Experimental and Modelling Studies on the Phase Behaviour of Mutual Solvents and Their Transport Through Porous Media in Oil/Brine/Mutual Solvent Systems in the Context of Scale Inhibitor Squeeze Treatments

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Abstract

Oilfield scale is a significant problem in oil production which arises due to temperature and pressure changes and mixing of incompatible brines when a well is produced. The most successful and commonly used strategy for mitigating against oilfield scale is the application of scale inhibitor squeeze treatments. A squeeze treatment is applied to the production well, and involves several stages, which are: pre-flush, main treatment, over-flush, shut-in and back-production. During a treatment, a scale inhibitor adsorbs or precipitates into the formation, and its desorption/dissolution into the produced water when the well is put back into production prevents scale formation. A well must be re-squeezed before the scale inhibitor concentration in the produced water falls below the minimum inhibition concentration (MIC) required to prevent scaling.

This work focuses on the pre-flush stage of a squeeze treatment, in which mutual solvents are applied in order to prepare the well for a treatment. This is the least investigated aspect of squeeze treatments, and the one with the greatest opportunity for potential optimisation. Fundamental to understanding how to best apply mutual solvents (MS) in squeeze treatments, to achieve squeeze lifetime enhancements and to mitigate any formation damage risks, is understanding MS phase behaviour, the transport of MS through the porous medium and MS/mineral surface conditioning effects (e.g. wetting changes).

In this work, the phase behaviour of various mutual solvents is investigated in oil/brine/mutual solvent systems. Effects of salinity and chemistry are determined at field relevant conditions. The influence of scale inhibitors on phase behaviour is also investigated and mutual solvent blend design is examined. The work also develops a quantitative understanding of the phase behaviour of mutual solvents and employs that in the development of semi-empirical and thermodynamic models for describing the phase behaviour. Practical analytical tools are also developed to aid mutual solvent investigations as well as analysis in the presence of mutual solvents. Transport studies of MS in sand packs are used to investigate the transport of mutual solvents in single and multiphase systems. Numerous field solutions can be obtained from this work, but more importantly, this work enables and forms the basis for future mutual solvent investigations in the context of scale inhibitor squeeze treatments.
Dedication

To my mum, Baheya Ahmed Ebrahim, and my uncle, Abbas Ahmed Ebrahim.

*Daily, I aspire to fulfil the greatest lesson I learned from you – that:
The best I can do for myself is to work for the sake of learning,
And the best I can do for others is to learn for the sake of working.
To acquire knowledge, and therein lies my joy;
And to dedicate my life to the service of others, and therein lies my purpose.*

To my sister, Anwaar Arab.

*Trying to describe the warmth and silliness of our friendship,
the best I thought of was:

“I love you, you love me; We’re a happy family.
With a great big hug and a kiss from me to you;
Won’t you say you love me too?”*

To my family in Edinburgh, Oleg Ishkov, Anna Ishkova and Sophia Ishkova.

*You taught me, how much you taught,
Forever, to you, I’ll be grateful.
You taught me, so much you taught,
Without you, my life so fateful.*

And because I am a romantic fool, to a girl I am yet to meet.

*But my eyes will drink, when they see you;
But my feelings will flood, in the passing of your soul;
And my vision, in your eventual presence, will be whole;
And I hope, our days to come, will please you.*
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# Nomenclature

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<th>Definition</th>
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</thead>
<tbody>
<tr>
<td>[MIC]</td>
<td>Minimum inhibitor concentration</td>
</tr>
<tr>
<td>[SI]</td>
<td>Scale inhibitor concentration</td>
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</table>

## Chapter 2

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tr>
<td>$P_{o/w}$</td>
<td>Partition coefficient of the mutual solvent in n-octanol to water</td>
</tr>
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## Chapter 3

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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</thead>
<tbody>
<tr>
<td>$C_0$</td>
<td>Initial concentration</td>
</tr>
<tr>
<td>$D_o$</td>
<td>Outside diameter</td>
</tr>
<tr>
<td>$P_{o/w}$</td>
<td>Partition coefficient of the mutual solvent in n-octanol to water</td>
</tr>
<tr>
<td>$P_{o/w}(MS_i)$</td>
<td>Partition coefficient of mutual solvent (i)</td>
</tr>
<tr>
<td>$P_{o/w}(m − MS)$</td>
<td>Theoretical partition coefficient of a mutual solvent blend</td>
</tr>
<tr>
<td>$S_{or}$</td>
<td>Residual oil saturation</td>
</tr>
<tr>
<td>$c_i$</td>
<td>Concentration of ion (i)</td>
</tr>
<tr>
<td>$x_i$</td>
<td>Fraction of mutual solvent (i)</td>
</tr>
<tr>
<td>$z_i$</td>
<td>Charge of ion (i)</td>
</tr>
<tr>
<td>$\Delta[TDS]$</td>
<td>Three-phase total dissolved solids interval</td>
</tr>
<tr>
<td>$\Delta T$</td>
<td>Three-phase temperature interval</td>
</tr>
<tr>
<td>$C$</td>
<td>Final concentration</td>
</tr>
<tr>
<td>$I$</td>
<td>Ionic strength</td>
</tr>
<tr>
<td>$L$</td>
<td>Length</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
</tr>
<tr>
<td>$TDS$</td>
<td>Total dissolved solids</td>
</tr>
<tr>
<td>$WC$</td>
<td>Water cut</td>
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</table>

## Chapter 4

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
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<tr>
<td>$(x_i^k)_0$</td>
<td>Volume fraction of component (i) in phase (k) at ($t = 0$)</td>
</tr>
<tr>
<td>$C_k$</td>
<td>The intercept of three-phase analysis for phase (k)</td>
</tr>
<tr>
<td>$R_{kn}$</td>
<td>Phase fraction of phase (k) in sample (n)</td>
</tr>
<tr>
<td>$V^{k(n)}$</td>
<td>Volume of phase (k) at iteration (n)</td>
</tr>
</tbody>
</table>
\[ V_k \] Phase volume; \( k = u, m, l \) for upper, middle and lower phases
\[ V_{k}^{(n)} \] Volume of component \( k \) in phase \( k \) at iteration \( n \)
\[ V_{k}^{(n-1)} \] Volume of component \( k \) in phase \( k \) at iteration \( n-1 \)
\[ V_{kn} \] Volume of phase \( k \) in sample \( n \)
\[ V_n \] Feed volume in sample \( n \)
\[ m_k \] Slope of three-phase analysis for phase \( k \)
\[ x_{i=k}^k \] Volume fraction of component \( i = k \) in phase \( k \)
\[ x_{i}^k \] Volume fraction of component \( i \) in phase \( k \)
\[ x_{i}^{kn} \] Volume fraction of component \( i \) in phase \( k \) in sample \( n \)
\[ z_j \] Fixed feed volume of component \( j \)
\[ \rho_{i} \] Density \( i = o, B, MS \); for oil, brine and mutual solvent
\[ \Delta V_{i=k}^{(n)} \] Disturbance to the feed volume of component \( i = k \) at iteration \( n \)
\[ \Delta V_{i=k}^{(n)} \] Disturbance to the feed volume of component \( i \neq k \) at iteration \( n \)
\[ \Delta V_k^F \] Disturbance to the feed volume of component \( k \) at \( t = 0 \)
\[ C \] Number of components
\[ F \] Number of degrees of freedom
\[ P \] Number of phases
\[ V \] Feed volume
\[ X \] Three-phase composition vector
\[ t \] Time

**Chapter 5**

\( (X_{CP}, Y_{CP}) \) The centroid of the three-phase region in Cartesian coordinates
\( (X_f, Y_f) \) Feed composition in Cartesian coordinates
\( (X_m, Y_m) \) Phase composition in Cartesian coordinates
\( (x_{df}, y_{df}) \) Feed composition correction in the PDM in Cartesian coordinates*
\( (\Delta x_{df}, \Delta y_{df}) \) Feed composition correction excess in the PDM in Cartesian coordinates*

* PDM = Phase Displacement Method

\( (X, Y) \) Composition in Cartesian coordinates
\( [TS]_k \) Concentration of the tracer TS in the \( (k) \)-rich phase
\( L_C \) Corrected lower phase volume
\( P_o/MS \) Partition coefficient of a tracer between oil-rich and mutual solvent-rich phases
\( U_C \) Corrected upper phase volume

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\( V_o \) Volume of the overall mixture
\( V_S \) Volume of the source sample
\( V_{i\,0}^Z \) Estimated volume of component \((i)\) in phase \((Z)\)
\( V_i^F \) Volume of component \((i)\) in the feed
\( V_k \) Volume of phase \((k)\)
\( V_t \) Volume of the target mixture
\( Z_C \) Corrected feed volume
\( e_{2}^{CE} \) Subset of the 2nd convergence parameter for component balance corrections for phase \((Z)\)
\( e_{i}^{ZF} \) 1st convergence parameter for component balance corrections for component \((i)\)
\( x_{MS}^F \) Volume fraction of the mutual solvent in the feed
\( x_{MS}^Z \) Volume fraction of the mutual solvent in the phase exhibiting constant composition
\( x_{i\,0}^Z \) Estimated fraction of component \((i)\) in phase \((Z)\)
\( x_i^F \) Fraction of component \((i)\) in the feed
\( x_i^O \) Volume fraction of component \((i)\) in the overall mixture
\( x_i^S \) Volume fraction of component \((i)\) in the source sample
\( x_i^Z \) Volume fraction of component \((i)\) in phase \((Z)\)
\( x_{i}^t \) Volume fraction of component \((i)\) in the target mixture
\( \Delta V_i \) Volume of component \((i)\) used in the phase displacement
\( C \) Intercept
\( DP \) Decimal point precision for component balance corrections
\( F \) Feed volume
\( L \) Lower phase volume
\( U \) Upper phase volume
\( Z \) Phase volume
\( dX \) Minimisation steps for component balance corrections
\( dr \) Phase separation parameter for estimating phase separation in a two-phase system
\( ind \) The 2nd convergence parameter for component balance corrections
\( m \) Slope
\( n \) Mixing factor (source sample to target mixture) or the number of degrees of freedom

**Chapter 6**

\( \overline{a_0} \) Initial values set for \((a_{ji})\) used to calculate \((\overline{a})\) for a given system
\( \overline{a_{cm}} \) The \((a_{ji})\) set in \((R''\)) corresponding the minimum of \((ObjR)\)
\( \overline{a_{Fm}} \) The \((a_{ji})\) set at stage \((z)\) corresponding the minimum of \((ObjR)\)
\( x_{ij}^{\text{dom}j} \)  Fraction of component (i) in phase rich in dominant component (j)

\( x_{ijk}^{\text{cal}} \)  Calculated fraction of component (i) in phase (j) for sample (k)

\( x_{ijk}^{\text{exp}} \)  Experimental fraction of component (i) in phase (j) for sample (k)

\( x_{ij}^k \)  Fraction of component (i) phase (k)

\( z_{\text{domi}} \)  Feed fraction of dominant component (i)

\( \gamma_i \)  Activity coefficient of component (i)

\( \gamma_i^C \)  Combinatorial part of the activity coefficient of component (i)

\( \gamma_i^R \)  Residual part of the activity coefficient of component (i)

\( \gamma_i^k \)  Activity coefficient of component (i) in phase (k)

\( \theta_i \)  Area fraction of component (i)

\( \tau_{ji} \)  UNIQUAC parameter for the interaction of (j) with (i)

\( \Delta g_{\text{mix}} \)  Dimensionless Gibbs free energy for a mixture

\( N(R'') \)  Number of values in range (\( R'' \))

\( ObjE \)  Squared and weighted nonlinear equilibrium condition

\( ObjF \)  Objective function

\( ObjG \)  Squared and weighted dimensionless Gibbs free energy

\( ObjR \)  Composite objective function for calculating the (\( a_{ji} \)) parameters

\( R \)  User specified range for (\( a_{ji} \)) calculation

\( S \)  The number of the values that (\( a_{ji} \)) can take within range (\( R \))

\( T \)  Temperature

\( WF1 \)  Weighting factor for (\( ObjG \))

\( WF2 \)  Weighting factor for (\( ObjE \))

\( dS_0 \)  The step size for expanding range (\( R' \))

\( dS_z \)  The step size at stage (\( z \))

\( da_z \)  The parameter defining the region of uncertainty around all (\( a_{ji} \)) at stage (\( z \))

\( lb(R_{ji}^n) \)  The lower bound on (\( R_{ji}^n \))

\( ub(R_{ji}^n) \)  The upper bound on (\( R_{ji}^n \))

\( z \)  Coordination number

\( \alpha \)  The whole number positive multiplier used to define (\( da_z \))

\( \eta \)  Initialisation component-balance parameter

**Chapter 7**

\( A' \)  Ideal area intensity for the analyte

\( A_i \)  Area intensity for the analyte for run (i)
\( A_i' \)  Ideal area intensity for the analyte for run \((i)\)
\( A_m \)  Average area intensity for the analyte
\( IS' \)  Ideal area intensity for the internal standard
\( c_{\infty} \)  Speed of light
\( c_m \)  Average differentiation ratio
\( f_i \)  Quantity ratio for run \((i)\)
\( x_{MS}^{GC} \)  Fraction of mutual solvents with respect to the organic fraction of the sample
\( x_{MS}^s \)  Fraction of mutual solvents in the sample
\( x_b^s \)  Fraction of brine in the sample
\( x_o^s \)  Fraction of oil in the sample
\( h \)  Planck’s constant
\( DF \)  Dilution factor
\( DP \)  Number of decimal places
\( E \)  Energy
\( IS_i \)  Area intensity for the internal standard for run \((i)\)
\( IS_m \)  Average area intensity for the internal standard
\( N \)  Total number of runs
\( c \)  The differentiation ratio
\( f \)  The quantity ratio
\( v \)  Frequency
\( \lambda \)  Wavelength

**Chapter 8**

\( S_{or} \)  Residual oil saturation
\( S_{wi} \)  Initial water saturation
\( PV \)  Pore volume

**Chapter 9**

\( P_{o/w} \)  Partition coefficient of the mutual solvent in n-octanol to water

**Key Abbreviations**

A  Analyte
ASOG  Analytical Solution of Groups
BM  Benchmark
D  Diluent
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>DW</td>
<td>De-ionised Water</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy Dispersive X-ray</td>
</tr>
<tr>
<td>ESEM</td>
<td>Environmental Scanning Electron Microscopy</td>
</tr>
<tr>
<td>FID</td>
<td>Flame Ionisation Detection</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatography</td>
</tr>
<tr>
<td>ICP</td>
<td>Inductively Coupled Plasma</td>
</tr>
<tr>
<td>IS</td>
<td>Internal Standard</td>
</tr>
<tr>
<td>KF</td>
<td>Karl-Fischer</td>
</tr>
<tr>
<td>LLE</td>
<td>Liquid-Liquid Equilibrium</td>
</tr>
<tr>
<td>LLI</td>
<td>Liquid-Liquid-Liquid Equilibrium</td>
</tr>
<tr>
<td>MGFW</td>
<td>Modified Glenelg Formation Water</td>
</tr>
<tr>
<td>MH</td>
<td>Multipar H</td>
</tr>
<tr>
<td>MS</td>
<td>Mutual Solvent</td>
</tr>
<tr>
<td>MSI</td>
<td>Multi-Start Minimisation</td>
</tr>
<tr>
<td>MT</td>
<td>Main Treatment</td>
</tr>
<tr>
<td>NFFW</td>
<td>Nelson Forties Formation Water</td>
</tr>
<tr>
<td>NRTL</td>
<td>Non-Random Two-Liquid</td>
</tr>
<tr>
<td>NSSW</td>
<td>North Sea Seawater</td>
</tr>
<tr>
<td>OES</td>
<td>Optical Emission Spectroscopy</td>
</tr>
<tr>
<td>OM</td>
<td>Overall Mixture</td>
</tr>
<tr>
<td>PDM</td>
<td>Phase Displacement Method</td>
</tr>
<tr>
<td>RSD</td>
<td>Relative Standard Deviation</td>
</tr>
<tr>
<td>SFNSSW</td>
<td>Sulphate-free North Sea Seawater</td>
</tr>
<tr>
<td>SFSW</td>
<td>Sulphate-Free Seawater</td>
</tr>
<tr>
<td>SI</td>
<td>Scale Inhibitor</td>
</tr>
<tr>
<td>SS</td>
<td>Source Sample</td>
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<tr>
<td>SW</td>
<td>Seawater</td>
</tr>
<tr>
<td>TM</td>
<td>Target Mixture</td>
</tr>
<tr>
<td>TPE</td>
<td>Tetraphenylethylene</td>
</tr>
<tr>
<td>TS</td>
<td>Trans-Stilbene</td>
</tr>
<tr>
<td>UNIFAC</td>
<td>UNIQUAC Functional Group Activity Coefficient</td>
</tr>
<tr>
<td>UNIQUAC</td>
<td>Universal Quasi-Chemical Activity Coefficient</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>Vis</td>
<td>Visible</td>
</tr>
</tbody>
</table>
Publications


N.B. This is a list of publications emerging from this work at the time of submitting this thesis. Additional publications based on this work are planned after this submission.
Chapter 1: Introduction

1.1. THE CONTEXT: OILFIELD SCALES

Before a well is put into production, the reservoir fluids are in thermodynamic equilibrium. This equilibrium is perturbed once the production starts. The perturbation may involve both physical and chemical changes, giving rise to different types of both organic and inorganic scales. These changes present significant flow assurance risks which must be considered to maintain oil production. Physical and chemical changes to reservoir fluids are inevitable as part of oilfield operations. As such, flow assurance in this respect addresses the consequences of these changes.

The term “oilfield scales” is typically used to denote inorganic scales formed in aqueous solutions (Cowan and Weintritt, 1976; Vetter, 1977; Vetter, 1976; Vetter and Crichlow, 1979; Vetter, 1975; Vetter and Phillips, 1970). The risks associated with these to both the near-wellbore region and the production facilities are very well documented in the literature. Intervention and loss of production costs due to the formation of inorganic scales can be crippling (Crabtree et al., 1999; Graham and Collins, 2004; Graham et al., 2002b). A commonly cited field example is that described by Brown (1998), in which a production well (producing at 4770 m³/d) in the North Sea (Miller field) lost production entirely within 24 hours due to scaling. Moreover, preventive measures – even when applied appropriately – may still dominate operational costs in some cases (Jordan et al., 2001). All of this highlights a preference for prevention over intervention, and a considerable drive towards the optimisation of prevention measures.

Organic scales (e.g. asphaltenes, gas hydrates, waxes, organic carboxylates, naphthenates) also pose important risks, but these are treated separately (Kelland, 2014), and are not directly relevant to this work (N.B. inorganic deposits cause more damage than organic deposits).

The most commonly encountered inorganic scales in the field are calcium carbonate (CaCO₃) and barium sulphate (BaSO₄) (Charleston, 1970; Cowan and Weintritt, 1976; Shen and Crosby, 1983; Vetter, 1976; Weintritt and Cowan, 1967). Their formation proceeds through distinctly different mechanisms. The formation of CaCO₃ is primarily driven by pressure drop, which causes the evolution of carbon dioxide (CO₂) from the produced brine when the pressure in the system falls below the bubble point. This is
described by reaction 1.1, where CO₂ loss can be seen to clearly drive CaCO₃ precipitation. Moreover, the problem is exacerbated by an increase in the pH as CO₂ is lost from the solution. This is due to a reduction in the concentration of carbonic acid (H₂CO₃) as illustrated by reaction 1.2. Since the solubility of CaCO₃ reduces with increasing pH, this drives further CaCO₃ precipitation (Atkinson and Mecik, 1997; Kelland, 2014; Meyers, Skillman and Herring, 1985; Payne, 1987; Tanner and Wittingham, 1986; Wat et al., 1992).

\[ Ca^{2+}(aq) + 2 HCO_3^- (aq) \leftrightarrow CaCO_3(s) + CO_2(g) + H_2O(l) \]  
\[ CO_2(g) + H_2O(l) \leftrightarrow H_2CO_3(aq) \leftrightarrow HCO_3^-(aq) + H^+(aq) \]  

As for BaSO₄, mixing of incompatible brines drives its precipitation. This is described by reaction 1.3. The source of barium ions is usually the formation brine, and the sulphate ions will come from injected seawater. The injection of seawater into the reservoir to maintain its pressure is common practice in offshore operations. While sulphate reduction technology is available, it is associated with very high capital and operational costs. In some cases, its use is a necessity due to the inability of alternative methods to manage the scaling risks (e.g. very high [Ba²⁺]). However, it does not eliminate sulphate scaling risks entirely and has no influence on carbonate scaling (Davis, Lomax and Plummer, 1996; Graham and Collins, 2004; Hardy and Simm, 1996; Jordan, Collins and Mackay, 2008; Vu, Hurtevent and Davis, 2000).

In relation to reaction 1.3, strontium and calcium may also precipitate with sulphate ions. However, barium presents the highest risk due to its lower solubility in comparison (Mackay et al., 2005).

\[ Ba^{2+}(aq) + SO_4^{2-} (aq) \leftrightarrow BaSO_4(s) \]  

Various scale management methods and strategies exist. Of these, chemical treatments known as scale inhibitor (SI) squeeze treatments are one of the most common and effective means by which carbonate and sulphate scaling can be delayed or prevented (Carvalho et al., 2017; Charleston, 1970; Cowan and Weintritt, 1976; Shen and Crosby, 1983; Sorbie, Yuan and Jordan, 1994; Vetter, 1976; Weintritt and Cowan, 1967). A typical treatment will comprise of five main stages (Jordan et al., 1995a; Vazquez, Fursov and Mackay, 2016). These are described briefly below and illustrated in Figure 1.1:

1. Pre-flush (spearhead) stage: This stage involves the injection of a mutual solvent into a producer well. This is thought to prepare the formation for a treatment and
will be discussed in detail in Chapter 2. This stage may be followed by a dilute SI pre-flush.

2. Main treatment (MT) stage: In this stage, a brine with 2.5-20% active [SI] is injected into the formation.

3. Over-flush stage: This stage is meant to push the main treatment to the desired depth into the formation.

4. Shut-in stage: The shut-in period (6-24 hours) allows for SI retention into the formation. This can happen through adsorption or precipitation mechanisms, or a combination of both.

5. Back-production stage: Normal production operations resume once a treatment has been completed. The SI and scaling ions concentrations are routinely monitored to ensure that the well is protected and to plan future treatments. A well must be treated before the SI concentration drops below the minimum inhibition concentration (MIC).

![Diagram of squeeze treatment stages]

**Figure 1.1:** A typical squeeze treatment.

In relation to the scale inhibitors, two conventional chemistries used in squeeze applications for the SI are: phosphonates (e.g. DETPMP) and polymers (e.g. PPCA). Both types inhibit scale formation through a combination of nucleation inhibition (i.e. causing unfavourable thermodynamics for crystal formation) and crystal growth inhibition (i.e. blocking active
crystal growth sites) mechanisms. However, phosphonates function primarily as crystal growth inhibitors, whereas polymers function primarily as nucleation inhibitors (Graham, Sorbie and Jordan, 1997; Sorbie and Laing, 2004). The adsorption/desorption of a SI is affected by several factors, including: SI chemistry and application pH, formation brine chemistry and pH, formation mineralogy and wettability and the temperature; the precipitation of a SI is affected by: the SI chemistry and application pH, the brine chemistry and the temperature (Graham, Sorbie and Jordan, 1997; Jordan et al., 1995a).

Squeeze treatments have been the subject of extensive research since the advent of the technology. Much of this research focused on the mechanisms of scale formation and hence scale prediction, the mechanisms of SI retention, factors affecting SI retention/release, the modelling of this retention/release, and the design and placement of a treatment based on all of the findings. In this sense, it is argued that the main treatment stage has been the focus of research efforts, along with some study of the over-flush and back-production stages. In contrast, the pre-flush stage has received very limited attention, and much of the fundamentals and the science related to it remain unexplored.

The pre-flush stage, which is the focus of this work, may have profound influences on the squeeze treatment. The amphiphile (mutual solvent; MS) deployed at this stage sets the scene for the treatment. Its physical interactions with the reservoir fluids and the formation substrate could influence both the SI retention, and consequently the lifetime of a treatment. This will be explored further in Chapter 2 where the literature concerned with MS research and MS application in squeeze treatments is reviewed.

Because of this, MS research is currently seen as a high priority research topic within the production chemistry community in the context of squeeze treatments research. Research areas of interest include: the phase behaviour of mutual solvents, their propagation through porous media, and their surface conditioning effects on the formation rock. All of these research areas are interconnected and must be supplemented by analytical tools and modelling techniques (Figure 1.2). All aspects of mutual solvent research for squeeze treatment applications are still at their infancy, and considerable work will be needed before squeeze treatment optimisations will be possible. This thesis develops the basis of MS research. This is done with a particular focus on the phase behaviour of MS (in systems of oil/brine/MS) and the modelling of this phase behaviour. Mutual solvent analysis and transport will also be addressed, although to a lesser extent with respect to phase behaviour investigations.
1.2. THEESIS OUTLINE

In Chapter 1, the context of the research described in this thesis is provided. The remaining chapters serve the following functions:

- Chapter 2 explores the literature on mutual solvent research relevant to the research context described in Chapter 1. The aims of the research will be outlined at the end of this chapter.

- Chapter 3 employs qualitative phase behaviour studies to develop a fundamental understanding of the phase behaviour of mutual solvents. Salinity and brine chemistry effects are investigated. The influence of SI on the phase behaviour at different concentrations is explored, and aspects of mutual solvent blend design are discussed.

- Chapter 4 develops a quantitative understanding of the phase behaviour of mutual solvents, which serves as a framework for modelling this phase behaviour.

- Chapter 5 exploits the findings in Chapter 4 to develop the experimental techniques and mathematical procedures required to map the phase behaviour of mutual solvents semi-empirically.
• Chapter 6 investigates the use of a thermodynamic model for describing the phase behaviour in oil/brine/MS systems. It does this by capitalising on the framework from Chapter 4 and the results from Chapter 5.

• Chapter 7 develops a practical analytical tool to analyse for mutual solvents, thereby enabling the validation and verification of the work outlined in the previous chapters. It also enables analysis in the presence of mutual solvents, hence enabling the transport studies in Chapter 8.

• Chapter 8 provides preliminary transport studies which focus on the propagation of mutual solvents and single/multi-phase displacements in oil/brine/MS systems.

• Chapter 9 summarises the findings and their significance. It also outlines the case for future research through a number of potentially high impact recommendations directly enabled by this work.
Chapter 2: Literature Review

2.1. THE CHEMISTRY OF MUTUAL SOLVENTS

The term “mutual solvent – MS” in the context of squeeze treatments refers to simple non-ionic amphiphiles. While this term covers a wide range of organic chemistries, preference in squeeze treatments is given to glycol ethers, although other simple compounds fitting the definition may be used (e.g. some alcohols and ketones). Table 2.1 compiles a list of mutual solvents used in the oil industry. This list was put together with the aid of information provided by Dow (2002), ReachCentrum (2012) and The-American-Chemistry-Council (2000) and based on uses and production volumes. Glycol ethers are preferred as mutual solvents since their dual functionality as alcohols and ethers enable unique physical characteristics, in particular: their excellent mutual oil/water solubility, their thermal stability and the ability to access a wide range of physical properties (e.g. boiling point, density, viscosity, surface tension) based on their chemistry (Dow, 2001).

Ethylene glycols are classed into two series denoting their chemical precursors, namely: the E-Series (“E” w.r.t. ethylene oxide) and the P-Series (“P” w.r.t. propylene oxide). These are typically reacted with alcohols such as n-alkanols to produce the wide range of chemical compounds covered by both series. Varying the molar ratio of the ethylene/propylene oxide to the alcohol is an additional parameter to accessing more chemistries (Dow, 2001; Dow, 2002; IHS-Markit, 2017). Example reactions are provided below. Using butan-1-ol as the alcohol, reactions 2.1 and 2.3 denote E-Series glycol ethers and reactions 2.2 and 2.4 denote P-Series glycol ethers at 1:1 and 2:1 molar ratios respectively.

\[
\text{butan-1-ol} + \text{ethylene oxide} + 1. \triangleq \rightarrow \text{2-butoxyethanol-1-ol (ethylene glycol monobutyl ether)}
\]

\[
\text{butan-1-ol} + \text{propylene oxide} + 1. \triangleq \rightarrow \text{1-butoxypropan-2-ol (propylene glycol monobutyl ether)}
\]

\[
\text{butan-1-ol} + \text{ethylene oxide} + 2. \triangleq \rightarrow \text{2-(2-butoxyethoxy)ethanol-1-ol (diethylene glycol monobutyl ether)}
\]
Table 2.1: Mutual solvents in the oil industry and their structures (MSDS $P_{o/w}$ values are experimental; predicted $P_{o/w}$ values via ALOGPS v2.1 (Tetko and Tanchuk, 2002)).

<table>
<thead>
<tr>
<th>Name</th>
<th>CAS No.</th>
<th>Structure</th>
<th>$\log_{10}(P_{o/w})$</th>
<th>MSDS</th>
<th>Predicted</th>
</tr>
</thead>
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<tr>
<td>2-(2-Hexyloxyethoxy) ethanol Diethylene glycol monohexyl ether (DGHE)</td>
<td>112-59-4</td>
<td><img src="image1" alt="Structure" /></td>
<td>1.65</td>
<td>1.65</td>
<td></td>
</tr>
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<td>112-25-4</td>
<td><img src="image2" alt="Structure" /></td>
<td>1.97</td>
<td>1.82</td>
<td></td>
</tr>
<tr>
<td>2-(2-Butoxyethoxy) ethyl acetate Diethylene glycol monobutyl ether acetate (DGBEA)</td>
<td>124-17-4</td>
<td><img src="image3" alt="Structure" /></td>
<td>1.70</td>
<td>1.42</td>
<td></td>
</tr>
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<td>2-Butoxyethanol acetate Ethylene glycol monobutyl ether acetate (EGBEA)</td>
<td>112-07-2</td>
<td><img src="image4" alt="Structure" /></td>
<td>1.51</td>
<td>1.63</td>
<td></td>
</tr>
<tr>
<td>1-Pentanol N-Amyl alcohol</td>
<td>71-41-0</td>
<td><img src="image5" alt="Structure" /></td>
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<td>1.47</td>
<td></td>
</tr>
<tr>
<td>2-Butoxyethanol Ethylene glycol monobutyl ether (EGMBE)</td>
<td>111-76-2</td>
<td><img src="image6" alt="Structure" /></td>
<td>0.80</td>
<td>0.78</td>
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</tr>
<tr>
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<td>112-34-5</td>
<td><img src="image7" alt="Structure" /></td>
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<td>0.63</td>
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<tr>
<td>2-[2-(2-Butoxyethoxy) ethoxy] ethanol Triethylene glycol monobutyl ether (TGBE)</td>
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<td>0.63</td>
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<td>0.70</td>
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<tr>
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<tr>
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<td><img src="image11" alt="Structure" /></td>
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<td>Name</td>
<td>Code</td>
<td>Structures</td>
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<td>0.41</td>
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<td>2807-30-9</td>
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<td>0.08</td>
<td>0.08</td>
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<td></td>
<td>0.10</td>
<td>0.04</td>
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<td>-0.20</td>
<td>-0.29</td>
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<td>2-Ethoxyethanol</td>
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<td>-0.28</td>
<td></td>
</tr>
<tr>
<td>Ethylene glycol monoethyl ether (EGEE)</td>
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<td>-0.32</td>
<td>-0.28</td>
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<tr>
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<td>Ethyl alcohol</td>
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<td>-0.40</td>
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<td>-0.08</td>
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<td>-0.16</td>
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<tr>
<td>Diethylene glycol monoethyl ether (DGEE)</td>
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<td>-0.16</td>
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<td>-0.67</td>
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<td>Diethylene glycol monomethyl ether (DEGME)</td>
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<td>-1.53</td>
<td></td>
</tr>
<tr>
<td>Monoethylene glycol (MEG)</td>
<td></td>
<td></td>
<td>-1.40</td>
<td>-1.53</td>
<td></td>
</tr>
</tbody>
</table>
2.2. THE USES OF MUTUAL SOLVENTS

Mutual solvents are found in most industries. Their uses cover a wide range of applications, and they may be used as both solvents and chemical intermediates. Examples of solvent uses include formulations of pharmaceutical and beauty products, paints, dyes, inks, cleaning products, herbicides and insecticides and solvents for chemical reactions. As solvents, main end-product examples include their use in the automotive industry in hydraulic and cooling systems and as antifreeze in the aviation industry. Moreover, as chemical intermediates, mutual solvents provide synthesis routes to numerous families of compounds including: ethers, esters, alkoxy alkyl halides, polyether alcohols and hemiacetals/acetals (Dow, 2001; IHS-Markit, 2017; IHS-Markit, 2018).

In the oil industry, mutual solvents are also used extensively. On the production side, the following uses have been identified with reference to the literature:

- In Huff’n’Puff surfactant formulations for improved oil recovery (IOR) applications (Shuler et al., 2016; Wang et al., 2008).
- As a pre-flush in polymeric water shut-off technologies (Dalrymple et al., 2002).
- In the formulations of foamers for liquid unloading in gas wells (Jelinek and Schramm, 2005), and in the formulations of foam diverters for acid well stimulation (Nasr-El-Din, 2000).
- As a pre-flush in squeeze treatments (Chapman et al., 1997; Collins, 1998; Jordan, Graff and Cooper, 2000).
- In the formulation of the aqueous phase or as a demulsifier in emulsified scale inhibitor squeeze treatments (Collins, 2005; Collins and Vervoort, 2003).
- As water-wetting agents for oil removal in acid stimulation treatments and for enabling the removal of spent acid in gas well stimulation (Kelland, 2014; Nasr-El-Din et al., 2004; Collins et al., 2001a).
- Cleaning up the surfaces of iron sulphide deposits to enable their removal (Miller, 2005).
- To resolve formation damage issues relating to viscoelastic surfactant gel treatments with high surfactant loading (Nasr-El-Din et al., 2006).
• To relieve solvency issues associated with the use of acids to manage naphthenate deposition (Kelland, 2014).

• As thermodynamic hydrate inhibitors (Cha et al., 2013).

• In blends used in hot-oiling for chemical wax removal (Walton, 1989).

• In standard tests for evaluating the performance of a demulsifier (Wu et al., 2004).

• For improving the performance of biocides (Jones and Talbot, 2004).

• For improving the performance of drag reduction agents (Hellsten and Harwigsson, 1999).

• In enhanced oil recovery (EOR) applications (Negin, Ali and Xie, 2017).

In acid stimulation treatments, the use of mutual solvents – especially EGMBE – is most relevant and comparable to its use in squeeze treatments. They are predominantly used to reduce the risk of water-block in tight formations, and to enable maintaining a water-wet formation (Gidley, 1971; Kalfayan, 2000). As with squeeze treatments, the use of mutual solvents is not optimised, and rules of thumb are followed based on operational experience. Most operators would not exceed a mutual solvent concentration of 10%, with most operating over the 3-5% range (Kalfayan, 2000). Commercial mutual solvent blends are designed for the purpose of targeting strong water-wet characteristics, but it is generally recommended to use pure mutual solvents or simple blends to avoid unforeseen issues (Kalfayan, 2000). Precipitation risks from mutual solvent/brine incompatibilities are also known to occur, but no detailed investigations have been carried out. Most investigations look at the possibility of controlling precipitation using mutual solvents in acid stimulation applications (Hall and Dill, 1988). Finally, mutual solvents use in acid stimulation treatments is known to strip adsorbed additives such as corrosion inhibitors, which may have implications to squeeze treatments and must be addressed by mutual solvent research (Hall, 1975; Kalfayan, 2000).

Many other uses for mutual solvents exist in the petroleum industry beyond the context of production chemicals. In terms of their uses in production processes, the identified uses generally serve the same functions. These are summarised below:

• Displacing the formation fluids (oil/water).
- Removing oil deposits from surfaces/substrates.
- Removing water block and emulsion damage.
- Removing wettability-alteration damage and changing the wettability in some cases from oil-wet to water-wet.
- Improving solvency and reducing surface tension.
- Achieving faster well clean-up after treatments.

These functions will be reviewed in greater detail in section 2.3 in the context of scale inhibitor squeeze treatments.
2.3. MUTUAL SOLVENTS IN SQUEEZE TREATMENTS

The evidence for squeeze lifetime enhancement due to the use of mutual solvents in the pre-flush is overwhelming in the literature. However, this is often confused with enhanced scale inhibitor (SI) retention. This phrasing seems to suggest a mechanism by which the application of MS in the pre-flush causes the SI to bind more strongly to the formation rock, leading to slower desorption kinetics when the well is produced. While this is possible (e.g. if the MS itself provides additional binding sites for SI adsorption), no evidence for this exists. It is more appropriate to say that the functions of the MS – rather than the MS itself – may lead to more SI retention in the treated formation. The reported mechanisms for squeeze lifetime enhancement through MS pre-flush applications are interrelated and described by:

1. The displacement of oil prior to the main treatment (MT). This exposes more rock to the SI containing MT, thereby enabling more SI to adsorb (or precipitate in the case of precipitation squeeze treatment) per unit volume of treated rock. Related to this, MS use can also help displacing heavy oil deposits (Tjomsland et al., 2008).

2. Altering the wettability of the formation rock from oil-wet to water-wet. This would enable the water-soluble SI to access active sites on the rock, leading to more favourable adsorption kinetics (Jordan et al., 1995b; Jordan et al., 1994).

In addition to improving the squeeze lifetime, other functions are also attributed to the use of MS in squeeze treatments. These include:

1. Preventing water-block attributed to the application of an aqueous squeeze treatment. This is particularly an issue in water sensitive formations (e.g. low water-cut), whereby the application of an aqueous treatment damages the relative permeability to the oil post-treatment (Scott and Littlewood, 2000; Collins et al., 2001b; Jordan, Graff and Cooper, 2001). The flowback of the MS when the well is back-produced prevents these relative permeability effects by lowering the surface tension and enabling the mobilisation of the residual water (King and Lee, 1988; Nasr-El-Din, 2003). Therefore, while non-aqueous treatments are an option in these scenarios, MS enables the use of more conventional treatments without water block formation damage risks encountered without them (Jordan, Graff and Cooper, 2001). In fact, even when non-aqueous treatments are used, MS is needed to enable
successful treatment without solvency/injectivity issues (Jordan, Graff and Cooper, 2001; Bogaert et al., 2006; Frigo et al., 2005; Graham et al., 2002a).

2. Even if the formation is not water sensitive, MS use can lead to faster well clean-up by enabling faster production of the injected brines during the treatment (Jordan, Graff and Cooper, 2001). Well clean-up refers to the time it takes a well to return to the pre-treatment production rate.

Achieving longer squeeze lifetime reduces the number of squeeze treatments required over the lifetime of the field. Moreover, faster well clean-up and avoidance of water block issues reduce the amount of deferred oil due to squeeze treatments over production lifetime. Both of these combine to deliver significant cost savings enabled by MS use, thereby enabling more profitable and economical operations.

As an example for the benefits of MS use, the largest known published study involving MS application in the field involved 125 producer wells in the Cedar Lake Unit Field in Texas. The wells in this study (Przybylinski et al., 1996) were divided into three groups: control wells (no MS/surfactant pre-flush), MS pre-flush wells and surfactant pre-flush wells. In this study, 95% of wells treated with MS gave better well clean-up time vs. 68% of wells treated with surfactant, with MS treated wells averaging 86% and 76% faster well clean-up with respect to the control and surfactant treated wells respectively. In terms of squeeze lifetime enhancement, MS treated wells averaged 57% and 27% longer squeeze lifetimes with respect to the control and surfactant treated wells respectively. This implies that the MS and the surfactant in this study share similar mechanisms for the observed effects, with MS delivering far superior performance – the details of which are unknown. It is worth mentioning that superior MS performance over surfactants is not universal. For instance, one recent study which targets wettability alterations in carbonate rocks shows superior performance of surfactant vs. MS (Ghosh, Alklih and Li, 2016; Ghosh, Li and Alklih, 2016). However, this may be an artefact of the MS concentration used (4% EGMBE). In fact, in both cases, it is unknown if the chemicals involved, and the concentrations and volumes used in the treatments are appropriate for direct deductive comparisons. Research instead should focus on understanding the mechanisms of the observed effects, and these can be used to design better treatments.
The described key functions above are reported consistently across many publications based on both coreflood data and field applications.\(^1\) Several issues exist with these, most importantly:

1. All known experimental studies on MS use in the pre-flush stage of a squeeze treatment are conducted as part of a campaign for field application. No known work has been done to isolate the mechanisms of squeeze lifetime enhancement due to MS use directly. While the reported mechanisms for squeeze lifetime enhancements (i.e. oil displacement and wettability changes) are certainly important and participating factors, their relative contributions as well as the existence of hidden factors cannot be gauged with the current level of knowledge.

2. No sensitivity studies are carried out. Almost all studies investigate the use of a single MS or MS blend, most of which are based on EGMBE, and assume that performance will be the same across all treatments. However, EGMBE is known to display a wide range of phase behaviour and wetting characteristics at different temperatures, salinities and oil content in the matrix (Kahlweit et al., 1989; Kahlweit et al., 1988a). Therefore, its ability to perform both oil displacement and wettability changes may be drastically different across different scenarios. An exception is the work of Jordan, Graff and Cooper (2001) in which two MS are investigated (i.e. EGMBE and DEGMBE); however, the results of this assessment are not reported. Moreover, Nasr-El-Din, Lynn and Al-Dossary (2002) demonstrated how EGMBE vs. a blend perform very differently in terms of formation damage potential for the same application. Additional sensitivities include: substrate type, SI type, pre-flush volume, MS concentration in the pre-flush and brine chemistry to mention a few.

Additional not commonly mentioned factors that could influence the squeeze lifetime due to a MS pre-flush have been identified. Firstly, the MS itself could adsorb to the substrate or influence the adsorption/desorption of other chemicals (e.g. SI, corrosion inhibitors, surfactants) (Graham et al., 2010; Graham et al., 2012; Hall, 1975; King and Lee, 1988).

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\(^1\) References denoting the functions/benefits of MS in various experiments and field applications:
(Jordan et al., 1995b; Przybylinski et al., 1996; Chapman et al., 1997; Collins et al., 1997a; Collins et al., 1997b; Bourne et al., 1998; Collins, Williams and Bourne, 1998; Collins, 1998; Bourne, Booth and Brunger, 1999; Bourne et al., 1999; Collins et al., 1999; Graham et al., 1999; Williams, Collins and Wade, 1999; Jordan, Graff and Cooper, 2000; Poynton et al., 2000; Scott and Littlewood, 2000; Collins et al., 2001a; Collins et al., 2001b; Jordan, Graff and Cooper, 2001; Graham et al., 2002a; Nasr-El-Din, 2003; Frigo et al., 2005; Bogaert et al., 2006; Bogaert et al., 2007; Jordan et al., 2007; Bogaert et al., 2008; Fleming et al., 2008; Jordan, Mackay and Vazquez, 2008; Tjomsland et al., 2008; Fleming et al., 2009; Jordan and Mackay, 2009; Vazquez et al., 2009; Graham et al., 2010; Graham et al., 2012).
Graham et al. (2010) showed how high concentrations of MS in the pre-flush returns can lead to significant stripping of the adsorbed SI during the main treatment.

Secondly, the presence of clay minerals in the formation matrix can have significant impact on squeeze lifetime enhancements when a MS pre-flush is applied. For instance, formation matrices containing kaolinite show some of the longest known squeeze lifetimes when a MS pre-flush is used (Fleming et al., 2009; Fleming et al., 2008). The application of MS alters the wettability of the preferentially oil-wet kaolinite, thereby providing further squeeze lifetime increases beyond those that would occur in their absence (Jordan et al., 1994; Bantignies, Moulin and Dexpert, 1997). Therefore, formulation mineralogy can be used to assess how well a treatment will be influenced by a MS pre-flush. Note that caution must be exercised when assessing the influence of a MS pre-flush on squeeze lifetime enhancement, as this is an implicit function of the [MIC] of the treatment. For instance, the presence of favourable clay minerals for squeeze lifetime enhancement (e.g. kaolinite) delivers longer squeeze lifetimes over intermediate [MIC]; at very low [MIC], the SI returns with and without the clay minerals converge which would mean no lifetime enhancements occurred. Hence, any comparisons (e.g. across different field applications) should be done on the same basis.

Thirdly, a mechanism that may play a role in squeeze lifetime enhancements due to MS use in the pre-flush is the influence of MS on dissolution of the formation substrate. It is known that MS, such as EGMBE, can lead to enhanced dissolution rates of calcite and barite minerals in dissolver treatments (Jordan et al., 2002). For example, in the presence of 0.1 N HCl, 10% MS (EGMBE) in the treatment can increase the dissolution rate of calcite and dolomite by up to 9% and 29%, respectively (Taylor, Al-Ghamdi and Nasr-El-Din, 2003; Taylor, Al-Ghamdi and Nasr-El-Din, 2004). The acidic nature of most squeeze treatments may mean that MS-induced enhanced dissolution rates of the substrate during the treatment cannot be ruled out. It may contribute pH and compositional (Ca$^{2+}$/Mg$^{2+}$) changes that would alter the adsorption kinetics. Observations involving enhanced squeeze lifetime when acidic additives (e.g. 10% polyaspartic acid) are included in the pre-flush/over-flush (Sutherland and Jordan, 2016) are in line with this proposition. In addition to the mechanism suggested by the authors of this work, the pH changes due to the polyaspartic acid presence may contribute to the observed squeeze lifetime enhancement. Finally, potential incompatibilities between the MS in the pre-flush and the SI in the main treatment can lead to the precipitation of the SI into the formation. Should this occur without formation damage, a prolonged squeeze lifetime is expected. This is due to precipitation...
squeeze treatments generally exhibiting longer squeeze lifetime compared to their adsorption counterpart.

Unrelated to squeeze lifetime enhancement, the MS can also serve additional functions. Two examples in the literature include: a) to prevent formation damage by emulsion formation on back-production in some squeeze applications, e.g. where iron bearing minerals are encountered, and surfactants are used in the treatment (Lynn, Nasr-El-Din and Hashem, 2002; Tjomsland et al., 2008); b) enable the blending of incompatible products for applications involving few chemical injection lines (Jordan et al., 2003; Feasey et al., 2006; Jordan et al., 2006); c) to avoid injectivity problems and to provide initial production stimulation in some cases post-treatment (Jordan et al., 2007; Bogaert et al., 2008; Bogaert et al., 2006; Bogaert et al., 2007; Frigo et al., 2005).

Despite all the benefits of MS applications, caution must be exercised in their use to prevent unintended formation damage. Several formation damage mechanisms associated with MS use have been reported. These include: a) MS incompatibilities with the reservoir fluids (in terms of phase behaviour) which may lead to residual oil/water saturation (Bennion, Thomas and Bietz, 1996); b) the participation of the MS in emulsion formation in the presence of surfactants or the failure of MS to prevent emulsion formation due to poor treatment design (Lynn, Nasr-El-Din and Hashem, 2002; Nasr-El-Din, 2003); c) damage due to both organic (e.g. asphaltenes; (Bogaert et al., 2008; Nasr-El-Din, 2003)) and inorganic scaling (e.g. sulphate salts; (Nasr-El-Din, 2003)). Topside issues relating to high MS concentrations after a treatment are also mentioned (Miles et al., 2003).

All of the above-mentioned risks may be manageable with proper understanding of the phase behaviour of MS and their transport. Currently, poor understanding of MS phase behaviour aspects can lead to significant production losses. Nasr-El-Din, Lynn and Al-Dossary (2002) document a case in which a vendor-recommended MS blend (over pure EGMBE) showed potential for significant formation damage (i.e. 85% permeability loss due to formation of an emulsion stabilised with precipitates) that would not be encountered with EGMBE alone. In terms of efficiency aspects, the blend seemed to perform no better than EGMBE. Another example in Nasr-El-Din (2003) showed the potential of a MS blend recommended by a service company for tight carbonate reservoir applications to induce both organic and inorganic precipitation; whereas the same was not observed with EGMBE alone. It is unknown if the blend would perform any better than EGMBE in this example in terms of efficiency. These examples illustrate how poor understanding of the phase
behaviour and the associated risks can lead to poor commercial products with potentially severe consequences to oil production.

The phase behaviour of amphiphiles in pure systems of oil (e.g. alkane) and water has been studied extensively, and the influence of various parameters (e.g. size of alkane, type of MS, temperature, pressure) on the phase behaviour has been addressed. The influence of salinity has also been addressed in very simple systems (e.g. single salt systems). The reader is referred to the following references for more details: (Kahlweit, Strey and Busse, 1993; Kahlweit et al., 1988a; Kahlweit et al., 1988b; Kahlweit et al., 1989; Burauer et al., 1999; Sassen et al., 1989). Formation of three liquid phases is well documented in these systems and has significant impact on the surface tension and wetting properties of the MS system. In the context of squeeze treatments, while this is known to occur (Collins et al., 1999; Scott and Littlewood, 2000), it is rarely – if at all – considered. This is partly attributed to the poor understanding of the phase behaviour of MS at field relevant conditions (i.e. multi-component systems involving oils and formation/seawater brines). It is unknown under which conditions three phases will form, and whether this is desirable. Scott and Littlewood (2000) postulate that formation of three phases will enable the MS to perfectly wet the formation rock, thereby maximising wettability and oil displacement benefits. However, no evidence for this in squeeze applications exists, and issues associated with the three-phase flow that would ensue are unknown.

It has so far been illustrated that the gap in knowledge relating to the MS phase behaviour in squeeze applications affects: a) the ability to design suitable MS blends; b) consideration of phase behaviour aspects on MS performance. Additional parameters affected by this include: c) the inability to model the influence of MS pre-flush on a squeeze treatment appropriately; d) issues relating to the field relevance of coreflood studies designed to assess SI treatment performance when MS is used as a pre-flush. These additional issues are discussed below.

Firstly, in terms of the modelling, the only known attempt to model the influence of MS application on squeeze treatments is the work of Vazquez et al. (2009). The surfactant model implemented for this study is described in Vazquez et al. (2008). The model assumes a constant partition factor for the MS during oil/water displacement. Based on this, new relative permeability curves are calculated as a function of the [MS] in the oil/brine phases. In practice, the MS will not have a constant partition factor and the [MS] will be dictated by phase separation. Moreover, the model only allows for two-phase flow and oil and water are not allowed to intermix; whereas in reality, single-, two- and three-phase flows
are possible. Additionally, the model assumes no mass transfer for the SI across phases. However, the ability of MS to solubilise oil and water means that a non-aqueous phase may contain significant amount of water (e.g. 20%), and hence some SI. While the model can capture field data through curve fitting, it cannot be used to investigate or to design a priori a pre-flush that would deliver an optimised squeeze treatment.

Secondly, in terms of coreflood studies for field applications, an ability to model the MS returns during the back-production is essential. Two examples are provided to illustrate the importance of this parameter. In the first example, Graham et al. (2010) showed how field data indicates squeeze lifetime enhancement while a coreflood study for the same application indicates squeeze lifetime deterioration when MS is used. Simulating the [MS] in the returns in the coreflood study was found to be the culprit and was deemed unrepresentative of the field situation. To achieve an ability to model [MS] in the back-production stage, an ability to model the phase behaviour of the MS is required. In the second example, Bogaert et al. (2008) showed how MS pre-flush in a coreflood study can show no signs of formation damage; however, [MS] in returns can cause significant formation damage. In this example, the MS and the oil were found to be incompatible (i.e. asphaltenes) only at low [oil]. Therefore, an ability to model the [MS] in the returns will allow more representative coreflood studies to be developed for field applications.

In addition to enabling MS selection/MS blend design, MS research should ultimately lead to an ability to design squeeze treatments while optimising the following pre-flush parameters: a) the volume of MS pre-flush; b) the concentration of the MS in the pre-flush. The functions associated with these parameters should enable: a) maximising oil/brine displacement; b) maximising wettability alterations; c) minimising SI stripping due to MS returns; d) minimising formation damage; e) minimising well-clean up time; f) minimising the cost of the treatment. Any additional parameters identified through MS research should be used to update this list.

By comparison, current state of the art design practices for squeeze treatments optimise the main treatment and the over-flush parameters only. The pre-flush is not considered at all in the optimisation (Jordan, Mackay and Vazquez, 2008; Jordan and Mackay, 2009; Vazquez, Fursov and Mackay, 2016). Therefore, treatment design practices in the field vary considerably. For instance, MS concentrations in the pre-flush can be anywhere between 10-100% v/v, and the volume of the pre-flush varies too as seen in the reported examples in the literature.
All of this highlights the potential for substantial improvements to current squeeze design practices by incorporating aspects of pre-flush design. However, before this is possible, the fundamentals of MS use in the context of squeeze treatments must be explored. Key to this work, and with reference to the above discussion, is understanding the phase behaviour of MS in oil/brine/MS systems, and enabling its modelling.
2.4. RESEARCH AIMS

The aim of this thesis is to develop the leading edge in mutual solvent research. As identified from the literature review, it is paramount that this development is done with a focus on the phase behaviour of mutual solvents to enable and to facilitate research in other areas. Therefore, the following objectives were set:

1. To classify the variety of mutual solvents available based on a field relevant parameter. This should be done in a way that highlights the wide range of options available in terms of mutual solvent selection.

2. To investigate the influence of directly relevant parameters – in the context of squeeze treatments – on the phase behaviour of mutual solvents. This should enable understanding what should be expected from the phase behaviour of mutual solvents under different conditions.

3. To study mechanisms for formation damage related to the phase behaviour of mutual solvents; most importantly, the effects of MS selection and brine chemistry should be considered.

4. To investigate phase behaviour design using mutual solvent blending and the influence of common scale inhibitors on the phase behaviour.

5. To develop a quantitative understanding of the phase behaviour of mutual solvents in complex oil/brine/MS systems, and to investigate means to model this phase behaviour.

6. To develop practical analytical methods for mutual solvent analysis that would enable the verification of MS models and transport investigations.

7. To perform preliminary transport studies investigating the displacement of oil and brine using mutual solvents with reference to the phase behaviour.

The direct impact of achieving these objectives would be:

1. Appreciating the influence of mutual solvent selection on the phase behaviour under different scenarios. Therefore, developing a better understanding of solvency issues to be expected in different applications.
2. Mitigating risks associated with mutual solvent use, particularly ones attributed to incompatibilities with the brine.

3. Developing preliminary understanding for mutual solvent blend design.

4. Enabling the design of experiments to investigate the transport of mutual solvents.

5. Enabling the design of more representative coreflood studies for field applications.

6. Enabling the development of existing mutual solvent models to better describe the influence of a mutual solvent pre-flush on a squeeze treatment.

7. Providing a foundation for the analytical methods that would enable future studies on topics such as mutual solvent adsorption/propagation.
Chapter 3: Qualitative Experimental Studies on the Phase Behaviour of Mutual Solvents

3.1. OVERALL AIMS AND OBJECTIVES

The lack of the analytical tools required to investigate the phase behaviour in the complex oil/brine/mutual solvent systems hindered research into the parameters influencing the phase behaviour in the context of scale inhibitor squeeze treatments. Key parameters of direct relevance to field applications include:

- The salinity effects on the phase behaviour of mutual solvents in oil/brine/mutual solvent systems.

- The brine chemistry effects on the liquid phase behaviour and the inorganic precipitates formed in the presence of mutual solvents.

- The general effects expected from the presence of the two most common scale inhibitors in oil/brine/mutual solvent systems.

- The phase behaviour of mutual solvents in blends of more than one mutual solvent.

- The effects of temperature on the phase behaviour of oil/brine/mutual solvent systems.

The development of analytical techniques for the analysis of oil/brine/mutual solvent systems is considered as part of this PhD. However, since this work is at its infancy, qualitative phase behaviour experiments should enable progress and advancements in mutual solvent applications in the field. In qualitative phase behaviour experiments, the different regions on the phase diagram are mapped through preparation of samples covering all areas of the phase diagram and allowing them to equilibrate. While this method is expensive and time consuming, it represents the most feasible route to develop understanding of the phase behaviour of mutual solvents. Hence, it is used to investigate the parameters of interest outlined above.
3.2. MUTUAL SOLVENTS

Ten mutual solvents (MS) were selected based on their standard (i.e. n-octanol/water at 20-25°C and 1 atm; (OECD, 1995; OECD, 2004; OECD, 2006)) partition coefficients (P<sub>o/w</sub>). The selection of the mutual solvents was done with the aim of covering a wide range of (P<sub>o/w</sub>) values. Correlations between the qualitative phase behaviour of the mutual solvents and their respective (P<sub>o/w</sub>) were subsequently investigated. The selected mutual solvents for the work described in this chapter, as well as their sources, purities, (P<sub>o/w</sub>) and structures, are provided in Table 3.1.

Figure 3.1 outlines the selected mutual solvents based on their standard relative solubilities (oil/water). It also highlights the predictability of the (P<sub>o/w</sub>) using the ALOGPS v2.1 programme developed by Tetko and Tanchuk (2002), with roughly 95% precision (R<sup>2</sup> = 0.92). In both Table 3.1 and Figure 3.1, the (P<sub>o/w</sub>) values are expressed in the logarithmic form (base 10) to achieve a relatable symmetry (e.g. when log<sub>10</sub> P<sub>o/w</sub> = 0, the mutual solvent is equally soluble in oil and water; when log<sub>10</sub> P<sub>o/w</sub> = 1, the mutual solvent is 10 times more soluble in oil; when log<sub>10</sub> P<sub>o/w</sub> = -1, the mutual solvent is 10 times more soluble in water). This symmetry is emphasised in Figure 3.1 with boundary lines highlighting the relative solubilities of the mutual solvents in oil and water.
Table 3.1: A full list of the investigated mutual solvents (Supplier: VWR).

<table>
<thead>
<tr>
<th>Mutual Solvent</th>
<th>Product Code</th>
<th>Purity</th>
<th>log_{10} P_{o/w}</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Butoxyethanol acetate Ethylene glycol monobutyl ether acetate (EGBEA)</td>
<td>8.01395.1000</td>
<td>≥98.0%</td>
<td>1.51</td>
<td></td>
</tr>
<tr>
<td>2-Butoxyethanol Ethylene glycol monobutyl ether (EGMBE)</td>
<td>A17976.0F</td>
<td>≥99.0%</td>
<td>0.80</td>
<td></td>
</tr>
<tr>
<td>2-(2-Butoxyethoxy) ethanol Diethylene glycol monobutyl ether (DGBE)</td>
<td>8.03129.2500</td>
<td>≥98.0%</td>
<td>0.60</td>
<td></td>
</tr>
<tr>
<td>2-Propanol Isopropyl alcohol (IPA)</td>
<td>20880.290</td>
<td>≥99.8%</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>2-Propoxyethanol Ethylene glycol monopropyl ether (EGPE)</td>
<td>8.43947.1000</td>
<td>≥99.0%</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>Propan-2-one Acetone</td>
<td>20067.320</td>
<td>100.0%</td>
<td>-0.20</td>
<td></td>
</tr>
<tr>
<td>Ethanol Ethyl alcohol</td>
<td>20821.330</td>
<td>≥99.0%</td>
<td>-0.30</td>
<td></td>
</tr>
<tr>
<td>2-(2-Methoxyethoxy) ethanol Diethylene glycol monomethyl ether (DEGME)</td>
<td>8.03128.1000</td>
<td>≥98.0%</td>
<td>-0.47</td>
<td></td>
</tr>
<tr>
<td>2-Methoxyethanol Ethylene glycol monomethyl ether (EGME)</td>
<td>1.00859.2500</td>
<td>≥99.5%</td>
<td>-0.74</td>
<td></td>
</tr>
<tr>
<td>Ethane-1,2-diol Monoethylene glycol (MEG)</td>
<td>24041.320</td>
<td>≥99.7%</td>
<td>-1.40</td>
<td></td>
</tr>
</tbody>
</table>
Figure 3.1: The experimental and the predicted log_{10} (P_{o/w}) values for a number of mutual solvents. The selected mutual solvents for this work are highlighted using the circular red markers (●). The experimental values are obtained from MSDS sheets for a number of mutual solvents. The predictions are obtained from ALOGPS v2.1 (Tetko and Tanchuk, 2002).
3.3. EXPERIMENTAL CONDITIONS

Qualitative phase diagrams were constructed for all of the selected mutual solvents at laboratory conditions (22.5°C and 1 atm) with oil and different brines. For this purpose, clean mineral oil (Multipar H; supplied by Brenntag; C_{11}-C_{12}, isoalkanes, <2% aromatics) was used. As for the brines, three brines of different chemistries and salinities were used, namely: North Sea Seawater (NSSW; SO_{4}^{2-} rich; TDS ≈ 36,000 ppm); Nelson Forties Formation Water (NFFW; Ca^{2+} rich; TDS ≈ 91,000 ppm); and Glenelg Formation Water (MGFW; contains HCO_{3}^{-}; TDS ≈ 264,000 ppm). The compositions of the brines are provided in Table 3.2. Phase diagrams were constructed for all the mutual solvents with de-ionised water as well (DW; TDS ≈ 0 ppm). The oil, brines, and mutual solvents were all filtered prior to use in the experiments to remove any solids (brine was filtered at 0.45 μm, while the oil and the MS were filtered at 2.7 μm).

To investigate the brine chemistry effects on the liquid phase behaviour, selected qualitative experiments were repeated for the same NSSW/MGFW brines in the absence of the sulphate/bicarbonate ions respectively.

Table 3.2: The salinities and chemistries of the brines used in the salinity mapping study.

<table>
<thead>
<tr>
<th>Ionic Concentration (ppm)</th>
<th>Brine</th>
<th>NSSW</th>
<th>NFFW*</th>
<th>MGFW**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na^{+}</td>
<td>10,890</td>
<td>31,275</td>
<td>68,700</td>
<td></td>
</tr>
<tr>
<td>Ca^{2+}</td>
<td>428</td>
<td>2,000</td>
<td>20,000</td>
<td></td>
</tr>
<tr>
<td>Mg^{2+}</td>
<td>1,368</td>
<td>739</td>
<td>2,500</td>
<td></td>
</tr>
<tr>
<td>K^{+}</td>
<td>460</td>
<td>654</td>
<td>8,000</td>
<td></td>
</tr>
<tr>
<td>Ba^{2+}</td>
<td>0</td>
<td>296</td>
<td>3,700</td>
<td></td>
</tr>
<tr>
<td>Sr^{2+}</td>
<td>0</td>
<td>771</td>
<td>2,000</td>
<td></td>
</tr>
<tr>
<td>SO_{4}^{2-}</td>
<td>2,960</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>HCO_{3}^{-}</td>
<td>0</td>
<td>0</td>
<td>180</td>
<td></td>
</tr>
<tr>
<td>Cl^{-}</td>
<td>19,774</td>
<td>55,279</td>
<td>159,297</td>
<td></td>
</tr>
<tr>
<td><strong>Total TDS</strong></td>
<td>35,880</td>
<td>90,987</td>
<td>264,377</td>
<td></td>
</tr>
</tbody>
</table>

*NFFW was reduced in calcium (from 5,038 ppm to 2,000 ppm) in order to achieve consistency with historic work involving scale inhibitor investigations.

**MGFW was reduced in sodium (from 80,000 ppm to 68,700 ppm) in order to achieve a lower salinity that allows studying the three-phase region in oil/brine/mutual solvent systems.
3.4. GENERAL EXPERIMENTAL METHODS

3.4.1. Qualitative Phase Diagrams

For the experiment, 10 ml samples containing oil + brine + MS were prepared at 10% intervals (using Gilson Type 401 Diluter for high precision; ±0.5 μl). The samples were mixed and the number of liquid phases was recorded at equilibrium. Any inorganic precipitation was also noted. This information aided the construction of the qualitative phase diagrams in which the liquid and solid phase boundaries are roughly determined.

To produce a qualitative ternary phase diagram, 66 samples were prepared by varying the feed compositions of oil, brine and mutual solvent at 10% v/v increments to an overall volume of 10 ml. The relative volumes of the sample constituents were measured using an electrical dispenser fitted with a 10 ml syringe (Gilson Type 401 Diluter for high precision; ±0.5 μl). Borosilicate glass test tubes (D_o × L = 16 mm × 125 mm) sealed with PTFE lids were used to store the samples. Once prepared, the samples were shaken vigorously, and left to equilibrate for at least 24 hours. The volumes of each of the resulting phases was tracked down to 0.1 ml precision, and ensured to be non-changing prior to recording the results. For each sample, the results collected were the volumes of the liquid phases, as well as whether a solid phase was present, e.g. due to salt dropout. Experiments were subsequently conducted for the purposes of characterising the inorganic solids.

3.4.2. Characterisation of the Inorganic Precipitates

In order to characterise the inorganic precipitates formed, two identical 100 ml set of samples were prepared. For simplicity, this was done generally at 90:10% v/v mutual solvent to brine ratio, which generally gave the highest mass of precipitate (at 10% v/v intervals). For each mutual solvent, the first set of samples was left to equilibrate for 24 hours before proceeding. After that, the precipitates were collected by filtering the samples through a 2.7 μm filter paper, and were micro-analysed qualitatively for topography and elemental composition using Environmental Scanning Electron Microscopy – Energy Dispersive X-ray (ESEM-EDX). The second set of samples was left to equilibrate separately for 24 hours. Since the mass of the precipitates was small, the supernatant was analysed instead by diluting in distilled water and analysing for all the cations in NSSW and the sulphate anion using Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) analysis.
3.5. SALINITY MAPPING

3.5.1. Salinity Mapping: Aims

The key aim of this study is to understand how different mutual solvents behave in systems of different salinities in the presence of oil, and to classify the phase behaviour in groups based on a relatable parameter. Field relevant brine salinities/compositions are investigated, and the results should inform understanding on the phase behaviour features of the identified groups of mutual solvents.

3.5.2. Results and Discussion

In terms of the impact of salinity on the phase behaviour, mutual solvents can be divided into three groups, namely MS with: high preferential oil solubility, high preferential water solubility or no preferential solubility/intermediate preferential oil solubility. These definitions are dependent on the experimental conditions. For instance, changing the temperature will change the partition coefficient, making a mutual solvent more oil soluble than water soluble (Kahlweit, Strey and Busse, 1990; Collins et al., 1999). As such, the definitions are not inherent properties of the mutual solvents under investigation. Instead, they are the properties of a mutual solvent with a similar partition coefficient at the conditions of interest.

The value of this approach is the ability to extend the findings of the salinity mapping to any experimental conditions by using the partition coefficient as a reference parameter to describe the influence of salinity. For example, a MS whose log$_{10}$ P$_{o/w}$ $\approx$ 1 at 90°C is predicted to exhibit largely similar qualitative phase behaviour as a MS whose log$_{10}$ P$_{o/w}$ $\approx$ 1 at 22.5°C in terms of salinity effects in this context. However, this can be extended to any parameter of interest, e.g. fixing the salinity and varying the temperature, the pressure or the oil quality.

With this in mind, the influence of salinity on the three groups of mutual solvents are described below with examples from the experimental results.

3.5.2.1. MS with High Preferential Oil Solubility at the Test Conditions

MS with high preferential oil solubility are insensitive to the salinity effects. This can be seen clearly in Figure 3.2. This shows the phase behaviour of EGBEA (log$_{10}$ P$_{o/w}$ = 1.51) with Multipar H and a given brine. As the salinity increases from 0 ppm to 264,000 ppm (Figure 3.2a to Figure 3.2d), there are no observable effects on the qualitative phase
behaviour and the phase diagrams remain largely the same. The high partition coefficient of EGBEA indicates its very low solubility in water. Therefore, at the test conditions, EGBEA does not behave like a mutual solvent, and increasing the salinity of the brine will not influence its phase behaviour due to its inability to enter the aqueous phase in any appreciable amounts.

Figure 3.2: The influence of salinity on the phase behaviour of EGBEA (log$_{10}$ P$_{o/w}$ = 1.51) at 22.5°C and 1 atm: (a) DW; (b) NSSW; (c) NFFW; (d) MGFW.

3.5.2.2. MS with High Preferential Water Solubility at the Test Conditions

MS with high preferential water solubility also experience negligible salinity effects on their qualitative phase behaviour. An example is provided for EGME (log$_{10}$ P$_{o/w}$ = -0.74) in Figure 3.3. This is counter-intuitive as the high solubility of EGME, for example, in the aqueous phase at the test conditions would lead one to expect its phase behaviour to be altered by the increase in salinity. However, qualitatively, it appears that EGME is sufficiently water soluble to a point beyond which increasing the salinity cannot noticeably alter its qualitative liquid phase behaviour, i.e. the number of liquid phases and where they
appear on the phase diagram. **Quantitatively**, the phase behaviour will be influenced in this case by the change in salinity (Figure 3.3a to Figure 3.3d), i.e. the tie-lines on the phase diagram will almost certainly be affected.

Figure 3.3: The influence of salinity on the phase behaviour of EGME (log$_{10}$ P$_{o/w}$ = -0.74) at 22.5°C and 1 atm: (a) DW; (b) NSSW; (c) NFFW; (d) MGFW.

The qualitative diagrams of ethanol, DEGME and MEG follow the same trends (Figure 3.4, Figure 3.5 and Figure 3.6 respectively).
Figure 3.4: The influence of salinity on the phase behaviour of Ethanol ($\log_{10} P_{\text{oil}} = -0.30$) at 22.5°C and 1 atm: (a) DW; (b) NSSW; (c) NFFW; (d) MGFW.
Figure 3.5: The influence of salinity on the phase behaviour of DEGME \((\log_{10} P_{o/w} = -0.47)\) at 22.5°C and 1 atm: (a) DW; (b) NSSW; (c) NFFW; (d) MGFW.
Figure 3.6: The influence of salinity on the phase behaviour of MEG (log10 \( P_{o/w} = -1.40 \)) at 22.5°C and 1 atm: (a) DW; (b) NSSW; (c) NFFW; (d) MGFW.

3.5.2.3. MS with No Preferential Solubility/Intermediate Oil Solubility at the Test Conditions

These MS experience the effects of salinity in a qualitatively observable sense. The effects generally manifest at very high salinities, and tend to become more evident as the partition coefficient of the mutual solvent increases (i.e. increased preferential oil solubility). Examples are provided in Figure 3.7 and Figure 3.8. With DGBE (log10 \( P_{o/w} = 0.60 \)), the qualitative phase behaviour remains more or less the same as the salinity increases from 0 ppm to 91,000 ppm (Figure 3.7a to Figure 3.7c). At 264,000 ppm, DGBE is found to be partially insoluble with the brine and a three-liquid-phase region covers a wide central area of the phase diagram (Figure 3.7d).
Figure 3.7: The influence of salinity on the phase behaviour of DGBE (log$_{10}$ $P_{o/w}$ = 0.60) at 22.5°C and 1 atm: (a) DW; (b) NSSW; (c) NFW; (d) MGFW.

EGMBE (log$_{10}$ $P_{o/w}$ = 0.80), which has a higher preferential oil solubility than DGBE, follows a similar trend (Figure 3.8). However, this occurs at much lower salinities. Going from 0 ppm to 36,000 ppm, EGMBE becomes partially insoluble in the brine, and a large three-phase region forms (Figure 3.8a and Figure 3.8b). Increasing the salinity further to high salinity values (e.g. 91,000 ppm and 264,000 ppm) causes the EGMBE to become insoluble with the brine, thereby exhibiting a similar phase behaviour to that of mutual solvents with high preferential oil solubility (Figure 3.8c and Figure 3.8d).
Figure 3.8: The influence of salinity on the phase behaviour of EGMBE ($\log_{10} P_{o/w} = 0.80$) at 22.5°C and 1 atm: (a) DW; (b) NSSW; (c) NFFW; (d) MGFW.

The mutual solvents IPA, EGPE and acetone follow the same trends, showing three-phase region only at very high salinities (as with DGBE) due to their increased preferential solubility in the brine compared with EGMBE. Their qualitative diagrams are provided in Figure 3.9, Figure 3.10 and Figure 3.11 respectively.
Figure 3.9: The influence of salinity on the phase behaviour of IPA ($\log_{10} P_{o/w} = 0.10$) at 22.5°C and 1 atm: (a) DW; (b) NSSW; (c) NFFW; (d) MGFW.
Figure 3.10: The influence of salinity on the phase behaviour of EGPE (log_{10} P_{w/o} = 0.08) at 22.5°C and 1 atm: (a) DW; (b) NSSW; (c) NFFW; (d) MGFW.
Figure 3.11: The influence of salinity on the phase behaviour of Acetone ($\log_{10} P_{o/w} = -0.20$) at 22.5°C and 1 atm: (a) DW; (b) NSSW; (c) NFFW; (d) MGFW.

3.5.2.4. Overall Salinity Effects as a Function of ($P_{o/w}$) of the Mutual Solvent

Based on all qualitative salinity mapping studies discussed in section 3.5.1, a summary of the qualitative liquid phase behaviour effects as a function of a benchmark $\log_{10} P_{o/w}$ (MS) value is provided in Table 3.3.

As explained before, the insensitivity of the qualitative liquid phase to the salinity effects in the cases of high preferential oil/water solubilities is attributed to either: 1) the inability of the mutual solvent to enter the aqueous phase in the case of high preferential oil solubility; 2) the very high solubility of the mutual solvent in the water to a point beyond which increasing the salinity cannot salt-out significant amounts of the mutual solvent from the aqueous phase.

In other cases where three-phase formation occurs (i.e. no/low/intermediate preferential oil solubility), it is perfectly reasonable that an increase in preferential oil solubility would lead
to three-phase formation at lower salinities. This is a direct result of an increased sensitivity of the oil/brine/MS system to the salting-out of the mutual solvent from the aqueous phase as the salinity increases.

Since the three-phase region appears and disappears as the salinity increases (e.g. the EGMBE system shown in Figure 3.59), it is postulated that at a fixed brine chemistry, three-phase formation will occur over a well-defined (Δ[TDS]) interval. A lower limit of salinity will determine the onset of three-phase formation, and a higher limit of salinity will determine the disappearance of the three-phase region. It is also suggested that mutual solvents with no/limited preferential affinities to oil/water will generally form three-phases at very high salinities as demonstrated by this work.

Table 3.3: Summary of the qualitative liquid phase behaviour effects as a function of log10 P_{o/w} (MS).

<table>
<thead>
<tr>
<th>Benchmark log10 P_{o/w} (MS)</th>
<th>Designation</th>
<th>Effects</th>
</tr>
</thead>
</table>
| ~ > 1.25                    | High preferential oil solubility | - No effects on the qualitative liquid phase behaviour  
- Complete binary oil miscibility at all concentrations  
- Complete immiscibility otherwise |
| ~ 0.75 to 1.25              | Intermediate preferential oil solubility | - Three-phase formation at low/intermediate salinities |
| ~ -0.25 to 0.75             | No/low preferential oil solubility | - Three-phase formation at high salinities |
| ~ < -0.25                   | High Preferential water solubility | - No effects on the qualitative liquid phase behaviour  
- Complete binary brine miscibility at all concentrations  
- Complete immiscibility otherwise |

The same logic can be constructed and applied to other parameters influencing the phase behaviour in oil/brine/mutual solvent systems, e.g. temperature, pressure and oil quality.

3.5.3. Salinity in Context

Out of context, the effects of salinity summarised in section 3.5.2.4 are in fact misleading at best, and erroneous at worst. Therefore, it is essential to contextualise the described effects. To do so, the science behind why the salinity has the effects discussed in section 3.5.2.4 must be explored. The influence of salts on the solubility of hydrophobes is well understood. For the partially hydrophobic amphiphiles, explanations in the literature were offered based on the Hard-Soft-Acid-Base (HSAB) Theory (Pearson, 1968a; Kahlweit et al., 1988a). Water is a hard solvent, whereas amphiphiles are soft solvents due to their
partial non-polarity (Pearson, 1968b). Oils are softer solvents than amphiphiles as they lack polar functional groups. As for solutes, examples of hard and soft acids are provided in Table 3.4. The same for hard and soft bases is provided in Table 3.5.

**Table 3.4: Classification of Lewis acids (Pearson, 1968a).**

<table>
<thead>
<tr>
<th>Hard</th>
<th>Soft</th>
</tr>
</thead>
<tbody>
<tr>
<td>H&lt;sup&gt;+&lt;/sup&gt;, Li&lt;sup&gt;+&lt;/sup&gt;, Na&lt;sup&gt;+&lt;/sup&gt;, K&lt;sup&gt;+&lt;/sup&gt;</td>
<td>Cu&lt;sup&gt;+&lt;/sup&gt;, Ag&lt;sup&gt;+&lt;/sup&gt;, Au&lt;sup&gt;+&lt;/sup&gt;, Tl&lt;sup&gt;+&lt;/sup&gt;, Hg&lt;sup&gt;+&lt;/sup&gt;</td>
</tr>
<tr>
<td>Be&lt;sup&gt;2+&lt;/sup&gt;, Mg&lt;sup&gt;2+&lt;/sup&gt;, Ca&lt;sup&gt;2+&lt;/sup&gt;, Sr&lt;sup&gt;2+&lt;/sup&gt;, Mn&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>Pd&lt;sup&gt;2+&lt;/sup&gt;, Cd&lt;sup&gt;2+&lt;/sup&gt;, Pt&lt;sup&gt;2+&lt;/sup&gt;, Hg&lt;sup&gt;2+&lt;/sup&gt;, CH&lt;sub&gt;3&lt;/sub&gt;Hg&lt;sup&gt;+&lt;/sup&gt;, Co(CN)&lt;sub&gt;5&lt;/sub&gt;&lt;sup&gt;2-&lt;/sup&gt;, Pt&lt;sup&gt;4+&lt;/sup&gt;, Te&lt;sup&gt;4+&lt;/sup&gt;</td>
</tr>
<tr>
<td>Al&lt;sup&gt;3+&lt;/sup&gt;, Sc&lt;sup&gt;3+&lt;/sup&gt;, Ga&lt;sup&gt;3+&lt;/sup&gt;, In&lt;sup&gt;3+&lt;/sup&gt;, La&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>Tl&lt;sup&gt;3+&lt;/sup&gt;, Tl(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;, BH&lt;sub&gt;3&lt;/sub&gt;, Ga-(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>N&lt;sup&gt;3+&lt;/sup&gt;, Cl&lt;sup&gt;3+&lt;/sup&gt;, Gd&lt;sup&gt;3+&lt;/sup&gt;, Lu&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>GaCl&lt;sub&gt;3&lt;/sub&gt;, GaI&lt;sub&gt;3&lt;/sub&gt;, InCl&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>Cr&lt;sup&gt;2+&lt;/sup&gt;, Co&lt;sup&gt;3+&lt;/sup&gt;, Fe&lt;sup&gt;3+&lt;/sup&gt;, As&lt;sup&gt;3+&lt;/sup&gt;, CH&lt;sub&gt;3&lt;/sub&gt;Sn&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>RS&lt;sup&gt;+&lt;/sup&gt;, RSe&lt;sup&gt;+&lt;/sup&gt;, RTTe&lt;sup&gt;+&lt;/sup&gt;</td>
</tr>
<tr>
<td>Si&lt;sup&gt;4+&lt;/sup&gt;, Ti&lt;sup&gt;4+&lt;/sup&gt;, Zr&lt;sup&gt;4+&lt;/sup&gt;, Th&lt;sup&gt;4+&lt;/sup&gt;, U&lt;sup&gt;4+&lt;/sup&gt;</td>
<td>I&lt;sup&gt;-&lt;/sup&gt;, Br&lt;sup&gt;-&lt;/sup&gt;, HO&lt;sup&gt;-&lt;/sup&gt;, RO&lt;sup&gt;-&lt;/sup&gt;</td>
</tr>
<tr>
<td>Pu&lt;sup&gt;4+&lt;/sup&gt;, Ce&lt;sup&gt;3+&lt;/sup&gt;, Hf&lt;sup&gt;4+&lt;/sup&gt;, WO&lt;sup&gt;4+&lt;/sup&gt;, Sn&lt;sup&gt;4+&lt;/sup&gt;</td>
<td>Sn&lt;sup&gt;4+&lt;/sup&gt;, Sn&lt;sup&gt;2+&lt;/sup&gt;, VO&lt;sup&gt;2+&lt;/sup&gt;, MoO&lt;sup&gt;3+&lt;/sup&gt;</td>
</tr>
<tr>
<td>UO&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;2+&lt;/sup&gt;, (CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Sn&lt;sup&gt;2+&lt;/sup&gt;, VO&lt;sup&gt;2+&lt;/sup&gt;, MoO&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>I&lt;sub&gt;2&lt;/sub&gt;, Br&lt;sub&gt;2&lt;/sub&gt;, ICN, etc.</td>
</tr>
<tr>
<td>BeMe&lt;sub&gt;2&lt;/sub&gt;, BF&lt;sub&gt;3&lt;/sub&gt;, B(OR)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>trinitrobenzene, etc.</td>
</tr>
<tr>
<td>Al(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;, AlCl&lt;sub&gt;3&lt;/sub&gt;, AlH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>chloranil, quinones, etc.</td>
</tr>
<tr>
<td>RPO&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;, ROPO&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;</td>
<td>tetracyanoethylene, etc.</td>
</tr>
<tr>
<td>RSO&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;, RO&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;, SO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>O&lt;sup&gt;-&lt;/sup&gt;, Cl&lt;sup&gt;-&lt;/sup&gt;, Br&lt;sup&gt;-&lt;/sup&gt;, I&lt;sup&gt;-&lt;/sup&gt;, N&lt;sup&gt;-&lt;/sup&gt;, RO&lt;sup&gt;-&lt;/sup&gt;, RO&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</td>
</tr>
<tr>
<td>I&lt;sup&gt;-&lt;/sup&gt;, I&lt;sup&gt;5+&lt;/sup&gt;, Cl&lt;sup&gt;7+&lt;/sup&gt;, Cl&lt;sup&gt;9+&lt;/sup&gt;</td>
<td>M&lt;sup&gt;+&lt;/sup&gt; (metal atoms)</td>
</tr>
<tr>
<td>RCO&lt;sup&gt;+&lt;/sup&gt;, CO&lt;sub&gt;2&lt;/sub&gt;, NC&lt;sup&gt;+&lt;/sup&gt;</td>
<td>bulk metals</td>
</tr>
<tr>
<td>HX (hydrogen bonding molecules)</td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;, carbenes</td>
</tr>
</tbody>
</table>

**Borderline**

| Fe<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup>, Sn<sup>2+</sup>, Sb<sup>3+</sup>, Bi<sup>3+</sup> | Rh<sup>3+</sup>, Ir<sup>3+</sup>, B(CH<sub>3</sub>)<sub>3</sub>, SO<sub>2</sub>, NO<sup>+</sup>, Ru<sup>2+</sup>, Os<sup>2+</sup>, Re<sup>3+</sup>, C<sub>6</sub>H<sub>5</sub><sup>+</sup>, GaH<sub>3</sub> |
The principle for explaining the salinity effects is very simple, and follows the basic and commonly used rule “like dissolves like”. As such, salts can be categorised in two groups: lyotropic salts which make hydrophobes less soluble in water, and hydrotropic salts which make hydrophobes more soluble in water. Lyotropic salts are salts of hard acids and hard bases, while hydrotropic salts are salts of hard acids and soft bases or hard bases and soft acids (Kahlweit et al., 1988). Taking all of this into account, increasing the TDS of a brine can very much do both, enhance or reduce the solubility of an amphiphile in the brine; much will depend on the actual chemistry of the brine. Thus, a brine can be described as being rich in either lyotropes or hydrotropes.

Table 3.6: Classification of the Lewis acids and bases dominating formation and seawater brines.

<table>
<thead>
<tr>
<th>Ions</th>
<th>Lewis Acid</th>
<th>Lewis Base</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Soft</td>
<td>Hard</td>
</tr>
<tr>
<td>Na⁺</td>
<td>✔</td>
<td></td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>✔</td>
<td></td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>✔</td>
<td></td>
</tr>
<tr>
<td>K⁺</td>
<td>✔</td>
<td></td>
</tr>
<tr>
<td>Ba²⁺</td>
<td>✔</td>
<td></td>
</tr>
<tr>
<td>Sr²⁺</td>
<td>✔</td>
<td></td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td></td>
<td>✔</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>✔</td>
<td></td>
</tr>
</tbody>
</table>

However, in practical field scenarios and with reference to Table 3.4 and Table 3.5, hydrotropes-rich brines will never be encountered. Soft acids and bases are, if at all present in the brine, will only exist in trace amounts in the field. As seen in Table 3.6, and as a
proof of concept, all the dominant ions encountered in the field are hard acids and bases, i.e. all practically encountered brines are lyotropes-rich brines. Hence, in the context of practical field scenarios, it is fair to say that as the TDS of the brine increases, the solubility of the amphiphilic mutual solvent will always decrease.

Another key point to highlight is that the P_{o/w} used to benchmark the phase behaviour of mutual solvents is a relative parameter, i.e. two mutual solvents can exhibit the same P_{o/w}, however, different specific solubilities in the oil and the brine. The effect of this will not be observed in oil/brine/MS mixtures on a qualitative basis. This is because the relative solubilities captured by the P_{o/w} will always be the dominant effect in these cases. The absolute solubilities will only be important in defining the binary oil/MS and oil/brine solubilities, and as such, it will not impact the overall findings described in section 3.5.2.
3.6. BRINE CHEMISTRY EFFECTS

3.6.1. Liquid Phase Behaviour Effects

Brines of similar salinities but different chemistries will not necessarily give the same phase behaviour. Here, the ionic composition of the brine becomes important in predicting the phase behaviour. An example is provided in Figure 3.12. Two brines of identical TDS are compared, namely: NSSW brine, and Sulphate-Free NSSW (SFNSSW) brine whose sodium levels were increased to match NSSW brine TDS. Figure 3.12b highlights the higher solubility of EGMBE in the SFNSSW brine with reference to the normal NSSW brine in Figure 3.12a, i.e. no binary brine-MS partial insolubility.

These effects cannot be attributed to the polarity of sulphate ions. Sulphate ions have a symmetrical tetrahedral structure, with the central sulphur atom surrounded by four oxygen atoms. The preferred Lewis structure of sulphate has six resonances as shown in Figure 3.13 (Brady, Russell and Holum, 2000; House, 2013). Since the electronegativity of oxygen is the same for the four oxygen atoms, the sulphate ion cannot have a permanent dipole. Therefore, it is essentially nonpolar.
Instead, the effects observed in Figure 3.12 can be explained almost entirely with reference to the Hofmeister Series (Hofmeister, 1888). The Hofmeister series describes the efficiency of lyotropic ions in salting out hydrophobes. Amphiphiles (e.g. mutual solvents) are partially hydrophobic, and hence this series applies. The order of this series for anions (Baldwin, 1996) is given by equation (3.1) below:

\[ SO_4^{2-} > OH^-; F^- > Cl^- > Br^- > NO_3^- > ClO_4^- > I^- \]  

From the series above, it can be concluded that sulphates are more efficient than chlorides in salting out amphiphiles. This explains the observations in Figure 3.12.

Furthermore, it is also suggested that ionic strength will also play a small role in this case. This is since removing the divalent (SO_4^{2-}) ions and replacing them with (Na^+) and (Cl^-) monovalent ions to keep the TDS constant would still have the effect of reducing the SFNSSW ionic strength (by roughly 2.5% with respect to NSSW), with the ionic strength given by equation (3.2) below:

\[ I = \frac{1}{2} \sum_{i=1}^{n} c_i z_i^2 \]  

3.6.2. Mutual Solvent Driven Inorganic Precipitation

From the salinity mapping investigations discussed in section 3.5, three scenarios of mutual solvent driven inorganic precipitation were identified:

1. Precipitation of sulphate salts. This is caused by any mutual solvent in the presence of sulphate ions, e.g. in seawater.
2. Precipitation of non-sulphate salts. This is caused only by highly polar mutual solvents at intermediate salinities. At very high salinities, all mutual solvents will precipitate non-sulphate salts.
3. Co-precipitation of sulphate and non-sulphate salts. This happens when a highly polar mutual solvent is mixed with a brine which contains sulphate ions such as seawater.

Experiments to investigate this were conducted for all mutual solvents and the results were fully consistent. The precipitation scenarios described above are best illustrated by the following three examples:

1. EGMBE mixed with NSSW (sulphate-rich brine) in a 90:10% v/v proportions.
2. Acetone mixed with NFFW (sulphate-free brine) in a 90:10% v/v proportions.
3. Acetone mixed with NSSW (sulphate-rich brine) in a 90:10% v/v proportions.

The qualitative phase diagrams of these systems with mineral oil, as well as an analysis of the precipitates formed as outlined in section 3.4.2 will be provided below.

3.6.2.1. Qualitative Phase Diagrams Illustrating the Precipitation Scenarios

The qualitative phase diagrams of EGMBE and acetone with mineral oil and: (a) NSSW; (b) NFFW, are provided in Figure 3.14 and Figure 3.15 respectively. In a sulphate-rich (NSSW) brine, a large precipitation region is observed on the phase diagram (Figure 3.14a and Figure 3.15a) as opposed to a very small or absent precipitation region in a sulphate-free (NFFW) brine (Figure 3.14b and Figure 3.15b). This is despite the sulphate-free (NFFW) brine used in the example being 2.5 times more saline than the sulphate-rich (NSSW) brine, thereby indicating the role of the sulphate ion rather than the effect of salinity or ionic strength.

Taking the brine compositions into account (Table 3.2), Figure 3.14 and Figure 3.15 perfectly illustrate the three precipitation scenarios outlined before. Figure 3.14b indicates that EGMBE is unable to precipitate any chloride salts in the more saline NFFW. The anions in NSSW are sulphates and chlorides. Ruling out the role of the chloride ions in creating the precipitation region observed on Figure 3.14a, the inorganic precipitates must be salts of sulphate ions (i.e. the first precipitation scenario).

Figure 3.15b highlights the ability of acetone to precipitate chloride salts. A small precipitation region is observed at 90% acetone concentration in the sulphate-free NFFW. With the chlorides being the only other anion in NFFW, these precipitates must be salts of chloride ions (i.e. the second precipitation scenario). Therefore, in NSSW where sulphate
ions are present, acetone has the potential to precipitate both sulphate and chloride ions (i.e. the third precipitation scenario).

Figure 3.14: The impact brine chemistry on precipitation – the phase diagram of EGMBE ($\log_{10} P_{o/w} = 0.80$) at 22.5°C and 1 atm with mineral oil and: (a) NSSW (sulphate-rich); (b) NFFW (sulphate-free).

Two additional examples illustrating these effects are highlighted in Figure 3.16 and Figure 3.17. With the preferentially oil soluble DGBE (Figure 3.16), sulphate precipitation occurs at almost all DGBE concentrations, resulting in a large precipitation region in the sulphate-rich NSSW (Figure 3.16a). A much smaller precipitation region is observed when the brine is the sulphate-free MGFW (7.3 times more saline than NSSW) as seen in Figure 3.16b. Note that with DGBE, precipitation does not occur when the brine is the sulphate-free NFFW (2.5 times more saline than NSSW).
Likewise with ethanol, the sulphate problem is evident (Figure 3.17). Ethanol has a greater tendency than acetone to precipitate chloride salts at intermediate salinities as observed in Figure 3.17b. Therefore, in NSSW, when ethanol is the mutual solvent, co-precipitation of sulphate and chloride salts will occur over a wider region on the phase diagram.

3.6.2.2. ESEM/EDX Analysis of the Inorganic Precipitates

For the sulphate precipitation case, an example involving EGMBE mixed with NSSW (sulphate-rich brine) at 90:10% v/v proportions is presented. An ESEM picture and the results of an EDX elemental micro-analysis (converted to molar basis) are presented in Figure 3.18.
The ESEM illustrates the heterogeneity of the precipitates, which implies that their chemical make-up can involve more than one salt. The qualitative molar compositions confirm this, showing the presence of all the cations present in NSSW, and the absence of any chloride precipitation. Therefore, only sulphate salts are present. The qualitative EDX results indicate that the salts are dominated by Na$_2$SO$_4$ and CaSO$_4$, with traces of MgSO$_4$ and K$_2$SO$_4$.

The results for DGBE are provided as another example in Figure 3.19, with a close-up on the precipitates. The fine crystals of sulphate are difficult to image closely with high contrast using ESEM due to their nature. However, the results of the EDX for DGBE are consistent with the results for EGMBE.

![Image](image.png)

**Figure 3.18:** The ESEM of the precipitates from a 90:10% v/v mixture of EGMBE to NSSW at t = 24 hour, with the EDX results provided in molar concentrations.
Figure 3.19: The ESEM of the precipitates from a 90:10% v/v mixture of DGBE to NSSW at t = 24 hour, with the EDX results provided in molar concentrations.

For the non-sulphate precipitation case, an example involving acetone mixed with NFFW (sulphate-free brine) at 90:10% v/v proportions is presented. The results are shown in Figure 3.20. The precipitates observed were cubic and homogenous. The elemental analysis highlights the nature of the salts, which are dominated by NaCl. Trace amounts of CaCl$_2$ and KCl are also detected. Additional examples are provided for ethanol and IPA in Figure 3.21 and Figure 3.22. The results are fully consistent with the acetone example, and the ESEM picture shows clearly the cubic crystal structure of NaCl.
Figure 3.20: The ESEM of the precipitates from a 90:10% v/v mixture of Acetone to NFFW at $t = 24$ hour, with the EDX results provided in molar concentrations.

<table>
<thead>
<tr>
<th>Ion</th>
<th>[Molar], %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$</td>
<td>56.33</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>0.21</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>0.00</td>
</tr>
<tr>
<td>K$^+$</td>
<td>0.23</td>
</tr>
<tr>
<td>SO$_2^-$</td>
<td>0.00</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>43.23</td>
</tr>
</tbody>
</table>

Figure 3.21: The ESEM of the precipitates from a 90:10% v/v mixture of Ethanol to NFFW at $t = 24$ hour, with the EDX results provided in molar concentrations.

<table>
<thead>
<tr>
<th>Ion</th>
<th>[Molar], %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$</td>
<td>61.83</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>0.00</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>0.00</td>
</tr>
<tr>
<td>K$^+$</td>
<td>0.00</td>
</tr>
<tr>
<td>SO$_2^-$</td>
<td>0.00</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>38.17</td>
</tr>
</tbody>
</table>
Figure 3.22: The ESEM of the precipitates from a 90:10% v/v mixture of IPA to NFFW at t = 24 hour, with the EDX results provided in molar concentrations.

For the mixed precipitation case, an example involving acetone mixed with NSSW (sulphate-rich brine) at 90:10% v/v proportions is presented. The results are shown in Figure 3.23. It can be clearly seen from the ESEM picture and the EDX analysis that NaCl is co-precipitating with Na$_2$SO$_4$ and CaSO$_4$. The results for ethanol and IPA were fully consistent with the results of acetone. These are the only studied mutual solvents which co-precipitate sulphate and chloride salts when possible. What distinguishes them from other mutual solvents is their higher polarity.
3.6.2.3. ICP-OES Analysis of the Inorganic Precipitates

This analysis will focus on the first precipitation scenario, i.e. sulphate precipitation only. This is in order to establish qualitatively the relative contributions of the precipitated sulphate salts with respect to the brine composition. With the second precipitation scenario, the precipitates are almost entirely NaCl as confirmed by the ESEM/EDX analysis.

The results of analysis of the supernatant are summarised in Figure 3.24. These results are used to calculate \( \frac{C}{C_0} \) representing the ions reacted to form the inorganic precipitates. The results are provided in Figure 3.25. The results indicate almost complete precipitation of the calcium ion in the brine with the sulphate ions. Therefore, the precipitates are dominated by CaSO\(_4\), with the other sulphate salts present in appreciable but variable amounts. Therefore, significant CaSO\(_4\) precipitation should be expected in the presence of the mutual solvent and a sulphate-rich brine.

Despite the higher solubility of CaSO\(_4\) compared to conventional oilfield scales, it has the risk of causing significant formation damage (Mahmoud, 2014). Therefore, injection of the mutual solvent in sulphate-rich environments should consider this. The use of scale inhibitors is the most effective strategy in these scenarios since: 1) sulphate salts are observed at most MS concentrations, therefore limiting the MS concentration will not help...
in most cases; 2) sulphate precipitation happens with all mutual solvents tested, therefore choice of mutual solvent is not a mitigation parameter.

With NaCl precipitation however, this is unlikely to cause formation damage due to the very high solubility of NaCl. However, it is important to highlight that the severity of a NaCl precipitation (in terms of mass precipitated) can be much higher than that of a CaSO$_4$ precipitation. This is illustrated for the 90:10% v/v MS to brine mixtures in Figure 3.26, where samples involving NaCl precipitation in NFW show a higher degree of precipitation. NaCl precipitation can be easily avoided through MS dilution or MS selection. This is because, unlike the sulphate problem, precipitation tends to happen at very high MS concentrations only at intermediate salinities, and only occurs for the highly polar mutual solvents.

![Unreacted ions due to the mutual solvent via ICP-OES](image)

*Figure 3.24: The ICP-OES of the supernatant from a 90:10% v/v mixture of MS to NSSW at t = 24 hour.*
Figure 3.25: The precipitates from a 90:10% v/v mixture of MS to NSSW at t = 24 hour.

Figure 3.26: The precipitates from a 90:10% v/v mixture of MS to brine at t = 24 hour.
3.7. SCALE INHIBITOR EFFECTS

3.7.1. Scale Inhibitor Effects: Aims

The aim of the experiments described in this section is to provide a general understanding of the main effects of scale inhibitors (SI) on the phase behaviour in oil/brine/mutual solvent systems. Two classes of scale inhibitors are directly relevant to this work, namely: polymers and phosphonates. Of these, PPCA (polymer) and DETPMP (phosphonate) are the most commonly used SI in oil field applications for SI squeeze treatments. Therefore, their effects on the phase behaviour of oil/brine/mutual solvent systems at various concentrations is of great interest.

3.7.2. Methodology

The general experimental procedure is described in section 3.4. The mutual solvent chosen for SI effects investigations is EGMBE due to its common use in the pre-flush stage of a treatment. The phase behaviour was studied with Multipar H oil and NSSW at laboratory conditions (22.5°C and 1 atm). The scale inhibitor was added to the brine prior to mapping the phase diagram qualitatively. It is important to highlight that the addition of the SI to the brine means that the concentration of the SI in any test sample would be dictated by the fraction of the brine in the sample. This mimics scenarios in oil field applications where the scale inhibitor is delivered into the formation within a brine.

Due to the effects of pH on the inhibition efficiency of the scale inhibitor, the pH of the brine was fixed at 5.5 for all experiments through pH adjustments. For both, PPCA and DETPMP, the following active concentrations were investigated separately: 1000 ppm, 5000 ppm, 10000 ppm, 15000 ppm, 20000 ppm, 30000 ppm, 40000 ppm and 50000 ppm. The details of the SI used in the experiment are provided in Table 3.7, and their structures are provided in Table 3.8. All tests were performed over a 24 hours period.

Table 3.7: Details of the SI used in the experiments.

<table>
<thead>
<tr>
<th>Mutual Solvent</th>
<th>Supplier</th>
<th>Batch No.</th>
<th>Activity</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphino (Poly Carboxylic Acid) – PPCA, i.e. Bellasol S40</td>
<td>BWA</td>
<td>2015084995</td>
<td>40.3%</td>
<td>Phosphonate</td>
</tr>
<tr>
<td>Diethylene Triamine Penta (Methylene Phosphoric acid) – DETPMP, i.e. Dequest 2066A</td>
<td>Italmatch</td>
<td>4K370</td>
<td>47.0%</td>
<td>Phosphonate</td>
</tr>
</tbody>
</table>
Table 3.8: Structures of the SI used in the experiments.

<table>
<thead>
<tr>
<th>Scale Inhibitor</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diethylene Triamine Penta (Methylene Phosphoric acid) – DETPMP, i.e. Dequest 2066A</td>
<td><img src="image" alt="Structure of DETPMP" /></td>
</tr>
<tr>
<td>Phosphino (Poly Carboxylic Acid) – PPCA, i.e. Bellasol S40</td>
<td><img src="image" alt="Structure of PPCA" /></td>
</tr>
</tbody>
</table>

3.7.3. Results and Discussion

3.7.3.1. Base Case for the Investigation

Consider the phase behaviour of EGMBE with Multipar H oil and NSSW (Figure 3.27), precipitation was found to occur at or above 40% \( v/v \) EGMBE feed concentration. The precipitates are sulphate salts dominated by \( \text{CaSO}_4 \) with smaller amounts of other sulphate salts (section 3.6.2). This is the base case for investigations involving both PPCA and DETPMP.
Figure 3.27: The liquid phase behaviour of EGMBE ($\log_{10} P_{o/w} = 0.80$) with mineral oil and NSSW at 22.5°C and 1 atm

3.7.3.2. Effects of PPCA on Phase Behaviour

The results for PPCA at 1000 ppm, 5000 ppm, 10000 ppm, 15000 ppm, 20000 ppm, 30000 ppm, 40000 ppm and 50000 ppm are shown in Figure 3.28, Figure 3.29, Figure 3.30, Figure 3.31, Figure 3.32, Figure 3.33, Figure 3.34 and Figure 3.35 respectively. Overall, the PPCA is found to have small effects on the liquid phase behaviour of the system with reference to the base case (Figure 3.27). The partial immiscibility between NSSW-EGMBE is influenced by this, showing an overall increase, as well as an overall increase in the size of the three-phase region. The inorganic precipitation region on the phase diagram is reduced to only very high [EGMBE] concentrations with increasing PPCA concentration. However, it takes high concentrations of PPCA to achieve this effect. PPCA is predominantly a nucleation inhibitor (Shaw, Sorbie and Boak, 2010). When these tests were conducted, initially no scaling is observed. However, at 24 hours at the highest tested concentration for PPCA (Figure 3.35), precipitation is observed at 90:10% v/v EGMBE:NSSW. This indicates that PPCA achieves inhibition initially, and the observed precipitation is not the result of incompatibility at the tested concentrations. Instead, it is the result of loss of inhibition efficiency of PPCA as it incorporates in crystal lattices over time (Graham, Sorbie and Jordan, 1997).
Figure 3.28: Phase behaviour of EGMBE with Multipar H and NSSW+PPCA at 1,000 ppm active concentration (22.5°C and 1 atm).

Figure 3.29: Phase behaviour of EGMBE with Multipar H and NSSW+PPCA at 5,000 ppm active concentration (22.5°C and 1 atm).
Figure 3.30: Phase behaviour of EGMBE with Multipar H and NSSW+PPCA at 10,000 ppm active concentration (22.5°C and 1 atm).

Figure 3.31: Phase behaviour of EGMBE with Multipar H and NSSW+PPCA at 15,000 ppm active concentration (22.5°C and 1 atm).
Figure 3.32: Phase behaviour of EGMBE with Multipar H and NSSW+PPCA at 20,000 ppm active concentration (22.5°C and 1 atm).

Figure 3.33: Phase behaviour of EGMBE with Multipar H and NSSW+PPCA at 30,000 ppm active concentration (22.5°C and 1 atm).
Figure 3.34: Phase behaviour of EGMBE with Multipar H and NSSW+PPCA at 40,000 ppm active concentration (22.5°C and 1 atm).

Figure 3.35: Phase behaviour of EGMBE with Multipar H and NSSW+PPCA at 50,000 ppm active concentration (22.5°C and 1 atm).
3.7.3.3. Effects of DETPMP on Phase Behaviour

The results for DETPMP at 1000 ppm, 5000 ppm, 10000 ppm, 15000 ppm, 20000 ppm, 30000 ppm, 40000 ppm and 50000 ppm are shown in Figure 3.36, Figure 3.37, Figure 3.38, Figure 3.39, Figure 3.40, Figure 3.41, Figure 3.42 and Figure 3.43 respectively. At 1000 ppm (Figure 3.36), precipitation grows on the EGMBE and brine side of the phase diagram, to dominate the entire phase diagram at 5000 ppm (Figure 3.37). The precipitation remains markedly high at 10000 ppm (Figure 3.38), but starts to recede at 15000 ppm (Figure 3.39) until it disappears completely at [DETPMP] ≤ 20000 ppm (Figure 3.40). Above 20000 ppm (Figure 3.41, Figure 3.42 and Figure 3.43), there is no precipitation up to 50000 ppm.

As to the effects of the DETPMP on the liquid phase behaviour, the partial insolubility of EGMBE in the brine increases due to salting out effects of the mutual solvent analogous to the salinity effects described in section 3.5. This continues until the EGMBE becomes completely insoluble in the brine at [DETPMP] ≤ 40,000 ppm (Figure 3.42). The three-phase region is largest at low DETPMP concentration, but starts to shrink very slightly with increasing DETPMP concentration.

The precipitation observed on the phase diagram, its emergence with DETPMP presence (Figure 3.37) and disappearance around 20000 ppm DETPMP (Figure 3.40) can be explained by looking at the chemistry and phase behaviour of DETPMP with calcium. DETPMP is predominantly a crystal growth scale inhibitor (Graham, Boak and Sorbie, 2003). It can chelate with divalent and trivalent cations, e.g. (Ca$^{2+}$) and (Mg$^{2+}$) (Nowack and Stone, 2006). The calcium/magnesium complexes attach to active crystal growth sites of an already formed crystal, rendering further crystal growth infeasible (Graham, Boak and Sorbie, 2003). DETPMP is well known for its ability to inhibit BaSO$_4$ (Graham, Boak and Sorbie, 2003), which has an orthorhombic crystal structure (Fendler, 2008). Na$_2$SO$_4$ and K$_2$SO$_4$ also have the same orthorhombic crystal structure (Garrett, 2001; Schultz et al., 2006). Therefore, the inhibition of the sulphate salts by DETPMP in mixtures of NSSW and EGMBE happens by two mechanisms. The sequestering of calcium/magnesium by DETPMP inhibits CaSO$_4$ and MgSO$_4$ formation. As for Na$_2$SO$_4$ and K$_2$SO$_4$, their inhibition proceeds through the attachment of Ca/Mg-DETPMP complexes to active growth sites on the orthorhombic crystals.
The above hypothesis for Na$_2$SO$_4$ and K$_2$SO$_4$ inhibition is also supported by the fact that
the sequestering of Ca$^{2+}$ by the DETPMP should further promote their precipitation
according to Le Châtelier's principle (as highlighted by the reactions below). Despite this,
they remains in the solution, and hence this is the effect of the DETPMP.

\[
2 \text{Na}^+_{(aq)} + \text{SO}_4^{2-}_{(aq)} \leftrightarrow \text{Na}_2\text{SO}_4_{(s)} \quad 3.3
\]

\[
2 \text{K}^+_{(aq)} + \text{SO}_4^{2-}_{(aq)} \leftrightarrow \text{K}_2\text{SO}_4_{(s)} \quad 3.4
\]

\[
\text{Ca}^{2+}_{(aq)} + \text{SO}_4^{2-}_{(aq)} \leftrightarrow \text{CaSO}_4_{(s)} \quad 3.5
\]

As described before, a surge in precipitation above that driven by EGMBE was observed
(Figure 3.27, Figure 3.36, Figure 3.37, Figure 3.38 and Figure 3.39). This is prior to the
inhibition of EGMBE driven precipitation (Figure 3.40, Figure 3.41, Figure 3.42 and Figure
3.43). The additional precipitates are in fact the Ca-DETPMP and Mg-DETPMP complexes, which return to the solution with increasing DETPMP concentration due to the
sequestration of (Ca$^{2+}$) (Sorbie et al., 1993), and some of the (Mg$^{2+}$). The phase behaviour
of DETPMP with calcium is well described in the literature, and it is influenced by
additional factors such as the temperature and the pH (Vetter, 1973; Pardue, 1991; Sorbie
et al., 1993). Therefore, this work only provides a snapshot of the phase behaviour effects
in oil/brine/mutual solvent systems in the presence of DETPMP. However, the basic
principles remain the same.

The phase diagram shown in Figure 3.44 (work of Sorbie et al. (1993)) is of particular
importance. From this, it can be speculated that precipitation in a system of DETPMP,
brine and EGMBE will reduce initially at low DETPMP concentration, before the Ca-
DETPMP and Mg-DETPMP complexes start to precipitate. If this is the case, then two no-
precipitation regions may exist depending on the calcium, namely: 1) at very low
[DETPMP], where [DETPMP] is high enough to inhibit EGMBE driven sulphate precipitation but not too high that Ca-DETPMP and Mg-DETPMP would start precipitating; and 2) at very high [SI]. Further investigations of this are beyond the scope
of this work, and the observed effects would vary depending on the system parameters from
oil, pH, temperature, [Ca$^{2+}$] and the presence other divalent ions to name a few. The value
of the findings in this work is in highlighting potential benefits for adding a phosphonate scale inhibitor to a mutual solvent blend and the associated formation damage risks.
However, the details of this will need to be decided on a case by case basis for any related
field applications.
Figure 3.36: Phase behaviour of EGMBE with Multipar H and NSSW+DETPMP at 1,000 ppm active concentration (22.5°C and 1 atm).

Figure 3.37: Phase behaviour of EGMBE with Multipar H and NSSW+DETPMP at 5,000 ppm active concentration (22.5°C and 1 atm).
Figure 3.38: Phase behaviour of EGMBE with Multipar H and NSSW+DETPMP at 10,000 ppm active concentration (22.5°C and 1 atm).

Figure 3.39: Phase behaviour of EGMBE with Multipar H and NSSW+DETPMP at 15,000 ppm active concentration (22.5°C and 1 atm).
Figure 3.40: Phase behaviour of EGMBE with Multipar H and NSSW+DETPMP at 20,000 ppm active concentration (22.5°C and 1 atm).

Figure 3.41: Phase behaviour of EGMBE with Multipar H and NSSW+DETPMP at 30,000 ppm active concentration (22.5°C and 1 atm).
Figure 3.42: Phase behaviour of EGMBE with Multipar H and NSSW+DETPMP at 40,000 ppm active concentration (22.5°C and 1 atm).

Figure 3.43: Phase behaviour of EGMBE with Multipar H and NSSW+DETPMP at 50,000 ppm active concentration (22.5°C and 1 atm).
Figure 3.44: The influence of pH on the phase diagram of DETPMP with Ca$^{2+}$ at 95°C (Sorbie et al. (1993)).
3.8. MUTUAL SOLVENT BLENDS

3.8.1. Mutual Solvent Blends: Aims

The aim of the experiments described in this section is to provide an understanding of how mutual solvents behave in blends. In the simplest cases, blends can comprise of a single mutual solvent and a scale inhibitor, or two or more mutual solvents. Blends can also involve several scale inhibitors and mutual solvents. This is in addition to additives such as emulsion breakers and water. However, the focus of the investigations will be the simple cases for mutual solvent blends which would be applicable to general scenarios in field applications.

The incentive for this research is the ultimate goal of understanding the criteria for targeting specific phase behaviour through mutual solvent blend design. Ideally, the targeted specific phase behaviour is the phase behaviour that makes a “good” mutual solvent which can achieve the intended effects of avoiding formation damage while extending the squeeze lifetime.

3.8.2. “Good” Mutual Solvents

The question on what makes a “good” mutual solvent has not been addressed specifically in the past. Primarily, the literature on mutual solvents in relation to squeeze treatments is heavily focused on their role in enhancing Scale Inhibitor (SI) adsorption (Collins et al., 1999; Collins and Hewartson, 2002; Vazquez et al., 2009; Vazquez et al., 2011; Collins et al., 1997a). Very little detailed attention has been given as to what makes a “good” mutual solvent.

Some context must be provided before attempting to assign “good” or “bad” traits to mutual solvents. For instance, good mutual solvents cannot be described fully in the context of their ability to enhance SI adsorption. This is because the role of mutual solvents in enhancing SI adsorption is not yet well understood. Other examples include the description of mutual solvents in the context of near-wellbore conditioning, well clean-up, topside handling and environmental effects.

In the discussion that follows, an attempt is made to describe “good” mutual solvents. In particular, the context of this is the phase behaviour of the mutual solvent in oil and brine. As such, a good mutual solvent would be one that manifests any phase behaviour properties
that may be perceived or justified as being beneficial to any aspect of squeeze treatments. The key phase behaviour parameters are:

1. The solubility of the mutual solvent in the relevant oil and brine.
2. The preferential partitioning of the mutual solvent at the reservoir conditions.
3. Three-phase formation.
4. Any mutual solvent driven precipitation.

Firstly, as to the solubility of the mutual solvent in the relevant oil and brine, it appears that complete solubility of the mutual solvents in both the oil and the brine would be a very “good” property. However, the answer may not be this straightforward. Complete solubility of mutual solvents in binary mixtures with the oil and the brine is good for multiphase flow avoidance. It also helps accessing larger areas of the near-wellbore regions. This is because the mutual solvent may be able to access the residual oil and brine which the mutual solvent could mobilise and hence change their relative permeabilities.

However, the solubility of the mutual solvent in the brine can be sacrificed in some cases. An example is when brine chemistry or salinity are very sensitive to mutual solvents, such that inorganic (salt) precipitation and potential formation damage can be caused by any mutual solvent which is highly soluble into the brine phase. In such case, a mutual solvent with limited solubility into the brine might be a better choice. Under this scenario, oil displacement, while less efficient in theory, would still be possible with this mutual solvent without risking any formation damage.

Secondly, as to the partitioning of the mutual solvent (which is also tied to the previous point), preferential partitioning in the oil at the reservoir conditions might be desired. This would help in oil displacement which is thought to be one of the most important functions of mutual solvents (Collins and Hewartson, 2002). Residual oil displacement from the near-wellbore region increases the surface area available for SI adsorption, and potentially the squeeze lifetime. However, if mutual solvent and formation rock interactions were found to be fundamental for enhancements in SI adsorption, and the formation rock is water-wet, preferential water partitioning might be more desirable. This is not yet known.

Thirdly, in regards to three-phase formation, multiphase flow is generally undesirable. However, it is unknown whether this phenomenon would assist in improving the efficiency of oil displacement, and research is ongoing. EGMBE, which is known to form three liquid phases over a wide range of conditions, is an industrial standard for applications at the pre-
flush stage of a treatment. This may change as understanding of what makes a good mutual solvent improves.

Finally, mutual solvent driven precipitation of any inorganic solids is generally thought to give a potential risk of formation damage. Therefore, a good mutual solvent in this regard would be one that does not cause the ions in the brine to precipitate as salts. In mutual solvent blends with a SI, the results may be different. A controlled precipitation of the SI by the mutual solvent in the near-wellbore region may enhance the squeeze lifetime. However, no data in the literature has been found to support this hypothesis.

Overall, it can be seen that even when the context for describing a good mutual solvent is well defined, the decision as to what makes a good mutual solvent can be ambiguous and case specific. Nevertheless, for the purposes of the discussion in this section, a good mutual solvent will be hypothetically assumed to be one with the following traits:

1. Completely soluble in oil at the reservoir condition.
2. Completely soluble in brine at the reservoir condition.
3. Preferentially soluble in the oil at the reservoir conditions.
4. Three-phase forming mutual solvent at the reservoir conditions over a wide area of the phase envelope.
5. A mutual solvent that does not promote any inorganic precipitation.

These assumptions are only assumed to enable the discussions within this section. Much research is needed to expand knowledge in this area.

3.8.3. Methodology

Two set of experiments were conducted. Both sets centralised on using EGMBE as the primary component in a blend containing multiple mutual solvents. In the first set of experiments, two blends (90:10% v/v EGMBE:Ethanol and 60:20:20% v/v EGMBE:IPA:Ethanol) were investigated for a general understanding of the key effects of additives to EGMBE on the phase behaviour. The second set of experiments develops the general understanding required for systematically targeting specific phase behaviour using four mutual solvent blends, namely: 90:10% v/v EGMBE:EGBEA, 80:20% v/v EGMBE:EGBEA, 90:10% v/v EGMBE:MEG and 80:20% v/v EGMBE:MEG. EGBEA is a highly preferentially oil soluble mutual solvent, while MEG is highly preferentially water soluble mutual solvent. Their selection was made to study the most extreme effects on the
phase behaviour to understand what can be achieved from a blend dominated by EGMBE and other MS additives.

3.8.4. Results and Discussion

In a 90:10% v/v blend of EGMBE and Ethanol (Figure 3.46), and with reference to the base case which is the phase behaviour of EGMBE with Multipar H oil and NSSW (Figure 3.45a), the ethanol contributes several phase behaviour changes. On the plus side, the 90:10% v/v EGMBE:Ethanol blend is fully soluble in the brine, whereas EGMBE is partially insoluble in the brine. Moreover, the third phase region is larger by a third on a qualitative point to point basis. On the negative side, precipitation is more profound with the blend rather than with pure EGMBE, with sulphate salts starting to precipitate at much lower mutual solvent concentrations.

Figure 3.45: The liquid phase behaviour of EGMBE (log10 P_o/w = 0.80) at 22.5°C and 1 atm: (a) NSSW base case; (b) SFNSSW base case.
In SFNSSW brine (Figure 3.47), the 90:10% v/v EGMBE:Ethanol blend performs poorly against the base case which is the phase behaviour of EGMBE with Multipar H oil and SFNSSW brine (Figure 3.45b). Precipitation is not a relevant selection parameter here since both EGMBE and the blend do not cause precipitation. The poor performance claim (with reference to the desired attributes defined in 3.8.2) is based on the idea that the three-phase region shrinks by approximately 44% (on qualitative basis) when the blend is used as opposed to using EGMBE alone.
Similarly, the 60:20:20% v/v blend of EGMBE:IPA:Ethanol was tested with SFNSSW. The idea behind the blend was to combine EGMBE with a preferentially oil soluble mutual solvent and a preferentially water soluble mutual solvent that are fully soluble in the brine and the oil respectively. This was done for the purposes of investigating whether this blend design would reduce the size of the multiphase region within the phase diagram to the furthest extent possible (for transport purposes).

The results (Figure 3.48) highlight the elimination of the miscibility gap to EGMBE between SFNSSW and mineral oil and hence no three-phase formation. However, the two-phase region dominates the multicomponent phase behaviour. The theoretical benchmark partition coefficient ($\log_{10} P_{o/w}$) of the blend is 0.44. This was calculated using a simple mixing rule based on the fraction of each constituent in the blend:

$$\log_{10} P_{o/w}(m − MS) = \sum_{i=1}^{n} x_i \log_{10} P_{o/w}(MS_i)$$  

The phase behaviour of the blend (Figure 3.48) is consistent with this theoretical value, indicating a slight affinity to the oil. Hence, it can be conjectured at a working level that the constituents of a multi-mutual-solvent (m-MS) blend behave collectively as single mutual solvent with an overall partition coefficient weighted by the amounts of each

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**Figure 3.47**: Phase behaviour of 90:10 % v/v EGMBE:Ethanol at with Multipar H and SFNSSW (22.5°C and 1 atm).
amphiphile in the blend. If true, this will be useful in predicting the phase behaviour of any mutual solvent blend with reference to the partition coefficient.

Figure 3.48: Phase behaviour of 60:20:20 % v/v EGMBE:IPA:Ethanol at with Multipar H and SFNSSW (22.5°C and 1 atm).

The four mutual solvent blends discussed hereinafter have the theoretical benchmark partition coefficients provided in Table 3.9. All of the blends partition with an affinity to the oil according to the benchmark partition coefficient values. The effective partitioning of each blend is not studied and beyond the scope of this thesis. For the phase behaviour of the blend with mineral oil and NSSW, the base case is that shown in Figure 3.45a. As for the phase behaviour of the blend with mineral oil and SFNSSW, the base case is that shown in Figure 3.45b. Both base cases examine the phase behaviour of EGMBE alone.

Table 3.9: Theoretical benchmark partition coefficients for the investigated blends.

<table>
<thead>
<tr>
<th>Classification</th>
<th>Blend</th>
<th>log₁₀ P(m − MS)</th>
<th>Affinity to oil w.r.t. EGMBE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Higher affinity to the oil than that of EGMBE</td>
<td>90:10% v/v EGMBE:EGBEA</td>
<td>0.87</td>
<td>8.75% more</td>
</tr>
<tr>
<td></td>
<td>80:20% v/v EGMBE:EGBEA</td>
<td>0.94</td>
<td>17.50% more</td>
</tr>
<tr>
<td>Lower affinity to the oil than that of EGMBE</td>
<td>90:10% v/v EGMBE:MEG</td>
<td>0.58</td>
<td>27.50% less</td>
</tr>
<tr>
<td></td>
<td>80:20% v/v EGMBE:MEG</td>
<td>0.36</td>
<td>55.00% less</td>
</tr>
</tbody>
</table>
In the blend 90:10% v/v EGMB:EGBEA (Figure 3.49), the 10% EGBEA in EGMBE has few effects on the phase behaviour. The partial insolubility of the blend in the brine is higher than that of EGMBE. This is due to the relatively poor solubility of EGBEA in the brine. Moreover, the miscibility gap of EGMBE between Multipar H and NSSW is reduced over low oil and intermediate blend concentrations, leading to a smaller three-phase region. Precipitation is only marginally reduced by EGBEA. Since precipitation is controlled by the mutual solvent availability in the aqueous phase to some extent, and EGBEA is poorly soluble in NSSW brine (section 3.5.2), the reduction in precipitation is not the effect of EGBEA. Instead, it is the effect of less EGMBE at any test mixture compared to the case where EGMBE is used alone. Increasing the EGBEA in the blend to 20% (Figure 3.50) leads to: 1) the complete elimination of the three-phase region; and 2) the complete insolubility of the blend (as whole) in NSSW. The inorganic precipitation is only marginally affected as expected.

Figure 3.49: Phase behaviour of 90:10% v/v EGMB:EGBEA at with Multipar H and NSSW (22.5°C and 1 atm).
Figure 3.50: Phase behaviour of 80:20 % v/v EGMBE:EGBEA at with Multipar H and NSSW (22.5°C and 1 atm).

In SFNSSW brine, the blends 90:10% v/v EGMBE:EGBEA (Figure 3.51) and 80:20% v/v EGMBE:EGBEA (Figure 3.52) demonstrate the effects of reduced ionic strength of the brine and also that of having no sulphate content. The 90:10% v/v EGMBE:EGBEA blend is slightly more soluble in de-sulphated brine compared to normal NSSW brine. The same would apply to the 80:20% v/v EGMBE:EGBEA blend, but the effects are not observed on the phase diagram due to the high content of the water insoluble EGBEA in the blend. Both blends do not exhibit any precipitation as precipitates with EGMBE cannot form in the absence of sulphate ions at intermediate salinities (section 3.6).
Figure 3.51: Phase behaviour of 90:10 % v/v EGMBE:EGBEA at with Multipar H and SFNSSW (22.5°C and 1 atm).

Figure 3.52: Phase behaviour of 80:20 % v/v EGMBE:EGBEA at with Multipar H and SFNSSW (22.5°C and 1 atm).
In the blend 90:10% v/v EGMBE:MEG (Figure 3.53), the 10% MEG in EGMBE has both positive and negative effects on the phase behaviour. The blend is completely soluble in NSSW brine whereas EGMBE alone is partially insoluble in the brine. Moreover, the three-phase region is slightly larger (~16.7%). This is the effect of increased miscibility gap of EGMBE between Multipar H and NSSW, i.e. the MEG displaces some of the EGMBE out of the brine, but the solubility of the EGMBE to the oil is not altered by the MEG in the oil due to its poor affinity to the oil. On the downside, MEG worsens the sulphate precipitation problem significantly due to its high solubility in the brine, making it a poorer solvent for sulphate salts.

At 20% MEG in the blend (Figure 3.54), the three-phase region starts to shrink at low brine and intermediate blend concentrations. This implies that the miscibility gap of EGMBE between Multipar H and NSSW brine grows to a maximum with the addition of MEG, decreasing subsequently with further addition of MEG as the three-phase forming miscibility gap on the brine side starts to reduce. The precipitation region on the phase diagram only grows slightly between 10% and 20% MEG in the blend. This indicates some flexibility in choosing the MEG concentration without further worsening precipitation risks.

Figure 3.53: Phase behaviour of 90:10% v/v EGMBE:MEG at with Multipar H and NSSW (22.5°C and 1 atm).
In SFNSSW brine, with regards to the phase behaviour of the blends 90:10% v/v EGMBE:MEG (Figure 3.55) and 80:20% v/v EGMBE:MEG (Figure 3.56), there are no surprises. Precipitation ceases due to the absence of sulphate ions. Moreover, the no sulphate content and reduced ionic strength of the brine reduce the three-phase forming miscibility gap on the brine side. This effect, while it occurs in both blends, is only apparent with the 20% MEG in EGMBE blend.
Figure 3.55: Phase behaviour of 90:10 % v/v EGMBE:MEG at with Multipar H and SFNSSW (22.5°C and 1 atm).

Figure 3.56: Phase behaviour of 80:20 % v/v EGMBE:MEG at with Multipar H and SFNSSW (22.5°C and 1 atm).
It is important to note that the investigations described here highlight the ability to maintain the three-phase region of EGMBE while manipulating the affinity of the mutual solvent blend within certain constraints. The three-phase region can also be made smaller either at low oil or low brine concentrations depending on how the blend is made. These findings are remarkably useful from a blend design standpoint. Two illustrative conceptual case studies are described below. For the purposes of this discussion, it is important to highlight that the residual oil saturation ($S_{or}$) describes initial binary (oil/water) conditions in the reservoir before the MS is introduced, whereas the water cut (WC) describes flow conditions towards the topside separator after the MS is introduced, with the MS concentration dropping to zero in the flowback as the well is produced over time.

Firstly, consider the case where a reservoir has low/intermediate $S_{or}$ and low WC (Figure 3.57). In the reservoir, the mutual solvent would form mixtures of intermediate/high brine and intermediate mutual solvent concentrations due to the $S_{or}$ (assuming neat MS injection). However, on back production, the mutual solvent would form mixtures of low brine and intermediate mutual solvent concentrations due the WC. Therefore, it would be advantageous to blend EGMBE with an appropriate amount of a suitable preferentially water soluble mutual solvent. This would favour the conditions under which three-phase formation occurs in the reservoir if this is desirable, while avoiding three-phase formation on back production which could cause topside issues.

![Figure 3.57: Blend design case study (1) – Low to intermediate $S_{or}$ and low WC.](image)
Secondly and similarly, consider the case where a reservoir has intermediate/high $S_{or}$ and intermediate/high WC (Figure 3.58). In the reservoir, the mutual solvent would form mixtures of low/intermediate brine and intermediate mutual solvent concentrations due to the $S_{or}$ (also assuming neat MS injection). However, on back production, the mutual solvent would form mixtures of intermediate/high brine and intermediate mutual solvent concentrations due the WC. Hence, a favourable blend is where EGMBE is blended with an appropriate amount of a suitable preferentially oil soluble mutual solvent. Therefore, topside oil and water separation issues are avoided without impacting on the downhole performance of the mutual solvent.

Figure 3.58: Blend design case study (2) – Intermediate to high $S_{or}$ and intermediate to high WC.
3.9. TEMPERATURE EFFECTS

3.9.1. Temperature Effects: Context

In de-ionised water, the temperature effects on the phase behaviour of EGMBE are reasonably understood. For instance, phase diagrams are found in the literature for systems of n-dodecane/de-ionised water/EGMBE at different temperatures as shown in Figure 3.59.

EGMBE is initially completely soluble in both n-dodecane and de-ionised water. Three-phase formation in de-ionised water does not occur at room temperature which is consistent with the findings for EGMBE in section 3.5. Three-phase formation occurs over a temperature interval (ΔT). The minimum temperature for three-phase formation with n-dodecane and de-ionised water is 31.23°C and the highest is 72.89°C as indicated on Figure 3.59. It is also observed that the solubility of EGMBE shifts to n-dodecane, with EGMBE being partially insoluble in de-ionised water at high temperatures. This temperature effect for EGMBE and other mutual solvents is well-described in the literature (Kahlweit, Strey and Busse, 1990; Collins et al., 1999), and is caused by a shift of solubility of the mutual solvent from the water to the oil with increasing temperature.

Performing a detailed temperature mapping of the temperature effects on the qualitative phase behaviour is unnecessary. In practice, an assessment of the phase behaviour of a given mutual solvent with a specific oil and brine and at a specific temperature will be needed on a case by case basis. However, for the most commonly used mutual solvent, EGMBE, an understanding of the combined effects of salinity and temperature on the phase behaviour is useful and has not been properly investigated before for oil/brine/mutual solvent systems. This should inform understanding on how the temperature effects would vary, particularly on the three-phase region, at higher salinities.

For this purpose, at seawater salinity, the EGMBE system was investigated at different temperatures. The seawater was sulphate-free (SFNSSW) to avoid inorganic precipitation (refer to section 3.6). Moreover, mineral oil (Multipar H) was used in line with the experimental conditions described in section 3.3. Three temperatures were investigated (22.5°C, 45.0°C and 70.0°C) and the experimental methodology described in section 3.4 for producing qualitative phase diagrams was followed.
Figure 3.59: Effect of temperature on the phase behaviour of EGMBE with n-dodecane and de-ionised water (1 atm) (Burauer et al., 1999).

3.9.2. Results and Discussion

At 22.5°C (base case), EGMBE with Multipar H and SFNSSW shows a wide three-phase region (Figure 3.60) which would not normally exist at the same temperature in de-ionised water (Figure 3.8a). However, EGMBE is still completely soluble in both Multipar H and de-sulphated NSSW.
At 45.0°C (Figure 3.61), EGMBE becomes partially insoluble in the brine which is consistent with the temperature effect described in the literature and described in section 3.9.1. The three-phase region disappears entirely despite the relatively small temperature increase (+22.5℃ with reference to the base case). In de-ionised water, the three-phase region prevails up to approximately 73℃ (Burauer et al., 1999). This indicates that while the salinity of the brine lowers the temperature at which the three-phase region starts to appear, it also lowers the temperature at which it disappears.

This happens because of the analogy between the temperature and the salinity effects. Increasing the temperature reduces the solubility of EGMBE to water while increasing its solubility to the oil. Increasing the salinity salts out the EGMBE, thereby reducing its solubility in the brine. Nevertheless, the analogy breaks down in that increasing the salinity does not influence the solubility of EGMBE in the oil.
Figure 3.61: Phase behaviour of EGMBE ($\log_{10} P_{o/w} = 0.80$ with respect to benchmark conditions) at 45.0°C and 1 atm.

At 70.0°C (Figure 3.62), the partial insolubility of EGMBE increases even further. This behaviour is expected and consistent with the findings at 45.0°C (Figure 3.61). All in all, the findings described in this section highlight the importance of temperature as a factor in mutual solvent blend design. Targeting specific phase behaviour must be done at the reservoir conditions. If this is not achieved, the perceived phase behaviour at laboratory conditions will be distinctively different than that at reservoir conditions.
Figure 3.62: Phase behaviour of EGMBE (log10 P_o/w = 0.80 with respect to benchmark conditions) at 70.0°C and 1 atm.

For three-phase-forming amphiphiles of the type $C_iE_j$ (e.g. EGMBE, $C_4E_1$), the temperature at which three-phases start to form can be influenced by manipulating the ($i$) – carbon chain – and ($j$) – ethoxy groups – numbers (Kahlweit et al., 1988b; Kahlweit, Strey and Busse, 1993; Burauer et al., 1999). Increasing ($i$) would decrease the temperature at which three-phases start to form, and increasing ($j$) would increase that temperature (Burauer et al., 1999). Hence, if three-phase formation is desirable, using amphiphiles of higher ($j$) values could be a solution for maintained three-phase formation in a saline environment at the elevated reservoir temperature. However, this may not be needed as heavier crudes will form three-phases at higher temperatures in any case. It is worth mentioning that larger three-phase regions can also be achieved with higher ($j$) numbers (Burauer et al., 1999), i.e. switching to a different mutual solvent.

Pressure effects may also be taken into account although they are generally felt much less than those of temperature (Kahlweit, Strey and Busse, 1993), and hence can be reliably ignored in general. To a small degree, the three-phase region can be influenced by pressure and tends to widen with increasing pressure (Sassen et al., 1989). However, this is not always the effect as other references describe a shrinking three-phase region with increasing pressure (Kahlweit et al., 1989). It is more likely that three-phase formation occurs over a pressure range in a similar fashion to the temperature and salinity. The
pressure effects can be attributed to stronger hydrogen bonding between the mutual solvent and the water molecules at higher pressures (Sassen et al., 1989), which in turn will cause a small shift in the solubility of the mutual solvent from the oil to the water.
3.10. SUMMARY AND RESEARCH SIGNIFICANCE

The findings in this chapter can be summarised in the following points:

- Mutual solvents can be classified into groups based on their \((P_{o/w})\). The phase behaviour of the mutual solvents can be gauged qualitatively with reference to this classification. In this work, all the investigations worked carried out with reference to a benchmark \((P_{o/w})\) value for simplicity and for illustrative purposes. However, the findings can be expanded to any conditions by measuring the \((P_{o/w})\) value. This is very useful to develop a general appreciation for the expected phase behaviour from a particular mutual solvent without detailed selection. It is most useful in preliminary selections of mutual solvents at a given set of conditions.

- In practical field situations, an increase in the salinity will always have the effect of salting out the mutual solvent from the brine. The consequence of this is also fairly predictable with the available of a suitable reference case. This should aid understanding the kind of phase behaviour expected from a mutual solvent as the salinity changes, e.g. mixing of formation/seawater brines.

- The brine chemistry plays a role in determining the liquid phase behaviour of a mutual solvent to some extent. This can be generally ignored if the salinity difference is high. Otherwise, this needs to be considered. More importantly, inorganic precipitation induced by the mutual solvent showed distinct precipitation scenarios. These findings highlight potential risks associated with the use of mutual solvents, as well as mitigating strategies for avoiding all of the precipitation scenarios.

- PPCA and DETPMP have modest effects on the liquid phase behaviour of mutual solvents at field relevant concentrations. More importantly, they influence the precipitation region on the phase diagram of oil/brine/MS systems. MS blend design could exploit this to prevent unwanted precipitation due to the MS.

- Specific phase behaviour can be designed and targeted through mutual solvent blending. This is incredibly valuable finding and could form the basis for future blend design strategies once the desired phase behaviour is understood properly.

- Temperature effects in saline systems remain consistent with findings in the literature.
Chapter 4: Quantitative Experimental Studies on the Phase Behaviour of Mutual Solvents

4.1. OVERALL AIMS AND OBJECTIVES

While the phase behaviour of simple oils (e.g. an alkane)/water/amphiphiles is well understood, the complex phase behaviour of oil/brine/mutual solvent systems is not. The introduction of additional additives (e.g. scale inhibitors) further complicates the problem. Chapter 3 of this thesis sheds some light on the phase behaviour in these complex systems on a qualitative basis through static testing. This approach is highly valuable in providing a general understanding of the phase behaviour of these systems of interest. However, it is deficient in that:

1. Detailed compositions are unknown in qualitative experiments. Therefore, the properties of the two-phase regions and the three-phase region in oil/brine/mutual solvent systems are not addressed sufficiently.

2. For practical application, lacking the ability to work out the phase compositions for an oil/brine/mutual solvent system constitutes a huge problem. For example, modelling the propagation of the mutual solvent is not possible without an ability to resolve its phase diagram quantitatively in the presence of oil, brine and other additives.

In the absence of working analytical tools that would enable resolving these very complex systems practically and accurately, investigations in this section focused on inspecting variations in the phase volume in the two and three-phase regions. All of this was done with the objective of achieving a better quantitative understanding of complex oil/brine/mutual solvent systems.

The work in this chapter will feed into the ultimate aim of devising methods for resolving the phase diagram of oil/brine/mutual solvent systems to a working level, and to model this phase behaviour. The results provided in this section highlight the key findings of this work.
4.2. GENERAL EXPERIMENTAL METHODS

Consider the phase diagram of EGMBE with mineral oil and NSSW at 22.5°C and 1 atm (Figure 3.27). Besides EGMBE being a commonly used mutual solvent (which makes this semi-idealised system interesting to study), this system encompasses three two-phase regions (oil/brine, oil/EGMBE and brine/EGMBE). It also has a sizeable three-phase region. A point of strong interest is how a mixture transitions from being a two-phase mixture to a three-phase mixture. Studying this is complex, but simplifications can be made to achieve this goal as will be illustrated by the experimental criteria implemented for this work.

![Figure 4.1](image_url)

**Figure 4.1:** The liquid phase behaviour of EGMBE ($\log_{10} P_{o/w} = 0.80$) with mineral oil and NSSW at 22.5°C and 1 atm.

Two set of samples were selected with reference to the qualitative diagram of Multipar H/NSSW/EGMBE shown in Figure 3.27. The first set of samples (Set 1) comprised of two-phase and three-phase samples at constant brine concentration in the feed (30% v/v). The second set of samples (Set 2) were additional three-phase samples prepared to support the analysis of the results obtained from the first set. All samples are shown in Figure 4.2.

In total, $16 \times 50$ ml samples were prepared in VWR polypropylene (PP) test tubes with 0.5 ml graduations ($\pm 0.25$ ml error). A single channel 10.0 ml manual pipette was used to
prepare the samples. Once prepared, the samples were shaken and allowed to equilibrate for at least 24 hours prior to collecting the phase separation results.

The results of this experiment were used to plan and conduct more detailed experiments for various systems. This is discussed in section 4.6.

Figure 4.2: Samples selected for the phase transition analysis for a system of Multipar H/NSSW/EGMBE at 22.5°C and 1 atm.
4.3. RESULTS AND DISCUSSION

4.3.1. Phase Transition Analysis Results

At 30% v/v NSSW (Set 1 Samples), the phase volume results are provided and illustrated in Figure 4.3. The upper phase is oil-rich, the lower phase is brine-rich and the middle phase is MS-rich (due to the density differences, i.e. $\rho_o < \rho_{MS} < \rho_B$). As the % v/v of EGMBE increases in the feed, the samples go from being two-phase samples to three-phase samples. Three-phase formation starts above 10% v/v EGMBE at 30% v/v NSSW. With increasing EGMBE feed concentration, the middle phase swells, and the upper and lower phases shrink (Figure 4.4). The upper phase (the oil-rich phase) shrinks at higher rate than the lower phase (the brine-rich phase). This is consistent with the partition coefficient of EGMBE ($\log_{10} P_{o/w} = 0.80$) which suggests a preference to partitioning in oil over brine (and hence the oil-rich phase over the brine-rich phase). The middle phase eventually overtakes the upper phase above 50% v/v EGMBE.

![Figure 4.3: Phase volumes as a function of the % v/v EGMBE in the feed for Multipar H/NSSW/EGMBE at 22.5°C and 1 atm: two-phase and three-phase samples (Set 1) at 30% v/v NSSW in the feed.](image-url)
In the three-phase region (volumes highlighted in yellow in Figure 4.3), a consistent change in the volumes of all the phases is observed, i.e. for every 10% v/v EGMBE added to the feed for a 50 ml sample, the middle phase grows by 10 ml, the upper phase shrinks by 8 ml, and the lower phase shrinks by 2 ml. This suggests a linear correlation between the feed concentration of EGMBE and the phase volumes at constant brine concentration in the feed. Replotting the results in the three-phase region as linear correlations fully supports this suggestion as shown in Figure 4.5. Perfect linear correlations are observed for the phase volumes of all phases. The linear correlations are worsened by the inclusion of the two-phase samples in the plot as shown in Figure 4.6, suggesting that the linear correlation does not extend to the two-phase region. Further discussion of this will follow in the subsequent sections (4.3.2 and 4.3.3).
Figure 4.5: Phase volume as a function of the % v/v EGMBE in the feed for Multipar H/NSSW/EGMBE at 22.5°C and 1 atm: three-phase samples (Set 1) at 30% v/v NSSW in the feed.

Figure 4.6: Phase volume as a function of the % v/v EGMBE in the feed for Multipar H/NSSW/EGMBE at 22.5°C and 1 atm: two-phase and three-phase samples (Set 1) at 30% v/v NSSW in the feed.
4.3.2. Theory of Truly Ternary Three-Phase Forming Systems

The phase behaviour described above is consistent with the phase behaviour of truly ternary systems. A ternary system is truly ternary when A, B and C are pure components. When a truly ternary system exhibits three-phase formation, the three-phase region must be bounded by a three-phase triangle on the phase diagram as illustrated in Figure 4.7. Any mixture with a composition falling within the three-phase triangle would separate into three-phases at equilibrium. The compositions of the A-rich, B-rich and C-rich phases will always be constant at fixed conditions of temperature and pressure, and will be denoted by the vertices of the three-phase triangle.

This three-phase region property is demanded by the thermodynamics of non-reactive heterogeneous truly ternary systems, and it is best summarised by the Gibbs phase rule (Gibbs, 1878). According to the rule \( F = C - P + 2 \); where \( F \) is the number of degrees of freedom, \( C \) is the number of components and \( P \) is the number of phases), the three-liquid-phase region in a ternary system has only two degrees of freedom. Therefore, at fixed temperature and pressure, the three-liquid-phase compositions must be constant anywhere within the three-liquid-phase region.

![Figure 4.7: An illustrative phase diagram of a truly ternary three-phase forming system.](image-url)
Changes of the three-phase volumes within the three-phase region of a truly ternary system can be described mathematically through mass balances. Let \((z_j)\) be the fixed feed composition of component \((j)\), \((z_i)\) the variable feed compositions of the two remaining components \((i)\), and let the phase volume be given by \((V_k; k = u, m, l\) for upper, middle and lower phases). Assuming negligible volume changes due to mixing (i.e. volume conservation), the following equations can be written:

**Overall Balance on a Volume Basis**

\[
V = V_u + V_m + V_l
\]

\[4.1\]

**Component Balances for all Components on a Volume Basis**

\[
z_A V = x_A^u V_u + x_A^m V_m + x_A^l V_l
\]

\[4.2\]

\[
z_B V = x_B^u V_u + x_B^m V_m + x_B^l V_l
\]

\[4.3\]

\[
z_C V = x_C^u V_u + x_C^m V_m + x_C^l V_l
\]

\[4.4\]

**Derivation**

Let equation \(4.4\) be base equation, and use equations \(4.1\) and \(4.3\) to eliminate unwanted variables. From equation \(4.4\):

\[
V z_C = x_C^u V_u + x_C^m V_m + x_C^l V_l
\]

\[4.5\]

\[
V z_C - x_C^m V - (x_C^l - x_C^m) V_l = (x_C^u - x_C^m) V_u
\]

\[
V_u = \frac{V}{x_C^u - x_C^m} z_C - \left(\frac{x_C^m}{x_C^u - x_C^m}\right) V - \left(\frac{x_C^l - x_C^m}{x_C^u - x_C^m}\right) V_l
\]

Similarly, from equation \(4.3\):

\[
V_l = \frac{V}{x_B^u - x_B^m} z_B - \left(\frac{x_B^m}{x_B^u - x_B^m}\right) V - \left(\frac{x_B^l - x_B^m}{x_B^u - x_B^m}\right) V_u
\]

\[4.6\]

Let \((e)\) denote the eliminated phase using overall balance, and \((n)\) denote the eliminated phase using the component balance (note that: \(e = i\ or\ j\) and \(n = i\ or\ j\), i.e. they are interchangeable. Hence, generalising equations \(4.7\) and \(4.8\) gives:
\[ V_k = \left( \frac{V}{x_{i}^{k}-x_{i}^{f}} \right) z_i - \left( \frac{x_{i}^{f}}{x_{i}^{k}-x_{i}^{f}} \right) \left[ \left( \frac{V}{x_{j}^{k}-x_{j}^{f}} \right) z_j - \left( \frac{x_{j}^{f}}{x_{j}^{k}-x_{j}^{f}} \right) V_n \right] \] 

\[ V_n = \left( \frac{V}{x_{j}^{n}-x_{j}^{f}} \right) z_j - \left( \frac{x_{j}^{f}}{x_{j}^{n}-x_{j}^{f}} \right) \left[ \left( \frac{V}{x_{j}^{k}-x_{j}^{f}} \right) z_j - \left( \frac{x_{j}^{f}}{x_{j}^{k}-x_{j}^{f}} \right) V_k \right] \]

Solving the general case equations for \( V_k = f(z_i) \) using the generalised equations 4.7 and 4.8 (i.e. eliminating \( V_n \) using equation 4.8 substituted into equation 4.7):

\[ V_k = \left( \frac{V}{x_{i}^{k}-x_{i}^{f}} \right) z_i - \left( \frac{x_{i}^{f}}{x_{i}^{k}-x_{i}^{f}} \right) \left[ \left( \frac{V}{x_{j}^{k}-x_{j}^{f}} \right) z_j - \left( \frac{x_{j}^{f}}{x_{j}^{k}-x_{j}^{f}} \right) V_k \right] \]

\[ V_k = \left( \frac{x_{i}^{n}-x_{i}^{f}}{x_{i}^{k}-x_{i}^{f}} \right) \left( \frac{x_{j}^{k}-x_{j}^{f}}{x_{j}^{n}-x_{j}^{f}} \right) V_k = \left( \frac{V}{x_{i}^{k}-x_{i}^{f}} \right) z_i - \left( \frac{x_{i}^{f}}{x_{i}^{k}-x_{i}^{f}} \right) \left[ \left( \frac{V}{x_{j}^{k}-x_{j}^{f}} \right) z_j - \left( \frac{x_{j}^{f}}{x_{j}^{k}-x_{j}^{f}} \right) V_k \right] \]

\[ V_k = \left( \frac{x_{i}^{n}-x_{i}^{f}}{x_{i}^{k}-x_{i}^{f}} \right) \left( \frac{x_{j}^{k}-x_{j}^{f}}{x_{j}^{n}-x_{j}^{f}} \right) V_k = \left( \frac{V}{x_{i}^{k}-x_{i}^{f}} \right) z_i - \left( \frac{x_{i}^{f}}{x_{i}^{k}-x_{i}^{f}} \right) \left[ \left( \frac{V}{x_{j}^{k}-x_{j}^{f}} \right) z_j - \left( \frac{x_{j}^{f}}{x_{j}^{k}-x_{j}^{f}} \right) V_k \right] \]

Therefore, in general the slope \( (m_k) \) and the intercept \( (C_k) \) are defined by the equations 4.9 and 4.10 given below:

\[ m_k(X,V) = \left( \frac{\frac{V}{x_{j}^{k}-x_{j}^{f}}}{1-\left( \frac{x_{i}^{n}-x_{i}^{f}}{x_{i}^{k}-x_{i}^{f}} \right) \left( \frac{x_{j}^{k}-x_{j}^{f}}{x_{j}^{n}-x_{j}^{f}} \right)} \right) \]

\[ C_k(z_j, X, V) = m_k \left[ \left( \frac{x_{i}^{n}-x_{i}^{f}}{x_{i}^{k}-x_{i}^{f}} \right) (z_j - x_{j}^{f}) - x_{i}^{f} \right] \]

The phase volume written as the equation of a straight line is given by equation 4.11 provided below:
\[ V_k = m_k(X, V) z_i + C_k(z_j, X, V) \]

Therefore, given the Gibbs phase rule and equations 4.9, 4.10 and 4.11, for a non-reactive truly ternary system at fixed temperature and pressure, when a three-liquid-phase region forms, the changes in the phase volumes are subject to equation 4.11 and must be linear due to the constant phase compositions.

### 4.3.3. Phase Transition Analysis Results in the Context of a Truly Ternary System

In the system of Multipar H/NSSW/EGMBE, both the oil (Multipar H) and the brine (NSSW) are multi-component mixtures. As such, this system is not a truly ternary system. However, the phase behaviour results in Figure 4.5 follow the trend expected of a truly ternary system. This suggests the quasi-ternary nature of the oil/brine/mutual solvent system under investigation.

Quasi-ternary systems are defined in this work as multicomponent systems that approximately exhibit the phase behaviour of a system containing three pure components only. For these systems, each main constituent of the system (e.g. each of the oil, brine and mutual solvent) will behave as “pseudo-components” irrespective of their detailed compositions.

Consider the system Multipar H/NSSW/EGMBE. The results in Figure 4.5 can be used to write six equations with reference to equations 4.9 and 4.10 as shown below (equations 4.12-4.17). The only unknowns in these equations are \( x_B^k \) and \( x_C^k \); six variables in total.

\[
m_u = \frac{\left( \frac{\nu}{x_C^m-x_C^u} \right)}{\left[ 1 - \left( \frac{x_C^m-x_C^u}{x_C^m-x_C^B} \right) \left( \frac{x_B^m-x_B^u}{x_B^m-x_B^C} \right) \right]}  \quad \text{4.12}
\]

\[
C_u = m_u \left[ \left( \frac{x_B^m-x_B^u}{x_B^m-x_B^C} \right) \left( z_B - x_B^m \right) - x_C^m \right]  \quad \text{4.13}
\]

\[
m_m = \frac{\left( \frac{\nu}{x_C^m-x_C^u} \right)}{\left[ 1 - \left( \frac{x_C^m-x_C^u}{x_C^m-x_C^B} \right) \left( \frac{x_B^m-x_B^u}{x_B^m-x_B^C} \right) \right]}  \quad \text{4.14}
\]

\[
C_m = m_m \left[ \left( \frac{x_B^m-x_B^u}{x_B^m-x_B^C} \right) \left( z_B - x_B^m \right) - x_C^m \right]  \quad \text{4.15}
\]
\[ m_t = \frac{\left( \frac{V}{x_c^m - x_C^m} \right)}{1 - \left( \frac{x_C^m - x_B^m}{x_C^m - x_B^m} \right)} \]  

4.16

\[ C_t = m_t \left[ \frac{x_C^m - x_B^m}{x_C^m - x_B^m} (z_B - x_B^m) - x_C^m \right] \]  

4.17

The equations above were solved numerically subject to the initial conditions (guess values) provided in Table 4.1. To do this, the initial conditions were used to calculate the slopes and intercepts of 4.12-4.17. These were compared with the experimental values in Figure 4.5, and the square of the error was minimised by allowing the phase compositions (initial conditions) to change within physical constraints, i.e. \(0 \leq x_t^k \leq 1\) (N.B. the function Solver in Microsoft Excel can be used for this purpose).

This approach was applied, and the quality of the calculated compositions in accurately representing the three-phase region for the system under investigation was assessed. The second set of samples (Set 2) shown in Figure 4.2 were used for this purpose. For this set, calculated phase volumes were compared against the experimental phase volumes for the \(\times 8\) three-phase samples in Set 2.

The results are shown in Figure 4.8, Figure 4.9 and Figure 4.10 for the Multipar H-rich, NSSW-rich and EGMBE-rich phases respectively. The maximum error was found to be 4.6% and the sum of the square of errors for all results is 37.9. These results highlight a reasonable reliability of the calculated three-phase compositions in representing the three-phase region, with generally low errors.

Table 4.1: The initial conditions and calculated compositions for the system Multipar H/NSSW/EGMBE at 22.5°C and 1 atm subject to the data in Figure 4.5 and using equations 4.12-4.17.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Initial Conditions Compositions, % v/v</th>
<th>Calculated Compositions, % v/v</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Multipar H</td>
<td>NSSW</td>
</tr>
<tr>
<td>Multipar H-Rich</td>
<td>90.00</td>
<td>0.00</td>
</tr>
<tr>
<td>NSSW-Rich</td>
<td>0.00</td>
<td>90.00</td>
</tr>
<tr>
<td>EGMBE-Rich</td>
<td>20.00</td>
<td>20.00</td>
</tr>
</tbody>
</table>
Figure 4.8: Experimental vs. calculated phase volumes for the Multipar H-rich phase in the three-phase region for the system Multipar H/NSSW/EGMBE at 22.5°C and 1 atm subject to the data in Figure 4.5 and using equations 4.12-4.17; Set 2 samples used.

Figure 4.9: Experimental vs. calculated phase volumes for the NSSW-rich phase in the three-phase region for the system Multipar H/NSSW/EGMBE at 22.5°C and 1 atm subject to the data in Figure 4.5 and using equations 4.12-4.17; Set 2 samples used.
Figure 4.10: Experimental vs. calculated phase volumes for the EGMBE-rich phase in the three-phase region for the system Multipar H/NSSW/EGMBE at 22.5°C and 1 atm subject to the data in Figure 4.5 and using equations 4.12-4.17; Set 2 samples used.
4.4. NUMERICAL SOLUTIONS TO THE THREE-PHASE PROBLEM

4.4.1. Introduction

An alternative way of solving the three-phase compositions than the method described in section 4.3.3 involves a numerical description of the liquid-liquid-liquid equilibrium (LLLE) taking place in the three-phase region. This approach builds-in the concept of achieving equilibrium while solving the mass balances numerically. The numerical three-phase equilibration model will be described and discussed in this section.

4.4.2. Model Description

In the model, the following is assumed for components A, B and C:

1. A is assumed to be immiscible with B.
2. C is assumed to be mutually miscible/partially miscible in both A and B.
3. The density order of the constituents are \( \rho_A < \rho_C < \rho_B \).
4. Volume changes due to mixing of non-ideal components are negligible.

This model is explained by the following points:

1. Initially, a mixture comprising of three-liquid-phases is at equilibrium. The feed composition of the mixture \( (z_i) \) is known due to sample selection. The three-phase volumes at equilibrium are known experimentally \( (V_i^k) \). Reasonable guess values (initial conditions) are made for the phase compositions, i.e. \( k \)-rich phase must be rich in \( (k) \). The initial phase separation (based on the guess values) is calculated as described in section 4.5

2. At \( (t = 0 \text{ s}) \), the equilibrium of the system is perturbed. This perturbation is in the form of changes to the feed composition of the mixture. The perturbation is expressed as changes in the volumes of components in the feed of the mixture. The new feed composition falls within the boundaries of the three-phase region.

3. The changes in the feed volumes are used to re-calculate new three-phase compositions (non-equilibrium compositions) by applying the change of the feed volume of component \( (k) \) to the \( k \)-rich phase. This is described by equation 4.18. The remaining phase compositions for each phase are calculated using equation 4.19.
4. The model restores equilibrium by describing equilibration as a series of discrete equilibration steps or cycles. In each cycle, the disturbances are transferred to the adjacent phases. This involves alternating between transferring the disturbances from the A-rich and B-rich phases to the C-rich phase and vice versa. This is illustrated in Figure 4.11.

5. The transfer of disturbances is performed until convergence is achieved. The solution converges when the calculated phase compositions match the initial guess values by setting tolerances on the deviations between the two.

Figure 4.11: The equilibration cycles of the numerical three-phase equilibration model.

The rules for transferring the disturbances are described by the following points:

1. The primary constituent of a phase is always retained within the phase.
2. Disturbances in the secondary constituents of a phase are always transferred to the adjacent phases to restore equilibrium.
3. A is never added to B due to immiscibility and vice versa.

The rules above are described by the following equations:

1. For the $k$-rich phase, the primary constituent of the phase ($i = k$) is retained within the phase. Therefore:

$$V_k^{k(n)} = V_k^{k(n-1)}$$
\[ \Delta V_{i=k}^n = 0 \]

2. The secondary constituents of the phase \((i \neq k)\) are re-calculated to restore the guess values for the phase compositions. Hence:

\[ \Delta V_{i \neq k}^n = V_i^{k(n)} - V_i^{k(n-1)} \]

But:

\[ V_i^k(n) = \left( x_i^k \right)_0 V^k(n) \]

\[ V^k(n) = \frac{V_k^{k(n)}}{(x_k^k)_0} = \frac{V_k^{k(n-1)}}{(x_k^k)_0} \]

Therefore:

\[ \Delta V_{i \neq k}^k = \left( x_i^k \right)_0 \frac{V_k^{k(n-1)}}{(x_k^k)_0} - V_i^{k(n-1)} \]

\[ \Delta V_{i \neq k}^k = \left( x_i^k \right)_0 \frac{V_k^{k(n-1)}}{(x_k^k)_0} - V_i^{k(n-1)} \]

At least two sets of three-phase volumes should be provided to the model, i.e. the experimental results for two feed compositions in the three-liquid phase region. The first set is used as a reference point, and the disturbances at time \((t = 0\ s)\) are described by the changes of the feed volumes going from the first set to the second set. Based on the guess values for the compositions, three-phase separations are calculated and compared with the experimental values. The square of the error is minimised within physical constraints, i.e. \(0 \leq x_i^k \leq 1\), in order to calculate the equilibrium three-phase compositions.

An illustration of the steps involved in the model is summarised by the logical diagram provided in Figure 4.12.
For the same system and set of data discussed in section 4.3.3, the results obtained from the numerical LLLE equilibration model are presented here. The data fed into the model are as summarised into Table 4.2. The initial conditions are kept the same as in section 4.3.3 to enable comparison. These, as well as the calculated compositions are provided in Table 4.3.

The quality of the calculated compositions in accurately representing the three-phase region for the system under investigation was also assessed using the samples in Set 2 shown in Figure 4.2. The results are shown in Figure 4.13, Figure 4.14 and Figure 4.15 for the Multipar H-rich, NSSW-rich and EGMBE-rich phases respectively. Compared to the graphical method in section 4.3.3, the maximum error in the calculated compositions was found to reduce from 4.6% to 1.2%, and the sum of the square of errors for all results reduced from 37.9 to 2.2. This represents a massive improvement in representing the three-phase region for the system Multipar H/NSSW/EGMBE at 22.5°C and 1 atm using the exact
same set of data, and thought to be the result of providing a numerical description of the equilibration in addition to solving the component balances.

Moreover, the results in Figure 4.16, Figure 4.17 and Figure 4.18 illustrate the fast convergence of the phase compositions for the Multipar H-rich, NSSW-rich and EGMBE-rich phases respectively. This is despite the strict convergence requirement set at $10^{-12}$ for the % v/v changes in the phase compositions.

**Table 4.2:** The data set for the numerical LLLE equilibration model for the system Multipar H/NSSW/EGMBE at 22.5°C and 1 atm (same data as in Figure 4.5).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Designation</th>
<th>Feed (ml)</th>
<th>Disturbance at (t = 0 s) w.r.t. Reference (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>1</td>
<td>Reference</td>
<td>25.0</td>
<td>15.0</td>
</tr>
<tr>
<td>2</td>
<td>Final Mixture 1</td>
<td>20.0</td>
<td>15.0</td>
</tr>
<tr>
<td>3</td>
<td>Final Mixture 2</td>
<td>15.0</td>
<td>15.0</td>
</tr>
<tr>
<td>4</td>
<td>Final Mixture 3</td>
<td>10.0</td>
<td>15.0</td>
</tr>
</tbody>
</table>

**Table 4.3:** The initial conditions and calculated compositions for the system Multipar H/NSSW/EGMBE at 22.5°C and 1 atm subject to the data in Table 4.2 and using the numerical LLLE equilibration model.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Initial Conditions Compositions, % v/v</th>
<th>Calculated Compositions, % v/v</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Multipar H</td>
<td>NSSW</td>
</tr>
<tr>
<td>Multipar H-Rich</td>
<td>90.00</td>
<td>0.00</td>
</tr>
<tr>
<td>NSSW-Rich</td>
<td>0.00</td>
<td>90.00</td>
</tr>
<tr>
<td>EGMBE-Rich</td>
<td>20.00</td>
<td>20.00</td>
</tr>
</tbody>
</table>
Figure 4.13: Experimental vs. calculated phase volumes for the Multipar H-rich phase in the three-phase region for the system Multipar H/NSSW/EGMBE at 22.5°C and 1 atm subject to the data in Table 4.2 and using the numerical LLLE equilibration model.

Figure 4.14: Experimental vs. calculated phase volumes for the NSSW-rich phase in the three-phase region for the system Multipar H/NSSW/EGMBE at 22.5°C and 1 atm subject to the data in Table 4.2 and using the numerical LLLE equilibration model.
Figure 4.15: Experimental vs. calculated phase volumes for the EGMBE-rich phase in the three-phase region for the system Multipar H/NSSW/EGMBE at 22.5°C and 1 atm subject to the data in Table 4.2 and using the numerical LLLE equilibration model.

Figure 4.16: Convergence of the A-Rich phase compositions during the final minimisation cycle of the numerical LLLE equilibration model for Final Mixture 1 in Table 4.2.
Figure 4.17: Convergence of the B-Rich phase compositions during the final minimisation cycle of the numerical LLLE equilibration model for Final Mixture 1 in Table 4.2.

Figure 4.18: Convergence of the C-Rich phase compositions during the final minimisation cycle of the numerical LLLE equilibration model for Final Mixture 1 in Table 4.2.
4.5. ANALYTICAL SOLUTIONS TO THE THREE-PHASE PROBLEM

4.5.1. Introduction

Both the graphical solution described in section 4.3.3 and the numerical LLLE equilibration model 4.4.3 rely on a numerical technique in resolving the three-phase compositions of a ternary/quasi-ternary system. However, an analytical solution can also be obtained without the need to rely on numerical methods. The analytical solution is derived and discussed in this section.

4.5.2. Derivation

This method relies on the principle that there are nine common variables for all three-phase samples representing the composition in each phase. Each sample that separates into three phases can be used to write three equations. Hence, only three samples are required to provide the nine equations required to solve for all compositions. Moreover, taking into account that compositions sum to one in each phase, the number of variables is reduced to only six variables, for which only two samples in the three-phase region are required to solve the equations. The derivation of the equations is illustrated below subject to the same assumption of volume conservation.

**Overall Balance on a Volume Basis for Sample (n)**

\[ V_n = V_{An} + V_{Bn} + V_{Cn} \]  \hspace{1cm} (4.22)

**Component Balances for all Components on a Volume Basis Sample (n)**

\[ x_{An}^F V_n = x_A^A V_{An} + x_A^B V_{Bn} + x_A^C V_{Cn} \]  \hspace{1cm} (4.23)

\[ x_{Bn}^F V_n = x_B^A V_{An} + x_B^B V_{Bn} + x_B^C V_{Cn} \]  \hspace{1cm} (4.24)

\[ x_{Cn}^F V_n = x_C^A V_{An} + x_C^B V_{Bn} + x_C^C V_{Cn} \]  \hspace{1cm} (4.25)

Let:

\[ R_{kn} = \frac{v_{kn}}{V_n} \]  \hspace{1cm} (4.26)

Using equation 4.22, equations 4.23, 4.24 and 4.25 can be re-written as:

\[ R_{An} x_A^A + R_{Bn} x_A^B + R_{Cn} x_A^C = x_{An}^F \]  \hspace{1cm} (4.27)
\[
R_A x^A_B + R_B n x^B_B + R_C n x^C_B = x^E_B \quad 4.28
\]
\[
R_A x^A_C + R_B n x^B_C + R_C n x^C_C = x^E_C \quad 4.29
\]

Equations 4.27, 4.28 and 4.29 can be written in the following matrix form:

\[
AX = b
\quad 4.30
\]

Therefore, for 3 samples in the three-phase region (3 samples × 3 equations = 9 equations):

\[
X_{9\times1} = \begin{bmatrix} x^A_A \\ x^B_B \\ x^C_C \\ x^A_A \\ x^B_B \\ x^C_C \\ x^A_A \\ x^B_B \\ x^C_C \end{bmatrix}
\quad 4.31
\]

\[
A_{9\times9} = \begin{bmatrix} R_A & R_B & R_C & 0 & 0 & 0 & 0 & 0 & 0 \\ R_A & R_B & R_C & 0 & 0 & 0 & 0 & 0 & 0 \\ R_A & R_B & R_C & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & R_A & R_B & R_C & 0 & 0 & 0 \\ 0 & 0 & 0 & R_A & R_B & R_C & 0 & 0 & 0 \\ 0 & 0 & 0 & R_A & R_B & R_C & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & R_A & R_B & R_C \\ 0 & 0 & 0 & 0 & 0 & 0 & R_A & R_B & R_C \\ 0 & 0 & 0 & 0 & 0 & 0 & R_A & R_B & R_C \end{bmatrix}
\quad 4.32
\]
\[
\begin{bmatrix}
  x_A^F \\
x_A^B \\
x_A^C \\
x_B^F \\
x_B^E \\
x_B^C \\
x_C^F \\
x_C^E \\
x_C^C
\end{bmatrix}
\]

\[b_{9\times1} = 4.33\]

Overall:

\[A_{9\times9} X_{9\times1} = b_{9\times1} \quad 4.34\]

Taking into account that the compositions of the constituents of each phase will always sum to one:

\[x_A^A + x_A^A + x_C^A = 1 \quad 4.35\]

\[x_B^B + x_B^B + x_C^B = 1 \quad 4.36\]

\[x_C^C + x_B^C + x_C^C = 1 \quad 4.37\]

Re-arranging:

\[x_C^A = 1 - (x_A^A + x_C^A) \quad 4.38\]

\[x_C^B = 1 - (x_A^B + x_B^B) \quad 4.39\]

\[x_C^C = 1 - (x_A^C + x_C^C) \quad 4.40\]

Substituting equations 4.38, 4.39 and 4.40 into equation 4.29, and re-arranging the resulting equation to achieve the required format for implementation in matrices:

\[R_{An} \left [ 1 - (x_A^A + x_A^A) \right ] + R_{Bn} \left [ 1 - (x_B^B + x_B^B) \right ] + R_{Cn} \left [ 1 - (x_C^C + x_C^C) \right ] = x_C^F \]

\[R_{An} - R_{An} x_A^A - R_{An} x_B^A + R_{Bn} - R_{Bn} x_B^B - R_{Bn} x_B^B + R_{Cn} - R_{Cn} x_C^C - R_{Cn} x_C^C = x_C^F \]

\[-R_{An} x_A^A - R_{An} x_B^A - R_{Bn} x_B^B - R_{Bn} x_B^B - R_{Cn} x_A^C - R_{Cn} x_B^C = x_C^F - (R_{An} + R_{Bn} + R_{Cn}) \]

\[R_{An} x_A^A + R_{Bn} x_A^A + R_{Cn} x_A^A + R_{An} x_B^B + R_{Bn} x_B^B + R_{Cn} x_B^B = (R_{An} + R_{Bn} + R_{Cn}) - x_C^F \]
But:

\[ R_{An} + R_{Bn} + R_{Cn} = 1 \]  

Then:

\[ R_{An} x_A^A + R_{Bn} x_A^B + R_{Cn} x_A^C + R_{An} x_B^A + R_{Bn} x_B^B + R_{Cn} x_B^C = 1 - x_C^F \]

Equation 4.42 can be used to simplify the matrices in equation 4.34 to yield:

\[ \bar{X}_{6 \times 1} = \begin{bmatrix} x_A^A \\ x_A^B \\ x_A^C \\ x_B^A \\ x_B^B \\ x_B^C \end{bmatrix} \]  

\[ \bar{A}_{9 \times 6} = \begin{bmatrix} R_{A1} & R_{B1} & R_{C1} & 0 & 0 & 0 \\ R_{A2} & R_{B2} & R_{C2} & 0 & 0 & 0 \\ R_{A3} & R_{B3} & R_{C3} & 0 & 0 & 0 \\ 0 & 0 & 0 & R_{A1} & R_{B1} & R_{C1} \\ 0 & 0 & 0 & R_{A2} & R_{B2} & R_{C2} \\ 0 & 0 & 0 & R_{A3} & R_{B3} & R_{C3} \\ R_{A1} & R_{B1} & R_{C1} & R_{A1} & R_{B1} & R_{C1} \\ R_{A2} & R_{B2} & R_{C2} & R_{A2} & R_{B2} & R_{C2} \\ R_{A3} & R_{B3} & R_{C3} & R_{A3} & R_{B3} & R_{C3} \end{bmatrix} \]

\[ \bar{b}_{9 \times 1} = \begin{bmatrix} x_{A1}^F \\ x_{A2}^F \\ x_{A3}^F \\ x_{B1}^F \\ x_{B2}^F \\ x_{B3}^F \\ 1 - x_{C1}^F \\ 1 - x_{C2}^F \\ 1 - x_{C3}^F \end{bmatrix} \]

Overall:
Equations 4.34 and 4.46 can be used to solve for the compositions given three or two samples in the three-phase region respectively. Alternatively, for \((n)\) samples in the three-phase region, the experimental data can be regressed to the conservation equations by minimising the square of the error. The regression form of equations 4.34 and 4.46 are provided below:

\[
\begin{bmatrix}
R_{A1} & R_{B1} & R_{C1} & 0 & 0 & 0 & 0 & 0 & 0 \\
R_{A2} & R_{B2} & R_{C2} & 0 & 0 & 0 & 0 & 0 & 0 \\
R_{A3} & R_{B3} & R_{C3} & 0 & 0 & 0 & 0 & 0 & 0 \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
R_{An} & R_{Bn} & R_{Cn} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & R_{A1} & R_{B1} & R_{C1} & 0 & 0 & 0 \\
0 & 0 & 0 & R_{A2} & R_{B2} & R_{C2} & 0 & 0 & 0 \\
0 & 0 & 0 & R_{A3} & R_{B3} & R_{C3} & 0 & 0 & 0 \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
0 & 0 & 0 & R_{An} & R_{Bn} & R_{Cn} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & R_{A1} & R_{B1} & R_{C1} \\
0 & 0 & 0 & 0 & 0 & 0 & R_{A2} & R_{B2} & R_{C2} \\
0 & 0 & 0 & 0 & 0 & 0 & R_{A3} & R_{B3} & R_{C3} \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
0 & 0 & 0 & 0 & 0 & 0 & R_{An} & R_{Bn} & R_{Cn}
\end{bmatrix}
\]
\[
b_{3n \times 1} = \begin{bmatrix}
  x_{A_1}^F \\
  x_{A_2}^F \\
  x_{A_3}^F \\
  \vdots \\
  x_{A_n}^F \\
  x_{B_1}^F \\
  x_{B_2}^F \\
  x_{B_3}^F \\
  \vdots \\
  x_{B_n}^F \\
  x_{C_1}^F \\
  x_{C_2}^F \\
  x_{C_3}^F \\
  \vdots \\
  x_{C_n}^F 
\end{bmatrix}
\]

\[
A_{3n \times 9} X_{9 \times 1} = b_{3n \times 1}
\]

\[
\bar{A}_{3n \times 6} = \begin{bmatrix}
  R_{A_1} & R_{B_1} & R_{C_1} & 0 & 0 & 0 \\
  R_{A_2} & R_{B_2} & R_{C_2} & 0 & 0 & 0 \\
  R_{A_3} & R_{B_3} & R_{C_3} & 0 & 0 & 0 \\
  \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
  R_{A_n} & R_{B_n} & R_{C_n} & 0 & 0 & 0 \\
  0 & 0 & 0 & R_{A_1} & R_{B_1} & R_{C_1} \\
  0 & 0 & 0 & R_{A_2} & R_{B_2} & R_{C_2} \\
  0 & 0 & 0 & R_{A_3} & R_{B_3} & R_{C_3} \\
  \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
  0 & 0 & 0 & R_{A_n} & R_{B_n} & R_{C_n} \\
  R_{A_1} & R_{B_1} & R_{C_1} & R_{A_1} & R_{B_1} & R_{C_1} \\
  R_{A_2} & R_{B_2} & R_{C_2} & R_{A_2} & R_{B_2} & R_{C_2} \\
  R_{A_3} & R_{B_3} & R_{C_3} & R_{A_3} & R_{B_3} & R_{C_3} \\
  \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
  R_{A_n} & R_{B_n} & R_{C_n} & R_{A_n} & R_{B_n} & R_{C_n}
\end{bmatrix}
\]
\[
\vec{b}_{3n \times 1} =
\begin{bmatrix}
  x_{A1}^F \\
  x_{A2}^F \\
  x_{A3}^F \\
  \vdots \\
  x_{An}^F \\
  x_{B1}^F \\
  x_{B2}^F \\
  x_{B3}^F \\
  \vdots \\
  x_{Bn}^F \\
  1 - x_{C1}^F \\
  1 - x_{C2}^F \\
  1 - x_{C3}^F \\
  \vdots \\
  1 - x_{Cn}^F
\end{bmatrix}
\]

\[
\vec{A}_{3n \times 6} \vec{x}_{6 \times 1} = \vec{b}_{3n \times 1}
\]

Equations 4.49 and 4.52 should significantly improve the accuracy of the computed compositions over their counterparts (equations 4.34 and 4.46 respectively). Moreover, equation 4.52 should yield similar or higher quality results for the same number of samples investigated compared to equation 4.49 due to higher degrees of freedom (degrees of freedom increase by 3 for every sample when using equation 4.52 over equation 4.49).  
Note that the implementation of both equations must satisfy physical constraints, i.e. \(0 \leq x_i^k \leq 1\).

**4.5.3. Model Results**

Equations 4.49 and 4.52 were run for the same set of data in section 4.3.3 and section 4.4.3 for comparison purposes.  
In both cases, the equations failed to yield a physical solution. They lack a description of the equilibrium status of this system (i.e. phase enrichment and the binary miscibility) as with the numerical LLLE equilibration model (section 4.4). They also lack an initial specification of the phase enrichments as with both the LLLE equilibration model and the graphical solution (section 4.3.3).  
As such, this results in poor solutions.  
The data set (Set 1) used for solving equations 4.49 and 4.52 are at constant brine concentration in the feed does not help in providing an adequate description of the three-phase region in the absence of any equilibrium information.
Solving equations 4.49 and 4.52 for the three samples listed in Table 4.4 instead results in the physical solutions provided in Table 4.5, i.e. the analytical approach works best when samples of non-repeating values of \( x_i \) for each component \( i \) are used. Only then, the three-phase region can be sufficiently represented without a mathematical description of equilibrium included in the formulation. Table 4.5 also includes the solution of the analytical approach when all the three-phase samples in Set 1 and Set 2 are implemented in the calculations.

As done in section 4.3.3 and section 4.4.3, the quality of the calculated compositions was assessed with reference to the samples in Set 2 (Figure 4.2). When the samples in Table 4.5 are used, the maximum error was found to be 1.3% and the sum of the square of errors for all results is 1.7%. This is marginally better than (if not on par with) the results obtained from the numerical LLLE equilibration model. When all the samples in Set 1 and Set 2 (Figure 4.2) are implemented in the analytical approach, the maximum error is found to be 0.8% and the sum of the square of errors for all results is 0.8. This is expected since feeding more data into the regression should result in an improved solution if the experimental errors across all data are identical. Breakdown of all the results for this scenario are provide in Figure 4.19, Figure 4.20 and Figure 4.21.

It is noted that when the analytical approach is implemented correctly (i.e. supplying feed data representative of the three-phase region as discussed before), equations 4.49 and 4.52 yield identical results, indicating that equation 4.49 possesses a high enough degree of freedom above which the results cannot be improved. This discussion also highlights that when physical solutions cannot be achieved using the analytical approach, the numerical LLLE equilibration model approach can be used effectively (i.e. when the experimental data set is limited and its selection is constrained).

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Composition, % v/v</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Multipar H</td>
</tr>
<tr>
<td>Set 1 – 4</td>
<td>20.0</td>
</tr>
<tr>
<td>Set 2 – 1</td>
<td>30.0</td>
</tr>
<tr>
<td>Set 2 – 5</td>
<td>50.0</td>
</tr>
</tbody>
</table>

Table 4.4: Three-phase samples at dissimilar feed compositions for all constituents.
Table 4.5: The calculated compositions for the system Multipar H/NSSW/EGMBE at 22.5°C and 1 atm using the analytical approach for the samples in Table 4.4 and for all samples in Figure 4.2.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Table 4.4 Case Compositions, % v/v</th>
<th>Set 1+ Set 2 Case Compositions, % v/v</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Multipar H</td>
<td>NSSW</td>
</tr>
<tr>
<td>Multipar H-</td>
<td>87.83</td>
<td>2.17</td>
</tr>
<tr>
<td>Rich</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NSSW-</td>
<td>0.87</td>
<td>89.13</td>
</tr>
<tr>
<td>Rich</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EGMBE-</td>
<td>20.43</td>
<td>19.57</td>
</tr>
<tr>
<td>Rich</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.19: Experimental vs. calculated phase volumes for the Multipar H-rich phase in the three-phase region for the system Multipar H/NSSW/EGMBE at 22.5°C and 1 atm for all Set 1 and Set 2 samples (Figure 4.2) using the analytical approach.
Figure 4.20: Experimental vs. calculated phase volumes for the NSSW-rich phase in the three-phase region for the system Multipar H/NSSW/EGMBE at 22.5°C and 1 atm for all Set 1 and Set 2 samples (Figure 4.2) using the analytical approach.

Figure 4.21: Experimental vs. calculated phase volumes for the EGMBE-rich phase in the three-phase region for the system Multipar H/NSSW/EGMBE at 22.5°C and 1 atm for all Set 1 and Set 2 samples (Figure 4.2) using the analytical approach.
4.6. QUASI-TERNARY OIL/BRINE/MUTUAL SOLVENT SYSTEMS

4.6.1. Introduction

The investigations described in this section will highlight the range of applicability of the quasi-ternary phase behaviour assumption in oil/brine/mutual solvent systems. This is very important to understand when this assumption is valid, and will form the basis for mapping out the phase diagram using semi-empirical and thermodynamic models as extensions of the work described in this chapter (Chapter 5 and Chapter 6 respectively).

4.6.2. Methodology

The systems outlined in Table 4.4 were investigated for quasi-ternary phase behaviour. For the purposes of this investigation, for each study three sets of samples were prepared. For each set, either the oil, brine or MS were kept constant in the feed. All samples were prepared up to a volume of 20 ml using Gilson Type 401 Diluter for precision. The three-liquid-phase volumes of all samples were recorded at equilibrium down to ±0.005 ml precision, and subsequently used for investigating whether the system exhibits quasi-ternary phase behaviour.

For each investigation, phase volume plots at fixed oil/brine/mutual solvent concentrations in the feed were produced. A linear change consistent with equation 4.4 is adequate proof of quasi-ternary phase behaviour.

Table 4.6: Systems investigated for quasi-ternary phase behaviour (22.5°C and 1 atm).

<table>
<thead>
<tr>
<th>System</th>
<th>Designation</th>
<th>Highlight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Multipar H/MGFW/DBGE</td>
<td>System B</td>
<td>High salinity (~264,000 ppm)</td>
</tr>
<tr>
<td>Multipar H/( NSSW+5% active DETPMP)/EGMBE</td>
<td>System C</td>
<td>Phosphonate scale inhibitor</td>
</tr>
<tr>
<td>Multipar H/(NSSW+5% active PPCA)/EGMBE</td>
<td>System D</td>
<td>Polymeric scale inhibitor</td>
</tr>
<tr>
<td>Multipar H/NSSW/(80:20% v/v EGMBE:MEG)</td>
<td>System E</td>
<td>Mutual solvent blend</td>
</tr>
<tr>
<td>Medium Crude Oil/NSSW/EGMME</td>
<td>System F</td>
<td>Crude system</td>
</tr>
</tbody>
</table>

4.6.3. Results and Discussion

Three-phase formation in the system can be demonstrated by Figure 4.22. This is for System F. Here, the oil-rich, brine-rich and mutual solvent-rich phases can be clearly distinguished in pictures. For other systems, clear three-phase formation was also observed. However, it was not possible to capture this in pictures due to difficulties in capturing the interface in the picture. Figure 4.22 is provided for visual illustration, and
shows clear separation and well-defined interfaces between all the phases. This phase separation was immediate after preparing and shaking the samples, and no centrifugation was applied. This also applied in all the investigated cases.

All the results for all systems (Figure 4.23, Figure 4.24 and Figure 4.25 for System B; Figure 4.26, Figure 4.27 and Figure 4.28 for System C; Figure 4.29, Figure 4.30 and Figure 4.31 for System D; Figure 4.32, Figure 4.33 and Figure 4.34 for System E; Figure 4.35, Figure 4.36 and Figure 4.37 for System F) are perfectly consistent with quasi-ternary phase behaviour. This is despite the high complexity of these systems.

For simpler cases involving oil/brine/mutual solvent only (System B), it is suggested that their quasi-ternary phase behaviour is due to the limited partitioning of the detailed composition of each constituent, i.e. the oil’s and the brine’s detailed compositions experience limited partitioning between the phases, whereby the oil’s organic compounds remain mostly in the oil-rich phase, and the brine’s ions remain mostly in the brine-rich phase. This is also helped by the binary immiscibility of the oil and the brine.

In more complex cases involving the presence of scale inhibitors (System C and System D), the scale inhibitor, like the brine’s ions, will mostly follow the brine. The mutual solvent blend investigated (System E) seem to behave collectively like a single component as well. Surely, the partitioning of the mutual solvents making up the blend will vary considerably. Nevertheless, the phase behaviour produced is consistent with the pseudo-component behaviour of the blend, and can be modelled accordingly. This is perfectly consistent with the findings in Chapter 3 section 3.8.4 involving the predictability of the phase behaviour of a blend based on the theoretical partition coefficient of the blend.

As with the brine, increasing the complexity of the oil (System F) seems to not affect the ability of the system to display quasi-ternary phase behaviour. All of the systems highlighted here are field relevant in the context of mutual solvent application at the pre-flush stage of a squeeze treatment. As such, the ability to describe all of these systems in the context of quasi-ternary phase behaviour will prove useful for applications involving the modelling of these systems.
Figure 4.22: Three-phase formation for System F at various feed compositions.

The constant A in feed set
$R_{sq}(A\text{-Rich}) = 0.9758$, $R_{sq}(B\text{-Rich}) = 0.9962$, $R_{sq}(C\text{-Rich}) = 0.9996$

Figure 4.23: Phase volumes (measured to the nearest 0.01 ml) vs. feed concentration of the brine at constant oil feed concentration (30% v/v) for System B at 22.5°C and 1 atm.
Figure 4.24: Phase volumes (measured to the nearest 0.01 ml) vs. feed concentration of the oil at constant brine feed concentration (30% v/v) for System B at 22.5°C and 1 atm.

Figure 4.25: Phase volumes (measured to the nearest 0.01 ml) vs. feed concentration of the oil at constant mutual solvent feed concentration (30% v/v) for System B at 22.5°C and 1 atm.
Figure 4.26: Phase volumes (measured to the nearest 0.01 ml) vs. feed concentration of the brine at constant oil feed concentration (30% v/v) for System C at 22.5°C and 1 atm.

Figure 4.27: Phase volumes (measured to the nearest 0.01 ml) vs. feed concentration of the oil at constant brine feed concentration (30% v/v) for System C at 22.5°C and 1 atm.
Figure 4.28: Phase volumes (measured to the nearest 0.01 ml) vs. feed concentration of the oil at constant mutual solvent feed concentration (30% v/v) for System C at 22.5°C and 1 atm.

Figure 4.29: Phase volumes (measured to the nearest 0.01 ml) vs. feed concentration of the brine at constant oil feed concentration (30% v/v) for System D at 22.5°C and 1 atm.
Figure 4.30: Phase volumes (measured to the nearest 0.01 ml) vs. feed concentration of the oil at constant brine feed concentration (30% v/v) for System D at 22.5°C and 1 atm.

Figure 4.31: Phase volumes (measured to the nearest 0.01 ml) vs. feed concentration of the oil at constant mutual solvent feed concentration (30% v/v) for System D at 22.5°C and 1 atm.
Figure 4.32: Phase volumes (measured to the nearest 0.01 ml) vs. feed concentration of the brine at constant oil feed concentration (30% v/v) for System E at 22.5°C and 1 atm.

Figure 4.33: Phase volumes (measured to the nearest 0.01 ml) vs. feed concentration of the oil at constant brine feed concentration (30% v/v) for System E at 22.5°C and 1 atm.
Figure 4.34: Phase volumes (measured to the nearest 0.01 ml) vs. feed concentration of the oil at constant mutual solvent feed concentration (30% v/v) for System E at 22.5°C and 1 atm.

Figure 4.35: Phase volumes (measured to the nearest 0.01 ml) vs. feed concentration of the brine at constant oil feed concentration (30% v/v) for System F at 22.5°C and 1 atm.
Figure 4.36: Phase volumes (measured to the nearest 0.01 ml) vs. feed concentration of the oil at constant brine feed concentration (30% v/v) for System F at 22.5°C and 1 atm.

Figure 4.37: Phase volumes (measured to the nearest 0.01 ml) vs. feed concentration of the oil at constant mutual solvent feed concentration (30% v/v) for System F at 22.5°C and 1 atm.
4.7. SUMMARY AND RESEARCH SIGNIFICANCE

The findings in this chapter can be summarised in the following points:

- Systems of oil/brine/mutual solvents are quasi-ternary, i.e. they behave like truly ternary systems, i.e. each of the oil, brine and mutual solvents behave collectively as a single pseudo-component.

- An immediate consequence of this finding is the constant phase compositions of the oil-rich, brine-rich and mutual-solvent rich phases anywhere in the three-phase region. As such graphical, numerical and analytical methods were constructed to resolve three-phase compositions.

- The graphical method is the simplest method. The numerical method, through a description of equilibrium, allows accurate three-phase compositions calculation when the experimental phase separation data set is constrained. The analytical method is easier to programme (simple component balances in matrix form), and gives the best results when the experimental phase separation data set is adequate.

- The quasi-ternary phase behaviour property was found to extend to systems with varying levels of complexity, therefore highlighting the field relevance of this finding.

- The discovered quasi-ternary phase behaviour enables massive simplifications to be made when attempting to model oil/brine/mutual solvent systems. Therefore, it can form the backbone for developing methods to work out the phase-compositions and to model the phase behaviour in complex oil/brine/mutual solvent systems. This was done in Chapter 5 and Chapter 6.

- The constant three-phase compositions means that the mutual solvent will always be concentrated in its respective phase within the three-phase region, which may have implications for oil displacement using a mutual solvent.
Chapter 5: Semi-Empirical Methods for Resolving the Phase Envelope of Oil/Brine/Mutual Solvent Systems

5.1. OVERALL AIMS AND OBJECTIVES

The quasi-ternary phase behaviour property of oil/brine/mutual solvent systems provides significant opportunities to resolve and model the phase behaviour of these systems. The simplest of these is in the form of a component balance semi-empirical model, which relies on phase separation data in working out the phase compositions.

In the three-phase region, this has already been discussed and highlighted. The analytical approach outlined in Chapter 4 section 4.5 describes the component balances that can be used to work out the boundaries of the three-phase region. This will be further illustrated in the discussions in this section.

Moreover, in the two-phase regions of the phase envelope, the equations of the analytical approach are not applicable. In these regions, the phase compositions will not be constant regardless of the feed composition. Therefore, method development is required to formulate both:

1. Experimental methods to produce the phase separation data that would enable detailed phase composition analysis in the two-phase regions of a phase envelope.

2. Mathematical and the modelling strategies that would tie-in with the experimental methods devised for the purposes of resolving the two-phase region.

These aspects are covered by the discussions in this section. The data provided in this section will be used to investigate the use of thermodynamic models for capturing the phase behaviour in quasi-ternary systems in Chapter 6.
5.2. THE EXPERIMENTAL STRATEGY

5.2.1. General Concept

Resolving the two-liquid-phase region/regions of a quasi-ternary system of oil-brine/mutual solvent requires the system to exhibit three-liquid-phase equilibria at accessible experimental conditions. The composition of the three-liquid-phase region can be resolved with ease using the analytical approach in Chapter 4 section 4.5. Once this is done, the **Phase Displacement Method (PDM)** can be used to resolve the unknown composition of any mixture for this particular system. The criterion for this is illustrated in Figure 5.1. The following definitions are required to explain the procedure in Figure 5.1:

1. **Source Sample (SS):** This is a sample of unknown compositions of oil/brine/mutual solvent obtained at the experimental conditions of interest. The PDM aims to resolve the composition of this sample. The SS is ideally comprised of a single liquid phase, but it can be a multi-phase mixture.

2. **Target Mixture (TM):** This a mixture of a known composition. The TM separates into three-phases at equilibrium at reference experimental conditions. The reference experimental conditions will not necessarily match the experimental conditions of interest. For the PDM, the TM is taken roughly as the centre-point of the three-phase triangle.

3. **Overall Mixture (OM):** This mixture is formed by combining the SS with the TM at known ratio (1:n).

When a volume of SS is mixed with (n) volumes of TM, as highlighted in Figure 5.1, the composition of the OM will tend to the composition of the TM as (n) grows bigger. This is key to determining the composition of the SS. The SS is a single phase mixture, while the TM is a three-phase mixture at equilibrium. The value of (n) can be designed such that mixing the SS and the TM in (1:n) proportions will always result in the OM to be a three-phase sample at the three-liquid-phase forming conditions. This phase transition is required to work out the composition of the SS, and for this reason, this method was dubbed the Phase Displacement Method. When TM is taken as roughly the centre-point of the three-phase triangle, an optimal value for (n) is 4. The mathematical analysis for selecting this value of (n) is provided in section 5.2.2.
Figure 5.1: An illustration of the basic methodology of the phase displacement method.

Working out the composition of the SS in this experimental methodology can be done by investigating the three-liquid-phase separation of the OM. This is done using the simple component balance given by equation 5.1. Therefore, resolving the phase compositions in the two-liquid-phase regions involves sampling each phase, and then using the PDM to work out the composition of the phases.

\[ x_i^S = \frac{1}{V_s} \left( x_i^A V_A + x_i^B V_B + x_i^C V_C - \Delta V_i \right) \]  \hspace{1cm} 5.1

Where:

\[ \Delta V_i = x_i^T V_t \]  \hspace{1cm} 5.2

\[ V_t = n \ V \]  \hspace{1cm} 5.3

The derivation of equation 5.1 with reference to Figure 5.1 is illustrated below.

**Component Balance on a Volume Basis**

\[ x_i^S V_S + x_i^T V_t = x_i^O V_O \]  \hspace{1cm} 5.4

**Component Balance on Three-Phase Separation of the OM**

\[ x_i^O V_O = x_i^A V_A + x_i^B V_B + x_i^C V_C \]  \hspace{1cm} 5.5

Equation 5.1 is the result of substituting equation 5.2 and equation 5.5 in equation 5.4 and rearranging for \( x_i^S \).
5.2.2. The Mixing Ratio for the Phase Displacement Method

As mentioned before, the selection of \((n)\) should ensure that for any SS, mixing the SS with the TM in \((1:n)\) ratio would always ensure that the OM is a three-phase mixture. If \((n)\) is too small, the required one-to-three phase transition would not occur. If \((n)\) is too big, the OM would have equal volumes of each phase regardless of the SS composition, and \((x^S_i)\) would tend to zero as shown below.

If:

\[ V_t \gg V_S \]  

Then:

\[ V_t \approx V_o \]  
\[ x^O_i \approx x^t_i \]  

Given equations 5.7 and 5.8, the following can be concluded from equation 5.4:

\[ x^S_i \approx 0 \]  

The upper limit of the value of \((n)\) would be dictated by the precision of volume measurements. If the volume can be measured to the nearest 0.1 ml, as \((n)\) increases, changes in the volumes of the phases in the OM must be measurable. Note that the overall volume of the OM is also important. In the procedure for selecting \((n)\), the minimum overall volume of the OM was set to 10 ml, with 0.1 ml precision assumed. To select \((n)\), the following hypothetical criteria was considered:

- Let the centre-point (centroid) of the phase diagram be the centre-point (centroid) of the three-phase triangle. This point will also be the TM composition.
- Let the three-phase region be defined by compositions one third the distance between the centre-point of the phase diagram and its vertices.
- The “too-small \((n)\) limitation” can be investigated by defining a SS at one of the vertices of the phase diagram.
- The “too-big \((n)\) limitation” can be investigated by defining a SS at one of the vertices of the three-phase triangle.
The hypothetical criteria outlined above are illustrated by Figure 5.2.

Figure 5.2: An illustration of the system and criteria used for selecting the value of \( (n) \).

The aforementioned hypothetical criteria overestimate the distance for the “too-small \( (n) \) limitation”, i.e. a real phase sample in the two-phase region would never be a pure component. The criteria also underestimates the distance for the “too-big \( (n) \) limitation”, i.e. a real phase sample in the two-phase region would never be at the vertex of the three-phase triangle. This makes the criteria fit for the purposes of selecting \( (n) \). A mathematical investigation was conducted to assess the two limitations. The results are presented below.

For the “too-small \( (n) \) limitation”, the changes in the composition and the phase volumes of the OM mixture with increasing \( (n) \) are shown by Figure 5.3 and Figure 5.4 respectively. Most of the change in the composition of the OM occurs below \( (n = 6) \) as seen in Figure 5.3. Below or at \( (n = 2) \), negative phase volumes are generated when assuming three-phase compositions (Figure 5.4). This indicates that \( (n) \) must be above 2 to achieve a definitive one-to-three phase transition.
Figure 5.3: The Changes in the composition of the OM as a function of \((n)\) for the “too-small \((n)\) limitation”.

Figure 5.4: The Changes in the phase volumes of the OM as a function of \((n)\) for the “too-small \((n)\) limitation”.

For the “too-big \((n)\) limitation”, the changes in the composition and the phase volumes of the OM mixture with increasing \((n)\) are shown by Figure 5.5 and Figure 5.6 respectively. Most of the change in the composition of the OM occurs below \((n = 4)\) as seen in Figure 5.5. Detailed calculations (the results of which are shown in Figure 5.6) show that:
• Above \((n = 6)\), changes in the volumes of the A-rich and B-rich phases are not measurable when \((V_{OM})\) equals 10 volume units and the measurement is made to the nearest 0.1 volume units.

• Above \((n = 12)\), changes in the volumes of all phases are not measurable under the same conditions.

Putting all the findings together, the selection of \((n)\) must satisfy equation 5.10 provided below:

\[
2 < n < 6 \quad \text{5.10}
\]

If a natural number is desired for the value of \((n)\) for simplicity, then the options are \((n = 3, 4 \text{ or } 5)\). Any of these would suffice, and a mid-range value would be ideal. Hence, for the PDM method, the optimal mixing proportions of the SS to the TM is 1:4.

**Figure 5.5:** The Changes in the composition of the OM as a function of \((n)\) for the “too-big \((n)\) limitation”.
Figure 5.6: The Changes in the phase volumes of the OM as a function of \((n)\) for the “too-big \((n)\) limitation”.

5.2.3. Experimental Tools

The test tubes used for this work are Duran borosilicate test tubes, graduated down to 0.1 ml precision (i.e. ±0.05 ml uncertainty in phase volume measurements). The test tubes were sealed with polypropylene stoppers during mixing and equilibration. The use of these test tubes provides more accurate phase separation data for the purposes of working out the two/three-phase regions on the phase diagram, thereby reducing experimental errors. All sample preparations were carried out using Gilson Type 401 Diluter for this purpose as well (high precision; ±0.5 μl). For mapping out the three-phase region, 20 ml samples were prepared. For the phase displacement method, 25 ml samples were used at \((n = 4)\), i.e. 5 ml SS to 20 ml TM.

5.2.4. Verification and Estimation of Errors

Samples of known compositions were prepared and analysed using the PDM. For simplicity, the systems used in this analysis consisted of Multipar H/NSSW/EGMME (System A) and Multipar H/MGFW/DGBE (System B) both at \((22.5°C\) and 1 atm). At these conditions, both systems form a three-phase region making them convenient systems for this investigation. The three-phase compositions were resolved using the analytical approach described in Chapter 4 section 4.5 using \(\times 12\) three-phase samples.
The results for mapping the three-phase region are provided in Table 5.1 and Table 5.2 for System A and System B respectively. Using all the samples implemented in the regression, the maximum error in the calculated phase compositions is estimated to be 1.1% and 1.9% for System A and System B respectively. The PDM will rely on these compositions. Therefore, investigating the errors in the results obtained from the PDM is essential to demonstrate its usability.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Constituents, % v/v</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Multipar H</td>
</tr>
<tr>
<td>MH-Rich</td>
<td>89.32</td>
</tr>
<tr>
<td>NSSW-Rich</td>
<td>0.00</td>
</tr>
<tr>
<td>EGMBE-Rich</td>
<td>19.79</td>
</tr>
</tbody>
</table>

Table 5.1: Three-phase compositions for System A at 22.5°C and 1 atm.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Constituents, % v/v</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Multipar H</td>
</tr>
<tr>
<td>MH-Rich</td>
<td>94.82</td>
</tr>
<tr>
<td>MGFW-Rich</td>
<td>0.00</td>
</tr>
<tr>
<td>DGBE-Rich</td>
<td>17.29</td>
</tr>
</tbody>
</table>

Table 5.2: Three-phase compositions for System B at 22.5°C and 1 atm.

An essential step that must be undertaken prior to using the PDM is determining the composition of the TM. As discussed in section 5.2.2, this is taken as the centre-point (centroid) of the three-phase triangle to ensure that SS from any side of the three-phase triangle are displaced efficiently when mixed with TM. The equations for determining the centre-point are described below.

Firstly, the ternary compositions \((x_A, x_B, x_C)\) must be converted to Cartesian coordinates using equations 5.11 and 5.12:

\[ X = (x_B \times 100) + (x_C \times 100) \cos \left(\frac{\pi}{3}\right) \]

\[ Y = (x_C \times 100) \sin \left(\frac{\pi}{3}\right) \]

Then, in Cartesian coordinates, the equation of straight line for each of the three-phase tie-lines must be determined using equations 5.13, 5.14 and 5.15:
\[ Y = mX + C \]  
\[ m = \frac{y_2-y_1}{x_2-x_1} \]  
\[ C = Y - mX \]

The coordinates of the midpoint of each tie-line must also be calculated using equations 5.14, 5.16 and 5.17:

\[
X_m = \frac{1}{2\left(\frac{1}{m} + \frac{1}{m'}\right)} \left[ \frac{x_2^2 - x_1^2 + y_2^2 - y_1^2}{y_2 - y_1} - 2C \right] 
\]

\[ Y_m = mX_m + C \]

Then, with reference to Figure 5.7, the equations of the lines between the vertices of the three-phase triangle and the midpoint of the opposite triangle side must be defined (equations 5.13, 5.14 and 5.15). Finally, the centre-point of the three-phase triangle is given by any of the following two equations:

\[ X_{CP} = \frac{c_1-c_3}{m_3-m_1} \]

\[ X_{CP} = \frac{c_2-c_3}{m_3-m_2} \]

After calculating \((Y_{CP})\), the composition of the TM can be converted back to ternary coordinates using equations 5.11 and 5.12.

Figure 5.7: An illustrative diagram of the procedure for determining the centre-point (centroid) of a three-phase triangle.
The composition of the TM was calculated and rounded to the nearest 0.5%. This is provided in Table 5.3 for System A and Table 5.4 for System B. These tables also contain the compositions of the SS used in the investigations for both systems.

Table 5.3: The feed composition of the SS and the TM used in the investigation for System A.

| Sample | Constituents, % v/v | | |
|--------|---------------------|---|---|---|
|        | MH | NSSW | EGMBE |
| SS1    | 0.0 | 0.0  | 100.0 |
| SS2    | 0.0 | 50.0 | 50.0  |
| SS3    | 30.0 | 10.0 | 60.0  |
| SS4    | 50.0 | 45.0 | 5.0   |
| TM     | 36.0 | 37.0 | 27.0  |

Table 5.4: The composition of the SS and the TM used in the investigation for System B.

| Sample | Constituents, % v/v | | |
|--------|---------------------|---|---|---|
|        | MH | MGFW | DGBE |
| SS1    | 0.0 | 0.0  | 100.0 |
| SS2    | 10.0 | 30.0 | 60.0  |
| SS3    | 50.0 | 5.0  | 45.0  |
| SS4    | 50.0 | 50.0 | 0.0   |
| TM     | 37.5 | 37.0 | 25.5  |

Figure 5.8 and Figure 5.9 show the location of all samples on the phase diagram for System A and System B respectively. In addition, they show the location of the OM when 1:4 SS to TM displacements are performed. The three-phase separation of the OM was used to calculate the composition of all SS using equation 5.1 subject to equations 5.20 and 5.21 provided below. Equation 5.20 eliminates unphysical results (i.e. negative compositions), while equation 5.21 ensures that all compositions sum to one.

\[
x_{ir}^S = \begin{cases} 
  x_i^S, & x_i^S \geq 0 \\
  0, & x_i^S < 0 
\end{cases} \\

x_{iN}^S = \frac{x_{ir}^S}{\sum_i x_{ir}^S} \tag{5.20}
\]

\[
x_{iN}^S = \frac{x_{ir}^S}{\sum_i x_{ir}^S} \tag{5.21}
\]
Figure 5.8: The position of the SS, TM and OM on the phase diagram (System A).

Figure 5.9: The position of the SS, TM and OM on the phase diagram (System B).

The compositions of the SS determined using the PDM are compared with their known compositions in Table 5.5 and Table 5.6 for System A and System B respectively. A very good match was found, for all samples. The maximum errors in the results were roughly...
1.95% and 2.33% for System A and System B respectively. Both errors tie-in very well with the errors in the calculated three-phase compositions for both systems.

The low errors indicate the reliability of this method. Therefore, the PDM can be implemented for both sample and phase behaviour analysis with reasonable reliability.

**Table 5.5: Compositions of the SS (theoretical vs. experimental via PDM) for System A.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Constituents, % v/v</th>
<th>Absolute Difference, % v/v</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Theoretical</td>
<td>Experimental (PDM)</td>
</tr>
<tr>
<td></td>
<td>MH</td>
<td>NSSW</td>
</tr>
<tr>
<td>SS1</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>SS2</td>
<td>0.00</td>
<td>50.00</td>
</tr>
<tr>
<td>SS3</td>
<td>30.00</td>
<td>10.00</td>
</tr>
<tr>
<td>SS4</td>
<td>50.00</td>
<td>45.00</td>
</tr>
<tr>
<td></td>
<td>Maximum Error</td>
<td>±1.95</td>
</tr>
</tbody>
</table>

**Table 5.6: Compositions of the SS (theoretical vs. experimental via PDM) for System B.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Constituents, % v/v</th>
<th>Absolute Difference, % v/v</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Theoretical</td>
<td>Experimental (PDM)</td>
</tr>
<tr>
<td></td>
<td>MH</td>
<td>MGFW</td>
</tr>
<tr>
<td>SS1</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>SS2</td>
<td>10.00</td>
<td>30.00</td>
</tr>
<tr>
<td>SS3</td>
<td>50.00</td>
<td>5.00</td>
</tr>
<tr>
<td>SS4</td>
<td>50.00</td>
<td>50.00</td>
</tr>
<tr>
<td></td>
<td>Maximum Error</td>
<td>±2.33</td>
</tr>
</tbody>
</table>

### 5.3. THE MATHEMATICAL STRATEGY FOR TWO-PHASE MAPPING

#### 5.3.1. General Aims

Besides sampling each phase and using the PDM to work out their compositions, the calculated tie-lines must satisfy physical constraints and the conservation equations. This section illustrates the use of the PDM for mapping the two-phase region.

#### 5.3.2. Full Mathematical Procedure Outline

When a sample separates into two phases, each phase can be analysed independently using the PDM to work out its composition. The composition of both phases can then be used together to draw the two-phase tie-line on the phase diagram corresponding to the sample’s feed composition. For any tie-line on the phase diagram, the feed composition should lie somewhere on the line. The position of the feed point on the tie-line determines the relative
amounts of the resulting phases at equilibrium. In essence, this line is a graphical representation of the overall balance governing the phase separation.

The experimental and basic mathematical procedure (equation 5.1) for the PDM do not ensure meaningful results. To ensure meaningful results, the following standard errors must be accounted for and corrected:

1. Unphysical results (i.e. negative compositions): negative compositions close to zero are possible when performing the calculations using equation 5.1 due to the experimental error margins associated with the PDM. For example, when the composition of one of the components is very low, and the PDM underestimates it, a negative composition may be calculated. Unphysical compositions are rationalised by setting their value to zero (equation 5.20).

2. The sum of the compositions for a given phase may be more than one. This is typically a consequence of rationalisation (i.e. eliminating unphysical results). Alternatively, if the composition of one of the components is very high, and the PDM overestimates it, a composition greater than one may be calculated. Less than one results are also possible (e.g. when working with a binary sample, and the composition of non-existent components are set to zero). When the compositions do not sum to one, the compositions of all components in the phase are normalised (equation 5.21).

On the phase diagram, correcting for the standard errors described above corresponds graphically to the following:

1. When rationalisation is performed on a tie-line, the tie-line is truncated so that all the phase points (on either sides of the tie-line) lie within the ternary plane. Therefore, rationalisation changes the relative distance between the feed point and the phase points. This is because the tie-line may become shorter on one side of the feed point or the other.

2. When normalisation is performed on a tie-line, the slope of the tie-line changes as the position of one or more phase points changes on the phase diagram. The tie-line may also become longer or shorter. When the slope of a tie-line changes, the feed point will no longer lie on the tie-line.
Whenever the results from a PDM are rationalised, normalisation of the results is a mathematical necessity. Also as explained above, in some cases, normalisation may be required even when rationalisation is not performed. A change in the slope of a tie-line represents a breach of both overall and specific component balances. This must be corrected for in order for the results to be physically consistent. Performing overall balance corrections and component balance corrections is only necessary when applying the PDM for phase behaviour analysis, i.e. attempting to establish a tie-line on the phase diagram.

5.3.3. Overall Balance Corrections

The mathematical procedure for performing overall balance corrections is iterative in nature. The fundamental principle for this method is explained below with reference to Figure 5.10. The following definitions are required for this explanation:

- Let \((x_1, y_1)\) and \((x_2, y_2)\) be the phase points.
- Let \((x_f, y_f)\) be the feed point that does not align with the tie-line defined by the phase points.
- Let \((x_{df}, y_{df})\) be a point that lies on the tie-line, either horizontally or vertically across from the feed point.
- Let \((\Delta x_{df} = x_{df} - x_f)\) and \((\Delta y_{df} = y_{df} - y_f)\).

When the tie-line does not align with the feed point, the following cases could be encountered:

1. \((\Delta y_{df} < \Delta x_{df})\) for the tie-line as illustrated on Figure 5.10a.
2. \((\Delta x_{df} < \Delta y_{df})\) for the tie-line as illustrated on Figure 5.10b.
3. \((\Delta x_{df} = \Delta y_{df})\) could also occur. However, this is rarely encountered in practical scenarios (the slope of the tie-line has to be exactly 1 or -1).

The tie-line can be displaced either horizontally or vertically to correct for the overall balance errors subject to the following equation:
\[(x_i, y_i)_{\text{new}} = \begin{cases} 
(x_i, y_i), & \Delta x_{df} < \Delta y_{df} \\
(x_i, [y_i - \Delta y_{df}]), & \Delta y_{df} < \Delta x_{df} \\
([x_i - \Delta x_{df}], y_i) \text{ or } (x_i, [y_i - \Delta y_{df}]), & \Delta x_{df} = \Delta y_{df}
\end{cases}\]

Figure 5.10: Illustrative diagram of the mathematical procedure for overall balance corrections: (a) \(\Delta y_{df} < \Delta x_{df}\); (b) \(\Delta x_{df} < \Delta y_{df}\).

Displacing the tie-lines horizontally or vertically ensures that the phase separation is not impacted significantly (although it would change as will be explained in the next paragraph). This is because the alignment procedure keeps the feed point in the same relative horizontal or vertical position to the phase points. Also, performing the displacements according to equation 5.22 minimises the effects of the overall balance corrections on the calculated compositions by keeping the changes to a minimum.

Following the initial round of balance corrections, the action of displacing a tie-line horizontally or vertically may cause one of the phase points to exit the ternary plane (e.g. when the composition of one of the components is close to zero). As such, re-rationalising and re-normalising the results (equations 5.20 and 5.21) will be required. This will again offset the feed point of the tie-line, although to a smaller degree, and balance corrections will be required again.

A tolerance for the feed point horizontal and vertical offsets \((\Delta x_{df} \text{ and } \Delta y_{df})\) can be set. Once this is done, rationalisation, normalisation and balance corrections can be performed iteratively. A solution is reached once the set tolerances are met as illustrated in Figure 5.12.
5.3.4. Component Balance Corrections

The overall balance correction described in section 5.3.3 ensures the existence of the feed point and the calculated phase composition points on the same tie-line. However, it does not correct the individual component balances. Thus, this correction is required. To perform component balance corrections, a numerical component balance correction method was devised. The inputs are:

1. Estimated lower and upper phase compositions ($x_{i0}^Z$).
2. The feed volume and composition ($F$ and $x_i^F$).
3. The phase separation of the feed mixture at equilibrium, i.e. the volume of the lower and the upper phases ($L$ and $U$).

Once the corrections had been performed, the outputs are phase compositions which satisfy all component balances ($x_i^Z$). To achieve a numerical correction of the component balances, two convergence parameters were used to guide the correction. These are described below.

Let ($V_{i0}^Z$) be the phase volume of component ($i$) in phase ($Z$) based on ($x_{i0}^Z$):

$$V_{i0}^Z = x_{i0}^Z Z$$

The first convergence parameter ($e_i^{ZF}$) is calculated using equation 5.24 provided below:

$$e_i^{ZF} = V_i^L + V_i^U - V_i^F$$

The parameter ($e_i^{ZF}$) measures how much of a given component is estimated to be in the lower and upper phases with reference to how much of the component is known to have existed in the feed. As such, there are three cases for the value of ($e_i^{ZF}$):

1. ($e_i^{ZF} = 0$): There are no errors in the component balance of component ($i$).
2. ($e_i^{ZF} > 0$): ($x_{i0}^Z$) is an overestimation of ($x_i^Z$). In this case, ($x_{i0}^Z$) must be minimised.
3. ($e_i^{ZF} < 0$): ($x_{i0}^Z$) is an underestimation of ($x_i^Z$). In this case, ($x_{i0}^Z$) must be maximised.

The minimisation and the maximisation are performed at steps of ($dX$) which is given by:

$$dX = 10^{-DP}$$

N.B. ($DP$) is the number of desired decimal point precision (e.g. 4 decimal places).
The second convergence parameter requires calculating the phase volumes \((L\) and \(U\)) based on \((x_{i0}^Z)\). The Lever rule (which can be derived by combining the overall and the component balances) can be used for this purpose:

\[
L_C = \left(\frac{x_i^F - x_{i0}^U}{x_i^F - x_{i0}^L}\right) F \quad 5.26
\]

\[
U_C = F - L_C \quad 5.27
\]

A subset of the second convergence parameter \((e_Z^{CE})\) is calculated using equation 5.28 provided below:

\[
e_Z^{CE} = Z_C - Z \quad 5.28
\]

Where \((Z_C)\) is the calculated phase volumes \((L_C\) or \(U_C)\) and \((Z)\) is the experimental phase volumes \((L\) or \(U\)). With this determined, the second convergence parameter \((ind)\) is given by equation 5.29 with reference to equation 5.28:

\[
ind = e_L^{CE} - e_U^{CE} \quad 5.29
\]

The parameter \((ind)\) measures the difference between what is estimated to be the phase volumes based on \((x_{i0}^Z)\) and the known phase volumes from the experiments. As such, there are three cases for the value of \((ind)\):

1. When \((ind = 0)\), there are no component balance errors which require correction.
2. When \((ind > 0)\), the volume of the lower phase is more than it should be according to the experimental data, and the opposite holds for the upper phase.
3. When \((ind < 0)\), the volume of the lower phase is less than it should be according to the experimental data, and the opposite holds for the upper phase.

The component balance corrections follow the algorithm described in Figure 5.13.

5.3.5. Additional Corrections for Three-Phase Forming Systems

In three-phase systems, an additional correction of the tie-lines may be required. If a calculated tie-line breaches the three-phase region, and this breach does not tie in with the experimental data, a two-phase correction can be applied. This correction can be applied graphically by rotating the tie-lines horizontally or vertically about the feed point, thereby achieving the correction without influencing phase separations. This is illustrated in Figure 5.11.
A vertical correction is applied when the tie-line that requires correction is below the oil-brine three-phase border (Figure 5.11a). Otherwise, a horizontal correction is opted for (Figure 5.11b). To achieve the rotation mathematically, the equation of the three-phase border closest to the tie-line that requires correction must be determined (equations 5.13-5.15). To perform a vertical correction (Figure 5.11a):

\[(x_2)_{\text{new}} = x_2\]  
5.30

\[(y_2)_{\text{new}} = m_{\text{border}} (x_2)_{\text{new}} + c_{\text{border}}\]  
5.31

After this, an equation is calculated for the new tie-line using \((x_2, y_2)_{\text{new}}\) and \((x_f, y_f)\). To calculate \((x_1, y_1)_{\text{new}}\), the following equations are applied:

\[(x_1)_{\text{new}} = x_1\]  
5.32

\[(y_1)_{\text{new}} = m_{\text{tiele}} (x_1)_{\text{new}} + c_{\text{tiele}}\]  
5.33

A horizontal correction (Figure 5.11b) can be achieved similarly, but by keeping the \((y)\) coordinates fixed as shown below:

\[(y_2)_{\text{new}} = y_2\]  
5.34

\[(x_2)_{\text{new}} = \frac{(y_2)_{\text{new}} - c_{\text{border}}}{m_{\text{border}}}\]  
5.35

\[(y_1)_{\text{new}} = y_1\]  
5.36

\[(x_1)_{\text{new}} = \frac{(y_1)_{\text{new}} - c_{\text{tiele}}}{m_{\text{tiele}}}\]  
5.37

The three-phase corrections are assisted by solubility corrections made with reference to the three-phase corrections. The following conditions must be met by two-phase tie-lines:

**A-B Two-Phase Region**

\[x_{Al}^L = \begin{cases}  
  x_{Al}^L, & x_{Al}^L \leq x_A^B \\
  x_A^B, & x_{Al}^L > x_A^B
\end{cases}\]  
5.38

\[x_{Cl}^L = \begin{cases}  
  x_{Cl}^L, & x_{Cl}^L \leq x_C^B \\
  x_C^B, & x_{Cl}^L > x_C^B
\end{cases}\]  
5.39
\[
x_{Bi}^U = \begin{cases} x_{Bi}^U, \\ x_B^A, \\ x_{Bi}^U \leq x_B^A \\ x_{Bi}^U > x_B^A \\ 5.40 
\end{cases}
\]

\[
x_{Ci}^U = \begin{cases} x_{Ci}^U, \\ x_C^A, \\ x_{Ci}^U \leq x_C^A \\ x_{Ci}^U > x_C^A \\ 5.41 
\end{cases}
\]

A-C Two-Phase Region

\[
x_{Ci}^U = \begin{cases} x_{Ci}^U, \\ x_C^A, \\ x_{Ci}^U \geq x_C^A \\ x_{Ci}^U < x_C^A \\ 5.42 
\end{cases}
\]

B-C Two-Phase Region

\[
x_{Ci}^L = \begin{cases} x_{Ci}^L, \\ x_C^B, \\ x_{Ci}^L \geq x_C^B \\ x_{Ci}^L < x_C^B \\ 5.43 
\end{cases}
\]

Figure 5.11: Illustrative diagram of the mathematical procedure for two-phase corrections: (a) when the tie-line is below A-B; (b) when the tie-line is beside A-C or B-C.
5.3.6. Logical Diagrams

Figure 5.12: The full procedure (experimental and mathematical) for conducting phase analysis using the PDM (three-phase analysis not included).
Figure 5.13: The algorithm used for component balance corrections.
5.4. MAPPING THE PHASE ENVELOPE

5.4.1. Three-Phase Mapping

The systems implemented (Table 5.7) in this investigation are the same systems discussed in Chapter 4. All of these systems were shown to be quasi-ternary. The results of mapping the three-phase region using the analytical approach (Chapter 4 section 4.5) are provided in this section.

Table 5.7: Quasi-ternary systems mapped as part of semi-empirical work (22.5°C and 1 atm).

<table>
<thead>
<tr>
<th>System</th>
<th>Designation</th>
<th>Highlight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Multipar H/NSSW/EGMBE</td>
<td>System A</td>
<td>Low salinity (~36,000 ppm)</td>
</tr>
<tr>
<td>Multipar H/MGFW/DGBE</td>
<td>System B</td>
<td>High salinity (~264,000 ppm)</td>
</tr>
<tr>
<td>Multipar H/(NSSW+5% active DETPMP)/EGMBE</td>
<td>System C</td>
<td>Phosphonate scale inhibitor</td>
</tr>
<tr>
<td>Multipar H/(NSSW+5% active PPCA)/EGMBE</td>
<td>System D</td>
<td>Polymeric scale inhibitor</td>
</tr>
<tr>
<td>Multipar H/NSSW/(80:20% v/v EGMBE:MEG)</td>
<td>System E</td>
<td>Mutual solvent blend</td>
</tr>
<tr>
<td>Medium Crude Oil/NSSW/EGMBE</td>
<td>System F</td>
<td>Crude system</td>
</tr>
</tbody>
</table>

The qualitative phase diagrams of these systems are provided in Figure 5.14, Figure 5.15, Figure 5.16, Figure 5.17, Figure 5.18 and Figure 5.19 for System A, System B, System C, System D, System E and System F respectively. The samples used for mapping these systems at constant oil, brine or mutual solvent concentration are highlighted on the qualitative phase diagrams.

The results are shown and compared with the qualitative three-liquid-phase region data in Figure 5.20, Figure 5.23, Figure 5.26, Figure 5.29, Figure 5.32 and Figure 5.35 for System A, System B, System C, System D, System E and System F respectively. In all cases, almost all of the qualitative three-liquid-phase data points are found to lie within the three-liquid-phase triangle. The errors in the calculated three-phase compositions were estimated to be 1.1%, 1.9%, 6.3%, 1.7%, 3.9% and 5.5% for System A, System B, System C, System D, System E and System F respectively. The higher errors in more complex systems are not a surprise as small deviations from quasi-ternary phase behaviour will start to occur. Moreover, the errors remain acceptable for the purposes of the practical applications of this method.

It is noted that the mapped three-phase regions do not agree fully with the qualitative experimental data for highly non-ideal systems. This is particularly true for System C (Figure 5.26) and even more so for System E (Figure 5.32). Both systems are still quasi-
ternary, and behave like quasi-ternary systems where three-phases form. However, solubility effects play a role in these cases. For instance, with System E, the blend component MEG improves the ability of the mutual solvent-rich phase to accommodate more brine. Therefore, it has the effect of eliminating the three-phase region at low brine concentrations as discussed in Chapter 3 section 3.8. However, where this effect stops (e.g. above 20% NSSW in the feed for System E), three-phase formation resumes in a quasi-ternary fashion as demonstrated in Chapter 4 section 4.6.

The quality of the calculated three-liquid-phase phase compositions for all systems, denoted by the vertices of the three-liquid-phase triangles, is evident when back-calculating the feed compositions and comparing them to the known experimental values. This is done in Figure 5.21, Figure 5.24, Figure 5.27, Figure 5.30, Figure 5.33 and Figure 5.36 for System A, System B, System C, System D, System E and System F respectively. An excellent match is observed between the experimental feed compositions, and the feed compositions calculated based on the predicted three-liquid-phase compositions for all systems. This excellent match propagates to the three-phase separations as well as illustrated in Figure 5.22, Figure 5.25, Figure 5.28, Figure 5.31, Figure 5.34 and Figure 5.37 for the same systems respectively, which compare the experimental and calculated three-phase separations for several samples.

All of this highlights the validity of the quasi-ternary approach to provide a sufficient description of these very complex systems for practical applications. However, the discussed limitations (i.e. increased errors with increasing complexity) must be considered when these models are applied. Note that all the results presented in this section were subjected to a “quasi-ternary” error correction. This approach uses re-calculated experimental phase volumes in solving the component balance equations of the analytical approach. The re-calculation of the experimental phase volumes converts the near perfect correlation coefficients in the figures presented in Chapter 4 section 4.6 to perfect correlation coefficients. This assumes that the imperfection in the correlation coefficients is caused by the precision limitation of the experimental tools. In general, this approach delivers more reliable three-phase composition result in all cases, reducing the errors by up to 3% in some cases, therefore highlighting the validity of this correction.
Figure 5.14: The phase diagram of System A at 22.5°C and 1 atm; mapping samples highlighted.

Figure 5.15: The phase diagram of System B at 22.5°C and 1 atm; mapping samples highlighted.
Figure 5.16: The phase diagram of System C at 22.5°C and 1 atm; mapping samples highlighted.

Figure 5.17: The phase diagram of System D at 22.5°C and 1 atm; mapping samples highlighted.
Figure 5.18: The phase diagram of System E at 22.5°C and 1 atm; mapping samples highlighted.

Figure 5.19: The phase diagram of System F at 22.5°C and 1 atm; mapping samples highlighted.
Figure 5.20: Qualitative vs. quantitative three-phase region data for System A at 22.5°C and 1 atm.

Figure 5.21: Experimental vs. back-calculated feed compositions for several samples in the three-phase region; System A at 22.5°C and 1 atm.
Figure 5.22: Experimental vs. calculated normalised phase volumes for several samples in the three-phase region; System A at 22.5°C and 1 atm.

Figure 5.23: Qualitative vs. quantitative three-phase region data for System B at 22.5°C and 1 atm.
Figure 5.24: Experimental vs. back-calculated feed compositions for several samples in the three-phase region; System B at 22.5°C and 1 atm.

Figure 5.25: Experimental vs. calculated normalised phase volumes for several samples in the three-phase region; System B at 22.5°C and 1 atm.
Figure 5.26: Qualitative vs. quantitative three-phase region data for System C at 22.5°C and 1 atm.

Figure 5.27: Experimental vs. back-calculated feed compositions for several samples in the three-phase region; System C at 22.5°C and 1 atm.
Figure 5.28: Experimental vs. calculated normalised phase volumes for several samples in the three-phase region; System C at 22.5°C and 1 atm.

Figure 5.29: Qualitative vs. quantitative three-phase region data for System D at 22.5°C and 1 atm.
Figure 5.30: Experimental vs. back-calculated feed compositions for several samples in the three-phase region; System D at 22.5˚C and 1 atm.

Figure 5.31: Experimental vs. calculated normalised phase volumes for several samples in the three-phase region; System D at 22.5˚C and 1 atm.
Figure 5.32: Qualitative vs. quantitative three-phase region data for System E at 22.5˚C and 1 atm.

Figure 5.33: Experimental vs. back-calculated feed compositions for several samples in the three-phase region; System E at 22.5˚C and 1 atm.
Figure 5.34: Experimental vs. calculated normalised phase volumes for several samples in the three-phase region; System E at 22.5°C and 1 atm.

Figure 5.35: Qualitative vs. quantitative three-phase region data for System F at 22.5°C and 1 atm.
Figure 5.36: Experimental vs. back-calculated feed compositions for several samples in the three-phase region; System F at 22.5°C and 1 atm.

Figure 5.37: Experimental vs. calculated normalised phase volumes for several samples in the three-phase region; System F at 22.5°C and 1 atm.
5.4.2. Two-Phase Mapping

Mapping the full phase diagram of the systems described in Table 5.7 was done using the PDM, and the three-phase compositions determined in section 5.4.1. All the initial results were subjected to the error corrections discussed in section 5.3. The final results are provided in Figure 5.39, Figure 5.41, Figure 5.43, Figure 5.45, Figure 5.47 and Figure 5.49 for System A, System B, System C, System D, System E and System F respectively. For all systems, the consistency between the calculated and the experimental phase fractions are highlighted in Figure 5.40, Figure 5.42, Figure 5.44, Figure 5.46, Figure 5.48 and Figure 5.50 for the same systems respectively. The near perfect correlation coefficients in all figures are due to the component balance corrections which incorporate the experimental phase separations in the calculations.

Looking more closely at the phase envelopes, all results are thermodynamically consistent with what can be expected from a three-phase forming system; a three-phase triangle surrounded by three two-phase region, oil/brine-rich, oil/mutual solvent-rich and brine/mutual solvent-rich. System A (Figure 5.39) stands out as an exception, in which the two-phase tie-lines in the oil/mutual solvent-rich region indicated phase separation to oil-rich and brine-rich phases.

The results of the PDM in this region were verified indirectly using two different methods. Firstly, the phase separation in the region is consistent with the position of the feed point on the tie-line, resulting in a large upper phase (>95%) and a very small lower phase. If the phases were oil-rich and mutual-solvent rich, a less variable phase separation is expected based on the position of the feed points. Secondly, UltraViolet (UV) Trans-Stilbene (TS) tracer analysis at 316 nm (refer to Chapter 7) was conducted to investigate the nature of each of the resulting phases for all samples (i.e. oleic phase or aqueous phase). This investigation is described in detail below.

For several samples within the three-phase region on the equal oil/mutual solvent phase separation line (see Figure 5.38; samples on this line give equal volumes of oil-rich and mutual solvent-rich phases at equilibrium), the partitioning of TS between the oil-, brine- and mutual solvent-rich phases was analysed. The results are provided in Table 5.8. A constant concentration of TS in all phases was achieved. This is consistent with the quaternary nature of this system, i.e. no three-phase region composition variations would equate to equal partitioning of a tracer across all phases anywhere in the three-phase region. A slight affinity of TS to the oil-rich phase was recorded as opposed to the mutual solvent-
rich phase \( (\log_{10} P_{o/MS} = 0.17 \text{ on average}; \text{ the 0.02 standard deviation is in line with the mass balance errors shown in Table 5.9}). \) Moreover, the TS cannot enter the brine-rich phase \([TS]_B = 0.0 \text{ ppm}\). These results can be used as a guideline to decipher the phase enrichment of the phases obtained from samples in the two-phase region.

![Figure 5.38: The three-phase region of System A with three-phase test samples highlighted.](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>[TS] in Each Phase, ppm</th>
<th>( P_{o/MS} )</th>
<th>( \log_{10} P_{o/MS} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>Oil-Rich</td>
<td>Brine-Rich</td>
<td>MS-Rich</td>
</tr>
<tr>
<td>1</td>
<td>6.1</td>
<td>0.0</td>
<td>4.0</td>
</tr>
<tr>
<td>2</td>
<td>5.9</td>
<td>0.0</td>
<td>4.1</td>
</tr>
<tr>
<td>3</td>
<td>6.1</td>
<td>0.0</td>
<td>4.0</td>
</tr>
<tr>
<td>4</td>
<td>6.0</td>
<td>0.0</td>
<td>4.2</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Standard Deviation</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.8: TS analysis in the three-phase region for System A (50 ppm TS added to the sample; x10 dilution was performed oil-, brine- and MS-rich phases were diluted in oil, water and MS respectively).
Table 5.9: Mass balance errors for the TS analysis provided in Table 5.8.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Mass of Trans-Stilbene Based on Feed/Phase Volumes</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Feed</td>
<td>MS-Rich</td>
</tr>
<tr>
<td>#</td>
<td>mg</td>
<td>mg</td>
</tr>
<tr>
<td>1TS</td>
<td>0.120</td>
<td>0.048</td>
</tr>
<tr>
<td>2TS</td>
<td>0.140</td>
<td>0.058</td>
</tr>
<tr>
<td>3TS</td>
<td>0.160</td>
<td>0.064</td>
</tr>
<tr>
<td>4TS</td>
<td>0.180</td>
<td>0.076</td>
</tr>
</tbody>
</table>

In the two-phase region, the results in Table 5.10 are in perfect agreement with the results in Figure 5.39. All of the TS dosed into the sample remained with the upper phase, thereby indicating its oleic nature. The lower phases for all samples contained no amount of TS indicating its aqueous nature, even in the oil/mutual solvent-rich two-phase region, i.e. no mutual-solvent rich phase in this region.

Table 5.10: TS analysis in the two-phase region for System A (50 ppm TS added to the sample; x10 dilution was performed oil-, brine- and MS-rich phases were diluted in oil, water and MS respectively).

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>[TS] in Each Phase, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Region</td>
</tr>
<tr>
<td>#</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Oil/Brine</td>
</tr>
<tr>
<td>2</td>
<td>Oil/Brine</td>
</tr>
<tr>
<td>3</td>
<td>Oil/Mutual Solvent</td>
</tr>
<tr>
<td>4</td>
<td>Oil/Mutual Solvent</td>
</tr>
<tr>
<td>5</td>
<td>Brine/Mutual Solvent</td>
</tr>
<tr>
<td>6</td>
<td>Brine/Mutual Solvent</td>
</tr>
</tbody>
</table>

The reason for the above findings could lie in the fact that System A is quasi-ternary (i.e. not truly ternary). The system is a multicomponent mixture of more than three components. The oil/mutual solvent two-phase region could be where the quasi-ternary phase behaviour breaks and multicomponent (oil and brine components) effects start to manifest on the phase diagram. However, since this effect is not observed for all the other systems despite their greater complexity (Figure 5.41, Figure 5.43, Figure 5.45, Figure 5.47 and Figure 5.49), it is more likely that the two-phase region on the oil/mutual solvent side for this system is very small, and the samples analysed (samples 3 and 4) are in fact three-phase samples. If the mutual solvent-rich phase is dispersed into the large oil-rich phase, the oleic phase compositions highlighted in Figure 5.39 are possible.

For comparative purposes, the same TS UV analysis was performed for System B, albeit qualitatively rather than quantitatively due to background interferences from DGBE at 316
nm (refer to Chapter 7). The results in Table 5.11 show a partitioning profile of TS consistent with the phase envelope of the system resolved via the PDM (Figure 5.41).

In the oil/mutual solvent region, TS is found in both phases, the upper (oil-rich) and the lower (mutual solvent-rich) phases is consistent with their oleic nature. No deviations are observed from the quasi-ternary phase behaviour. This further suggests the potentially artificial nature of the observations in the case of System A, which are thought to be the result of a wider three-phase region than expected, and the entrainment of the small mutual solvent-rich phase within the larger oil rich phase.

Table 5.11: TS analysis in the two-phase region for System B (50 ppm TS added to the sample; x10 dilution was performed oil-, brine- and MS-rich phases were diluted in oil, water and MS respectively).

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Region</th>
<th>UV Absorbance in Each Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td></td>
<td>Lower</td>
</tr>
<tr>
<td>1</td>
<td>Oil/Brine</td>
<td>0.002</td>
</tr>
<tr>
<td>2</td>
<td>Oil/Brine</td>
<td>0.002</td>
</tr>
<tr>
<td>3</td>
<td>Oil/Mutual Solvent</td>
<td>0.500</td>
</tr>
<tr>
<td>4</td>
<td>Oil/Mutual Solvent</td>
<td>0.521</td>
</tr>
<tr>
<td>5</td>
<td>Brine/Mutual Solvent</td>
<td>0.006</td>
</tr>
<tr>
<td>6</td>
<td>Brine/Mutual Solvent</td>
<td>0.007</td>
</tr>
</tbody>
</table>

The results for all systems in this section will be compared with the results obtained from a thermodynamic model in Chapter 6.
Figure 5.39: Phase envelope of System A via the PDM at 22.5°C and 1 atm.

Figure 5.40: Experimental vs. calculated (PDM) phase fractions for System A at 22.5°C and 1 atm.
Figure 5.41: Phase envelope of System B via the PDM at 22.5°C and 1 atm.

Figure 5.42: Experimental vs. calculated (PDM) phase fractions for System B at 22.5°C and 1 atm.
Figure 5.43: Phase envelope of System C via the PDM at 22.5°C and 1 atm.

Figure 5.44: Experimental vs. calculated (PDM) phase fractions for System C at 22.5°C and 1 atm.
Figure 5.45: Phase envelope of System D via the PDM at 22.5°C and 1 atm.

Figure 5.46: Experimental vs. calculated (PDM) phase fractions for System D at 22.5°C and 1 atm.
Figure 5.47: Phase envelope of System E via the PDM at 22.5°C and 1 atm.

Figure 5.48: Experimental vs. calculated (PDM) phase fractions for System E at 22.5°C and 1 atm.
Figure 5.49: Phase envelope of System F via the PDM at 22.5°C and 1 atm.

Figure 5.50: Experimental vs. calculated (PDM) phase fractions for System F at 22.5°C and 1 atm.
5.4.3. Mapping the Phase Envelope of Strictly Two-Phase Forming Systems

PDM Mapping

As mentioned briefly in section 5.2.1, the experimental conditions of interest for the phase envelope mapping via the PDM can differ from the three-phase forming conditions. This means that even when the system under investigation does not exhibit three-phase formation at the experimental conditions of interest, the phase envelope of the system can still be mapped via the PDM as long as three-phase forming conditions for the system exist.

As an example, System A is a three-phase forming system at 22.5°C and 1 atm. At 45.0°C and 70.0°C, the three-phase region disappears (refer to Chapter 3 section 3.9). Using the three-phase forming conditions (22.5°C) as reference conditions (Figure 5.20) for the TM, the PDM was applied to map the phase envelope of these systems. Phase samples were collected at the experimental conditions of interest, while phase displacements were performed at the reference conditions.

Subject to the error corrections discussed in section 5.3, the results for System A at 45.0°C and 70.0°C are provided in Figure 5.51 and Figure 5.53 respectively. Also, as expected and due to the error corrections, the calculated and the experimental phase fractions are almost perfectly consistent as shown in Figure 5.52 and Figure 5.54 for the same temperatures respectively.

A closer inspection of Figure 5.51 and Figure 5.53 highlights the near constant aqueous phase composition. This is a direct consequence of the miscibility gap that exists between the oil and the brine in three-phase forming systems. The explanation for this is simple. The amount of mutual solvent that the aqueous phase can accommodate in this case has an upper limit. The tie-lines of System A under three-phase forming conditions (22.5°C) also indicate a relatively constant lower phase composition when an aqueous phase is attained (Figure 5.39). In this case, the three-phase region forms because at the low temperature of System A, the aqueous phase has reached its upper mutual solvent solubility limit. The oleic phase cannot accommodate all of the mutual solvent that cannot go into the aqueous phase. Due to this miscibility gap, the three-phase region forms, with one of the phases being rich in the mutual solvent. As the temperature increases, (e.g. to 45.0°C), this enhances the solubility of the mutual solvent in the oil, and hence the disappearance of the three-phase region.
As such, the relatively constant composition of the lower phase is reflective of the solubility limits. The opposite effect can also occur depending on the constituents of the system. This effect may be important in squeeze treatments. For example, consider the case where the aqueous phase always contains the same amount of mutual solvent in transport due to solubility limits, i.e. lower phase composition is roughly constant. In such case, more concentrated mutual solvent pre-flushes lead to higher mutual solvent concentrations in the oleic phase anywhere in the formation. This may aid in more efficient oil displacement during a pre-flush treatment.

On the other hand, if the solubility limit applies to the oil (i.e. upper phase composition is roughly constant), increasing the mutual solvent concentration in the pre-flush increases the mutual solvent concentration in the aqueous phase anywhere in the system, which may lead to greater inorganic precipitation. It may also have greater influences on the adsorption of the scale inhibitor in case of competitive mutual solvent/scale inhibitor adsorption during the main treatment stage of a squeeze treatment. Effects may stretch as far as the back-production, as higher concentrations of mutual solvent in the aqueous phase on back-production may strip the adsorbed scale inhibitor off the rock. Projections aside, this phase behaviour effect is important to consider in transport studies involving the mutual solvent.
Figure 5.51: Phase envelope of System A via the PDM at 45.0°C and 1 atm.

Figure 5.52: Experimental vs. calculated (PDM) phase fractions for System A at 45.0°C and 1 atm.
Figure 5.53: Phase envelope of System A via the PDM at 70.0°C and 1 atm.

Figure 5.54: Experimental vs. calculated (PDM) phase fractions for System A at 70.0°C and 1 atm.
Simplified Mapping

A side-line opportunity arising in the case of near constant oleic/aqueous phase compositions is the ability to use a very simple mass balance model to map out the phase envelope. A knowledge of the solubilities is required for this (i.e. binary oil/mutual solvent solubilities or binary brine/mutual solvent solubilities). The oil and the brine can be assumed immiscible.

An illustration of the procedure proposed for a simplified estimation of the phase envelope of a two-phase forming system when one of the phase compositions is constant is provided in Figure 5.55. Point A denotes the equal binary separation between the oil and the brine at equilibrium. Point B denotes the equal binary separation between the brine and the mutual solvent at equilibrium. Point M is the midpoint of line AB. At 90° angle with respect to the line AB, another point dM is defined. Therefore, the distance (dr) represents the vertical separation distance between point M and point dM with respect to line AB. A quadratic polynomial can describe the curve A-dM-B. Points falling on this curve represent the multicomponent equal two-phase separation.

Figure 5.55: Simplified two-phase mapping when one of the phase compositions are constant.
To work-out an estimation of the phase envelope, the following rules may be applied:

1. Scenario A (Figure 5.55): if the feed composition of the mutual solvent ($x_{MS}^F$) lies below the mutual solvent concentration in the fixed phase composition ($x_{MS}^{fx}$), the solubility limits within the fixed phase composition for the mutual solvent have not been met. Therefore, it may be assumed that:

$$x_{MS}^{fx} = x_{MS}^F$$

2. Scenario B (Figure 5.55): at feed compositions above the fixed phase composition of the mutual solvent, one of the phase compositions is fixed at the fixed phase composition.

Both scenarios are illustrated in Figure 5.55, and the assumptions above tie-in well with the observations in Figure 5.51 and Figure 5.53. To apply this simple model, a value for (dr) must be selected, making this a one parameter model. This value will be subject to a maximum, beyond which unphysical results are obtained. Matching qualitative or quantitative data can be used to determine (dr) in a trial and error fashion. Once this is specified, performing a simple component balance on the basis of equal phase separation allows all phase compositions to be calculated anywhere on the phase diagram.

This was performed for System A at 45.0°C and 70.0°C. The parameters used in this solution are provided in Table 5.12. The lower phase solubility limits and the binary separation data are measured experimentally using the PDM. The (dr) values are obtained via trial and error. As with the PDM, all the results shown in Figure 5.56 and Figure 5.58 at 45.0°C and 70.0°C respectively are reasonable in representing the phase envelope. The experimental phase separations are also consistent with the calculated values as shown in Figure 5.57 and Figure 5.59 for the same conditions respectively.

Table 5.12: The parameters used to calculate the results for System A using the (dr) model shown in Figure 5.56, Figure 5.57, Figure 5.58 and Figure 5.59.

<table>
<thead>
<tr>
<th>T, °C</th>
<th>Lower Phase Solubility Limits, % v/v</th>
<th>Brine/MS Binary Separation, % v/v</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Oil</td>
<td>Brine</td>
</tr>
<tr>
<td>45.0</td>
<td>0.01</td>
<td>91.99</td>
</tr>
<tr>
<td>70.0</td>
<td>0.01</td>
<td>94.49</td>
</tr>
</tbody>
</table>
Figure 5.56: Phase envelope of System A (dr basis) at 45.0°C and 1 atm.

Figure 5.57: Experimental vs. calculated (dr basis) phase fractions for System A at 45.0°C and 1 atm.
Figure 5.58: Phase envelope of System A (dr basis) at 70.0°C and 1 atm.

Figure 5.59: Experimental vs. calculated (dr basis) phase fractions for System A at 70.0°C and 1 atm.
5.5. SUMMARY AND RESEARCH SIGNIFICANCE

The findings in this chapter can be summarised by the following points:

- The quasi-ternary phase behaviour of oil/brine/mutual solvent systems can be used to devise a simple mass balance model to estimate the phase envelope of the system reasonably well without the need for complex modelling/analytical tools.

- This mass balance model must be applied in the context of: 1) an experimental procedure that generates the data required to estimate the phase envelope; 2) a rigorous mathematical procedure that ensures the physical consistency of the results obtained. Both the experimental and mathematical procedures were developed and demonstrated with success as part of this work.

- Phase envelope mapping was demonstrated successfully for both two-phase and three-phase forming systems using this method. The results of such analysis could be implemented in transport models immediately to investigate the propagation of the mutual solvent taking into account its phase behaviour.

- An advantage of the experimental procedure outlined for this method (PDM) is its ability to provide an excellent estimation of the composition of a sample containing oil/brine/mutual solvent, with the knowledge of the sample constituents and without any additional knowledge about the sample. Therefore, it can be applied to analyse the effluent from propagation studies involving mutual solvents displacing oils/brines, thereby providing more insights into the displacement. This was applied in Chapter 8.

- The constant phase composition of one of the phases in strictly two-phase forming conditions may have implications on oil displacement as well as scale inhibitor adsorption. Thus, this phase behaviour must be considered in cases in which it occurs.

- A very simple estimation of the phase envelope of strictly two-phase forming systems can be made using a one-parameter model, and taking into account the probable constant phase composition of one of the phases in strictly two-phase forming system. This simplified phase mapping also enables applications in transport studies as demonstrated in Chapter 8.