a	0.9961	1.0956	0.2250	0.56	2.2401
11	5.5	n/a	n/a	0.9990	1.0757	0.1684	0.61	2.4085
12	5.9	n/a	n/a	0.9947	1.0772	0.1825	0.67	2.5909
13	5.9	n/a	n/a	0.9941	1.0448	0.1077	0.73	2.6987
14	6.2	n/a	n/a	0.9923	1.0879	0.2151	0.79	2.9137
15	5.8	n/a	n/a	0.9905	1.0587	0.1481	0.85	3.0618
16	5.6	n/a	n/a	0.9938	1.0457	0.1105	0.90	3.1723
17	5.5	n/a	n/a	0.9976	1.0848	0.1940	0.95	3.3663
18	5.9	n/a	n/a	0.9967	1.0704	0.1612	1.01	3.5275
19	5.8	n/a	n/a	1.0054	1.0805	0.1645	1.07	3.6920
20	6.0	n/a	n/a	1.0040	1.0758	0.1566	1.13	3.8487
21	6.1	n/a	n/a	1.0045	1.0725	0.1476	1.19	3.9963
22	6.2	n/a	n/a	1.0090	1.0498	0.0857	1.25	4.0820
23	6.3	n/a	n/a	1.0120	1.1067	0.2128	1.31	4.2948
24	6.0	n/a	n/a	1.0151	1.0867	0.1562	1.37	4.4509
25	6.0	n/a	n/a	1.0151	1.0825	0.1462	1.43	4.5972
26	6.1	n/a	n/a	1.0136	1.0535	0.0837	1.49	4.6808
27	6.3	n/a	n/a	1.0141	1.1106	0.2173	1.55	4.8982
28	5.7	n/a	n/a	1.0129	1.0238	0.0221	1.60	4.9202
29	5.6	n/a	n/a	1.0131	1.0723	0.1271	1.66	5.0474
30	5.9	n/a	n/a	1.0137	1.0778	0.1385	1.72	5.1859
31	5.8	n/a	n/a	1.0174	1.0648	0.1003	1.77	5.2862
32	5.9	n/a	n/a	1.0161	1.0594	0.0912	1.83	5.3774
33	5.7	n/a	n/a	1.0197	1.0552	0.0740	1.89	5.4514
34	5.7	n/a	n/a	1.0192	1.0875	0.1484	1.94	5.5998
35	5.8	n/a	n/a	1.0164	1.0459	0.0611	2.00	5.6609

# **COLUMN DATA SHEET** (abbreviations as defined by sections 4.7 & 5)

**Trial No.:** 3      **Rate(ml/min)=** 50.0      **T(°C) =** 21.0

**Surfactant**      **C<sub>Triton</sub> (CMC) =** 0.00      **σ<sub>i</sub> (mN/m) =** n/a

**Pore Volume**      **M<sub>i</sub> (g) =** 885.41      **M<sub>f</sub> (g) =** 359.19      **M<sub>S</sub> (g)=** 526.22

**V<sub>P</sub> (ml) = V<sub>C</sub> - [M<sub>S</sub>/ρ<sub>S</sub>] =** 103.3      **V<sub>O,i</sub> (ml) = 0.75(V<sub>P</sub>) =** 77.5

**V<sub>O,r</sub> (ml) = V<sub>O,i</sub> - V<sub>O,d</sub> =** 26.0      **V<sub>O,d</sub> (ml) =** 51.5

**Oil Recovery**      **M<sub>O,e</sub>=M<sub>O+pan</sub> - M<sub>pan</sub>**      **M<sub>O,t</sub>=2M<sub>O,e</sub>/[1 - 1.16M<sub>O,e</sub>]**

**Pressure**

No.	V(ml)	σ	σ <sub>i</sub> / σ	M <sub>pan</sub>	M <sub>O+pan</sub>	M <sub>O,t</sub> (g)	Σ V <sub>P</sub>	Σ M <sub>O,t</sub>	Σ V <sub>pore</sub>	ΔP(Hg)
1	5.2	n/a	n/a	1.3246	1.4421	0.2721	0.05	0.2721	0.12	43.0
2	5.7	n/a	n/a	1.3431	1.4014	0.1251	0.11	0.3971	0.24	42.0
3	5.7	n/a	n/a	1.3376	1.3859	0.1023	0.16	0.4995	0.36	41.0
4	5.8	n/a	n/a	1.3435	1.3952	0.1100	0.22	0.6095	0.48	40.5
5	5.7	n/a	n/a	1.3444	1.3907	0.0979	0.27	0.7073	0.61	40.0
6	5.6	n/a	n/a	1.3193	1.3618	0.0894	0.33	0.7967	0.73	39.5
7	5.5	n/a	n/a	1.3137	1.3550	0.0868	0.38	0.8835	0.85	39.0
8	5.7	n/a	n/a	1.3411	1.3844	0.0912	0.43	0.9747	0.97	39.0
9	5.6	n/a	n/a	1.3415	1.3859	0.0936	0.49	1.0683	1.09	38.5
10	5.6	n/a	n/a	1.3390	1.3789	0.0837	0.54	1.1520	1.21	38.5
11	5.5	n/a	n/a	1.3426	1.3782	0.0743	0.60	1.2262	1.33	38.0
12	5.6	n/a	n/a	1.3266	1.3694	0.0901	0.65	1.3163	1.45	37.0
13	5.4	n/a	n/a	1.3269	1.3635	0.0764	0.70	1.3928	1.57	36.5
14	3.6	n/a	n/a	1.3158	1.3549	0.0819	0.74	1.4747	1.69	36.0
15	5.7	n/a	n/a	1.3455	1.3900	0.0938	0.79	1.5685	1.82	35.5
16	5.6	n/a	n/a	1.3478	1.3952	0.1003	0.85	1.6688	1.94	35.5
17	5.8	n/a	n/a	1.3418	1.3867	0.0947	0.90	1.7636		
18	5.8	n/a	n/a	1.3200	1.3629	0.0903	0.96	1.8539		
19	5.3	n/a	n/a	1.3150	1.3620	0.0994	1.01	1.9533		
20	5.6	n/a	n/a	1.3457	1.3823	0.0764	1.06	2.0297		
21	5.6	n/a	n/a	1.3195	1.3661	0.0985	1.12	2.1283		
22	5.6	n/a	n/a	1.3170	1.3642	0.0999	1.17	2.2281		
23	5.8	n/a	n/a	1.3459	1.3856	0.0832	1.23	2.3114		
24	5.7	n/a	n/a	1.3486	1.3990	0.1071	1.28	2.4184		
25	5.3	n/a	n/a	1.3452	1.3872	0.0883	1.34	2.5067		
26	5.6	n/a	n/a	1.3459	1.3918	0.0970	1.39	2.6037		
27	5.7	n/a	n/a	1.3451	1.3870	0.0881	1.45	2.6918		
28	4.2	n/a	n/a	1.3229	1.3669	0.0927	1.49	2.7845		
29	5.7	n/a	n/a	1.3263	1.3706	0.0934	1.54	2.8779		
30	5.6	n/a	n/a	1.3160	1.3609	0.0947	1.60	2.9726		
31	5.6	n/a	n/a	1.3199	1.3633	0.0914	1.65	3.0640		
32	5.6	n/a	n/a	0.9996	1.0426	0.0905	1.70	3.1546		
33	5.8	n/a	n/a	1.0176	1.0585	0.0859	1.76	3.2404		
34	5.6	n/a	n/a	1.0197	1.0649	0.0954	1.81	3.3358		
35	5.8	n/a	n/a	1.0140	1.0513	0.0780	1.87	3.4138		

# **COLUMN DATA SHEET** (abbreviations as defined by sections 4.7 & 5)

**Trial No.:** 4      **Rate**(ml/min)= 50.0      **T**(°C) = 21.5

**Surfactant**       $C_{\text{Triton}}$  (CMC) = 0.00       $\sigma_i$  (mN/m) = n/a

**Pore Volume**       $M_i$  (g) = 886.61       $M_f$  (g) = 357.03       $M_S$  (g) = 529.58

$V_P$  (ml) =  $V_C - [M_S/\rho_S]$  = 102.0       $V_{O,i}$  (ml) = 0.75( $V_P$ ) = 76.5

$V_{O,r}$  (ml) =  $V_{O,i} - V_{O,d}$  = 24.8       $V_{O,d}$  (ml) = 51.7

**Oil Recovery**       $M_{O,e} = M_{O+pan} - M_{pan}$        $M_{O,t} = 2M_{O,e}/[1 - 1.16M_{O,e}]$       **Pressure**

No.	V(ml)	$\sigma$	$\sigma_i / \sigma$	$M_{pan}$	$M_{O+pan}$	$M_{O,t}$ (g)	$\Sigma V_P$	$\Sigma M_{O,t}$	$\Sigma V_{pore}$	$\Delta P$ (Hg)
1	6.4	n/a	n/a	1.0070	1.1275	0.2802	0.06	0.2802	0.12	42.0
2	5.7	n/a	n/a	1.0101	1.0900	0.1761	0.12	0.4563	0.25	41.0
3	5.9	n/a	n/a	1.0128	1.0639	0.1086	0.18	0.5649	0.37	41.0
4	5.8	n/a	n/a	0.9959	1.0411	0.0954	0.23	0.6603	0.49	41.0
5	5.8	n/a	n/a	1.0119	1.0489	0.0773	0.29	0.7377	0.61	41.0
6	5.9	n/a	n/a	0.9901	1.0275	0.0782	0.35	0.8158	0.74	41.0
7	5.6	n/a	n/a	0.9891	1.0239	0.0725	0.40	0.8884	0.86	40.5
8	5.9	n/a	n/a	1.0047	1.0407	0.0751	0.46	0.9635	0.98	40.5
9	6.1	n/a	n/a	1.0058	1.0409	0.0732	0.52	1.0367	1.10	40.0
10	6.0	n/a	n/a	0.9902	1.0306	0.0848	0.58	1.1215	1.23	40.0
11	5.8	n/a	n/a	0.9879	1.0247	0.0769	0.64	1.1983	1.35	39.5
12	6.0	n/a	n/a	0.9906	1.0338	0.0910	0.69	1.2893	1.47	39.5
13	5.6	n/a	n/a	1.0003	1.0421	0.0879	0.75	1.3772	1.59	39.0
14	5.9	n/a	n/a	1.0116	1.0513	0.0832	0.81	1.4604	1.72	38.0
15	5.9	n/a	n/a	1.0114	1.0513	0.0837	0.87	1.5441	1.84	38.0
16	5.9	n/a	n/a	0.9910	1.0320	0.0861	0.92	1.6302	1.96	37.5
17	5.9	n/a	n/a	0.9922	1.0349	0.0899	0.98	1.7200		
18	6.0	n/a	n/a	0.9941	1.0322	0.0797	1.04	1.7997		
19	5.7	n/a	n/a	0.9944	1.0352	0.0857	1.10	1.8854		
20	5.8	n/a	n/a	0.9882	1.0249	0.0767	1.15	1.9621		
21	5.9	n/a	n/a	0.9862	1.0233	0.0775	1.21	2.0396		
22	6.0	n/a	n/a	0.9895	1.0309	0.0870	1.27	2.1266		
23	5.9	n/a	n/a	1.0077	1.0445	0.0769	1.33	2.2035		
24	5.9	n/a	n/a	1.0012	1.0401	0.0815	1.38	2.2849		
25	5.6	n/a	n/a	0.9883	1.0257	0.0782	1.44	2.3631		
26	5.9	n/a	n/a	0.9872	1.0259	0.0810	1.50	2.4442		
27	5.9	n/a	n/a	0.9935	1.0326	0.0819	1.56	2.5261		
28	4.3	n/a	n/a	0.9942	1.0324	0.0799	1.60	2.6060		
29	5.9	n/a	n/a	0.9848	1.0198	0.0730	1.66	2.6790		
30	5.9	n/a	n/a	0.9868	1.0265	0.0788	1.71	2.7578		
31	5.6	n/a	n/a	1.0092	1.0419	0.0680	1.77	2.8258		
32	5.3	n/a	n/a	1.0061	1.0415	0.0738	1.82	2.8996		
33	5.0	n/a	n/a	0.9877	1.0239	0.0756	1.87	2.9752		
34	6.0	n/a	n/a	1.0161	1.0515	0.0738	1.93	3.0490		
35	6.0	n/a	n/a	0.9900	1.0252	0.0734	1.99	3.1224		

**COLUMN DATA SHEET** (abbreviations as defined by sections 4.7 & 5)

Trial No.: 5      Rate(ml/min)= 5.0      T(°C) = 20.5

Surfactant      C<sub>Triton</sub> (CMC) = 1.00       $\sigma_i$  (mN/m) = 37.5Pore Volume      M<sub>i</sub> (g) = 885.97      M<sub>f</sub> (g) = 357.71      M<sub>S</sub> (g) = 528.26

$$V_P(\text{ml}) = V_C - [M_S/\rho_S] = 102.5 \quad V_{O,i}(\text{ml}) = 0.75(V_P) = 76.9$$

$$V_{O,r}(\text{ml}) = V_{O,i} - V_{O,d} = 25.1 \quad V_{O,d}(\text{ml}) = 51.8$$

Oil Recovery      M<sub>O,e</sub> = M<sub>O+pan</sub> - M<sub>pan</sub>      M<sub>O,t</sub> = 2M<sub>O,e</sub> / [1 - 1.16M<sub>O,e</sub>]

No.	V(ml)	$\sigma$	$\sigma_i / \sigma$	M <sub>pan</sub>	M <sub>O+pan</sub>	M <sub>O,t</sub> (g)	$\Sigma V_P$	$\Sigma M_{O,t}$
1	6.1	75.2	0.50	1.0121	1.0771	<b>0.1406</b>	<b>0.06</b>	<b>0.1406</b>
2	6.2	74.9	0.50	0.9915	1.1356	<b>0.3460</b>	<b>0.12</b>	<b>0.4867</b>
3	5.8	75.0	0.50	1.0100	1.0977	<b>0.1953</b>	<b>0.18</b>	<b>0.6819</b>
4	6.2	74.8	0.50	1.0116	1.1426	<b>0.3090</b>	<b>0.24</b>	<b>0.9909</b>
5	5.9	74.7	0.50	0.9892	1.0739	<b>0.1879</b>	<b>0.29</b>	<b>1.1787</b>
6	5.9	74.9	0.50	1.0093	1.1215	<b>0.2580</b>	<b>0.35</b>	<b>1.4367</b>
7	6.0	75.3	0.50	0.9893	1.1309	<b>0.3389</b>	<b>0.41</b>	<b>1.7756</b>
8	5.7	75.2	0.50	0.9689	1.0391	<b>0.1528</b>	<b>0.47</b>	<b>1.9284</b>
9	6.0	74.9	0.50	0.9897	1.0736	<b>0.1859</b>	<b>0.52</b>	<b>2.1143</b>
10	6.1	74.8	0.50	0.9919	1.0853	<b>0.2095</b>	<b>0.58</b>	<b>2.3238</b>
11	6.0	74.7	0.50	0.9897	1.0871	<b>0.2196</b>	<b>0.64</b>	<b>2.5434</b>
12	6.0	74.7	0.50	0.9907	1.0903	<b>0.2252</b>	<b>0.70</b>	<b>2.7687</b>
13	5.8	74.6	0.50	1.0067	1.0882	<b>0.1800</b>	<b>0.76</b>	<b>2.9487</b>
14	5.9	74.8	0.50	1.0053	1.0428	<b>0.0784</b>	<b>0.82</b>	<b>3.0271</b>
15	6.0	74.9	0.50	1.0106	1.0927	<b>0.1815</b>	<b>0.87</b>	<b>3.2086</b>
16	6.0	74.7	0.50	0.9958	1.0208	<b>0.0515</b>	<b>0.93</b>	<b>3.2601</b>
17	5.8	74.8	0.50	1.0033	1.0916	<b>0.1968</b>	<b>0.99</b>	<b>3.4568</b>
18	5.8	75.0	0.50	0.9916	1.0604	<b>0.1495</b>	<b>1.05</b>	<b>3.6064</b>
19	6.0	74.8	0.50	1.0175	1.0436	<b>0.0538</b>	<b>1.10</b>	<b>3.6602</b>
20	6.0	74.7	0.50	0.9928	1.0446	<b>0.1102</b>	<b>1.16</b>	<b>3.7704</b>
21	6.1	74.6	0.50	0.9691	1.0235	<b>0.1161</b>	<b>1.22</b>	<b>3.8865</b>
22	5.9	60.5	0.62	1.0120	1.0595	<b>0.1005</b>	<b>1.28</b>	<b>3.9871</b>
23	5.8	53.8	0.70	1.0031	1.0258	<b>0.0466</b>	<b>1.34</b>	<b>4.0337</b>
24	5.6	52.3	0.72	1.0023	1.0030	<b>0.0014</b>	<b>1.39</b>	<b>4.0351</b>
25	5.6	49.9	0.75	1.0054	1.0577	<b>0.1114</b>	<b>1.45</b>	<b>4.1465</b>
26	6.0	47.9	0.78	1.0054	1.0312	<b>0.0532</b>	<b>1.50</b>	<b>4.1997</b>
27	5.8	46.5	0.81	1.0101	1.0222	<b>0.0245</b>	<b>1.56</b>	<b>4.2242</b>
28	5.9	45.3	0.83	1.0024	1.0174	<b>0.0305</b>	<b>1.62</b>	<b>4.2547</b>
29	5.6	44.5	0.84	0.9943	1.0201	<b>0.0532</b>	<b>1.67</b>	<b>4.3079</b>
30	5.7	44.5	0.84	1.0118	1.0384	<b>0.0549</b>	<b>1.73</b>	<b>4.3628</b>
31	5.6	43.9	0.85	0.9929	1.0128	<b>0.0407</b>	<b>1.78</b>	<b>4.4036</b>
32	5.9	43.8	0.86	0.9989	1.0317	<b>0.0682</b>	<b>1.84</b>	<b>4.4717</b>
33	5.8	44.1	0.85	1.0162	1.0379	<b>0.0445</b>	<b>1.90</b>	<b>4.5163</b>
34	5.9	43.6	0.86	1.0064	1.0333	<b>0.0555</b>	<b>1.95</b>	<b>4.5718</b>
35	5.8	43.8	0.86	1.0179	1.0349	<b>0.0347</b>	<b>2.01</b>	<b>4.6065</b>



**COLUMN DATA SHEET** (abbreviations as defined by sections 4.7 & 5)

Trial No.: 6      Rate(ml/min)= 5.0      T(°C) = 22.0

Surfactant      C<sub>Triton</sub> (CMC) = 1.00       $\sigma_i$  (mN/m) = 37.5Pore Volume      M<sub>i</sub> (g) = 887.45      M<sub>f</sub> (g) = 359.84      M<sub>S</sub> (g) = 527.61V<sub>P</sub> (ml) = V<sub>C</sub> - [M<sub>S</sub>/ρ<sub>S</sub>] = 102.8      V<sub>O,i</sub> (ml) = 0.75(V<sub>P</sub>) = 77.1V<sub>O,r</sub> (ml) = V<sub>O,i</sub> - V<sub>O,d</sub> = 26.0      V<sub>O,d</sub> (ml) = 51.1Oil Recovery      M<sub>O,e</sub> = M<sub>O+pan</sub> - M<sub>pan</sub>      M<sub>O,t</sub> = 2M<sub>O,e</sub> / [1 - 1.16M<sub>O,e</sub>]

No.	V(ml)	σ	σ <sub>i</sub> / σ	M <sub>pan</sub>	M <sub>O+pan</sub>	M <sub>O,t</sub> (g)	Σ V <sub>P</sub>	Σ M <sub>O,t</sub>
1	5.9	74.9	0.50	1.0205	1.0460	<b>0.0526</b>	<b>0.06</b>	<b>0.0526</b>
2	6.1	74.8	0.50	0.9875	1.1387	<b>0.3667</b>	<b>0.12</b>	<b>0.4193</b>
3	5.9	74.7	0.50	0.9888	1.1259	<b>0.3261</b>	<b>0.17</b>	<b>0.7453</b>
4	6.0	74.8	0.50	1.0057	1.1266	<b>0.2812</b>	<b>0.23</b>	<b>1.0266</b>
5	5.7	74.9	0.50	0.9959	1.0904	<b>0.2123</b>	<b>0.29</b>	<b>1.2389</b>
6	6.0	74.8	0.50	0.9875	1.1161	<b>0.3023</b>	<b>0.35</b>	<b>1.5412</b>
7	5.9	74.7	0.50	1.0142	1.1232	<b>0.2496</b>	<b>0.40</b>	<b>1.7907</b>
8	5.8	74.6	0.50	0.9936	1.0652	<b>0.1562</b>	<b>0.46</b>	<b>1.9469</b>
9	5.9	74.7	0.50	0.9911	1.1108	<b>0.2780</b>	<b>0.52</b>	<b>2.2249</b>
10	5.9	74.8	0.50	1.0027	1.1039	<b>0.2293</b>	<b>0.58</b>	<b>2.4542</b>
11	5.8	74.6	0.50	1.0133	1.0816	<b>0.1484</b>	<b>0.63</b>	<b>2.6026</b>
12	5.9	74.7	0.50	1.0121	1.1006	<b>0.1973</b>	<b>0.69</b>	<b>2.7998</b>
13	5.7	74.6	0.50	0.9957	1.0983	<b>0.2329</b>	<b>0.74</b>	<b>3.0327</b>
14	5.7	74.6	0.50	0.9977	1.0596	<b>0.1334</b>	<b>0.80</b>	<b>3.1661</b>
15	6.0	74.5	0.50	0.9931	1.0581	<b>0.1406</b>	<b>0.86</b>	<b>3.3067</b>
16	5.8	74.6	0.50	1.0113	1.0951	<b>0.1856</b>	<b>0.91</b>	<b>3.4924</b>
17	6.1	74.7	0.50	0.9996	1.0698	<b>0.1528</b>	<b>0.97</b>	<b>3.6452</b>
18	6.0	74.6	0.50	1.0034	1.0711	<b>0.1469</b>	<b>1.03</b>	<b>3.7922</b>
19	5.7	74.5	0.50	1.0118	1.0801	<b>0.1484</b>	<b>1.09</b>	<b>3.9405</b>
20	6.0	74.6	0.50	0.9864	1.0199	<b>0.0697</b>	<b>1.15</b>	<b>4.0102</b>
21	5.9	62.1	0.60	0.9996	1.0165	<b>0.0345</b>	<b>1.20</b>	<b>4.0447</b>
22	5.9	54.8	0.68	1.0081	1.0437	<b>0.0743</b>	<b>1.26</b>	<b>4.1190</b>
23	5.9	51.0	0.74	1.0090	1.0421	<b>0.0688</b>	<b>1.32</b>	<b>4.1878</b>
24	5.8	49.1	0.76	1.0069	1.0494	<b>0.0894</b>	<b>1.37</b>	<b>4.2772</b>
25	5.7	47.4	0.79	0.9885	0.9929	<b>0.0088</b>	<b>1.43</b>	<b>4.2861</b>
26	6.0	46.3	0.81	1.0131	1.0211	<b>0.0161</b>	<b>1.49</b>	<b>4.3022</b>
27	5.9	45.3	0.83	0.9878	0.9943	<b>0.0131</b>	<b>1.55</b>	<b>4.3153</b>
28	5.9	44.8	0.84	1.0121	1.0692	<b>0.1223</b>	<b>1.60</b>	<b>4.4376</b>
29	6.0	44.3	0.85	0.9882	1.0111	<b>0.0470</b>	<b>1.66</b>	<b>4.4847</b>
30	5.9	43.9	0.85	1.0030	1.0499	<b>0.0992</b>	<b>1.72</b>	<b>4.5839</b>
31	6.0	43.7	0.86	0.9904	1.0080	<b>0.0359</b>	<b>1.78</b>	<b>4.6198</b>
32	5.8	43.5	0.86	1.0064	1.0278	<b>0.0439</b>	<b>1.83</b>	<b>4.6637</b>
33	5.9	43.4	0.86	1.0040	1.0393	<b>0.0736</b>	<b>1.89</b>	<b>4.7373</b>
34	5.8	43.3	0.87	1.0044	1.0326	<b>0.0583</b>	<b>1.95</b>	<b>4.7956</b>
35	6.0	43.3	0.87	1.0168	1.0791	<b>0.1343</b>	<b>2.01</b>	<b>4.9299</b>

# **COLUMN DATA SHEET** (abbreviations as defined by sections 4.7 & 5)

**Trial No.:** 7      **Rate**(ml/min)= 50.0      **T**(°C) = 20.3

**Surfactant**       $C_{\text{Triton}} \text{ (CMC)} = 1.00$        $\sigma_i \text{ (mN/m)} = 37.5$

**Pore Volume**       $M_i \text{ (g)} = 886.72$        $M_f \text{ (g)} = 358.20$        $M_s \text{ (g)} = 528.52$

$V_P \text{ (ml)} = V_C - [M_s/\rho_s] = 102.4$        $V_{O,i} \text{ (ml)} = 0.75(V_P) = 76.8$

$V_{O,r} \text{ (ml)} = V_{O,i} - V_{O,d} = 25.6$        $V_{O,d} \text{ (ml)} = 51.2$

**Oil Recovery**       $M_{O,e} = M_{O+pan} - M_{pan}$        $M_{O,t} = 2M_{O,e}/[1 - 1.16M_{O,e}]$

**Pressure**

No.	V(ml)	$\sigma$	$\sigma_i / \sigma$	$M_{pan}$	$M_{O+pan}$	$M_{O,t} \text{ (g)}$	$\Sigma V_P$	$\Sigma M_{O,t}$	$\Sigma V_{pore}$	$\Delta P \text{ (Hg)}$
1	8.1	74.6	0.50	1.0156	1.1837	0.4176	0.08	0.4176	0.12	49.0
2	5.4	74.5	0.50	1.0092	1.0801	0.1545	0.13	0.5722	0.24	45.0
3	5.7	74.6	0.50	1.0079	1.0819	0.1619	0.19	0.7341	0.37	43.0
4	5.8	74.4	0.50	1.0099	1.0777	0.1472	0.24	0.8812	0.49	42.0
5	5.2	74.2	0.51	1.0118	1.0650	0.1134	0.29	0.9946	0.61	41.5
6	5.7	74.6	0.50	1.0089	1.0645	0.1189	0.35	1.1135	0.73	41.0
7	5.8	74.5	0.50	1.0100	1.0607	0.1077	0.41	1.2212	0.85	40.5
8	5.4	74.7	0.50	1.0100	1.0618	0.1102	0.46	1.3315	0.98	39.5
9	5.7	74.8	0.50	1.0120	1.0666	0.1166	0.52	1.4480	1.10	37.0
10	5.6	74.6	0.50	1.0134	1.0647	0.1091	0.57	1.5571	1.22	35.5
11	5.6	74.5	0.50	1.0168	1.0666	0.1057	0.62	1.6628	1.34	34.0
12	5.6	74.7	0.50	1.0141	1.0653	0.1089	0.68	1.7717	1.46	33.0
13	5.8	74.3	0.50	1.0139	1.0639	0.1062	0.74	1.8779	1.59	32.0
14	5.4	74.4	0.50	1.0128	1.0625	0.1055	0.79	1.9833	1.71	31.5
15	5.7	74.5	0.50	1.0122	1.0652	0.1129	0.84	2.0963	1.83	31.5
16	5.6	67.3	0.56	1.0126	1.0634	0.1080	0.90	2.2043	1.95	31.0
17	5.7	63.2	0.59	1.0104	1.0633	0.1127	0.95	2.3170		
18	5.8	59.8	0.63	1.0121	1.0673	0.1180	1.01	2.4349		
19	5.7	57.2	0.66	1.0147	1.0711	0.1207	1.07	2.5556		
20	5.4	54.1	0.69	1.0128	1.0618	0.1039	1.12	2.6595		
21	5.5	51.3	0.73	1.0104	1.0596	0.1044	1.17	2.7639		
22	5.7	48.9	0.77	1.0110	1.0581	0.0996	1.23	2.8635		
23	5.8	47.5	0.79	1.0144	1.0558	0.0870	1.29	2.9505		
24	5.7	46.5	0.81	1.0139	1.0542	0.0846	1.34	3.0351		
25	5.6	46.0	0.82	1.0157	1.0543	0.0808	1.40	3.1159		
26	5.3	45.5	0.82	1.0136	1.0500	0.0760	1.45	3.1919		
27	5.7	45.1	0.83	1.0113	1.0493	0.0795	1.50	3.2714		
28	5.6	44.2	0.85	1.0126	1.0505	0.0793	1.56	3.3507		
29	5.7	43.8	0.86	1.0108	1.0461	0.0736	1.61	3.4243		
30	5.5	43.8	0.86	1.0100	1.0468	0.0769	1.67	3.5012		
31	5.8	43.7	0.86	1.0084	1.0426	0.0712	1.72	3.5724		
32	5.3	43.5	0.86	1.0108	1.0446	0.0704	1.78	3.6428		
33	5.8	43.3	0.87	1.0082	1.0432	0.0730	1.83	3.7157		
34	5.6	43.2	0.87	1.0051	1.0400	0.0727	1.89	3.7885		
35	5.8	43.1	0.87	1.0016	1.0367	0.0732	1.94	3.8616		

**COLUMN DATA SHEET** (abbreviations as defined by sections 4.7 & 5)**Trial No.:** 8      **Rate**(ml/min)= 50.0      **T**(°C) = 20.0**Surfactant**       $C_{\text{Triton}}$  (CMC) = 1.00       $\sigma_i$  (mN/m) = 37.5**Pore Volume**       $M_i$  (g) = 886.80       $M_f$  (g) = 358.05       $M_S$  (g) = 528.75 $V_P$  (ml) =  $V_C - [M_S/\rho_S]$  = 102.3       $V_{O,i}$  (ml) = 0.75( $V_P$ ) = 76.8 $V_{O,r}$  (ml) =  $V_{O,i} - V_{O,d}$  = 26.3       $V_{O,d}$  (ml) = 50.5**Oil Recovery**       $M_{O,e} = M_{O+pan} - M_{pan}$        $M_{O,t} = 2M_{O,e}/[1 - 1.16M_{O,e}]$ **Pressure**

No.	V(ml)	$\sigma$	$\sigma_i / \sigma$	$M_{pan}$	$M_{O+pan}$	$M_{O,t}$ (g)	$\Sigma V_P$	$\Sigma M_{O,t}$	$\Sigma V_{pore}$	$\Delta P$ (Hg)
1	5.4	74.2	0.51	0.9931	1.1446	<b>0.3676</b>	<b>0.05</b>	<b>0.3676</b>	0.12	48.0
2	4.8	73.7	0.51	0.9889	1.0454	<b>0.1209</b>	<b>0.10</b>	<b>0.4885</b>	0.24	44.5
3	5.6	73.5	0.51	1.0198	1.0687	<b>0.1037</b>	<b>0.15</b>	<b>0.5922</b>	0.37	44.0
4	5.7	74.5	0.50	1.0212	1.0702	<b>0.1039</b>	<b>0.21</b>	<b>0.6961</b>	0.49	43.0
5	5.6	74.8	0.50	1.0176	1.0670	<b>0.1048</b>	<b>0.26</b>	<b>0.8009</b>	0.61	42.0
6	5.7	73.5	0.51	1.0146	1.0669	<b>0.1114</b>	<b>0.32</b>	<b>0.9123</b>	0.73	41.5
7	5.4	73.8	0.51	1.0121	1.0709	<b>0.1262</b>	<b>0.37</b>	<b>1.0385</b>	0.86	40.5
8	4.4	74.3	0.50	1.0116	1.0672	<b>0.1189</b>	<b>0.42</b>	<b>1.1574</b>	0.98	40.0
9	5.6	74.6	0.50	1.0176	1.0662	<b>0.1030</b>	<b>0.47</b>	<b>1.2604</b>	1.10	36.5
10	5.7	74.8	0.50	1.0163	1.0678	<b>0.1095</b>	<b>0.53</b>	<b>1.3699</b>	1.22	34.5
11	5.6	74.7	0.50	1.0143	1.0666	<b>0.1114</b>	<b>0.58</b>	<b>1.4813</b>	1.34	33.0
12	5.7	74.5	0.50	1.0158	1.0653	<b>0.1050</b>	<b>0.64</b>	<b>1.5863</b>	1.47	32.0
13	5.3	74.2	0.51	1.0144	1.0612	<b>0.0990</b>	<b>0.69</b>	<b>1.6853</b>	1.59	31.0
14	5.6	74.1	0.51	1.0135	1.0604	<b>0.0992</b>	<b>0.74</b>	<b>1.7845</b>	1.71	30.5
15	5.7	74.3	0.50	1.0096	1.0550	<b>0.0958</b>	<b>0.80</b>	<b>1.8803</b>	1.83	30.0
16	5.7	74.0	0.51	1.0065	1.0541	<b>0.1008</b>	<b>0.86</b>	<b>1.9811</b>	1.95	29.5
17	5.8	74.2	0.51	1.0038	1.0464	<b>0.0896</b>	<b>0.91</b>	<b>2.0707</b>		
18	5.9	66.5	0.56	1.0053	1.0509	<b>0.0963</b>	<b>0.97</b>	<b>2.1670</b>		
19	5.3	61.8	0.61	1.0092	1.0485	<b>0.0824</b>	<b>1.02</b>	<b>2.2494</b>		
20	4.4	58.7	0.64	1.0032	1.0428	<b>0.0830</b>	<b>1.06</b>	<b>2.3324</b>		
21	3.6	56.4	0.66	0.9970	1.0366	<b>0.0830</b>	<b>1.10</b>	<b>2.4154</b>		
22	5.6	53.3	0.70	0.9965	1.0354	<b>0.0815</b>	<b>1.15</b>	<b>2.4969</b>		
23	5.8	51.2	0.73	0.9957	1.0360	<b>0.0846</b>	<b>1.21</b>	<b>2.5814</b>		
24	5.7	49.4	0.76	1.0166	1.0583	<b>0.0876</b>	<b>1.27</b>	<b>2.6691</b>		
25	5.3	48.1	0.78	1.0109	1.0499	<b>0.0817</b>	<b>1.32</b>	<b>2.7508</b>		
26	5.6	47.0	0.80	1.0105	1.0497	<b>0.0821</b>	<b>1.37</b>	<b>2.8329</b>		
27	5.7	46.4	0.81	1.0129	1.0519	<b>0.0817</b>	<b>1.43</b>	<b>2.9146</b>		
28	5.3	45.6	0.82	1.0154	1.0529	<b>0.0784</b>	<b>1.48</b>	<b>2.9930</b>		
29	5.7	45.0	0.83	1.0128	1.0494	<b>0.0764</b>	<b>1.54</b>	<b>3.0694</b>		
30	5.6	44.6	0.84	1.0133	1.0497	<b>0.0760</b>	<b>1.59</b>	<b>3.1455</b>		
31	5.5	44.4	0.84	1.0137	1.0488	<b>0.0732</b>	<b>1.64</b>	<b>3.2186</b>		
32	5.6	44.2	0.85	1.0144	1.0498	<b>0.0738</b>	<b>1.70</b>	<b>3.2925</b>		
33	5.8	44.0	0.85	1.0169	1.0532	<b>0.0758</b>	<b>1.76</b>	<b>3.3683</b>		
34	5.6	43.8	0.86	1.0181	1.0556	<b>0.0784</b>	<b>1.81</b>	<b>3.4467</b>		
35	5.7	43.6	0.86	1.0163	1.0493	<b>0.0686</b>	<b>1.87</b>	<b>3.5153</b>		

# **COLUMN DATA SHEET** (abbreviations as defined by sections 4.7 & 5)

**Trial No.:** 9      **Rate(ml/min)=** 5.0      **T(°C)** = 20.5

**Surfactant**       $C_{\text{Triton}} \text{ (CMC)} = 0.50$        $\sigma_i \text{ (mN/m)} = 41.5$

**Pore Volume**       $M_i \text{ (g)} = 887.33$        $M_f \text{ (g)} = 356.15$        $M_S \text{ (g)} = 531.188$

$V_P \text{ (ml)} = V_C - [M_S/\rho_S] = 101.4$        $V_{O,i} \text{ (ml)} = 0.75(V_P) = 76.1$

$V_{O,r} \text{ (ml)} = V_{O,i} - V_{O,d} = 25.0$        $V_{O,d} \text{ (ml)} = 51.1$

**Oil Recovery**       $M_{O,e} = M_{O+\text{pan}} - M_{\text{pan}}$        $M_{O,t} = 2M_{O,e}/[1 - 1.16M_{O,e}]$

No.	V(ml)	$\sigma$	$\sigma_i / \sigma$	$M_{\text{pan}}$	$M_{O+\text{pan}}$	$M_{O,t} \text{ (g)}$	$\Sigma V_P$	$\Sigma M_{O,e}$
1	6.0	74.8	0.55	0.9923	1.0487	0.1207	0.06	0.1207
2	5.9	74.7	0.56	0.9927	1.1767	0.4679	0.12	0.5886
3	5.9	74.8	0.55	0.9934	1.1614	0.4173	0.18	1.0059
4	6.2	74.9	0.55	0.9979	1.1109	0.2601	0.24	1.2660
5	5.8	74.8	0.55	0.9887	1.1185	0.3056	0.29	1.5716
6	6.1	74.7	0.56	0.9941	1.1141	0.2788	0.35	1.8504
7	5.9	74.6	0.56	0.9846	1.1084	0.2891	0.41	2.1396
8	6.1	74.7	0.56	0.9921	1.1187	0.2968	0.47	2.4363
9	5.9	74.8	0.55	0.9949	1.0949	0.2262	0.53	2.6626
10	5.9	74.6	0.56	0.9934	1.0981	0.2384	0.59	2.9009
11	5.8	74.7	0.56	0.9928	1.0869	0.2113	0.65	3.1122
12	6.1	74.6	0.56	0.9929	1.0692	0.1674	0.71	3.2796
13	6.1	74.6	0.56	0.9878	1.0862	0.2222	0.77	3.5018
14	6.1	74.5	0.56	0.9909	1.0675	0.1681	0.83	3.6699
15	6.2	74.6	0.56	0.9895	1.0422	0.1123	0.89	3.7822
16	6.1	74.7	0.56	0.9878	1.0877	0.2260	0.95	4.0082
17	6.3	74.6	0.56	0.9858	1.0570	0.1552	1.01	4.1634
18	5.9	74.5	0.56	0.9860	1.0280	0.0883	1.07	4.2517
19	5.7	74.6	0.56	0.9908	1.0410	0.1066	1.12	4.3583
20	5.8	74.7	0.56	0.9870	1.0399	0.1127	1.18	4.4710
21	5.9	74.6	0.56	0.9820	1.0486	0.1444	1.24	4.6154
22	6.0	74.5	0.56	0.9817	1.0212	0.0828	1.30	4.6982
23	6.1	74.6	0.56	0.9846	1.0214	0.0769	1.36	4.7751
24	5.7	66.5	0.62	0.9862	1.0058	0.0401	1.41	4.8152
25	5.7	60.0	0.69	0.9863	1.0054	0.0391	1.47	4.8542
26	5.9	56.5	0.73	0.9859	1.0403	0.1161	1.53	4.9704
27	5.4	54.2	0.77	0.9866	1.0013	0.0299	1.58	5.0003
28	5.9	52.8	0.79	0.9887	1.0040	0.0312	1.64	5.0314
29	5.9	51.4	0.81	0.9944	1.0262	0.0660	1.70	5.0975
30	5.7	50.0	0.83	0.9891	1.0206	0.0654	1.76	5.1629
31	6.0	49.1	0.85	0.9915	1.0398	0.1023	1.81	5.2652
32	5.7	48.3	0.86	0.9916	1.0598	0.1481	1.87	5.4133
33	6.0	47.9	0.87	0.9896	1.0231	0.0697	1.93	5.4830
34	6.0	47.5	0.87	0.9924	1.0580	0.1420	1.99	5.6250
35	6.0	47.3	0.88	1.0000	1.0299	0.0619	2.05	5.6870

# **COLUMN DATA SHEET** (abbreviations as defined by sections 4.7 & 5)

**Trial No.:** 10    **Rate(ml/min)=** 50.0    **T(°C)** = 20.5

**Surfactant**     $C_{\text{Triton}} \text{ (CMC)} = 0.50$      $\sigma_i \text{ (mN/m)} = 41.5$

**Pore Volume**     $M_i \text{ (g)} = 884.64$      $M_f \text{ (g)} = 355.52$      $M_S \text{ (g)} = 529.12$

$V_P \text{ (ml)} = V_C - [M_S/\rho_S] = 102.2$      $V_{O,i} \text{ (ml)} = 0.75(V_P) = 76.6$

$V_{O,r} \text{ (ml)} = V_{O,i} - V_{O,d} = 26.4$      $V_{O,d} \text{ (ml)} = 50.2$

**Oil Recovery**     $M_{O,e} = M_{O+\text{pan}} - M_{\text{pan}}$      $M_{O,t} = 2M_{O,e}/[1 - 1.16M_{O,e}]$

**Pressure**

No.	V(ml)	$\sigma$	$\sigma_i / \sigma$	$M_{\text{pan}}$	$M_{O+\text{pan}}$	$M_{O,t} \text{ (g)}$	$\Sigma V_P$	$\Sigma M_{O,t}$	$\Sigma V_{\text{pore}}$	$\Delta P \text{ (Hg)}$
1	6.5	74.7	0.56	0.9878	1.1446	<b>0.3833</b>	<b>0.06</b>	<b>0.3833</b>	0.12	40.0
2	5.9	74.8	0.55	0.9891	1.0691	<b>0.1764</b>	<b>0.12</b>	<b>0.5597</b>	0.24	39.0
3	5.6	74.5	0.56	0.9917	1.0435	<b>0.1102</b>	<b>0.18</b>	<b>0.6699</b>	0.37	39.0
4	5.7	74.6	0.56	0.9941	1.0405	<b>0.0981</b>	<b>0.23</b>	<b>0.7680</b>	0.49	39.0
5	5.6	74.6	0.56	0.9920	1.0416	<b>0.1053</b>	<b>0.29</b>	<b>0.8733</b>	0.61	39.0
6	5.6	74.5	0.56	0.9897	1.0423	<b>0.1120</b>	<b>0.34</b>	<b>0.9853</b>	0.73	38.0
7	5.8	74.8	0.55	0.9877	1.0405	<b>0.1125</b>	<b>0.40</b>	<b>1.0978</b>	0.86	37.5
8	5.4	74.7	0.56	0.9865	1.0359	<b>0.1048</b>	<b>0.45</b>	<b>1.2026</b>	0.98	37.0
9	5.6	74.6	0.56	0.9876	1.0373	<b>0.1055</b>	<b>0.51</b>	<b>1.3081</b>	1.10	36.5
10	5.7	74.6	0.56	0.9889	1.0434	<b>0.1164</b>	<b>0.56</b>	<b>1.4244</b>	1.22	34.5
11	5.6	74.7	0.56	0.9871	1.0398	<b>0.1123</b>	<b>0.62</b>	<b>1.5367</b>	1.35	33.5
12	5.6	74.8	0.55	0.9853	1.0355	<b>0.1066</b>	<b>0.67</b>	<b>1.6433</b>	1.47	33.0
13	5.7	74.7	0.56	0.9870	1.0392	<b>0.1111</b>	<b>0.73</b>	<b>1.7544</b>	1.59	32.5
14	5.3	74.8	0.55	0.9860	1.0310	<b>0.0950</b>	<b>0.78</b>	<b>1.8494</b>	1.71	32.0
15	5.7	74.8	0.55	0.9906	1.0410	<b>0.1071</b>	<b>0.83</b>	<b>1.9564</b>	1.83	31.5
16	5.5	74.7	0.56	0.9909	1.0373	<b>0.0981</b>	<b>0.89</b>	<b>2.0545</b>	1.96	31.5
17	5.8	74.8	0.55	0.9930	1.0445	<b>0.1095</b>	<b>0.95</b>	<b>2.1641</b>		
18	5.8	70.0	0.59	0.9933	1.0404	<b>0.0996</b>	<b>1.00</b>	<b>2.2637</b>		
19	5.6	65.6	0.63	0.9946	1.0447	<b>0.1064</b>	<b>1.06</b>	<b>2.3701</b>		
20	5.3	62.0	0.67	0.9951	1.0410	<b>0.0970</b>	<b>1.11</b>	<b>2.4671</b>		
21	5.6	58.9	0.70	0.9954	1.0413	<b>0.0970</b>	<b>1.16</b>	<b>2.5640</b>		
22	5.6	56.0	0.74	0.9934	1.0380	<b>0.0941</b>	<b>1.22</b>	<b>2.6581</b>		
23	5.8	54.5	0.76	0.9908	1.0348	<b>0.0927</b>	<b>1.27</b>	<b>2.7508</b>		
24	5.6	53.3	0.78	0.9899	1.0311	<b>0.0865</b>	<b>1.33</b>	<b>2.8374</b>		
25	5.6	52.3	0.79	0.9909	1.0335	<b>0.0896</b>	<b>1.38</b>	<b>2.9270</b>		
26	5.3	50.7	0.82	0.9880	1.0271	<b>0.0819</b>	<b>1.44</b>	<b>3.0089</b>		
27	5.7	49.3	0.84	0.9888	1.0298	<b>0.0861</b>	<b>1.49</b>	<b>3.0950</b>		
28	5.6	48.8	0.85	0.9903	1.0296	<b>0.0824</b>	<b>1.55</b>	<b>3.1774</b>		
29	5.7	48.5	0.86	0.9913	1.0291	<b>0.0791</b>	<b>1.60</b>	<b>3.2564</b>		
30	5.6	48.4	0.86	0.9907	1.0294	<b>0.0810</b>	<b>1.66</b>	<b>3.3375</b>		
31	5.8	48.2	0.86	0.9897	1.0264	<b>0.0767</b>	<b>1.71</b>	<b>3.4141</b>		
32	5.3	48.0	0.86	0.9900	1.0250	<b>0.0730</b>	<b>1.77</b>	<b>3.4871</b>		
33	5.8	47.9	0.87	0.9890	1.0280	<b>0.0817</b>	<b>1.82</b>	<b>3.5688</b>		
34	5.6	47.7	0.87	0.9883	1.0232	<b>0.0727</b>	<b>1.88</b>	<b>3.6415</b>		
35	5.8	47.5	0.87	0.9890	1.0250	<b>0.0751</b>	<b>1.93</b>	<b>3.7167</b>		

**COLUMN DATA SHEET** (abbreviations as defined by sections 4.7 & 5)Trial No.: 11    Rate(ml/min)= 5.0     $T(^{\circ}\text{C}) = 20.0$ Surfactant     $C_{\text{Triton}} \text{ (CMC)} = 2.00$      $\sigma_i \text{ (mN/m)} = 33.5$ Pore Volume     $M_i \text{ (g)} = 884.59$      $M_f \text{ (g)} = 354.82$      $M_S \text{ (g)} = 529.77$  $V_P \text{ (ml)} = V_C - [M_S/\rho_S] = 102.0$      $V_{O,i} \text{ (ml)} = 0.75(V_P) = 76.5$  $V_{O,r} \text{ (ml)} = V_{O,i} - V_{O,d} = 26.0$      $V_{O,d} \text{ (ml)} = 50.5$ Oil Recovery     $M_{O,e} = M_{O+\text{pan}} - M_{\text{pan}}$      $M_{O,t} = 2M_{O,e}/[1 - 1.16M_{O,e}]$ 

No.	V(ml)	$\sigma$	$\sigma_i / \sigma$	$M_{\text{pan}}$	$M_{O+\text{pan}}$	$M_{O,t} \text{ (g)}$	$\Sigma V_P$	$\Sigma M_{O,t}$
1	5.9	74.8	0.45	1.0055	1.0740	<b>0.1488</b>	<b>0.06</b>	<b>0.1488</b>
2	5.4	74.6	0.45	1.0064	1.1919	<b>0.4727</b>	<b>0.11</b>	<b>0.6216</b>
3	6.1	74.3	0.45	1.0049	1.1996	<b>0.5030</b>	<b>0.17</b>	<b>1.1246</b>
4	5.8	74.5	0.45	1.0036	1.1744	<b>0.4260</b>	<b>0.23</b>	<b>1.5506</b>
5	5.3	74.7	0.45	1.0035	1.1447	<b>0.3377</b>	<b>0.28</b>	<b>1.8883</b>
6	5.8	75.0	0.45	1.0025	1.1265	<b>0.2897</b>	<b>0.34</b>	<b>2.1780</b>
7	5.8	74.6	0.45	1.0087	1.1478	<b>0.3317</b>	<b>0.39</b>	<b>2.5097</b>
8	5.5	74.8	0.45	1.0084	1.1100	<b>0.2304</b>	<b>0.45</b>	<b>2.7401</b>
9	3.8	74.9	0.45	1.0076	1.1208	<b>0.2606</b>	<b>0.48</b>	<b>3.0007</b>
10	5.3	75.0	0.45	1.0074	1.1230	<b>0.2670</b>	<b>0.54</b>	<b>3.2677</b>
11	5.9	74.9	0.45	1.0064	1.0993	<b>0.2082</b>	<b>0.59</b>	<b>3.4759</b>
12	6.6	75.2	0.45	1.0075	1.1142	<b>0.2435</b>	<b>0.66</b>	<b>3.7195</b>
13	5.6	74.9	0.45	1.0053	1.0792	<b>0.1617</b>	<b>0.71</b>	<b>3.8811</b>
14	5.4	75.1	0.45	1.0078	1.0920	<b>0.1866</b>	<b>0.77</b>	<b>4.0678</b>
15	6.1	75.1	0.45	1.0104	1.1000	<b>0.2000</b>	<b>0.83</b>	<b>4.2678</b>
16	5.9	74.6	0.45	1.0147	1.0969	<b>0.1817</b>	<b>0.88</b>	<b>4.4495</b>
17	5.7	74.8	0.45	1.0140	1.0772	<b>0.1364</b>	<b>0.94</b>	<b>4.5859</b>
18	5.9	75.0	0.45	1.0119	1.0525	<b>0.0852</b>	<b>1.00</b>	<b>4.6711</b>
19	5.9	74.4	0.45	1.0095	1.0492	<b>0.0832</b>	<b>1.06</b>	<b>4.7543</b>
20	5.9	63.3	0.53	1.0115	1.0565	<b>0.0950</b>	<b>1.11</b>	<b>4.8493</b>
21	5.9	54.6	0.61	1.0131	1.0388	<b>0.0530</b>	<b>1.17</b>	<b>4.9023</b>
22	5.7	50.5	0.66	1.0119	1.0562	<b>0.0934</b>	<b>1.23</b>	<b>4.9957</b>
23	5.9	47.8	0.70	1.0092	1.0992	<b>0.2010</b>	<b>1.29</b>	<b>5.1967</b>
24	5.8	45.3	0.74	1.0054	1.0315	<b>0.0538</b>	<b>1.34</b>	<b>5.2505</b>
25	5.9	44.0	0.76	1.0062	1.0779	<b>0.1564</b>	<b>1.40</b>	<b>5.4069</b>
26	6.0	43.2	0.78	1.0071	1.0609	<b>0.1148</b>	<b>1.46</b>	<b>5.5217</b>
27	6.0	42.6	0.79	1.0073	1.0371	<b>0.0617</b>	<b>1.52</b>	<b>5.5834</b>
28	6.0	42.1	0.80	1.0051	1.0308	<b>0.0530</b>	<b>1.58</b>	<b>5.6364</b>
29	5.9	41.7	0.80	1.0035	1.0221	<b>0.0380</b>	<b>1.64</b>	<b>5.6744</b>
30	6.0	41.4	0.81	1.0068	1.0392	<b>0.0673</b>	<b>1.69</b>	<b>5.7417</b>
31	6.1	41.2	0.81	1.0032	1.0172	<b>0.0285</b>	<b>1.75</b>	<b>5.7702</b>
32	5.9	41.1	0.82	1.0024	1.0342	<b>0.0660</b>	<b>1.81</b>	<b>5.8362</b>
33	6.0	41.0	0.82	1.0057	1.0360	<b>0.0628</b>	<b>1.87</b>	<b>5.8990</b>
34	5.8	40.9	0.82	1.0075	1.0295	<b>0.0452</b>	<b>1.93</b>	<b>5.9442</b>
35	5.9	40.8	0.82	1.0010	1.0224	<b>0.0439</b>	<b>1.99</b>	<b>5.9881</b>

**COLUMN DATA SHEET** (abbreviations as defined by sections 4.7 & 5)

Trial No.: 12    Rate(ml/min)= 50.0    T(°C) = 20.2

Surfactant     $C_{\text{Triton}} \text{ (CMC)} = 2.00$      $\sigma_i \text{ (mN/m)} = 33.5$ Pore Volume     $M_i \text{ (g)} = 883.57$      $M_f \text{ (g)} = 354.84$      $M_S \text{ (g)} = 528.73$  $V_P \text{ (ml)} = V_C - [M_S/\rho_S] = 102.3$      $V_{O,i} \text{ (ml)} = 0.75(V_P) = 76.8$  $V_{O,r} \text{ (ml)} = V_{O,i} - V_{O,d} = 25.8$      $V_{O,d} \text{ (ml)} = 51.0$ Oil Recovery     $M_{O,e} = M_{O+\text{pan}} - M_{\text{pan}}$      $M_{O,t} = 2M_{O,e}/[1 - 1.16M_{O,e}]$ Pressure

No.	V(ml)	$\sigma$	$\sigma_i / \sigma$	$M_{\text{pan}}$	$M_{O+\text{pan}}$	$M_{O,t} \text{ (g)}$	$\Sigma V_P$	$\Sigma M_{O,t}$	$\Sigma V_{\text{pore}}$	$\Delta P \text{ (Hg)}$
1	8.0	74.7	0.45	1.0048	1.2094	<b>0.5366</b>	<b>0.08</b>	<b>0.5366</b>	0.12	50.0
2	5.6	74.5	0.45	1.0056	1.1044	<b>0.2232</b>	<b>0.13</b>	<b>0.7597</b>	0.24	47.0
3	5.8	75.3	0.44	1.0660	1.0875	<b>0.0441</b>	<b>0.19</b>	<b>0.8038</b>	0.37	47.0
4	5.8	74.8	0.45	1.0139	1.0717	<b>0.1239</b>	<b>0.25</b>	<b>0.9277</b>	0.49	44.0
5	5.7	74.7	0.45	1.0083	1.0853	<b>0.1691</b>	<b>0.30</b>	<b>1.0968</b>	0.61	42.0
6	5.8	74.6	0.45	1.0038	1.0811	<b>0.1698</b>	<b>0.36</b>	<b>1.2667</b>	0.73	41.0
7	5.9	74.7	0.45	1.0044	1.0756	<b>0.1552</b>	<b>0.42</b>	<b>1.4219</b>	0.85	39.5
8	5.5	74.8	0.45	1.0070	1.0748	<b>0.1472</b>	<b>0.47</b>	<b>1.5691</b>	0.98	35.0
9	5.1	74.7	0.45	1.0071	1.0710	<b>0.1380</b>	<b>0.52</b>	<b>1.7071</b>	1.10	33.0
10	5.8	74.9	0.45	1.0051	1.0707	<b>0.1420</b>	<b>0.58</b>	<b>1.8491</b>	1.22	32.5
11	5.7	75.1	0.45	1.0044	1.0688	<b>0.1392</b>	<b>0.63</b>	<b>1.9883</b>	1.34	32.0
12	5.6	75.1	0.45	1.0046	1.0620	<b>0.1230</b>	<b>0.69</b>	<b>2.1113</b>	1.47	31.0
13	5.7	74.8	0.45	1.0046	1.0662	<b>0.1327</b>	<b>0.74</b>	<b>2.2440</b>	1.59	30.5
14	5.5	74.7	0.45	1.0043	1.0605	<b>0.1202</b>	<b>0.80</b>	<b>2.3642</b>	1.71	30.0
15	5.8	68.3	0.49	1.0024	1.0594	<b>0.1221</b>	<b>0.85</b>	<b>2.4863</b>	1.83	29.5
16	5.7	60.1	0.56	1.0031	1.0651	<b>0.1336</b>	<b>0.91</b>	<b>2.6199</b>	1.95	29.5
17	5.9	56.5	0.59	0.9951	1.0559	<b>0.1308</b>	<b>0.97</b>	<b>2.7507</b>		
18	6.0	51.6	0.65	0.9951	1.0521	<b>0.1221</b>	<b>1.02</b>	<b>2.8728</b>		
19	5.7	48.8	0.69	0.9995	1.0531	<b>0.1143</b>	<b>1.08</b>	<b>2.9871</b>		
20	5.4	46.9	0.71	1.0019	1.0446	<b>0.0899</b>	<b>1.13</b>	<b>3.0770</b>		
21	5.6	45.3	0.74	1.0051	1.0458	<b>0.0854</b>	<b>1.19</b>	<b>3.1624</b>		
22	5.7	44.0	0.76	1.0046	1.0439	<b>0.0824</b>	<b>1.24</b>	<b>3.2448</b>		
23	5.9	43.3	0.77	1.0106	1.0488	<b>0.0799</b>	<b>1.30</b>	<b>3.3247</b>		
24	5.7	42.7	0.78	1.0073	1.0453	<b>0.0795</b>	<b>1.36</b>	<b>3.4042</b>		
25	5.6	42.2	0.79	1.0090	1.0476	<b>0.0808</b>	<b>1.41</b>	<b>3.4850</b>		
26	5.4	41.8	0.80	1.0144	1.0481	<b>0.0701</b>	<b>1.46</b>	<b>3.5552</b>		
27	5.8	41.5	0.81	1.0146	1.0533	<b>0.0810</b>	<b>1.52</b>	<b>3.6362</b>		
28	5.7	41.3	0.81	1.0153	1.0493	<b>0.0708</b>	<b>1.58</b>	<b>3.7070</b>		
29	5.7	41.1	0.82	1.0121	1.0467	<b>0.0721</b>	<b>1.63</b>	<b>3.7791</b>		
30	5.6	41.0	0.82	1.0119	1.0486	<b>0.0767</b>	<b>1.69</b>	<b>3.8558</b>		
31	3.1	40.9	0.82	1.0142	1.0376	<b>0.0481</b>	<b>1.72</b>	<b>3.9039</b>		
32	5.4	40.8	0.82	1.0129	1.0470	<b>0.0710</b>	<b>1.77</b>	<b>3.9749</b>		
33	5.8	40.7	0.82	1.0127	1.0488	<b>0.0754</b>	<b>1.83</b>	<b>4.0502</b>		
34	5.7	40.6	0.83	1.0148	1.0496	<b>0.0725</b>	<b>1.88</b>	<b>4.1227</b>		
35	5.8	40.6	0.83	1.0165	1.0508	<b>0.0714</b>	<b>1.94</b>	<b>4.1942</b>		

## **APPENDIX B:**

Hexane extraction trials



## HEXANE EXTRACTION TRIALS

(abbreviations as defined in section 5.2)

**Evaporation Period: 18 hours**

Mass check for constant volume of mineral oil added to test tubes using pipette

Pan no.	M <sub>pan</sub>	M <sub>O+pan</sub>	M <sub>O+pan</sub> (18 hrs)	M <sub>pipette</sub>
1	1.3154	1.3877	1.3871	0.0717
2	1.3128	1.3878	1.3865	0.0737
3	1.3150	1.3894	1.3886	0.0736
4	1.3165	1.3941	1.3930	0.0765

**Average (g) 0.0739**

Mass of mineral oil determined from hexane extraction procedure

**Note:** - 1 mL lipophilic phase (oil & hexane) used for extractions

- Oil concentration of lipophilic extraction is M<sub>O,e</sub> per mL of hexane

- Mass oil originally in tube:  $M_{O,t} = 2 \cdot M_{O,e} / (1 - 1.16 \cdot M_{O,e})$

Replicate	C <sub>Triton</sub> (CMC)	M <sub>pan</sub>	M <sub>O+pan</sub>	M <sub>O,e</sub>	M <sub>O,t</sub>
1	0	1.3184	1.3529	0.0345	0.0719
2	0	1.3177	1.3504	0.0327	0.0748
3	0	1.3150	1.3504	0.0354	0.0738
4	0	1.3118	1.3473	0.0355	0.0740
5	0.5	1.3192	1.3563	0.0371	0.0775
6	0.5	1.3191	1.3535	0.0344	0.0717
7	0.5	1.3150	1.3516	0.0366	0.0764
8	0.5	1.3141	1.3503	0.0362	0.0756
9	1	1.3129	1.3521	0.0392	0.0821
10	1	1.3118	1.3480	0.0362	0.0756
11	1	1.3138	1.3493	0.0355	0.0740
12	1	1.3158	1.3517	0.0359	0.0749
13	2	1.3137	1.3538	0.0401	0.0841
14	2	1.3186	1.3572	0.0386	0.0808
15	2	1.3122	1.3496	0.0374	0.0782
16	2	1.3139	1.3518	0.0379	0.0793

**Calculated average mass oil originally in test tube (g): 0.0766**

**Percent difference from mass oil originally added to test tube: 3.6%**

## HEXANE EXTRACTION TRIALS

(abbreviations as defined in section 5.2)

Evaporation Period: 24 hours

Mass check for constant volume of mineral oil added to test tubes using pipette

Pan no.	M <sub>pan</sub>	M <sub>O+pan</sub>	M <sub>O+pan</sub> (18 hrs)	M <sub>pipette</sub>
1	1.3154	1.3877	1.3869	0.0715
2	1.3128	1.3878	1.3861	0.0733
3	1.3150	1.3894	1.3881	0.0731
4	1.3165	1.3941	1.3926	0.0761

**Average (g) 0.0735**

Mass of mineral oil determined from hexane extraction procedure

- Note:** - 1 mL lipophilic phase (oil & hexane) used for extractions  
 - Oil concentration of lipophilic extraction is M<sub>O,e</sub> per mL of hexane  
 - Mass oil originally in tube:  $M_{O,t} = 2 \cdot M_{O,e} / (1 - 1.16 \cdot M_{O,e})$

Replicate	C <sub>Triton</sub> (CMC)	M <sub>pan</sub>	M <sub>O+pan</sub>	M <sub>O,e</sub>	M <sub>O,t</sub>
1	0	1.3184	1.3525	0.0341	0.0710
2	0	1.3177	1.3500	0.0323	0.0738
3	0	1.3150	1.3499	0.0349	0.0727
4	0	1.3118	1.3470	0.0352	0.0734
5	0.5	1.3192	1.3558	0.0366	0.0764
6	0.5	1.3191	1.3533	0.0342	0.0712
7	0.5	1.3150	1.3514	0.0364	0.0760
8	0.5	1.3141	1.3500	0.0359	0.0749
9	1	1.3129	1.3518	0.0389	0.0815
10	1	1.3118	1.3477	0.0359	0.0749
11	1	1.3138	1.3491	0.0353	0.0736
12	1	1.3158	1.3515	0.0357	0.0745
13	2	1.3137	1.3536	0.0399	0.0837
14	2	1.3186	1.3568	0.0382	0.0799
15	2	1.3122	1.3493	0.0371	0.0775
16	2	1.3139	1.3517	0.0378	0.0791

**Calculated average mass oil originally in test tube (g): 0.0759**

**Percent difference from mass oil originally added to test tube: 3.3%**

## HEXANE EXTRACTION TRIALS

(abbreviations as defined in section 5.2)

Evaporation Period: 42 hours

Mass check for constant volume of mineral oil added to test tubes using pipette

Pan no.	M <sub>pan</sub>	M <sub>O+pan</sub>	M <sub>O+pan</sub> (18 hrs)	M <sub>pipette</sub>
1	1.3154	1.3877	1.3863	0.0709
2	1.3128	1.3878	1.3858	0.0730
3	1.3150	1.3894	1.3875	0.0725
4	1.3165	1.3941	1.3920	0.0755

**Average (g) 0.0730**

Mass of mineral oil determined from hexane extraction procedure

- Note:** - 1 mL lipophilic phase (oil & hexane) used for extractions  
 - Oil concentration of lipophilic extraction is M<sub>O,e</sub> per mL of hexane  
 - Mass oil originally in tube:  $M_{O,t} = 2 \cdot M_{O,e} / (1 - 1.16 \cdot M_{O,e})$

Replicate	C <sub>Triton</sub> (CMC)	M <sub>pan</sub>	M <sub>O+pan</sub>	M <sub>O,e</sub>	M <sub>O,t</sub>
1	0	1.3184	1.3520	0.0336	0.0699
2	0	1.3177	1.3494	0.0317	0.0724
3	0	1.3150	1.3495	0.0345	0.0719
4	0	1.3118	1.3466	0.0348	0.0725
5	0.5	1.3192	1.3554	0.0362	0.0756
6	0.5	1.3191	1.3529	0.0338	0.0704
7	0.5	1.3150	1.3511	0.0361	0.0754
8	0.5	1.3141	1.3496	0.0355	0.0740
9	1	1.3129	1.3511	0.0382	0.0799
10	1	1.3118	1.3471	0.0353	0.0736
11	1	1.3138	1.3486	0.0348	0.0725
12	1	1.3158	1.3511	0.0353	0.0736
13	2	1.3137	1.3530	0.0393	0.0824
14	2	1.3186	1.3565	0.0379	0.0793
15	2	1.3122	1.3491	0.0369	0.0771
16	2	1.3139	1.3512	0.0373	0.0780

**Calculated average mass oil originally in test tube (g): 0.0749**

**Percent difference from mass oil originally added to test tube: 2.6%**

## HEXANE EXTRACTION TRIALS

(abbreviations as defined in section 5.2)

**Evaporation Period: 48 hours**

Mass check for constant volume of mineral oil added to test tubes using pipette

Pan no.	M <sub>pan</sub>	M <sub>O+pan</sub>	M <sub>O+pan</sub> (18 hrs)	M <sub>pipette</sub>
1	1.3154	1.3877	1.3861	0.0707
2	1.3128	1.3878	1.3856	0.0728
3	1.3150	1.3894	1.3873	0.0723
4	1.3165	1.3941	1.3918	0.0753

**Average (g) 0.0728**

Mass of mineral oil determined from hexane extraction procedure

- Note:** - 1 mL lipophilic phase (oil & hexane) used for extractions  
 - Oil concentration of lipophilic extraction is M<sub>O,e</sub> per mL of hexane  
 - Mass oil originally in tube:  $M_{O,t} = 2 \cdot M_{O,e} / (1 - 1.16 \cdot M_{O,e})$

Replicate	C <sub>Triton</sub> (CMC)	M <sub>pan</sub>	M <sub>O+pan</sub>	M <sub>O,e</sub>	M <sub>O,t</sub>
1	0	1.3184	1.3518	0.0334	0.0695
2	0	1.3177	1.3494	0.0317	0.0724
3	0	1.3150	1.3493	0.0343	0.0714
4	0	1.3118	1.3464	0.0346	0.0721
5	0.5	1.3192	1.3552	0.0360	0.0751
6	0.5	1.3191	1.3527	0.0336	0.0699
7	0.5	1.3150	1.3509	0.0359	0.0749
8	0.5	1.3141	1.3494	0.0353	0.0736
9	1	1.3129	1.3509	0.0380	0.0795
10	1	1.3118	1.3469	0.0351	0.0732
11	1	1.3138	1.3484	0.0346	0.0721
12	1	1.3158	1.3511	0.0353	0.0736
13	2	1.3137	1.3528	0.0391	0.0819
14	2	1.3186	1.3562	0.0376	0.0786
15	2	1.3122	1.3489	0.0367	0.0767
16	2	1.3139	1.3509	0.0370	0.0773

**Calculated average mass oil originally in test tube (g): 0.0745**

**Percent difference from mass oil originally added to test tube: 2.4%**

## **APPENDIX C:**

### Sample calculations

## SAMPLE CALCULATIONS (Heading numbers correspond with those of thesis)

All sample calculations are performed for the 0 CMC solution delivered at  $50 \text{ mL} \cdot \text{min}^{-1}$ , other than for section 7.1.2. In section 7.1.2, the 0.5 CMC solution delivered at  $5 \text{ mL} \cdot \text{min}^{-1}$  is used to calculate the lowest Peclet Number ( $N_p$ ) for all the trial conducted, as well as for the corresponding longitudinal hydrodynamic dispersion coefficient ( $D_L$ ).

All symbols are as defined in the thesis text.

### 7.1.1 Reynolds number ( $N_R$ )

$$q_A = Q / A_C = [(50 \times 10^{-6} \text{ m}^3 \cdot \text{min}^{-1}) (\text{min} / 60 \text{ s})] / [1.20 \times 10^{-3} \text{ m}^2] = 6.98 \times 10^{-4} \text{ m} \cdot \text{s}^{-1}$$

$$N_R = [\rho_A q_A d_p] / \mu_A = [(998 \text{ kg} \cdot \text{m}^{-3})(6.98 \times 10^{-4} \text{ m} \cdot \text{s}^{-1})(7.0 \times 10^{-4} \text{ m})] / (0.984 \text{ mN s} \cdot \text{m}^{-2}) = 0.50$$

### 7.1.2 Peclet Number ( $N_p$ )

$$q_A = Q / A_C = [(5 \times 10^{-6} \text{ m}^3 \cdot \text{min}^{-1}) (\text{min} / 60 \text{ s})] / [1.20 \times 10^{-3} \text{ m}^2] = 6.98 \times 10^{-5} \text{ m} \cdot \text{s}^{-1}$$

$$n_e = n (1 - S_{N,r}) = (0.339) [1 - 0.251] = 0.254$$

$$v_A = q_A / n_e = (6.98 \times 10^{-5} \text{ m} \cdot \text{s}^{-1}) / (0.254) = 2.75 \times 10^{-4} \text{ m} \cdot \text{s}^{-1}$$

$$N_p = [v_A d_p] / D_d = [(2.75 \times 10^{-4} \text{ m} \cdot \text{s}^{-1})(7.0 \times 10^{-4} \text{ m})] / (2.24 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}) = 860$$

$$D_L = 1.8 N_p D_d = 1.8 (860) (2.24 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}) = 3.5 \times 10^{-7} \text{ m}^2 \cdot \text{s}^{-1}$$

### 7.1.3 Capillary number ( $N_C$ )

$$N_C = [\mu_A q_A] / \gamma_{AN} = [(0.984 \text{ mN s} \cdot \text{m}^{-2})(6.98 \times 10^{-4} \text{ m} \cdot \text{s}^{-1})] / (47.7 \text{ mN} \cdot \text{m}^{-1}) = 1.4 \times 10^{-5}$$

#### 7.1.4 Bond number ( $N_B$ )

$$k = [d_p^2 n^3] / [180(1 - n)^2] = [(7.0 \times 10^{-4} \text{m})^2 (0.339)^3] / [180(1 - 0.339)^2] = 2.4 \times 10^{-10} \text{ m}^2$$

$$S_e = [S_A - S_{A,r}] / [1 - S_{A,r}] = [0.749 - 0.25] / [1 - 0.25] = 0.665$$

$$k_{rA} = S_e^3 = (0.665)^3 = 0.295$$

$$k_e = k_{rA} k = (0.295) (2.4 \times 10^{-10} \text{ m}^2) = 7.1 \times 10^{-11} \text{ m}^2$$

$$N_B = [\Delta\rho g k_e] / \gamma_{AN} = [(998 - 862) \text{ kg} \cdot \text{m}^{-3} (9.806 \text{ m} \cdot \text{s}^{-2}) (7.1 \times 10^{-11} \text{ m}^2)] / (47.7 \text{ mN} \cdot \text{m}^{-1}) = 2.0 \times 10^{-6}$$

#### 7.1.5 Total trapping number ( $N_T$ )

$$N_T = N_C + N_B = 1.4 \times 10^{-5} + 2.0 \times 10^{-6} = 1.6 \times 10^{-5}$$