PHASE INVERSION AND WETTABILITY IN TESTING THE EXTENDER OIL FOR THE FLOTATION OF COARSE POTASH ORE FRACTIONS

by Leonardo Barroilhet Cahuas

B.Sc., Universidad de Santiago de Chile, 2010

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF APPLIED SCIENCE

in

The Faculty of Graduate and Postdoctoral Studies (Mining Engineering)

THE UNIVERSITY OF BRITISH COLUMBIA

(Vancouver)

September 2015

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Abstract

The effects of amines on the phase inversion of oil/NaCl-KCl saturated-brine emulsions stabilized by KCl particles and on the wettability of KCl surfaces in brine were investigated. Contact angle at the oil/saturated-brine/KCl line of contact, interfacial tension at the oil/saturated-brine interface, and phase inversion measurements were performed to study the applicability of the phase inversion method in the selection of the extender oil(s) for subsequent coarse potash ore flotation tests.

Two commercial amines, dodecyl and octadecyl, and two technical amines, TD and HTD, were tested as additives to oil in the preparation of the extender, and three hydrocarbons (cyclohexane, n-decane, and Diesel oil).

The contact angle results demonstrated that amines adsorb onto KCl with a clear effect of the equilibration time. The increasing of contact angle with amine concentration was influenced by two equilibrium phenomena: a "fast equilibrium" resulting from the diffusion of large amine molecules to the interfaces and a "slow equilibrium" caused by dissolution/recrystallization of mostly NaCl fine crystallites onto KCl surfaces in saturated brine.

This project discusses the existence of eight intermediate states that describe sequentially the changes in KCl wettability caused by the amine adsorption. Each state occurs at a particular amine concentration, which is characteristic of each amine in oil formulation. The contact angles were linked with the emulsion stability, which was described by the final emulsion volume. KCl particles were gradually made hydrophobic and the contact angle and emulsion stability increase until equilibrium with amine concentration.

The obtained results suggest that water-in-oil (W/O) emulsions are produced at the equilibrium, while oil-in-water (O/W) emulsions are mostly unstable. The emulsion stability was experimentally found to depend on temperature and additional mixing time; the former lead to the coalescence phenomena, while the latter caused the phase inversion from O/W to W/O emulsions.

This project confirms that the phase inversion technique could constitute a quick and reliable lab testing methodology to screen various amines in oil formulations.

Preface

This dissertation is original, unpublished, and independent work by the author, L. Barroilhet Cahuas. The author conducted all the experiments described in this thesis.

Chapters 1, 2, and 3 present respectively an introduction to the research, literature review, and experimental program designed for the purpose of this study by the author.

Chapter 4 involves the results of three different type of tests performed by the author to study oil/saturated-brine/KCl systems. These tests include contact angle measurements, interfacial tension measurements, and phase inversion tests.

Chapter 5 includes the analysis of the research data carried out by the author.

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Acknowledgements

I offer my enduring gratitude to the faculty, staff and my fellow students at the Norman B. Keevil Institute of Mining Engineering who have inspired me to continue my work in this field. I owe particular thanks to Professor Janusz S. Laskowski, my research supervisor, for his expert opinion, guidance, valuable comments, suggestions, and provisions that benefited me in the completion and success of this project.

I wish to extend my immeasurable appreciation and deepest gratitude to Ms. Sally Finora for enlarging my vision of science and providing coherent answers to my endless questions.

I would also like to express my sincere gratitude to Ms. Avishan Atrafi for her contribution to this thesis in the interfacial tension measurements.

To my committee, Dr. Marek Pawlik, Dr. Dirk van Zyl, and Dr. Dunbar Scott, I am extremely grateful for your assistance and suggestions throughout my project.

I gratefully acknowledge the financial support provided by Becas CONICYT for letting me fulfill my dream of being a student at UBC.

I would also like to thank to my parents in Chile for their continuous support and encouragement, and to my dear wife, Paulina, whose patient and love made all possible.

Finally, to Mr. Graham Bullen and his family, my first Canadian friends, thank you! I am deeply indebted for their help, support, care, and shelter.

To my wife, friend, and lover, Paulina

&

To my parents and sisters:

As we set out on this journey called life, we put all our effort into struggling and competition. The mindset of a better and encouraging tomorrow for a very few ones.

Life is, however, an instance for reflection, peace, and wisdom for everyone.

God creates us with love, and we have to carry only love in our back pack.

Our eyes always mislead us but our souls always envision the truth... *so, why are you in rush following the former and silencing the latter?*

Stop your walk... don't be afraid of tomorrow... close you eyes and listen to your soul... Because the only way to reach fullness is through God, and in turn the only way to achieve God is with reflection, peace, and wisdom.

All around you is a lie, an illusion, a trick of our mind. The truth was, is, and will be inside us. And the only truth is that God has created us to love each other but not to strive wantonly for a hopeful and non-existent tomorrow.

- Corinthians 13

1 Introduction

1.1 Potash ore flotation

Commercial potash ore flotation is carried out in saturated brine since main components of the sylvinite ores, sylvite (KCl) and halite (NaCl), are water-soluble salts. Long-chain primary amines are used for the fine fraction as collectors to selectively render KCl particles hydrophobic, while coarse fractions also require an additional collector, so-called extender oil, to improve further flotation of coarse sylvite particles. Potash Corporation of Saskatchewan (PCS is the world's largest potash producer) has utilized Esso 904 oil, which contains polycyclic carcinogenic aromatic compounds, as extender oil. Potash industry long term future relies on the development of new technologies that replace toxic chemical additives.

Extender oils have been extensively studied over years at UBC (Dai et al., 1992; Laskowski and Dai, 1993; Laskowski and Wang, 1997). These reports show that pre-emulsified oils with longchain amines added as an emulsifier can yield high-grade and high-recovery concentrates in the laboratory flotation tests, however, in-plant tests with those same formulations, applied under operating flotation conditions, have not yet been successful (Strathdee et al., 1982). One of the reasons for the problems in this area is the lack of a simple and reliable method of testing and selection of suitable oils.

Another important factor is the effect of temperature on these combinations for the stability of emulsions, i.e. the emulsion must be stable in the temperature range during winter and summer. It is well known that phase inversion of the emulsion, from O/W to W/O, is very sensitive to temperature (Binks and Rocher, 2009). Therefore, in potash ore flotation, two factors have to be well understood. Firstly, the oil must wet the surface of KCl particles to work as extender oil, and secondly this oil, which comes to the plant as oil containing amine emulsion in water, must be stable over the plant operating temperature ranges.

In this thesis, two wettability tests were carried out in selection of the possible extender(s) for subsequent coarse potash ore flotation tests. One test included the phase inversion method for the preparation of emulsions. The other test involved the sessile drop method for contact angle measurements. It is, therefore, to be pointed out that the problem of the extender oil selection was studied only from the KCl wettability point of view in this project.

1.2 Objectives

This thesis had the following research objectives:

1.2.1 General objective

 To develop the lab testing procedure for selection of the oil(s) which could be used as the extender oil(s) in potash ore flotation.

1.2.2 Specific objectives

- To study the applicability of the phase inversion method, in which oil/saturated-brine emulsions are stabilized by fine KCl particles, as a method of selection of the extender oil(s) for the use in potash ore flotation.
- 2) To study the effect of equilibration time on the contact angle at the oil/saturated-brine/KCl threephase line of contact with the use of the sessile drop method
- 3) To study the effect of equilibration time on the interfacial tension at the oil/saturated-brine interface with the use of the pendant drop method.
- 4) To test several commercial and technical long-chain amines as additives to oil in the preparation of the extender oil(s).
- 5) To test several hydrocarbons (oils) as amine solvents to model extender oil(s).
- 6) To examine the effect of different long-chain amines on the phase inversion of oil/saturated-brine emulsions stabilized by KCl particles.
- 7) To investigate the effect of the concentration of long-chain amines in oil on KCl wettability and on emulsion stability in an oil/saturated-brine/KCl system.

2 Literature review

2.1 Overview of the potash ore flotation

In the PCS processing plants (see Figure 1), the fine and coarse fractions of the ore are processed by flotation. The coarse ore fraction (typically +0.841 mm) is screened and tumbled in a mixing drum (see inset in Figure 1) with blinders (e.g. carboxy-methyl cellulose starch, guar gum, etc.), then an aqueous dispersion of long-chain AKZO amines (C_{16} - C_{22}) is used as collector; extender oil is added to float the coarse fraction. Esso 904 oil, used to date, exhibits unique collecting properties but contains toxic polycyclic aromatic compounds (Strathdee et al., 1982). Ambient temperature fluctuations between summer and winter sessions, which in some locations may be within 15 – 35 °C, affect the sylvite flotation results (Perucca, 2003).



Figure 1. Schematic block diagram of a conventional potash flotation plant (Perucca, 2003); reproduced by the permission of the Canadian Institute of Mining, Metallurgy and Petroleum (CIM).

Experimental evidence (Laskowski and Dai, 1993; Laskowski and Wang, 1997) suggests that it is possible to substitute very toxic products (e.g. Esso 904 oil) with more refined and less toxic formulations such as Esso 2600 oil and/or Esso 2600 oil with added amine (e.g. $R_{12}NH_2$). Nevertheless, those same combinations applied under operating flotation conditions have not yet been successful.

2.1.1 Effect of amine addition to oil on contact angle

One important factor in potash ore flotation is that oils must wet the surface of KCl particles in order to work as extender oil, however, attachment of oil droplets to hydrophilic particles is impossible (Laskowski and Ralston, 1992). Dai et al. (1992), Laskowski and Dai (1993), and Laskowski and Wang (1997) investigated the emulsion flotation in NaCl-KCl saturated brine and concluded that all the tested oils (i.e. Esso 904, Esso 1156, and Esso 2600 oils), with the exception of Esso 904, could not attach to the KCl hydrophilic surface, and so oil droplets can attach to the sylvite particles only if the KCl surface is previously rendered hydrophobic by long-chain primary amines. With the use of the extender oil containing amine, the oil interacts with KCl particles through the collector species present at the oil/saturated-brine and/or KCl/saturated-brine interfaces. According to Laskowski and Dai (1993) and Laskowski and Wang (1997), it may be, therefore, beneficial to introduce a certain quantity of amine together with oil (the concentration (wt) of amine in oil should not be less than 1 %).

Oils are difficult to disperse in brine, and long-chain amines are not soluble in brine either. Despite of this, the amine can be dissolved in the oil to form a so-called amine-in-oil emulsification (Laskowski and Wang, 1993). In such application, oil droplets act as the collector carrier, therefore, it becomes not only active but also selective (Dai et al., 1992; Laskowski et al., 2008).

Oil droplets adhere to the solid surface through the hydrophobic bonding with the nonpolar groups of the pre-adsorbed amine. The effect of amine addition to oil is to provide the functional groups that can adsorb at the KCl surface (Dai et al., 1992).

Figures 2 and 3 show the effect of the concentration of long-chain amines in oil on KCl wettability. These curves demonstrate that the solutions of oil containing amine can wet KCl surfaces (Dai et al., 1992; Laskowski and Dai, 1993).



Figure 2. The effect of the addition of the following flotation reagents on the wettability of KCl plates by oil droplets: (a) Armeen HTD amine and various additives to Esso oils, (b) dodecylamine $(R_{12}NH_2)$ to Esso 1156 oil, and (c) various surfactants to Esso 2006 oil (Dai et., 1992; Laskowski and Dai, 1993); reproduced by the permission of The Australian Institute of Mining and Metallurgy (AusIMM) and the Society for Mining, Metallurgy, and Exploration, Inc (SME).

Laskowski and Dai (1993) concluded that Esso oils could not adhere to the KCl surfaces without pre-adsorbed amines, and addition of $R_{12}NH_2$ to oil could favour the flotation of coarse potash ore (see Figure 3). The authors also concluded that polar compounds, especially those bearing nitrogen, were found to be the major constituents responsible for a good oil performance in the potash flotation.

Oil	Recov- ery* (%)	Θ_{air} (deg)		Polar	Nitro-
		No R ₁₂ NH ₂ in oil	1% R ₁₂ NH ₂ in oil	(wt%)	gen (ppm)
805	0	47	56	0.3	2
620**	-	57	63	0.4	-
2600**	26.2	69	63	2.2	164
670	-	73	58	9.0	-
1156	11.7	53	57		42
904	27.3	80	75	-	72

* The flotation results were obtained with oils containing no amine.

** Essoflex 620 and 670 are equivalent to Esso 805 and 2600, respectively, but contain more polar compounds.

Figure 3. The effect of the addition of dodecylamine $(R_{12}NH_2)$ to various oils on the wettability of KCl surfaces (Laskowski and Dai, 1993); reproduced by the permission of The Australian Institute of Mining and Metallurgy (AusIMM).

2.1.2 Effect of collector-extender oil mixture on flotation performance

Addition of Esso oils containing dodecylamine has beneficial effect on the flotation performance of oily collectors, increasing the recovery as shown in Figures 4 and 5.



Figure 4. The effect of dodecylamine $(R_{12}NH_2)$ addition on the flotation performance of Esso 1156 and Esso 2600 oils (Laskowski and Dai, 1993); reproduced by the permission of The Australian Institute of Mining and Metallurgy (AusIMM).

According to Strathdee et al. (1982), in spite of a substantial effort during the past 20 years, no significant change in the chemical class or formulation of extender oil composition has provided in-plant coarse particle flotation performance equivalent to that achieved with the industry standard asphaltene–based additive. Pre-emulsified collector/extender oil mixture can yield highgrade and high-recovery concentrates in the laboratory. However, in-plant tests with those same formulations in operating flotation circuits have not yet been successful.



Figure 5. Flotation recovery as a function of the concentration of Esso 2600 oil for different amine in oil formulations (Laskowski and Dai, 1993); reproduced by the permission of The Australian Institute of Mining and Metallurgy (AusIMM).

2.2 Emulsion stabilized by finely divided solids

2.2.1 Pickering emulsion

In 1907, Pickering was apparently the first to recognize that colloidal particles situated at the oil/water interface (see Figure 6) can stabilize emulsions, the so-called *Pickering emulsions*, similarly to emulsions in which soluble emulsifiers are used (Briggs, 1921). Many different solid materials have been extensively used to stabilize emulsions acting as *emulsifying agents*, these solids include iron oxides, silica, alumina, calcium carbonate, barium sulfate, clay minerals, carbon, and polystyrene as well as colloidal metals and crystalline organic compounds like glycerol tristearate and stearic acid (Abend et al., 1998).

Two conditions, which must be met before the emulsion stabilization by particles can take place, are (i) particles have to be finely divided, i.e. they must be very fine in comparison with the emulsion droplet, and (ii) the surface of the particles must be partially wettable by both oil and water (Briggs, 1921; Schulman and Leja, 1965; Levine et al., 1989). Emulsions may be classified according to the position of the phases. The emulsion type can be distinguished: *oil-in-water emulsions* (O/W), in which the oil is dispersed as small droplets in a continuous water phase, and *water-in-oil emulsions* (W/O), in which the water is dispersed as small droplets in a continuous oil phase.



Figure 6. Stabilization of emulsions by finely divided solids: (left) preferential wetting by water leading to an O/W emulsion; (right) preferential wetting by oil leading to a W/O emulsion (Binks, 2002).

Emulsion tests conducted by Tambe and Sharma (1993), in which the stability of oil/water emulsions was investigated for solutions of stearic acid ("acid") in n-decane, showed that in absence of any solid particles, no stable emulsion could be produced within the range of surfactant (stearic acid) concentrations (see Figure 7), thereby confirming that the formation and stability of these emulsions was largely a result of the presence of solid particles. Additionally, the effectiveness of the solid particles is influenced by the presence of the surfactant. This conclusion is in perfect agreement with Laskowski and Dai (1993) and Laskowski and Wang (1997) (see section 2.2.5).



Figure 7. The effect of solid particles: calcium carbonate, and bentonite (a) and silica, barium sulfate, and carbon graphite (b) on emulsion stability, which is described by the final emulsion volume, at varying stearic acid concentration (Tambe and Sharma, 1993); reproduced by the permission of the Elsevier.

2.2.2 Coalescence mechanism

Figure 8 shows the so-called drop coalescence plot, which consists of two well-defined sections, where N (Y axis) is the number of droplets that do not coalesce before time t (X axis). One section in which N decreases slowly with time (from A to B), followed by the other section of rapid decline (from B to C). Such a distribution curve indicates that the lifetimes of droplets are determined by two distinct processes: the drainage of the continuous phase initially present between the droplet and the interface, followed by the rupture of the film encapsulating the droplet, the so-called *coalescence phenomena*. According to Tambe and Sharma (1993), finely divided solids coat droplets by some kind of film or pellicle which tends to prevent coalescence phenomena (see section 2.2.2 for details) and consequently macroscopic phase separation. Therefore, fine ground particles can act as emulsion stabilizing agents or *emulsifiers*.



Figure 8. Drop coalescence plot (Tambe and Sharma, 1993); reproduced by the permission of Elsevier.

2.2.3 Emulsion stabilizing agent

As already mentioned, finely divided solids can potentially stabilize an emulsion by attaching to the water/oil interface directly or by a film already stabilizing the emulsion. Colloidal particles stabilize emulsions both by providing steric hindrance to the coalescence of emulsion droplets and by modifying the rheological properties of the interface (Tambe and Sharma, 1993). Fine solid particles constitute a dense but elastic film around the droplets of the dispersed phase (see Figure 6), and the presence of a continuous film of emulsifying agent is absolutely essential to the existence of all ordinary emulsions (Briggs, 1921).

The effectiveness of solid particles in stabilizing emulsions depends on their ability to migrate to the interfacial region, to remain there in a stable mechanical equilibrium, and to form a sufficiently dense layer of particles around the droplets (in the outside phase of the emulsion) which inhibits coalescence of the droplets (*rigid barrier acting against coalescence*). The magnitude of the mechanical barrier is determined by the energy (E) required to remove a particle from the interface that in turn is a function of the three-phase contact angle. The particle is mostly held in the interface when Θ =90° (see Figure 9). On either side of the 90° peak, the energy of attachment falls. This extreme variation of E (energy) with wettability has a major influence on the ability of particles of different wettabilities to stabilize emulsions. Pickering emulsions are believed to be unconditionally stable due to the large interfacial energy, E, that is required to move the particles away from the interface, hence, the pellicle of solid particles corresponds the state most energetically favourable.

The strength with which a particle is held at the oil/water interface is related not only to Θ but also to the tension of the interface, γ_{OW} (Binks and Lumsdon, 2000).



Figure 9. Energy with which a spherical particle is held at the oil/water interface as a function of the contact angle (Binks and Lumsdon, 2000); reproduced by the permission of the American Chemical Society (ACS) Publishing.

2.2.4 Final emulsion volume

Generally four phases are distinguishable after conducting mixing experiment procedures (e.g. hand or mechanical shaking, ultrasonication, or vortex mixing), as shown in Figure 10: a sediment of solid particles at the bottom, a layer of water, a creaming layer, and a coherent oil phase at the top (Abend et al., 1998).



Figure 10. Phase separation after sedimentation (Abend et al., 1998); reproduced by the permission of the Steinkopff Verlag Publishing.

The state of the emulsion is described by (i) the sediment height (volume fraction of sediment "sd", related to the total volume of the system), (ii) the final emulsion volume (volume of the creaming layer "cr" to total volume), and (iii) the degree of coalescence (volume of coherent oil phase "o" to total volume).

As an example, Figures 11 and 12 depicts an oil-in-water emulsion (O/W) stabilized with carbonyl iron paramagnetic particles (Melle et al., 2005), and an oil-in-water emulsion (O/W) stabilized with hematite particles (Maldivala et al., 2009), respectively.



Figure 11. Photograph of an oil-in-water emulsion stabilized with carbonyl iron paramagnetic particles at a concentration of 4% (wt) (Melle et al., 2005); reproduced by the permission of the American Chemical Society (ACS) Publishing.



Figure 12. Optical micrograph of oil droplets coated with hematite particles when deposited at an air/water interface. (Maldivala et al., 2009); reproduced by the permission of the Royal Society of Chemistry (RCS) Publishing.

2.2.5 Factors influencing emulsion stability

Some of the parameters that control the type and stability of the oil/water emulsions include particle wettability (see Figure 9), surfactant and particle concentration (see Figure 13), and the particle size (see Figure 15), just to mention the main ones (Tambe and Sharma, 1993; Melle et al., 2005). In those figures, the emulsion stability is described by the final emulsion volume (FEV), which in turn is defined as the volume of the creaming layer to the total volume. The emulsion stability increases with the final emulsion volume.

2.2.5.1 Effect of surfactant concentration on emulsion stability

Figure 13 shows that at a given particle concentration, as the surfactant (stearic acid) concentration (wt%) increases, the emulsion stability, in terms of the final emulsion volume, typically increases, demonstrating that the stability of the emulsions formed increased significantly when small amounts of surfactants.



Figure 13. The effect of carbon graphite (a) and silica particle (b) on emulsion stability, which is described by the final emulsion volume, at varying particle and stearic acid concentrations (Tambe and Sharma, 1994); reproduced by the permission of the Elsevier.

2.2.5.2 Effect of particle concentration on emulsion stability

Figure 13 also indicates that at a given surfactant (stearic acid) concentration, as the particle concentration increases, the emulsion stability that is described by the final emulsion volume, increases as well, confirming that <u>emulsion stability increases with an increase in the concentration of particles in the system</u>.

The log-normal distribution of droplet sizes can be effectively varied by adjusting the solid particle concentration while keeping the relative proportion of the oil and water constant. The average size of emulsions droplets decreases as the solid particle concentration increases (see Figure 14). A decrease in the size of emulsions droplets creates additional surface area that allows additional colloidal particles to be accommodated at the interface. This increase in the solid particle concentration at the interface, in turn, leads to more stable emulsions.



Figure 14. Change in the average droplet ("drops") size for large (squares) and small (circles) droplets with varying the paramagnetic particles concentration (Melle et al., 2005); reproduced by the permission of ACS Publications.

2.2.5.3 Effect of particle size on emulsion stability

Figure 15 shows that the effectiveness of the particles in stabilizing emulsions decreases with an increase in particle size.



Figure 15. The effect of particle size on the stability of emulsions, which is described by the final emulsion volume, stabilized by alumina particles. (Tambe and Sharma, 1994); reproduced by the permission of the Elsevier.

Tambe and Sharma (1994) claims that the emulsion stability increased with a decrease in particle size until a critical particle size was reached. Below this critical size Brownian effects are significant enough to affect the partitioning of particles at the oil/water interface.

2.3 Contact angle and fine solid wettability – a brief review

The contact angle at the oil/water/solid three-phase boundary is critical in controlling the stabilization by given solid particles (see Figure 6). Emulsion type (O/W or W/O) is believed to be determined by the particle wettability, expressed in terms of contact angle Θ that particles of the solid make with the oil/water interface. Binks and Lumsdon (2000) mentioned the following three studies that point to a direct link between contact angles Θ , measured on flat surfaces, and the resulting emulsion type: Schulman and Leja (1954), Koretsky and Kruglyakov (1971), and Tambe and Sharma (1993). These studies are in sections 2.3.1, 2.3.2, and 2.3.3, respectively. Recently published articles (see section 2.3.4) confirmed also the link referred to above.

2.3.1 Schulman and Leja (1954)

These authors studied the system: benzene/water/barium-sulfate (BaSO₄), in the presence of anionic or cationic surface-active agents (C_8 to C_{18}). The authors investigated the relation existing between the contact angle (*across the aqueous phase*) developed by a drop of oil deposited on a solid surface in water coated by a surfactant and the stabilization of oil-water emulsions by solid powders (of suitable size) similarly coated by the same agents, postulating that the relation is as follows:

- Water-continuous emulsions (O/W) are stabilized by the solid powder when the contact angle at the oil/water/solid interface is a little smaller than 90° (measured through the aqueous phase);
- (ii) Oil-continuous emulsions (W/O) are formed and stabilized by the solid powder when the contact angle is somewhat greater than 90°;
- (iii) If the particles are completely wetted by water or oil, they remain dispersed in either phase and no stable emulsions are formed.

Starting with O/W emulsions stabilized by sodium dodecyl sulfate alone, addition of BaSO₄ resulted in phase inversion to stable W/O emulsions with Θ around 120° (see Figure 16). The reverse phase inversion occurred on adding the solid to W/O emulsions stabilized by oleic acid alone (at low pH), resulting in Θ =60°. For conditions such that Θ was >160° (oleic acid at high pH), unstable W/O emulsions were formed.



No. of carbon atoms in the hydrocarbon chain.

Figure 16. Relation between contact angle and chain length of surface active agents M/1000 on $BaSO_4$ crystal surface (Schulman and Leja, 1954); reproduced by the permission of the Royal Society of Chemistry (RSC) Publishing.

2.3.2 Koretsky and Kruglyakov (1971)

These authors, studying the stability and coalescence of carbon tetrachloride/water emulsions with added spherical quartz particles, varied Θ systematically by addition of octadecylamine. The stability of O/W emulsions increased to a maximum as Θ increased from 40° to between 60° and 80°. For Θ between 85° and 95° both O/W and W/O emulsions were formed (probably representing the state around phase inversion) of considerably reduced stability. The authors stated that stable W/O emulsions would be expected for Θ in the range 95-115° but did not present any data.

2.3.3 Tambe and Sharma (1993)

These authors reported a thorough study of a decane/water/calcium-carbonate system. On addition of stearic acid, stable O/W emulsions formed with solid alone become less stable, inverting to W/O emulsions whose stability increases away from inversion. Significantly, Θ increased from 40° to over 130° in this range, and it was shown that the concentration of stearic acid required to reach 90° was the same as that needed for phase inversion (see Figure 17).



Figure 17. Contact angle of a calcite crystal as a function of the stearic acid concentration (Tambe and Sharma, 1994); reproduced by the permission of Elsevier.

2.3.4 Recently published articles - a brief review

2.3.4.1 Hu et al. (2015)

These authors have recently researched the effect of surfactants on the properties of Pickering emulsions stabilized by cellulose nanocrystals, for two surfactants, dodecyldimethylammonium bromide (DMAB) and cetyltrimethylammonium bromide (CTAB), respectively (see Figure 18). With increasing DMAB concentration, emulsions exhibit a double phase inversion (O/W to W/O [phase inversion 1], followed by W/O to O/W [phase inversion 2]), whereas with CTAB, all emulsions are oil-in-water (O/W).

The authors concluded that the surfactant type and concentration can be used to control whether the continuous phase of the emulsion is oil or water which extends the potential use of CNCs in emulsified products.



Figure 18. Three-phase contact angle of a 10 mL drop of surfactant solution on a spin coated CNC surface measured under dodecane for CTAB solutions (open squares) and DMAB solutions (closed diamonds) (Hu et al., 2015); reproduced by the permission of Elsevier.

2.3.4.2 Binks et al. (2013)

These authors have recently investigated the effect of the surfactant concentration on the double inversion of phases of Pickering emulsions stabilized by silica particles of diameter 0.404 microns for a cationic surfactant (C_{10} DMAB). Their experiments were conducted at equal volumes (1 mL) of n-decane and aqueous dispersions.

The authors concluded that the particles can undergo a hydrophilic-hydrophobic-hydrophilic transition corresponding closely to the O/W-W/O-O-W emulsions upon increasing the concentration of the surfactant. Their results link contact angles to the type of particle-stabilized emulsion, confirming macroscopic emulsion inversion on the microscopic level



Figure 19. Average contact angles at the decane/water interface (measured through water) for silica particles of radius 202 nm as a function of surfactant concentration. The angle in the absence of surfactant is 33°. The inset is log abscissa; also given is the type of emulsion formed on homogenizing the mixtures, and the horizontal dashed line refers to 90°. Error bars are the standard deviations in the measurements (Binks et al., 2013); reproduced by the permission of the American Chemical Society (ACS) Publishing.

2.4 Drop shape and phase inversion techniques

2.4.1 Sessile drop method

The drop shape analysis (DSA) is a convenient way to measure contact angles, thereby determining wettability of solids by liquids (see Figures 19 and 20 for details). The principal assumptions are:

- 1. The drop is symmetric about a central vertical axis: this means it is irrelevant from which direction the drop is viewed.
- 2. The drop is not in motion in the sense that viscosity or inertia is not playing a role in determining its shape: this means that interfacial tension and gravity are the only forces shaping the drop.



Figure 20. FTA1000 B Class drop shape instrument (left), an illustrative image captured for sessile drop analysis (right), and wettability and contact angle across the drop (below).
2.4.2 Pendant drop method

The pendant drop method is an optical method for determining the surface or interfacial tension of a drop of liquid by using the radii of curvature of a drop profile (Winkler, 2010). Figure 21 depicts a FTA drop shape instrument and an illustrative pendant drop.



Figure 21. FTA1000 B Class drop shape instrument (left) and an illustrative image captured for pendant drop analysis (right) (Liu et al., 2015); reproduced by the permission of Elsevier.

An increased pressure is produced inside the drop as a result of the interfacial tension between inner and outer phase. The pendant drop is deformed under the effect of gravity that acts to elongate the drop while interfacial tension opposes elongation because of the associated increase in interfacial area (Miller and Neogi, 1985), thereby affecting the main radii of curvature r_1 and r_2 . The correlation between the pressure difference Δp , the radii of curvature of the surface r_1 and r_2 and the interfacial tension is described by the Young- Laplace equation:

$$\Delta p = \sigma \cdot \left(\frac{1}{r_1} + \frac{1}{r_2}\right)$$

The shape of the drop is then determined from its video image (see Figures 21 and 28) using a Fta 32 video computer program. Figures 19 and 21 show a FTA 1000 drop shape instrument, while Figure 29 presents a snap shot of the interfacial tension window of a Fta32 video computer program (provided by First Ten Angstroms).

2.4.3 Phase inversion method

As it was mentioned earlier in section 2.1.2, the addition of Esso oils containing dodecyl amine increases the potash ore flotation recovery. In spite of being extensively studied (Dai et al., 1992; Laskowski and Dai, 1993; Laskowski and Wang, 1997) a method for testing various oils (as extender oils) has not yet been developed. The phase inversion method (P.I.M.) could be, therefore, tested as a way of studying how different oils and amine additions affect sylvite particles wettability. It must be pointed out that the phase inversion tests are very sensitive to the changes in temperature.

Takakuwa and Takamori (1963) proposed the P.I.M. as a procedure for studying the change in wettability of the fine solid particles caused by flotation reagents. The authors investigated the emulsion phases for two minerals, galena (PbS) and sphalerite (Zn,Fe)S, at varying concentrations of sodium ethyl xanthate and CuSO4, respectively. The principal advantages of the method are as follow:

- 1. Small amount of material are required.
- 2. Easy preparation of mineral for test.
- 3. Quick and reliable.
- 4. Simple experimental procedure.

The phase inversion method is based on generally known fact that oil/water emulsions are stabilized by a powdered solid, the so-called *Pickering emulsions* (see section 2.2.1 for details). The final result after mixing (either water-in-oil, W/O, or oil-in-water, O/W, emulsions) depends on the wettability of solid particles by oil (Binks and Lumsdon, 2000).

3.1 Reagents

All the reagents were used without any further purification in this thesis, and their properties (molecular weight, assay, melting point, and boiling point) are presented in this section as reported by their manufacturers.

3.1.1 Water-soluble salts

Potassium chloride (KCl) and sodium chloride (NaCl) had a molecular weight of 74.55 and 58.44, respectively. They were white, \geq 99.0% pure, powdery solids obtained in 3 kg poly bottles from Fisher Scientific International Inc.

Since sylvinite ores contain mainly NaCl and KCl water-soluble salts, all the experiments were conducted in saturated NaCl-KCl brine (see section 3.4.3) to reflect natural processing conditions (see section 2.1).

3.1.2 Long-chain amines

Dodecylamine ($C_{12}H_{25}NH_2$) and octadecylamine ($C_{18}H_{37}NH_2$) were two commercial, 98% pure, primary amines, supplied in 25 g glass bottles by Sigma-Aldrich Corporation, with molecular weights of 185.35 and 269.51, respectively. The melting point ranges were 27-29 °C for the former and 50-52 °C for the latter.

Armeen HTD (Hydrogenated Tallow Alkyl Amines) and Armeen TD (Tallow Alkyl Amines) were technical amines provided by Akzo Nobel with equivalent molecular weight of 263 and 267, respectively. It is to be noted that the equivalent weight was assumed to be equal to the molecular weight in this project. The melting points were 56 °C for the former and 40 °C for the latter.

Amines were used as collectors to render KCl particles hydrophobic.

3.1.3 Hydrocarbons

Three hydrocarbons of different chemical composition were selected for this study.

n-decane (C₁₀H₂₂), purchased in 500 mL glass bottles from Sigma-Aldrich Corporation, was \geq 99% pure, with a molecular weight of 142.29 and a boiling point of 174.1°C.

Cyclohexane (C₆H₁₂), provided in 3 L glass bottles by Fisher Scientific International Inc., was \geq 99% pure, with a molecular weight of 84.16 and a boiling point of 80.74°C.

Diesel oil was a technical product that may contain various hydrocarbons and also various impurities. It was bought at Shell gas station in Vancouver.

All these hydrocarbons were used as amine solvents to model extender oil which could be utilized in the flotation of coarse potash ore fractions.

3.2 KCl plates

Limited quantities of KCl plates of 15x30x4 mm were purchased to International Crystal Labs. For this reason, an used plate was gently removed after every sessile drop test and polished following the method described in section 3.4.2. In some cases, Fourier transform infrared spectroscopy (FTIR) was used to check possible surface contamination of the polished KCl plates through comparison with the infrared spectra of a new KCl plate.

3.3 Equipment and materials

3.3.1 Equipment

For the preparation of fine KCl (see section 3.4.6), coarse KCl particles were used (as given by the manufacturer, in section 3.1.1). The coarse material was ground using an electrical agate mortar and pestle supplied by RETSCH and screened using a Ro-Tap sieve shaker to pass 325 mesh screen as described in the pioneering work of Takakuwa and Takamori (1963).

For the experiments on the KCl weight and shaking mechanism for the phase inversion tests (see Appendix B), two mechanical shakers were used. One was an Orbital Environ-Shaker, the other was a KS 4000 IC control. They were manufactured by Lab-Line Instruments and IKA Works, respectively. The latter was also connected to a Polystat Circulating Bath provided by Cole-Parmer ($\pm 0.5^{\circ}$ C accuracy) for temperature control.

For the phase inversion tests (see section 3.8), a K-550-G vortex mixer manufactured by VWR International was used with variable speed control of 100-3200 rpm (see Figure 30).

Contact angles and interfacial tensions were measured using a FTA1000 B Class drop shape instrument (Figures 19 and 21) manufactured by First Ten Angstroms. The description of contact angle (sessile drop method) and interfacial tension (pendant drop method) measurements are presented in sections 3.6 and 3.7, respectively. The former and the latter used two cuvettes made out of glass of 90x45x50 mm and 15x30x4 mm, respectively, as containers.

For the analysis of the surface of polished KCl plates, an infrared spectrophotometer (Spectrum 100 FT-IR spectrophotometer manufactured by PerkinElmer) was used (see section 3.2).

A MR Hei-Standard magnetic stirrer with heating was bought from Heidolph USA and used for stirring and heating (see sections 3.4.3 and 3.4.4), while a FS30 ultrasonic cleaner manufactured by Fisher Scientific was utilized for sonication (see sections 3.4.4 and 3.4.5).

Finally, a Malvern Mastersizer 2000 particle size analyzer was used for particle size distribution analysis (see Appendix E).

3.3.2 Materials

Following the experiments on phase inversion, the emulsion type was determined by mere visualization using 40 mL Volatile Organic Analyte (VOA) sampling vials obtained from Restek Corporation. For the preparation of oil containing amine solutions (see Figures 23 and 24 for details), 125 mL Wheaton glass snap cap bottles, bought from Fisher Scientific International Inc., were utilized. These two bottles are referred to as "*VOA vials*" or "beakers" and "Wheaton bottles", respectively. The latter was also used for mechanical shaking (see section 3.5).

3.4 Methods

All experiments were conducted in saturated NaCl-KCl brine at room temperature ($22 \pm 3.0^{\circ}$ C). The pH range of oil containing amine solutions was from 5 to 6, however, this parameter was not included as variable in this project.

In this thesis, any solution of oil containing or not amine is referred to as "*organic phase*" or "*oil phase*", while saturated brine with or without fine KCl particles is called "*aqueous phase*". For the sake of convenience, the organic phase and the aqueous phase may be denoted as "O" and "W", respectively, as used widely in colloid chemistry.

3.4.1 Glassware cleaning

See Appendix A for the standard cleaning procedure with the use of nitric acid and ethanol.

3.4.2 KCl plate cleaning

Following the manufacturer's instructions, solutions of ethanol and cerium oxide were used to clean the KCl surface by fine polishing on a polishing pad (self-adhering). After polishing, the KCl surface was dried with a soft, clean, and dry cloth. Prior to any experiments, the KCl surface was completely cerium oxide-free.

3.4.3 Saturated brine

Saturated NaCl-KCl brine is referred to as "saturated brine" throughout the text.

The preparation of saturated brine was as follows (see Figure 22): 300 g of NaCl and 150 g of KCl were added to 1 liter of distilled water. The salts/water mixture was stirred between 250-500 rpm and then was left to stand for at least 1 hour. An excess of KCl+NaCl crystals left in the solution was a proof that the saturated brine was really saturated.

Saturated brine was finally kept in 4 liter beakers (sealed with parafilm) and allowed to equilibrate for additional at least 3 days.



Figure 22. Schematic methodology for the preparation of saturated brine.

3.4.4 Oil containing amine stock solutions

Typically, stock solutions of 1.000 % (wt) of amine in oil were prepared as follows (see Figure 23): in a Wheaton bottle, 0.146 g of amine was melted by heating (see section 3.1.2 for the melting points of amines). Then, 20 mL of oil was added to the previously melted amine, and the resulting mixture was placed on an ultrasonic bath until the amine was completely dissolved in the oil (sonication).



Figure 23. Schematic methodology for the preparation of oil containing amine stock solutions.

3.4.5 Oil containing amine diluted solutions

As indicated in section 3.8.3, three amine concentrations (wt%) in oil were typically selected in this project: 1.000 % (stock solution), 0.050 %, and 0.005 %. The last two are the so-called diluted solutions and were prepared from the stock solution (see section 3.4.4) as follows (see Figure 24): the volume of stock solution (see V₁ in Table 1) was pipetted into a clean 25 mL volumetric flask and then diluted through adding fresh oil to the 25 mL line. The diluted solution was transferred to a Wheaton bottle. These diluted solutions were sonicated so that amines were completely dissolved in oil.



Figure 24. Schematic methodology for the preparation of oil containing amine diluted solutions.

Table 1. The preparation of oil containing amine diluted solutions where: V_1 is the volume of stock solution, C_1 is the concentration of amine in oil in the stock solution, V_2 is the volume of the flask (25 mL), and C_2 is the amine concentration of the diluted solution (either 0.050 % or 0.005 %).

$V_1C_1 = V_2C_2$									
amine concentration (wt.%) in oil, C ₂	mL of stock solution, V_1								
1.000	-								
0.050	1.25								
0.005	0.125								

3.4.6 Fine KCl particles

Fine KCl particles - 325 mesh (below 44 μ m) were obtained as follows: 10 grams of coarse KCl (as provided by the manufacturer) were ground in an electrical agate mortar and pestle for 30-60 minutes. Then, these ground KCl particles were screened for 10-20 minutes to pass 325 mesh screen using a Ro-Tap sieve shaker. KCl particle size distribution is given in Appendix E.

3.5 Fine KCl weight and shaking mechanism

As it will be explained in section 3.8.4, the organic (oil) phase and the aqueous phase were shaken with the use of a vortex mixer, and for clarification the resulting mixture is referred to as *"emulsion"* in this work. The emulsion type and its judgment are discussed in section 4.3.

Figure 7 illustrates that in absence of any solid particles, no stable emulsions could be produced (see section 2.2.1). Fine KCl particles – 325 mesh were, hence, added to the aqueous phase (denoted by W) to stabilize oil/saturated-brine emulsions, i.e. *Pickering emulsions*, (see section for 2.2.5 details). However, a specific quantity of fine KCl particles is not well defined. Takakuwa and Takamori (1963) used an equivalent at 0.25 g, while Schulman and Leja (1954) claimed that the fine particle weight should be in the range from 2.5 to 5.0 g. The first set of the experiments on phase inversion method was, therefore, carried out to determine the weight of fine KCl particles required.

On the other hand, the aforementioned authors used mechanical and hand shaking to mix the organic and aqueous phases. The second set of experiments on phase inversion technique included the use of vortex mixing as an alternative for reducing unnecessary complexity.

Therefore, the outcome of these initial tests determined both the <u>weight of fine KCl particles</u> and the <u>shaking (mixing) procedure</u> for the subsequent experiments phase inversion tests (see sections 4.2 and 4.3). These results are given in Appendix B.

For the sake of convenience, in those two sets of experiments, solutions at 1.000 % (wt) of amine in cyclohexane were used at varying weights of fine KCl (see section 3.4.6). The oil/saturated-brine mixtures were mechanically shaken with the use of an Orbit-line and an IKA 4000 (see section 3.3) and also by hand following the method described below. In some cases, those mixtures were also shaken using a vortex mixer (see Figure 30).

Mechanical shaking:

As sample container, an Orbit-line shaker used Wheaton bottles, while an IKA 4000 shaker utilized Erlenmeyer flasks. The temperature and the speed of the two shakers were set up at 22°C and 450 rpm, respectively.

Firstly, 1, 2, 3, or 4 grams of fine KCl – 325 mesh were mixed with 10 mL of saturated brine, and the mixtures (the *aqueous phases*) were conditioned in the two shakers for 10 min.. Then, those mixtures were left to stand for additional at least 1 hour.

Secondly, those aqueous phases were mixed with 10 mL of solutions at 1.000 % (wt) of amine in oil (the *organic phase*), and the mixtures were shaken again using the two shakers for 60 min., transferred to VOA vials, left to stand for additional at least 1 hour, and finally judged by mere visualization (see section 4.3).

Hand shaking:

In VOA vials, 1, 2, 3, or 4 grams of fine KCl - 325 mesh were mixed with 10 mL of saturated brine, and the mixtures (the *aqueous phases*) were shaken by hand for 60 seconds and were left to stand for additional at least one hour.

Then, those aqueous phases were mixed with 10 mL of solutions at 1.000 % (wt) of amine in oil, and the resulting mixtures were hand shaken again for 30 seconds, left to stand for additional at least one hour, and finally judged also by mere visualization (see section 4.3).

Vortex mixing:

Similar methodology for hand shaking but with the use of a vortex mixer (see Figure 30) was performed for the solutions at 1.000 % (wt) of amine in cyclohexane. It is to be noted that Katepalli (2014) also used a vortex mixer to prepare emulsions.

3.6 Experimental phase I. Sessile drop method

3.6.1 Introduction

In the experimental phase I, oil/saturated-brine contact angles were measured directly using the sessile drop technique (see section 2.4.1 for details). In this method, a drop of oil containing amine was located at the tip of a needle and then placed on a smooth KCl surface immersed in brine (see Figure 25 for details). The shape of an oil drop lying on the KCl surface in brine was then monitored as a function of the time with a digital video camera (connected to a FTA instrument), from which the contact angles were determined using a Fta 32 video computer program.

3.6.2 Experimental set-up

The experimental set-up (see Figure 25) included a syringe connected to a syringe pump that allowed automatic control of the drop volume and pumping rate. A drop was placed underneath a smooth KCl surface, which was always completely immersed in saturated brine .



Figure 25. Schematic experimental set-up for sessile drop tests.

3.6.3 Operating conditions and FTA software settings

- Images before/after trigger: 25/250.
- Initial period after trigger (s): 1.
- Analysis type: Sessile Drop Profile.
- Drop Orientation: Upside Down Drop.
- Liquid-Vapor Curve Fit: Non-spherical Fit.
- Liquid-Solid Curve (Baseline) Fit: Tilting Baseline (not horizontal).

Figure 26 shows a snap shot of the Contact Angle Window from the Fta32 video computer program. As it was mentioned in section 2.4.1, one of the principal assumptions in this method is that the drop is symmetric about a central vertical axis. In some cases, nevertheless, a drop was asymmetric, and the non-spherical fit was selected. In turn, this curve fit can be divided into "left side only" and "right side only".

Figure 26 also presents that the liquid-solid curve consisted of two options, a horizontal line and a non horizontal line (tilting baseline).



Figure 26. Contact angle window of a Fta32 video computer program including settings for contact angle measurements.

3.6.4 Experimental methodology

See Figures 19 and 25 for details.

- 1. A KCl plate was placed horizontally on a holder made out of Teflon in a glass cuvette of 90x45x50 mm.
- 2. The cuvette was filled with saturated brine (see section 3.4.3) such that the KCl plate was completely immersed in saturated brine.
- 3. An excess of KCl and NaCl particles was always present in the cuvette to be sure that the brine was really saturated.
- 4. Prior to use, a 10 mL syringe was cleaned with acetone to dissolve any possible organic residual, e.g. from solutions of oil containing amine previously used, and with nitrogen to remove the acetone.
- 5. The syringe was filled with a fresh oil containing amine solution. This syringe was initially rinsed with that solution, which was discharged as "waste" to eliminate any possible residual of acetone or nitrogen particles. The full contents of the syringe were used for subsequent measurements.
- 6. Then, the syringe and the KCl plate were arranged such that their images fill the video screen or *view window* (see Figure 25 on the right side). The focus was adjusted until clear.
- 7. An oil drop was generated at the tip of the needle and placed on the KCl surface completely immersed in saturated brine.
- 8. The video was recorded using a Fta 32 video software by clicking on "run".
- 9. Extreme care was used in cleaning all materials after each experimental run.

The contact angle was measured for every capture (picture) with the use of the Fta 32 computer program that automatically created a graph of the contact angle as a function of the time (see Figure 27), with a total of 275 points (25 before trigger and 250 after trigger). At about 250 seconds, contact angles were assumed to reach equilibrium values. These results are in section 4.1.



Figure 27. Sessile drop contact angle as a function of the time curve calculated with the use of the *Fta32* video computer program with 250 points or pictures after trigger.

3.7 Experimental phase II. Pendant drop method

3.7.1 Introduction

The oil/saturated-brine interfacial tension measurements were conducted using the pendant drop method and a FTA drop shape instrument (see Figure 20 and 21). Both the technique and the equipment are described by Atrafi et al. (2012) and Liu et al. (2015). In this technique, a drop of oil containing amine was located at the tip of a needle in brine, and several images of this drop suspended from the needle were taken over time. The typical shape of a drop used for calculating the interfacial tension in the FTA software is presented in Figures 21 and 28. It is to be noted that the drop volume must be known prior to any experiments.

3.7.2 Experimental set-up

The experimental set-up consisted of an oil drop suspended from a needle in saturated brine. The needle diameter was 0.71 mm, and this value was used for the calibration of the piece of equipment.



Figure 28. Schematic experimental set-up for pendant drop tests.

3.7.3 Operating conditions and FTA software settings

- 1. Images before/after trigger: 5/20.
- 2. Initial period after trigger (s): 1.
- 3. Analysis type: Pendant Drop Shape and Use Quick Mode for Pendant Drop.
- 4. Magnification Calibration by Needle: Calibrate by Needle Diameter.
- 5. Liquid Data: Density (see Table 3) and Surface Tension (see Appendix D).

Figure 29 a snap shot of the Interfacial Tension Window from the Fta32 video computer program. The drop shape was analyzed and solved by the FTA software (Analysis type: Pendant Drop Shape). During a measurement the magnification of the image was taken into account for calculating the actual drop dimensions.



Figure 29. Fta32 video computer program settings for interfacial tension measurements.

3.7.4 Experimental methodology

See Figures 21 and 29 for details.

- A clean cuvette of 15x30x4 mm (see section 3.3.1) was filled with saturated brine (see section 3.4.3).
- 2. An excess of KCl and NaCl particles was always present in the cuvette to be sure that the brine was really saturated.
- 3. Prior to use, a 10 mL syringe was cleaned with acetone to dissolve any possible organic residual, e.g. used oil containing amine solutions, and with nitrogen to remove the acetone.
- 4. The syringe was filled with a fresh oil containing amine solution. This syringe was initially rinsed with that solution, which was discharged as "waste" to eliminate any possible residual of acetone or nitrogen particles. The full contents of the syringe were used for subsequent measurements
- 5. Then, the syringe was arranged so that its video on the screen quite fits (see Figure 28 on the right side).
- 6. At a given volume of liquid, an oil drop was generated in the needle of the syringe without detachment so that the drop was suspended in saturated brine. It must be pointed out that the volume of liquid was a significant parameter in this technique, unlike the sessile drop method (section 3.6.4).
- 7. The video was recorded using a Fta 32 video software by clicking on "run".
- 8. Extreme care was used in cleaning all materials after each experimental run.

3.8 Experimental phase III. Phase inversion method

3.8.1 Introduction

The experimental phase III involved the application of the so-called Phase Inversion Method (P.I.M.) as proposed originally by Takakuwa and Takamori (1963). The emulsions stabilized by fine KCl particles – 325 mesh, at varying amine concentration, were prepared with the use of a vortex mixer (see Figure 30). The description of the phase inversion method is in section 2.4.3. It was based on the fact that amines modify wettability of sylvite.

In the emulsion, solids report to the oil/water interface as shown in Figure 6, forming an oilwater-solid system. The contact angle at this three-phase line of contact determines the emulsion type either O/W or W/O (see section 2.3), where the terms "O" and "W" are referred to the organic phase and the aqueous phase, respectively

Hence, the idea was, simply, to determine the particular amine concentration (or *inversion point*) at which the phase inverts from O/W to W/O, or vice versa (all this in the presence of fine - 325 mesh KCl particles).

It is to be noted that some authors indicate the existence of two inversion points (see section 5.4.2). Firstly, from O/W to W/O emulsions, and secondly, from W/O back to O/W emulsions.

The P.I.M. was applied to two sets of tests. One initial set of experiments was performed between April 2014 and April 2015 to study the effect of temperature and additional shaking or *mixing* on the emulsion stability as well as the position of KCl particles in either phase and/or at the oil/saturated-brine interface (see section 4.3). The other final set of experiments was conducted on May 19, 2015 to study the correlation between the emulsion type and contact angles (see section 4.2 and Figure 70).

3.8.2 Experimental set-up

The experimental set-up embraced a three-phase mixture (see Figure 30). One phase was the organic (oil) phase, denoted as "O" that consisted of varying concentrations of amine in oil. The second phase was the aqueous phase, denoted as "W" that comprised one component, the saturated brine, and the third phase consisted of fine – 325 mesh KCl particles in saturated brine.



Figure 30. Schematic experimental set-up for the phase inversion tests.

3.8.3 Operating conditions

The initial experiments on phase inversion method showed that the KCl weight of 1.0 g and the shaking mechanism by vortex mixing (see section 3.5) were approximately proper. In addition, the operating conditions were: $22.0 \pm 3.0^{\circ}$ C, 10 mL of oil phase, and 10 mL of aqueous phase.

Three hydrocarbons (see section 3.1.3) and four amines (see section 3.1.2) were tested. For convenience, three concentrations (wt%) of amine in oil were selected: 1.000 % (stock solution), 0.050 %, and 0.005 %, this in total then constitutes 36 amine-in-oil combinations as tabulated in Figure 70.

3.8.4 Experimental methodology

See Figure 30 for details.

The preparation of the aqueous phase was as follows:

In a VOA vial, 1 gram of -325 mesh fine KCl was added to 10 mL of saturated brine, and the mixture was vigorously shaken for about 60 sec. with the use of a vortex mixer and was left to stand for additional at least 30 min.

The preparation of the organic (oil) phase was as follows:

In a volumetric flask (25 mL), the calculated volume of stock solution (see Table 1) was added. Then, pure oil (see section 3.1.3) was gently added so that the graduation line was even with the center (bottom) of the meniscus. Finally, the mixture was transferred to a Wheaton bottle. If necessary, the mixture was sonicated so that amines were completely dissolved in oil.

The preparation of emulsions was as follows: (Figure 31)

10 mL of the aforementioned organic phase were transferred to the VOA vial that contained the aqueous phase, and the resulting mixture, referred to as "*emulsion*", was vigorously shaken for about 60 min. with the use of a vortex mixer and then was left to stand for additional at least 1 day to equilibrate. After equilibration, the emulsion finally was judged by mere visualization (see section 4.3).



Figure 31. Schematic methodology for the preparation of emulsions.

The results of the phase inversion tests are in sections 4.2 (final experiments) and 4.3 (initial experiments).

4 Results

Three types of experiments were carried out in this thesis including contact angle measurements (see section 4.1.1), interfacial tension measurements (see section 4.1.2), and phase inversion tests (see section 4.2). In all these experiments, three hydrocarbons (see section 3.1.3) and four amines (see section 3.1.2) were tested. As research variables, three concentrations (wt%) of amine in oil were selected: 0.005 %, 0.050 %, and 1.000 %, unless otherwise stated, this in total constitutes at least 36 amine-in-oil combinations.

All experiments were conducted in NaCl-KCl saturated brine (see section 3.4.3) at room temperature ($22 \pm 3.0^{\circ}$ C). The pH range of those solutions was from 5 to 6, however, for the sake of convenience pH was not included as variable in this thesis.

Exactly the same oil containing amine solutions utilized in the sessile drop, pendant drop, and Wilhelmy plate tests were then used in phase inversion experiments. Extreme care was used to hold all parameters constant to minimize extraneous sources of systematic error that might influence the comparison between results.

4.1 Equilibrium in oil/saturated-brine systems

4.1.1 Effect of equilibration time on contact angle

Figures 32, 33, and 34 show the contact angle values as a function of the time for solutions of varying amine concentration (wt) in n-decane, cyclohexane and Diesel oil, respectively. Contact angles were measured upon contacting an oil drop with a smooth KCl surface immersed completely in saturated brine. This experimental procedure is described in section 3.6 (experimental phase I).

All contact angles were measured at the oil/saturated-brine/KCl three-phase line of contact (*across the aqueous phase*), with the use of a Fta32 video computer program. In this respect, initial contact angle curves consisted of 250 points after trigger (see Figure 27). For convenience, these curves were, nevertheless, simplified to only a few points as shown in Figures 32-34.

These simplified figures demonstrate that the contact angle increases with time and with the amine concentration. As the equilibrium phenomena involved will be discussed in section 5.3, they will not be described here. Depending on the amine concentration and on the chemical composition of the oil, contact angles reached the so-called equilibrium values at different times. These equilibrium contact angles are summarized in Figure 70. It is to be noted that all contact angles were assumed to reach equilibrium after 250 seconds. The rationale given for such an approach is that the variation of contact angle values after the last 250 seconds was not significant.

It can be seen that the contact angle curves are irregular particularly for dodecyl (C_{12}) amine and octadecyl (C_{18}) amine. Drops of oil containing amine (see Figures 19 and 25) were continuously "oscillating" during the experimental runs, thus making difficult the contact angle measurements by the Fta32 video computer program. This effect was to some extent related to the high complex aforementioned equilibrium phenomena that will be further discussed in section 5.3. In these difficult cases, those experimental runs were repeated but resulted in even poorer reproducibility (see section 5.3).

Insets in Figures 32-34 show sessile drops on smooth KCl surfaces immersed in brine, at 250 seconds, taken with the use of a digital video camera connected to the FTA drop shape instrument (Figure 25). In some cases at 1.000 % (wt) of amine in oil, drops spread almost completely on the KCl surface (see Figure 32) after a particular point in time, and contact angles could not be measured (see section 2.4.1 for the assumptions in the sessile drop method). This situation is illustrated with a hypothetical curve in a "dashed rectangle" in those figures.

Temperature was not rigidly controlled in sessile drop tests due to their high complexity, therefore, inherent changes in room temperature could introduce extraneous experimental error. The temperature could influence on adsorption and diffusion dynamics.



Figure 32. A drop of oil containing amine spread on the surface of a KCl plate in saturated brine.



Figure 33. Contact angle curves for a n-decane/saturated-brine/KCl system at various amine concentrations (wt%) determined with the use of sessile drop method.



Figure 34. Contact angle curves for a cyclohexane/saturated-brine/KCl system at various amine concentrations (wt%) determined with the use of sessile drop method.



Figure 35. Contact angle curves for a Diesel oil/saturated-brine/KCl system at various amine concentrations (wt%) determined with the use of sessile drop method.

4.1.2 The effect of equilibration time on interfacial tension

4.1.2.1 Interfacial tension for oil containing amine solutions

Figures 36, 37, and 38 present the interfacial tension values as a function of the time for solutions of varying amine concentration in cyclohexane and Diesel oil, respectively. Interfacial tensions were measured for a suspended oil drop that is located at the tip of a needle. This experimental procedure is described in section 3.7 (experimental phase II).

All interfacial tensions were measured at the oil/saturated-brine with the use of a FTA computer program Fta32 video. Unlike sessile drop method, in this technique the drop volume (abbreviated as V) must be known; this is also given in the chart legends (see Figures 36-38).

These figures demonstrate that the interfacial tension values decrease with time and with the amine concentration. In other words, the diffusion rate of large amine molecules from the bulk of the organic phase to the interface depended on the amine concentration as expected from the Flick's equation. These diffusion phenomena will be briefly discussed in section 5.2 for oil/saturated-brine systems.

In some cases, the drop generated at the tip of a needle detached immediately from the tip regardless of the volume of liquid. In other words, it was not possible to suspend a drop from a needle, thereby precluding interfacial tension measurements. This happened mostly for very low values of interfacial tension.

The temperature could influence on diffusion dynamics, and it was not rigidly controlled in pendant drop experiments because of their high complexity. As a consequence of this, inherent changes in room temperature could introduce extraneous experimental error.



Figure 36. Oil/saturated-brine interfacial tension (ST) curves for a n-decane/saturated-brine system at various amine concentrations (wt%) with the use of pendant drop method.



Figure 37. Oil/saturated-brine interfacial tension (ST) curves for a cyclohexane/saturated-brine system at various amine concentrations (wt%) determined with the use of pendant drop method.



Figure 38. Oil/saturated-brine interfacial tension (ST) curves for a Diesel/saturated-brine system at various amine concentrations (wt%) determined with the use of pendant drop method.

4.1.2.2 Interfacial tension for oils without amine

Figures 39 shows the interfacial tension (IFT) values as a function of the time for oils without amines including n-decane and Diesel oil. Interfacial tensions were correlated from the force exerted on a vertically suspended platinum plate that touches the oil/saturated-brine interface. This experimental procedure is given in Appendix D (from Krüss K11's manual).

The Krüss computer program automatically correlated those forces with the interfacial tension according to the equation for capillarity, i.e. $F = p\sigma \cos(\theta)$ where: F is the force acting on the microbalance, p is the perimeter of the plate, σ is the interfacial tension, and θ is the contact angle at the three-phase line of contact. Platinum plate can be optimally wetted on account of its very high surface free energy and, therefore, generally forms a θ of zero $\cos(0^\circ) = 1$ with liquids.

Buoyancy forces were assumed to be zero because of the thickness of the plate (0.4 mm), and the instrument automatically tarred the balance

Figures 39 shows IFT measurements over a long period for n-decane and Diesel oil without amine. The IFT curve for Diesel oil gently decreases over time unlike that for n-decane, which practically does not decrease in time. Diesel is a technical product which may contain various hydrocarbons and also various impurities, while n-decane is reagent grade oil.



Figure 39. Oil/saturated-brine interfacial tension curves for Diesel oil (circles) and n-decane (squares) without amines determined with the use of Wilhelmy plate technique.

4.2 Phase inversion tests

4.2.1 Final experiments on emulsions stabilized by fine KCl particles

For the preparation of emulsions, the organic (oil) and aqueous phases were shaken together with the use of a vortex mixer (see Figure 30). The experimental methodology is described in section 3.8. For the sake of clarification, the resulting oil/saturated-brine mixture after shaking is referred to as "*emulsion*" in this section.

Figures 40, 41, 42, and 43 show emulsions stabilized by fine KCl particles (see section 3.4.6) at varying concentration of dodecyl (C_{12}), octadecyl (C_{18}), HTD, and TD amines, respectively, and include four columns as follows.

From left to right, the first three columns present photographs taken one day, one month, and three months after the emulsion preparation (on May 19, 2015), respectively. Additional shaking or *mixing* was performed by hand for 30 seconds only for emulsions in the third column, and their photographs were taken immediately after that additional shaking.

The two most significant variables that affect the stability of emulsions are temperature and shaking time. The former and the latter are discussed in sections 4.3.2 and 4.3.3, respectively. In order to rigidly control the two variables, initially those final experiments were conducted on the same day (without interruptions) using always a thermometer and a stopwatch to minimize experimental error that might influence the resulting emulsion. The temperature of the oil/saturated-brine mixture and shaking time remained, hence, constant at 22.0 $\pm 0.5^{\circ}$ C and at 75 seconds, respectively.

Similar tests but between April, 2014 and April, 2015 (the initial experiments) are shown in the utmost right column with those in the third column in order to study the reproducibility of the results. The photographs in this fourth column were taken 10 minutes after the aforementioned additional shaking.

It is to be noted that those initial experiments were performed on different days, thus inherent changes in room temperature $(22.0 \pm 3.0^{\circ}C)$ could introduce extraneous experimental error. It can be determined, nevertheless, that the phase inversion tests show good reproducibility even though fluctuations in temperature were present.

All experiments used equal volumes of organic (oil) phase and aqueous phase (1:1 by volume). In this respect, Figures 40-43 also include a horizontal red line that approximately indicates the separation between both phases, thus the organic and aqueous phases are above and below the line, respectively. For cyclohexane/saturated-brine emulsions, however, the volume of the organic phase drastically decreased a couple of days after shaking because of volatilization phenomena (although the VOA vials or *beakers* were tightly closed with a plastic cap at all times).



Figure 40. Photographs of beakers at different dates containing dodecyl (C_{12}) amine-in-oil/saturated-brine solutions (1:1 in volume) at 22.0 ± 0.5 °C stabilized by fine KCl particles.

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Figure 41. Photographs of beakers at different dates containing octadecyl (C_{18}) amine-in-oil/saturated-brine solutions (1:1 in volume) at 22.0 ± 0.5 °C stabilized by fine KCl particles.

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Figure 42. Photographs of beakers at different dates containing HTD-in-oil/saturated-brine solutions (1:1 in volume) at 22.0 ± 0.5 °C stabilized by fine KCl particles.

52

	Prepared on May 19, 2015 unless otherwise stated on label														
Photo: 20/05/15			Photo: 23/06/15			Photo: 13/08/15				Photo: 13/08/15					
TD	TD	TD	TD	TD	TD	TD	TD	TD		TD	TD	TD	TD		
Cyclo	Cyclo	Cyclo	Cyclo.	Cyclo.	Cyclo.	Cyclo.	Cyclo.	Cyclo.		Cyclo.	Cyclo.	Cyclo.	Cyclo.		
1.000%	0.050%	0.005%	1.000%	0.050%	0.005%	1.000%	0.050%	0.005%		1.0%	1.0%	0.050%	0.005%		
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-	(a)		(b)			(c)			(d)						
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Decane	Decane	Decane	Decane	Decane	Decane	Decane	Decane	Decane	Decane	Decane	Decane	Decane	Decane	Decane	
1.000%	0.050%	0.005%	1.000%	0.050%	0.005%	1.000%	0.050%	0.005%	1.0%	1.0%	1.0%	1.000%	0.050%	0.005%	
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(e)			(f)			(g)			(h)						
TD	TD	TD	TD	TD	TD	TD	TD	TD	TD	TD	TD	TD	TD	TD	
Diesel	Diesel	Diesel	Diesel	Diesel	Diesel	Diesel	Diesel	Diesel	Diesel	Diesel	Diesel	Diesel	Diesel	Diesel	
1.000%	0.050%	0.005%	1.000%	0.050%	0.005%	1.000%	0.050%	0.005%	1.0%	1.0%	0.050%	0.05%	0.005%	0.005%	
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(i)			(j)			(k)			(1)						

Figure 43. Photographs of beakers at different dates containing TD-in-oil/saturated-brine solutions (1:1 in volume) at 22.0 ± 0.5 °C stabilized by fine KCl particles.

4.3 Emulsion type

Figures 40-43 demonstrate the existence of four distinguishable phases in accordance with Figure 10: (1) a sediment of solid KCl particles at the bottom, (2) a layer of saturated brine (the aqueous phase), (3) a creaming layer (white), and (4) a coherent oil phase at the top (the organic phase). Emulsions stabilized by fine KCl particles could be described in terms of the so-called final emulsion volume (FEV), which is defined as the volume of the creaming layer "cr" to the total volume. The FEV was experimentally found to depend on amine concentration.

At very low or zero amine concentration, the FEV was zero. As that concentration increased, the FEV also increased, and the creaming layer reported mostly to the organic (oil) phase. At higher amine concentrations, the creaming layer inverted, occupying the aqueous phase. In some cases, emulsions became, however, unstable and the creaming layer "constricted" a couple of seconds after shaking, reporting to the interface. The observations of Figures 40-43 suggest also that oil-in-water (O/W) emulsions were mostly unstable, while water-in-oil (W/O) emulsions were typically stable. Unstable emulsions may explain, in turn, the apparent double inversion of phases from O/W to W/O and back to O/W observed in this project (see Figures 52, 56, and 57). This observed double inversion point is in agreement with Binks and Rodrigues (2009), Binks et al. (2013), and Hu et al. (2015). The double inversion mechanism is briefly discussed in section 5.4.2.

Initial experiments on emulsion preparation suggest that all those changes in the FEV occurred mostly during the first seconds immediately after shaking following patterns (see section 4.3.1), and also during the following days with or without additional mixing (see section 4.3.3). The temperature of the solutions also influenced on the FEV (see section 4.3.2).

All those observed patterns or "*states*" were sequentially merged to make an overview (or a "*movie*") of changes on KCl wettability with the amine concentration and contact angle (see Figure 44). As the amine concentration increases, the contact angle increases as well, thereby modifying the KCl wettability (see section 4.1.1). In that overview, a situation is reached where oil-in-water (O/W) emulsions are inverted to water-in-oil emulsions (W/O). Then, the aforementioned double inversion of phases may occur (see section 5.4.2). Figure 44 includes dashed red arrows that indicate the directions of the contraction of the creaming layer, "cr", either downward or upward.

Tests for identification of emulsions (e.g. drop, conductivity, and dye solubility tests) could not be successfully applied in saturated brine, but more detailed discussion on them is beyond the scope of this work. The patterns that the KCl particles follow with time immediately after shaking makes possible to identify the type of the emulsion (using the FEV). This identification was in agreement with that in Figures 11-12, and 67-68. The stability of emulsions can, hence, be described by the final emulsion volume (see Figure 44).



Figure 44. Positions of the creaming layer ("cr") in an oil/saturated-brine/KCl system at various amine concentrations (wt%), showing changes in KCl wettability and contact angle. Dashed arrows illustrate the contractions of the creaming layer immediately after shaking (seconds).

As it was earlier mentioned, the emulsion stability in the illustrative scheme proposed (see Figure 44) can be described in terms of the final emulsion volume as follows (see Figure 10). It is to be noted that the scheme is in agreement with that prepared by Binks et al. (2013) in Figure 19 and Hu et al. (2015) in Figure 66.

- In the position or **state** (1), the final emulsion volume and therefore the creaming layer were zero. Thus, KCl particles were naturally (or inherently) hydrophilic and settled to the bottom after shaking forming a sediment layer. Contact angles were as those for oil without amines. The contact angles for the tested oils without amines were around 40-50°.
- In the position or **state** (2), as the amine concentration slightly increased, the final emulsion volume increased as well. This state is called "*hydrophilic*" because although KCl particles ceased to be naturally hydrophilic because of the amine addition, they are still hydrophilic. They gradually migrated to the oil/saturated-brine interface forming a thin creaming layer. Contact angles were still much lower than 90°. See section 4.3.1.1 for details.
- In the position or **state** (3), an additional increasing in the amine concentration raised the final emulsion volume even further. KCl particles either accumulated at the oil/saturated-brine interface or dispersed in the organic (oil) phase, thus the sediment layer of KCl particles present in the position (1) practically disappeared. This state is called "*mostly hydrophilic*" because some KCl particles were to some extent hydrophobic. Contact angles were expected to be lower than 90° but higher than those for positions (1) and (2). See section 4.3.1.2for details.

- In the positions (4.a and 4.b), the volume of the coherent organic (oil) phase decreased dramatically, increasing the final emulsion volume even further. This creaming layer occupying the oil phase was assumed to be an oil-in-water (O/W) emulsion. Figures 11-12, and 67-68 also indicate that the creaming layer reports to the organic phase for O/W emulsions. At positions or **states (4.a) and (4.b)**, KCl particles were preferably wettable by water (see Figure 6). Contact angles were a little smaller than 90°. See section 4.3.1.3 for details.
- In the positions (5.a and 5.b), the volume of the coherent oil phase increased drastically, and the final emulsion volume inverted from the organic phase to the aqueous phase. This creaming layer occupying the aqueous phase was assumed to be water-in-oil (W/O) emulsion. Figures 11-12, and 67-68 also indicate that the creaming layer reports to the aqueous phase for W/O emulsions. At positions or **states (5.a) and (5.b)**, KCl particles were preferably wettable by oil (see Figure 6), and contact angles were somewhat greater than 90°. See section 4.3.1.4 for details.
- Finally, the hypothetical state (6) represents the observed double inversion of phases from O/W to W/O emulsions (see Figures 19 and 66). Thus, KCl particles may render hydrophilic again, decreasing the contact angle from around 100° (for W/O emulsions) to lower than 90° (for O/W emulsions). Figures 2, 18, 19, and 66 validate that the contact angle curve can peak and then descend. Section 5.4.2 further discusses this apparent mechanism.

The results in Figures 40-43 are summarized in Figure 70, which includes the particular position of KCl particles and KCl wettability as well as contact angle measured with the use of the sessile drop technique (see section 3.6).
4.3.1 Emulsion stability

The film or *pellicle* encapsulating the droplet(s) may spontaneously break down over time, producing coalescence phenomena (see section 2.2.2). The strength with which a particle is held at the oil/water interface is related to the contact angle (Binks and Lumsdon, 2000). For contact angles much higher or lower than 90° (see Figure 9), the energy of attachment of solid particles decreases significantly, thereby leading to coalescence. The obtained results suggest that emulsions become unstable or "break" immediately after shaking or *mixing*. Initially, the creaming layer occupied the volume of both phases (about 40 mm in height). Then, this layer followed distinct patterns in time depending on the KCl wettability, which in turn determines the energy of attachment. The following sections illustrate the observed patterns during the first 10 seconds after the mixing.

For illustration purposes only, Figure 45 shows the final emulsion volume (FEV) as a function of the time (immediately after shaking) for different amine in oil solutions at room temperature. The curves for solutions of C_{12} amine in cyclohexane show that the higher the amine concentration is, the faster the creaming layer constricts in the state (3). The creaming layer reported to the interface 3 and 8 seconds later for those solutions at 0.050 % and 0.005 %, respectively. The curve for a solution of 0.050 % of C_{18} amine in Diesel illustrates that the FEV was zero after approximately 4 seconds. This state (2) exhibited the creaming layer contraction from the top and bottom to the interface (as a "sandwich") similarly as those for C_{12} amine in cyclohexane but with a clear sediment layer of KCl particles in the bottom. Finally, the curves for a solution of 1.000 % (wt) of C_{12} amine in n-decane and its duplicate present similar contraction rates.



Figure 45. Final emulsion volume as a function of the time immediately after shaking for amine in oil solutions.

4.3.1.1 Hydrophilic KCl particles

The position or **state** (2) was reached for solutions at 0.050 % of C_{18} , TD, and HTD amines in Diesel oil, and it was characterized by a clear sediment layer of solid KCl particles at the bottom. For the sake of comparison, Figure 46 shows solutions at 0.005 % and 0.050 % of C_{18} amine in Diesel oil. Figure 46.g demonstrates that the resulting oil/saturated-brine mixtures after shaking were similar for those solutions. The observation of their patterns over time, nevertheless, revealed that they followed state (1) and state (2), respectively.

All the solutions at 0.005 % of amine in Diesel oil reached the position or **state** (1), i.e. KCl particles were naturally hydrophilic, and they settled to the bottom. The creaming layer disappeared immediately after mixing (see Figure 46.b). See section 5.4.2.2 for further discussion.

Figures 40.1, 41.1, 42.1, 43.1, and 46.g show that the final emulsion volume for emulsions in the **state** (2) was practically zero, thus those emulsions were broken approximately 5 seconds after shaking or mixing. This fast emulsion drop coalescence could be attributed to the low energy of attachment of KCl particles at the interface, which in turn is explained by the sessile drop contact angles (see section 5.4.2).



Section 5.4.2.2 further discusses the KCl wettability in Diesel oil solutions.

Figure 46. Photographs of beakers showing sequentially the creaming layer contraction per second immediately after shaking for octadecylamine-in-Diesel/saturated-brine emulsions stabilized by fine KCl particles, without additional shaking. All solutions at room temperature.

4.3.1.2 KCl particles mostly hydrophilic

The position or state (3) was reached for the following solutions: at 0.005 % of amines in cyclohexane and n-decane, at 0.050 % of C_{12} amine in those oils, and at 0.050 % of C_{18} amine in cyclohexane (see Figure 70). At this particular state, KCl particles did not settle to the bottom unlike those particles in the state (2). For illustration purposes only, Figure 47 shows solutions at 0.005 % and 0.050 % of C_{12} amine in cyclohexane. Figure 47.i shows that the resulting mixture after shaking is similar for both solutions, and the observation of their patterns over time suggests that they followed the position (3). Figure 45 reveals, nevertheless, that the contraction rate of their creaming layers depends on the amine concentration. More detailed discussion of this rate is beyond the scope of this project.

Figures 40.d, 40.h, 41.d, 41.h, 42.d, 42.h, 43.d, 43.h, and 47.i demonstrate that the creaming layer reported mostly to the oil/saturated-brine interface, and the FEV was very small (~ 5 mm) but not zero. It was assumed that this creaming layer occupying the interface does not correspond to an emulsion. This assumption is in agreement with the sessile drop contact angles (see Figure 70).

The aqueous phase in those figures is clear, suggesting that KCl particles either accumulated at the oil/saturated-brine interface or dispersed in the organic (oil) phase.



Figure 47. Photographs of beakers showing sequentially the creaming layer contraction per second immediately after shaking for dodecylamine-in-cyclohexane/saturated-brine emulsions stabilized by fine KCl particles, without additional shaking. All solutions at room temperature.

4.3.1.3 KCl particles preferably wetted by water

When KCl particles were preferentially wetted by water (see Figure 6), they produced oil-inwater (O/W) emulsions immediately after shaking. Then, these emulsions followed three possible patterns. Firstly [**state (4.a**)], they remained stable over time. Only solutions of concentrations (wt) between 0.2 % – 0.5 % of TD amine in cyclohexane and at 0.036 % of HTD amine in Diesel oil produced state O/W emulsions in time (see Figures 58.h and 52, respectively). Secondly [**state** (**4.b**)], they became unstable in time (see Figure 55.g). Solutions at 0.050 % of amines in cyclohexane, 0.005 % of C₁₂ amine in n-decane, and 0.005 % and 0.050 % of C₁₂ amine in Diesel oil formed unstable O/W emulsions in time. Finally [**state** (**5.a**)], they inverted to stable W/O emulsions if additional shaking or mixing is applied. Solutions of n-decane containing between 0.1 % - 0.2 % of HTD and TD amines inverted to stable W/O emulsions (see Figures 56.h and 57.h, respectively).

These occurrence of every state depends on the strength with which KCl particles are held at the oil/saturated-brine interface. This energy of attachment in turn is determined by the KCl wettability. The link between the KCl wettability and the stability of emulsions is further discussed in section 5.4.2.3.



Figure 48. Photographs of beakers showing sequentially the creaming layer contraction per second immediately after shaking for TD-in-cyclohexane/saturated-brine emulsions stabilized by fine KCl particles, without (a-g) and with (h) additional shaking. All solutions at room temperature.



Figure 49. Photographs of beakers showing sequentially the creaming layer contraction per second immediately after shaking for TD-in-decane/saturated-brine emulsions stabilized by fine KCl particles, without (a-g) and with (h) additional shaking. All solutions at room temperature.

4.3.1.4 KCl particles preferably wetted by oil

When KCl particles were preferentially wetted by oil (see Figure 6), they produced water-inoil (W/O) emulsions immediately after shaking. Then, these emulsions followed also an apparent pattern that is described by the final emulsion volume (see Figures 50 and 51). Immediately after shaking, the creaming layer occupied three fourths of the total volume (~ 30 mm in height) and started to constrict from the top to the interface, i.e. the creaming layer was displaced downwards by the organic (oil) phase. For the sake of comparison, Figure 50 includes a solution of amine concentration (wt) at 0.005 % of HTD amine in decane, which reached the position (3), as well as similar tests at 1.000 % and 0.050 % amine concentration, which achieved the position or **state** (**5.a**). For the latter, the creaming layer constricted immediately after shaking (see Figure 50.a). For the former, this layer constricted gradually over seconds (see section 4.3.1.2). Figure 51 demonstrates that W/O emulsion may be also unstable at the **state** (**5.b**). At 1.0 % of C₁₂ amine in cyclohexane, the creaming layer remained in the aqueous phase. At 2.0 %, this layer constricted upwards to the interface and fell to the bottom. Finally, at 3.0 %, the creaming layer settled on the bottom. This instability could also lead to a double inversion point as discussed in section 5.4.2.



Figure 50. Photographs of beakers showing sequentially the creaming layer contraction per second immediately after shaking (a-f) and after 30 minutes (g) for HTD-in-decane/saturated-brine emulsions stabilized by fine KCl particles. All solutions at room temperature.



Figure 51. Photographs of beakers showing sequentially the creaming layer contraction per second immediately after shaking for dodecylamine-in-cyclohexane/saturated-brine emulsions stabilized by fine KCl particles, without (a-d) and with (e-g) additional shaking. All solutions at room temperature.

4.3.1.5 Apparent double inversion of phases

Binks and Rodrigues (2009) and Binks et al. (2013) indicated that the double inversion of emulsions occurs in systems of double chain cationic surfactants, and it is not possible however when a single-chain cationic surfactant is used. The authors used the following double-chain cationic surfactants of different chain lengths: di-octyldimethylammonium bromide (di-C8DMAB), di-decyldimethylammonium bromide (di-C10DMAB), and di-dodecyldimethylammonium bromide (di-C12DMAB). Hu et al. (2015) also investigated the double inversion of emulsions with didecyldimethylammonium bromide (DMAB) and cetyltrimethylammonium bromide (CTAB) as surfactants, concluding that only the former produced double inversion (see Figure 68). Even though, the double inversion of phases and the double-chain cationic surfactants are beyond the scope of this project, it must be pointed out that in Figure 2.c, the HF and dodecylamine curves clearly follows a parabola as those shown in Figures 18 and 19, validating that contact angle can decrease with amine concentration. Section 5.4.2 briefly discusses this mechanism.

Figure 52 shows the apparent double inversion, i.e. the **state** (6), from O/W to W/O and back to W/O emulsions for solutions of varying HTD amine concentration (wt%) in Diesel oil.

HTD	HTD	HTD	HTD	HTD	HTD
Diesel	Diesel	Diesel	Diesel	Diesel	Diesel
0.036%	0.125%	0.50%	1.0%	2.0%	4.0%
N. S.					149.84
					- Statistics
TIEK					

Figure 52. Photographs of beakers after 1 day containing HTD-in-Diesel/saturated-brine emulsions stabilized by fine KCl particles. Apparent double inversion from O/W to W/O and back to W/O emulsions occurs. All solutions at room temperature.

4.3.2 Effect of temperature on emulsion stability

Figures 53 shows the effect of the temperature of solutions of octadecyl (C_{18}) amine in cyclohexane on emulsion stability at different amine concentrations (wt). The final emulsion volume is demarcated using rectangles with red borders.

For solutions at 0.500 % (wt), stable water-in-oil (W/O) emulsion can be distinguished at 25 °C (position 5.a). At higher temperatures, the emulsion was broken, i.e. the interfacial film or pellicle that encapsulate the droplets was destroyed, the coalescence phenomena. KCl particles were completely wetted by water, and they become dispersed in the aqueous phase.

For solutions at 1.000 % (wt), at 25 °C and 35 °C water-in-oil (W/O) stable emulsion was produced. At higher temperatures, the coalescence phenomena occurred as well.

For solutions at 2.000 % (wt), at 25°C stable water-in-oil (W/O) emulsion can be observed (position 5.a). At 35 °C, the creaming layer started to shrink towards the oil/saturated-brine interface, suggesting an unstable W/O emulsion. At higher temperatures, the coalescence phenomena took place.



Figure 53. Photographs of beakers after 1 day showing the effect of temperature on emulsion stability for solutions of cyclohexane containing 0.500 % (a), 1.000 % (b), and 2.000 % (c) of octadecyl (C_{18}) amine. Prepared on August 8, 2015. Phographed on August 9, 2015.

Figures 54 presents the effect of the temperature of solutions of octadecyl (C_{18}) amine in n-decane on emulsion stability. The final emulsion volume is demarcated in red.

For solutions at 0.500 % and 1.000 % (wt), stable water-in-oil (W/O) emulsion can be distinguished between 25 °C and 45 °C (position 5.a). At 55 °C, the emulsion was broken, i.e. the coalescence phenomena (see Figure 8). KCl particles were completely wetted by water, and they settle to the bottom.

For solutions of 2.000 % (wt), stable water-in-oil (W/O) emulsion can be observed between 25 °C and 45 °C (position 5.a). At 55 °C, the creaming shrank completely at the oil/saturated-brine interface (position 6). The coalescence phenomena was not observed at this concentration.



Figure 54. Photographs of beakers after 1 day showing the effect of temperature on emulsion stability for solutions of n-decane containing 0.500 % (a), 1.000 % (b), and 2.000 % (c) of octadecyl (C_{18}) amine. Prepared on August 8, 2015. Phographed on August 9, 2015.

4.3.3 Effect of shaking time on emulsion stability

Section 4.3.1 shows the effect of time immediately after shaking (seconds) on the emulsion stability and suggests patterns (states) for all the different positions of KCl particles in either phase and/or at the oil/saturated-brine interface. Similar initial tests but presenting emulsions after days are shown in Figures 55- 62.

Figure 55, 56, and 57 show three initial experiments that were performed for solutions of concentration (wt) of 0.020 % - 0.075 % (column on the left), 0.1 % - 0.5 % (column in the middle), and of 0.5 % - 2.0 % (column on the right) of amine in oil, respectively.

The results of Figure 58 are based on two initial experiments, which were carried out for solutions of concentration (wt) at 0.1 % – 0.5% (column on the left) and 0.5 % – 2.0 % (column on the right) of TD amine in cyclohexane, respectively.

Figure 59 shows three initial experiments that were performed for solutions of concentration (wt) of 1.0 –4.0 % (column on the left), 4.0% – 5.5 % (column in the middle), and 0.5 % – 5.0 % (column on the right) of dodecyl (C_{12}) amine in decane, respectively.

Figures 60 presents three initial experiments, which were conducted for solutions of concentration (wt) of 0.033 % - 0.2 % (column on the left), 1 % - 0.5 % (column in the middle), and 0.0 % - 1.0 % (column on the right) of dodecyl (C₁₂) amine in cyclohexane, respectively.

All figures include four rows that involves photographs taken immediately, one or two days later, one or two days later (with additional shaking), and five days later (with additional shaking) the emulsion preparation, respectively. The dates of the emulsion preparation are shown in the first row. Solutions were shaken at room temperature ($22 \pm 3.0^{\circ}$ C).

Finally, Figures 61 and 62 show emulsions for solutions of octadecyl (C_{18}) amine in decane and in cyclohexane, respectively.

Final and initial experiments on emulsion preparation suggest that the range of amine concentrations (wt) at which phase inversion from O/W to W/O may occur is as shown in Table 2. Only the solutions of TD amine in n-decane exhibit discrepancies between the final and initial results. As it was earlier mentioned, these differences could be attributed to the effect of temperature and shaking time, just to mention the two main ones.

<u>HTD – in – cyclohexane</u>



(j) July 08, 2014

Figure 55. Photographs of beakers showing HTD-in-cyclohexane/saturated-brine emulsions stabilized by fine KCl particles taken immediately (a-c), one day later (d-f), one day later with additional shaking (g-i), and five days later the emulsion preparation (j) on dates shown in (a-c). All solutions at room temperature.

<u>HTD – in – n-decane</u>



Figure 56. Photographs of beakers showing HTD-in-decane/saturated-brine emulsions stabilized by fine KCl particles taken immediately (a-c), one day later (d-f), one day later with additional shaking (g-i), and five days later the emulsion preparation (j) on dates shown in (a-c). Apparent double inversion from O/W to W/O and back to W/O emulsions occurs (a-b). All solutions at room

temperature.

<u>TD – in – n-decane</u>



(j) July 08, 2014

Figure 57. Photographs of beakers showing TD-in-decane/saturated-brine emulsions stabilized by fine KCl particles taken immediately (a-c), one day later (d-f), one day later with additional shaking (g-i), and five days later the emulsion preparation (j) on dates shown in (a-c). Apparent double inversion from O/W to W/O and back to W/O emulsions occurs (a-b). All solutions at room temperature.

<u>TD – in – cyclohexane</u>

TD	TD	TD	TD	TD		TD	TD	TD	TD
Cyclo.	Cyclo.	Cyclo.	Cyclo.	Cyclo.		Cyclo.	Cyclo.	Cyclo.	Cyclo.
0.1%	0.2%	0.3%	0.4%	0.5%		0.5%	1.0%	1.5%	2.0%
1000	CI WILL	a Profile	a parti	TAXABLE IN		STATE OF	1.00		
1000				and the second second					
De lega De	COMP.	Concession of the	Same of	and the owner of the		1 miles	Same.	125-10	
(a) Lata 09, 2014						b) July	03 201/		
TD	TD	TD	TD	TD		TD	TD	TD	TD
Cyclo.	Cyclo.	Cyclo.	Cyclo.	Cyclo.		Cyclo.	Cyclo.	Cyclo.	Cyclo.
0.1%	0.2%	0.3%	0.4%	0.5%		0.5%	1.0%	1.5%	2.0%
Contraction of	TOP		TOTAL OF	Par I		IN STATE	THE OWNER	No.	1-01
	Contraction of the		No.				C.LANS	(STATE)	PLOT OF
TD	(c) J	uly 10, 2	2014 TD	TD	ſ	(TD	d) July TD	04, 2014 TD	
	TD Cyclo	Cvelo	TD Cyclo			Cyclo	Cyclo		TD Cyclo
Cyclo.	Cyclo.	Cyclo.	Cyclo.	Cyclo.		Cyclo.	Cyclo.	Cyclo.	Cyclo.
	0.2%	0 3%	0 /0/-	0 50/		0.5%	1.0%	1 5%	2.0%
0.1%	0.2%	0.3%	0.4%	0.5%		0.5%	1.0%	1.5%	2.0%
0.1%	0.2%	0.3%	0.4%	0.5%	l	0.5%	1.0%	1.5%	2.0%
0.1%	0.2%	0.3%	0.4%	0.5%	ļ	0.5%	1.0%	1.5%	2.0%
0.1%	0.2%	0.3%	0.4%	0.5%	l	0.5%	1.0%	1.5%	2.0%
0.1%	(e) J	0.3%	0.4%	0.5%		0.5%	1.0%	1.5%	2.0%
0.1%	(e) J	0.3%	0.4%	0.5%]	0.5%	1.0%	1.5% 04, 2014 TD	2.0%
0.1%	(e) J	0.3%	0.4%	0.5%		0.5% TD Cyclo.	1.0% (f) July (TD Cyclo.	1.5% 04, 2014 TD Cyclo.	2.0%
0.1%	0.2%	0.3%	0.4%	0.5%		0.5% TD Cyclo. 0.5%	1.0% (f) July (TD Cyclo. 1.0%	1.5% 04, 2014 TD Cyclo. 1.5%	2.0% TD Cyclo. 2.0%
	(e) J	0.3%	0.4%	0.5%		0.5% 0.5%	1.0% (f) July (TD Cyclo. 1.0%	1.5% 04, 2014 TD Cyclo. 1.5%	2.0% TD Cyclo. 2.0%
	(e) J	0.3%	0.4%	0.5%		0.5% 0.5%	1.0% (f) July (TD Cyclo. 1.0%	1.5% 04, 2014 TD Cyclo. 1.5%	2.0% TD Cyclo. 2.0%
	(e) J	0.3%	0.4%	0.5%	[0.5% TD Cyclo. 0.5%	1.0% (f) July (TD Cyclo. 1.0%	1.5% 04, 2014 TD Cyclo. 1.5%	2.0% TD Cyclo. 2.0%

(g) July 08, 2014

Figure 58. Photographs of beakers showing TD-in-cyclohexane/saturated-brine emulsions stabilized by fine KCl particles taken immediately (a-b), one day later (c-d), one day later with additional shaking (e-f), and five days later the emulsion preparation (g) on dates shown in (a-c). All solutions at room temperature.

Dodecylamine – in – n-decane



(j) June 30, 2014

(k) June 23, 2014

Figure 59. Photographs of beakers showing octadecylamine-in-decane/saturated-brine emulsions stabilized by fine KCl particles taken immediately (a-c), one day later (d-f), two days later (g-i), and five days later the emulsion preparation (j-k) on dates shown in (a-c). All solutions at room temperature.

<u>Dodecylamine – in – cyclohexane</u>



(j) June 30, 2014

(k) July 23, 2014

Figure 60. Photographs of beakers showing octadecylamine-in-cyclohexane/saturated-brine emulsions stabilized by fine KCl particles taken immediately (a-c), one day later (d-f), two days later (g-i), and five days later the emulsion preparation (j-k) on dates shown in (a-c). All solutions at room temperature.

<u>Octadecylamine – in – n-decane</u>

Figure 61 shows photographs of beakers containing emulsions over concentration (wt) range from 0.005 % to 2.0 % of octadecyl (C_{18}) amine in n-decane.

C18 Decane 0.005%	C18 Decane 0.01%	C18 Decane 0.05%	C18 Decane 0.1%	C18 Decane 0.5%	C18 Decane 1%	C18 Decane 2%
and the second						
Store .	140	and a	-			

Figure 61. Photographs of beakers after 1 day containing octadecylamine-in-decane/saturatedbrine emulsions stabilized by fine KCl particles. All solutions at room temperature.

<u>Octadecylamine – in – cyclohexane</u>

Figure 62 shows photographs of beakers containing emulsions over concentration (wt) range from 0.005 % to 2.0 % of octadecyl (C_{18}) amine in cyclohexane.

C18 Cyclo. 0.005%	C18 Cyclo. 0.01%	C18 Cyclo. 0.05%	C18 Cyclo. 0.1%	C18 Cyclo. 0.5%	C18 Cyclo. 1%	C18 Cyclo. 2%
-	100	-	-			

Figure 62. Photographs of beakers after 1 day containing octadecylamine-in-cyclohexane/saturated-brine emulsions stabilized by fine KCl particles. All solutions at room temperature.

5 Discussions

5.1 Experimental work

In this project, two wettability tests were conducted in process aimed at selecting an extender oil for the flotation of coarse potash ore fractions; these two included the phase inversion method (see section 3.8) and contact angle measurements with the use of sessile drop technique (see section 3.6). Pendant drop interfacial tension measurements (see section 3.7) were carried out to study the effect of equilibration time on the results.

Four amines, two commercial (reagent grades) and two technical, and three oils were tested at three different concentrations (wt) of amine in oil: 0.005 %, 0.050 % and 1.000 %, this in total then constitutes 36 amine-in-oil combinations as tabulated in Figure 70. Exactly the same oil containing amine solutions were used in all tests in order to minimize extraneous sources of systematic error that might influence the comparison of results. Prior to any experiments these solutions were sonicated for additional minutes to assure the complete dissolution of amines in oil.

The phase inversion tests are dependent on the temperature of the oil/saturated-brine mixtures prior to the shaking (see section 4.3.2). The main objective of this thesis is to investigate whether the phase inversion method can be used in the aforementioned selection process. For this purpose, the developed lab testing procedure was applied into two sets of experiments. One final set of tests were conducted on the same day (on May 19,2015); therefore, the temperature was rigidly controlled at about $22^{\circ}C \pm 0.5^{\circ}C$. The other initial set of experiments were carried out on different days (between April, 2014 and April, 2015) at room temperature ($22 \pm 3.0^{\circ}C$) that could not be controlled.

It is also to be noted that cyclohexane tended to evaporate from the liquid to form a separate vapor phase. The vapor pressure of cyclohexane and n-decane are 102.7 and 1.0 hPa, respectively, at 20°C. The Diesel oil vapor pressure is lower than 1.0 hPa. Therefore, the volume of cyclohexane (organic phase) could be reduced at about 30 %, affecting possibly the results.

For preventing vaporization, all containers, i.e. VOA vials or beakers and Wheaton bottles (see section 3.3.2), were closed with plastic caps that were cleaned with the use of soap and washed with a stream of copious distilled water. The soap that contains surface-active agents could contaminate the solutions despite rigorous cleaning procedures.

Prior to any experiments, KCl plates were polished with the use of solutions of ethanol and cerium oxide (see section 3.4.2). After polishing, KCl surfaces were quite rough and irregular particularly at its edges.

5.2 Interfacial tension measurements

Interfacial tension (IFT) is a central parameter in many colloidal systems including emulsions. When two immiscible liquids, e.g. oil and saturated brine, are shaken together, spherical droplets will form to maintain as small interfacial area as possible. When a surfactant is added to the system its molecules will adsorb at the interface tending to orient between the two phases with the polar ends in the aqueous phase and the non polar ends in organic (oil) phase, thus lowering the interfacial tension that may result in the formation of stable emulsions in time.

Results of this thesis demonstrate that interfacial tension curves for oils without amines (see Figures 39) exhibit higher IFT values than those with amine (see Figures 36-38). As the amine in oil formulations tested in this project decreased the interfacial tension (see Figure 36-38), they are expected to enhance emulsification. These colloidal systems are discussed in Section 5.4.

In the systems tested in this thesis the amines were used in the form of solutions in oil. When such a solution is contacted with brine the oil/brine interface forms and the amines start adsorbing at it at a rate determined mostly by diffusion

The slope of the IFT curves as a function of time indicates the aforementioned diffusion rate. It is well documented that as the surfactant concentration increases, the diffusion rate increases as well. Atrafi et al. (2012) measured interfacial tensions with the use of exactly the same FTA drop shape instrument (see Figures 19 and 21) for aqueous fatty acid solutions in order to determine the adsorption behavior of oleic acid at the gas/solution interface. Figure 63 shows that the higher the oleate concentration is, the faster the diffusion rate is and sooner the surface tension curve levels off. The interfacial tension measurements indicate, hence, the role of diffusion mechanism.



Figure 63. Dynamic surface tension as a function of oleate concentration at natural pH (Atrafi et al., 2012); reproduced by the permission of Elsevier.

Similar experiments but for oil containing amine solutions in saturated brine were carried out in this thesis (see section 3.7). Figure 39 demonstrates that the IFT values for n-decane without amine decreased from about 47 mN/m to 45 mN/m during the first 40 seconds whereas Figure 36 shows that IFT values for similar solutions but containing 1.000 % (wt) of amine are reduced from approximately 5 mN/m to 4 mN/m, reaching equilibrium values after 20-30 seconds. Similar changes of the measured contact angles over this initial period of time (see Figure 33) are caused by such equilibration processes, which in turn explain why those solutions containing 1.000 % (wt) of amine produced stable W/O emulsions (see Figures 40.h, 41.h, 42.h, and 43.h).

Figure 33 shows that solutions of 0.050 % (wt) of amine in n-decane reached equilibrium after 50-75 seconds. Their equilibrium contact angles, except for C_{12} amine, were similar to those at 1.000 % of amine, producing stable W/O emulsions (see Figures 40.h, 41.h, 42.h, and 43.h). The slope of these curves was, nevertheless, more gentle than those at 1.000 % of amine, supporting that the diffusion rate increases with amine concentration.

Figure 33 also demonstrates that solutions of 0.005% (wt) of amine in n-decane reached equilibrium at about 250 seconds. Their equilibrium contact angles are much lower than those at higher amine concentrations, and no emulsions were produced.

Figure 39 also shows that the IFT values for Diesel oil without amine decreased from about 22 mN/m to 16 mN/m during the first 40 seconds whereas Figure 38 demonstrates that IFT values for similar solutions but containing amines reduced approximately from 22 mN/m to 16 mN/m (at 0.005 % of amine). This practically zero decreases in interfacial tension may explain why solutions of concentration (wt) of 0.005 % of amine in Diesel oil exhibited contact angles similar to those for pure oils (around 45°) and also did not form emulsions (see Figures 40.1, 41.1, 42.1, and 43.1).

On the other hand, a comparison between curves without amine over 800 seconds (see Figure 39) indicate that IFT values for Diesel oil decreased significantly from about 22 mN/m to 8 mN/m. This result implies that Diesel oil (as bought at Shell gas station in Vancouver) contained surfactants unlike the reagent grade n-decane oil. Contents of surfactants in Diesel oil may explain why solutions of concentration (wt) of 1.000 % of amine in this oil did not produced stable W/O emulsions as expected from similar tests with n-decane cyclohexane (see Table 69).

Interestingly, solutions of HTD in Diesel oil (see Figure 52) produced both stable O/W and stable W/O emulsions when this oil was recently bought (in September 2014). It is to be noted that final experiments (see Figures 40-43) were performed on May 19, 2015. Diesel oil oxidation in storage is well documented in the literature. Jarviste et al. (2007) suggest the use of aluminum containers in which oxidation processes are considerably inhibited. It should be noted that Diesel oil was stored in a plastic container at all time in this project.

5.3 Equilibrium in oil/saturated-brine/KCl systems

For illustration purposes only, Figure 64 shows three contact angle curves from the Fta 32 computer program for a solution at room temperature of 0.05 % (wt) of dodecylamine in cyclohexane. These three curves were produced with the use of the sessile drop technique (see section 3.6). Three experimental runs (triplicates) were conducted for that solution while the KCl plate was removed prior to any of those runs. A comparison between these three curves show significant discrepancies. In these difficult cases, the "fresh" result was used for correlations with the phase inversion tests (see Figure 70).

Two types of apparently complex equilibrium processes may explain those changes observed when sample are kept for long and then repeated in the systems that involve KCl plate/particles in NaCl-KCl brine/oil-containing-amine. A "fast equilibrium" (seconds) resulting from the diffusion of large amine molecules to the interfaces and a "slow equilibrium" caused by dissolution/recrystallization of mostly NaCl fine crystallites onto KCl surfaces in NaCl-KCl saturated brine (Schreithofer and Laskowski, 2007).



(a)



Figure 64. Dynamic contact angle curves from the Fta 32 video computer program for solutions at room temperature of 0.050 % (wt) of dodecylamine in cyclohexane. Experiments are conducted on 4/19/15 at 7:26 p.m. (a), at 7:34 p.m. (b), and at 7:54 p.m, using fresh oil solutions, fresh saturated brine, and polished KCl plates.

5.3.1 Adsorption of amines at the oil/saturated-brine interface

Figures 33-35 shows that as the amine concentration increases, the equilibrium contact angle increases as well, which is in perfect agreement with Figure 17. Solutions of concentration (wt) of 1.000 % of amine in n-decane reached θ_{EQ} after 20-50 seconds whereas similar tests with 0.005 % and 0.050 % of amine increased gradually at a constant slope and reached θ_{EQ} at about 250 seconds.

According the Young's equation $\gamma_{so} = \gamma_{sL} + \gamma_{Lo} \cos \theta$, where θ is the contact angle, γ_{so} is the solid/oil interfacial tension, γ_{sL} is the solid/liquid interfacial tension , and γ_{Lo} is the liquid surface tension y. The relationship between adsorption and interfacial tensions is provided by the Gibbs adsorption equation, i.e. $\Gamma = -\frac{1}{RT} \left[\frac{d\gamma}{d \ln c} \right]$, where Γ is the surface excess concentration, R is the universal gas constant, T is the absolute temperature, and c is the concentration of surfactant.

As claimed by some researchers (de Bruyn et al., 1954; Laskowski et al., 2007), the contact angle can increase only if the solid/oil interfacial tension (γ_{so}), i.e. the adsorption at the solid/oil interface, is larger than at the solid/liquid interface (γ_{sL}).

It can then be inferred that upon contacting an oil drop with the smooth surface of a KCl plate (see Figures 19 and 25), the interactions between the cationic surfactants ($-NH_2$) and the negatively charged KCl surfaces promote migration of those cationic surfactants away from the oil/saturated-brine interface to the KCl/saturated-brine interface, leading to an increase in the contact angle.

Oil drops adhere to the solid surface through the hydrophobic bonding with the nonpolar groups of the pre-adsorbed amine. The effect of amine addition to oil is to provide the functional groups that can adsorb at the KCl surface (Dai et al., 1992).

Figures 33-35 show that all contact angles curves at 1.000 % (wt) of amine in oil dramatically ascent to contact angles higher than 100° within the first 50 seconds. Then, two distinct cases were observed. In the first case, the contact angle curves did not level off for solutions of C₁₂ amine in n-decane and in Diesel oil. In the other case, all those curves for the other formulations reached a plateau after approximately 50 seconds. Similar changes of the measured contact angles over this initial period of time were found for all the interfacial tension curves (see Figures 36-38), which descent and then achieved a plateau.

As it was earlier mentioned, the obtained results suggest that those differences in KCl wettability were caused by equilibration processes, i.e. diffusion (for interfacial and contact angle measurements) and dissolution/recrystallization (only for the latter).

Since all contact angle measurements were conducted to describe certain relative trend, the reproducibility of the obtained results was not as thoroughly examined.

5.3.2 NaCl fine crystallites at the KCl/saturated-brine interface

As shown by Schreithofer and Laskowski (2007), in the systems with KCl particles suspended in a KCl-NaCl saturated brine, a continuous dissolution/recrystallization takes place. The use of Atomic Force Microscopy (AFM) revealed that the topography of KCl/brine interface changes continuously. Through these tests it was possible to identify formation of fine NaCl crystallites on the KCl surfaces. These crystals were found to form when the specimen was withdrawn from the saturated solution. It can be expected such phenomena must have a very heavy bearing on the surface properties of KCl particles.

Two main types of surfaces could be distinguished, one that was microscopically 'smooth' (Figure 65.a) and the other macroscopically 'spotted' (Figure 65.c). The authors indicate that if the samples were not soaked quickly enough with lint-free filter paper after removal from the brine, these crystals grew too large (larger than 7.5 μ m in height) rendering the surface too rough.



Figure 65. Topography (*a*,*c*) image of KCl surface kept in brine for 30 minutes. The cubic structures are NaCl crystals that formed after the crystal was removed from the brine (Schreithofer and Laskowski); reproduced by the permission of Maney Publishing.

Prior to any experimental run, KCl plates were removed from the saturated brine and polished. Even though an infrared spectrophotometer was used for the analysis of the surface of polished KCl plates, the reuse of KCl plates may modify their surface not only by introducing possible reagents but also by rendering their surfaces too rough due to a continuous dissolution/recrystallization. It is to be noted that the number of KCl plates was limited (see section 3.2), and they were continuously reused.

5.4 Oil/saturated-brine emulsions stabilized by fine KCl

5.4.1 Final emulsion volume

The resulting oil/saturated-brine mixture after the use of vortex mixing (see section 3.8.4) is referred to as "emulsion" thoroughly the text. Oil/saturated-brine emulsions (1:1 by volume) were stabilized with fine KCl – 325 mesh. Figure 7 illustrates that in the absence of any solid particles, no stable emulsions could be formed (see section 2.2.5).

<u>The size of the particles</u> used for emulsification may be one of the most important factors affecting the effectiveness of colloidal particles in stabilizing emulsions because it controls the ability of the particle to reside at the interface (see section 2.2.5.3). Schulman and Leja (1954) claimed that for good emulsions it is necessary to have powders of particle size not greater than 1.0 micron and still smaller. In this respect, the particle size distribution for ground KCl particles is given in Appendix E and shows that these particles are mostly distributed around 1.0 micron. It is to be noted that particle size analysis was conducted in cyclohexane as solvent.

Another important factor affecting the emulsion stability is <u>the particle concentration</u> (see section 2.2.5.2). A specific quantity of fine particles is not well defined. Takakuwa and Takamori (1963) used an equivalent of 0.25 g, while Schulman and Leja (1954) claimed that the fine particles weight should be in the range from 2.5 to 5.0 g. Particular experiments on emulsion preparation in this project determined that 1.0 g of KCl was suitable (see Appendix B).

A third factor corresponds to <u>the surfactant concentration</u> (see section 2.2.5.1). Three different concentrations (wt) of amine in oil: 0.005 %, 0.050 % and 1.000 % were tested, unless otherwise stated.

On the other hand, several shaking mechanisms have been reported. Schulman and Leja (1954) used hand shaking, Takakuwa and Takamori (1963) utilized mechanical shakers, and most recently Katepalli (2014) used a vortex mixer. The aforementioned particular experiments on emulsion preparation were also carried out to compare different shaking mechanisms (see Appendix B). The obtained results suggested the use of vortex mixing (see Figure 30).

A lab testing procedure was, therefore, developed for selection of the oil(s) which could be used as the extender oil(s) in potash ore flotation. This lab testing methodology was applied in two sets of experiments. One initial set of experiments where emulsion stability (see Section 4.3.1) as well as the effect of temperature (see Section 4.3.2) and additional shaking time (see Section 4.3.3) on emulsion stability were studied. The other final set of experiments (see Section 4.2) involved validation and explanation of the initial results using the contact angles measured with the use of the sessile drop technique (see section 3.6). It is to be noted that initial and final experiments were conducted between April, 2014 and April, 2015 and on May 19, 2015, respectively.

In all these tests, emulsions showed the existence of four distinct phases (see Figure 10).

- 1. A sediment of KCl particles at the bottom,
- 2. a layer of saturated brine,
- 3. a creaming layer,
- 4. and, a coherent organic (oil) phase at the top.

The existence of those phases is in excellent agreement with the results of Abend et al. (1998), Melle et al. (2005), Maldivala et al. (2009), and Hu et al. (2015).

The final emulsion volume (FEV) is defined as the volume of the creaming layer related to the total volume of the system. In turn, emulsion stability can be related to the FEV.

Observations of the two aforementioned set of experiments allowed a correlation between the emulsion stability and the amine concentration and KCl wettability to be established. These correlations stipulate that:

- 1. Amines modify wettability of KCl surfaces (see Figures 2-3),
- 2. The strength with which a particle is held at the oil/water interface is related to the sessile drop contact angle (see Figure 9).
- 3. The position of KCl particles in either phase and/or at the interface determines the volume of the creaming layer (see Figure 44).
- 4. The FEV is defined in terms of the creaming layer.
- 5. The emulsion stability is, eventually, related to the FEV.

All these correlations are experimentally discussed in the following sections.

5.4.2 KCl wettability studies

It is widely accepted (see section 2.3 for details) that if the contact angle *across the aqueous phase* at the oil/water/solid interface is a little smaller than 90° the solid particles are held at the oil-water interface on the organic side and stabilize a water continuous emulsion (O/W). If the contact angle at oil/water/solid interface is somewhat greater than 90°, the particles are still held at the interface but on the aqueous phase and they now stabilize an W/O emulsion. If the particles are completely wetted either by the oil or by the water, they become dispersed in either phase respectively and, in these cases, no stable emulsions are formed (Schulman and Leja, 1954).

Hu et al. (2015) measured contact angles with the use of a Krüss Drop Shape Analysis System DSA10 for cetyltrimethylammonium bromide (CTAB) or didecyldimethylammonium bromide (DMAB) solutions (concentrations ranging from 0.25mM to 32 mM) at varying surfactant concentration. These solutions were contacted with a small piece of CNC-coated films. The authors summarized contact angle values as a function of the time in Figure 66 and indicated a double inversion point.



Figure 66. Contact angle as a function of the surfactant concentration for emulsions stabilized by cellulose nanocrystals (CNCs) (Hu et al., 2015); reproduced by the permission of Elsevier.

Figures 67 and 68 demonstrate how emulsions look like. Oil-in-water (O/W) emulsions reported mostly to the organic (oil) phase whereas water-in-oil (W/O) emulsions occupied typically the volume of the aqueous phase. Figure 69 shows that in some cases the creaming layer is formed at the oil/water interface.



Figure 67. Photograph of beakers after 24 h containing dodecane–water emulsions stabilized by mixtures of 2 wt.% Ludox HS-30 silica particles with di-C8DMAB (upper) or di-C12DMAB surfactant (lower). Double inversion from o/w to w/o and back to o/w emulsions occurs in both cases (Binks and Rodrigues, 2009); reproduced by the permission of Elsevier.



Figure 68. Water–dodecane emulsions (1:1 by volume) stabilized by 0.25 wt.% CNCs and surfactant (a) CTAB and (b) DMAB with concentrations from 0 to 16 mM (left to right, as indicated). All emulsions with CTAB are oil-in-water, whereas two phase inversions are seen in emulsions with DMAB; from o/w to w/o and back to o/w, with increasing surfactant concentration (Hu et al., 2015); reproduced by the permission of Elsevier.





Figure 69. Optical microscopy image of a water-in-squalane emulsion stabilized by 2 wt%Floraspheres after homogenisation for 30 s at 11,000 rpm. Scale bar = $100 \mu m$. (b) Vessel in (a) 1 min after emulsification; white phase is emulsion with oil and water above and below (Binks and Rocher, 2009); reproduced by the permission of Elsevier.

Figure 69 shows the equilibrium contact angles (at 250 seconds), measured on smooth KCl surfaces, and the resulting emulsion type. Discrepancies could be attributed to the "rough" surface of polished KCl plates, vaporization of hydrocarbons, fluctuations in room temperature, and cleaning of plastic materials for reuse (e.g. caps), just to mention a few ones.

Oil	Amine	Amine Concentration (wt%)	Position of KCl particles (Fig. 44)	KCl Wettability (Figures 40-44)	Contact Angle, degree (Figures 33-35)	Additonal Experiment on Figure(s)	
		1.000	5.b	Stable W/O (i)	104		
	C ₁₂	0.050	3 - 4.b	No Emulsion	78	60	
		0.005	3	No Emulsion	80		
		1.000	5.a	Stable W/O	95		
	C ₁₈	0.050	3 - 4.b	No Emulsion	65	53 and 62	
Carlahaman		0.005	3	No Emulsion	62		
Cyclonexane		1.000	5.a	Stable W/O	140		
	TD	0.050	4.b	Unstable W/O	117	58	
		0.005	3	No Emulsion	80		
		1.000	5.a	Stable W/O	>120		
	HTD	0.050	4.b	Unstable O/W (ii)	81	55	
		0.005	3	No Emulsion	54		
	C ₁₂	1.000	5.a	Stable W/O	95		
		0.050	. 3	No Emulsion	74	59	
		0.005	3 - 4.b	No Emulsion	68		
	C ₁₈	1.000	5.a	Stable W/O	109		
		0.050	5.a	Stable W/O	94	54 and 61	
n de cono		0.005	3	No Emulsion	70		
n-ue cane	TD	1.000	5.a	Stable W/O	>100		
		0.050	5.a	Stable W/O (iii)	90	57	
		0.005	3	No Emulsion	85		
		1.000	5.a	Stable W/O	>100		
	HTD	0.050	5.a	Stable W/O	95	56	
		0.005	5.a	Stable W/O (iv)	95		
		1.000	4.b	Unstable O/W	80		
	C ₁₂	0.050	4.b	Unstable O/W	80	-	
		0.005	1	No Emulsion	45		
	C ₁₈	1.000	5.a - 5.b	Unstable W/O	>100		
		0.050	2	No Emulsion	90	-	
D:		0.005	1	No Emulsion	51		
Dieseron		1.000	5.b	Unstable W/O	>120		
	TD	0.050	2	No Emulsion	70	-	
		0.005	1	No Emulsion	65		
		1.000	5.b	Unstable W/O	>120		
	HTD	0.050	2	No Emulsion	73	52	
		0.005	1	No Emulsion	49		

(i) See Figure 60.k

(ii) See Figure 55.g

(iii) See Figure 57.g

(iv) See Figure 56.g

Figure 70. KCl wettability and sessile drop contact angles.

Figure 70 shows that the stability of the emulsions formed increased significantly when amine was added to the system (see section 2.2.5.1).

On the other hand, Figure 16 illustrates the relation between contact angle and the number of carbon atoms in the hydrocarbon chain. In general, this relation is in agreement with the results in Figure 70; at 1.000 % of amine in oil dodecyl (C_{12}) amine shows the lowest contact angles, while 1.000 % of TD and HTD amines in oil present the highest values. At lower amine concentrations, it is not possible to establish that relation.

The KCl wettability over time during the first seconds immediately after shaking seems to follows particular patterns or *states* (see section 4.3). This project discusses the existence of eight intermediate states that describe sequentially the changes in KCl wettability caused by the long-chain amine adsorption. All these observed patterns were sequentially combined to make an overview of the changes on KCl wettability as a function of the amine concentration and contact angle as well (see Figure 44 for details).

Those patterns makes possible to identify the type of the emulsion (using the final emulsion volume). In this respect, Figure 44 indicates that the creaming layer for O/W and W/O emulsions reported to the organic (oil) and aqueous phases, respectively. The position of the creaming layer in either phase is in agreement with that in Figures 11-12 and 67-68, thereby validating the judgment carried out in this project.

The aforementioned eight intermediate states are discussed as follows.

- The state (1) was observed for solutions of 0.005 % (wt) of amine in Diesel oil. At very low or zero amine concentration, contact angles were as low as those for pure oils (between 40°– 50°), and the energy required to hold a spherical particle at the interface, i.e. the energy of attachment, was very low as well. Inherent hydrophilic KCl particles settled to the bottom, and no emulsion was formed.
- The state (2) was reached for solutions of Diesel oil containing 0.050 % (wt) of amine except for dodecylamine ($-C_{12}$). The strength with which a particle is held at the interface was still low, however, some KCl particles accumulated at the interface while the others settled to the bottom (see Figure 46.g).

- The state (3) was observed for solutions of amine in cyclohexane and n-decane. Immediately after shaking, the creaming layer occupied the total volume (see Figures 47.a). The organic and water phases displaced then that layer from the top and the bottom (as a "sandwich"), respectively, until the final emulsion volume (FEV) was just a few millimeters at the interface. This apparent pattern is shown in Figure 47, i.e. the reduction of the final emulsion volume, as a function of the time immediately after shaking. The energy at this point was enough to hold all KCl particles at the interface without a sediment layer. KCl particles were partially wettable by oil and by saturated brine, and no emulsion was formed (see Figure 47.h).
- The further increasing in the amine concentration leads to the **state** (**4**). KCl particles were preferably wetted by water (see Figure 6), and contact angles were a little smaller than 90°. Immediately after shaking stable oil-in-water (O/W) emulsions were formed. Then, three distinct cases were observed after additional shaking. In the first case [**state** (**4.a**)], those emulsions remained stable over time (see Figure 48.h). The obtained results suggest that this stability occurs in a narrow range of concentrations, and a slight increase in the amine concentration leads either to the second case [**state** (**3**)], instability over time, or to the third case [**state** (**4.b**)], phase inversion from O/W to W/O (see Figure 49.h).

Only solutions of concentrations (wt) between 0.2 % and 0.5 % of TD amine in cyclohexane and of concentration of 0.036 % of HTD amine in Diesel Oil formed stable O/W emulsions over time. It must be pointed out that these emulsions might be used as extenders (see section 2.1) because they are stable within a time of days, and their droplets wet KCl particles in saturated brine.

• At higher amine concentrations, KCl particles were preferably wetted by oil (see Figure 6); water-in-oil (W/O) emulsions were produced at contact angles higher than 90°, typically between 100°-120°, in this project. These W/O emulsions were mostly stable over a wide range of amine concentrations (see Figures 55.h-i, 56.g-i, and 57.g-i) unlike O/W emulsions. The obtained results suggest that this **state (5.a)** corresponds to equilibrium. Figures 33-35 demonstrate that solutions of amine concentration (wt) of 1.000 %, except for dodecylamine in Diesel oil, reached equilibrium contact angles larger than 90° after approximately 50 seconds. These results are in perfect correlation with the phase inversion tests where all those solutions produced stable W/O emulsions, while solutions of dodecylamine in Diesel oil did not form emulsions (see Figure 40.l). For the sake of convenience, Figure 60.k was selected to show emulsions of 1.000 % of C₁₂ amine in cyclohexane. Similar emulsions in Figure 40.e must be handled with care because of the vaporization of the organic phase.

Figures 56.f (for amine concentrations (wt) 1.5%-2.0%) show unstable W/O emulsions in which the creaming layer was constricted from the bottom to interface and "stuck" to the interface. A slight increase in the amine concentration caused the removal of the creaming layer, which finally settled to the bottom (see Figure 51.c at 2.0%) and reached the **state** (5.b). Figure 53.c demonstrates that an increase from 25 °C to 35 °C for solutions of 2.0% of C₁₈ amine in cyclohexane the W/O emulsions were not stable.

Figures 52 and 59 suggest a hypothetical state (6) where W/O emulsions may invert to O/W emulsions, which in turn may invert back to W/O emulsions until equilibrium. The mechanism of double inversion of phases was previously reported by Binks and Rodrigues (2009) and Hu et al. (2015). This mechanism implies that the contact angle curve peaks, reaches a maximum value and then decreases (similar to a parabolic curve) with amine concentration. In this respect, Hu et al. (2015) show that contact angle curves for solutions of CTAB and DMAB follow a parabola that peaks in 70° and 120° , respectively (see Figure 18). The former produced only O/W emulsions, while the latter formed a double inversion of phases. The observation of those curves implies that contact angles for O/W and W/O emulsions are about 70° and 120°, respectively, which is in perfect agreement with the existence of eight intermediate states (see Figure 44). Even though the double inversion of phases is beyond the objectives of this project, it must be pointed out that Figure 2.c shows that contact angle curves can effectively follow a parabola similar to that in Figure 18 (for CTAB solutions) with amine concentration for oil/NaCl-KCl saturated-brine/KCl systems. For C_{12} amine the contact angle curve peaks around 70°, suggesting that the double phase inversion mechanism cannot occur for dodecylamine (reagent grade) solutions. This is in perfect agreement with Binks and Rodrigues (2009). The authors claims that the double inversion of emulsions is not possible when a single-chain cationic surfactant is used.

In this study, such mechanism was observed for solutions of HTD and TD amines (see Figures 52, 56, and 57), suggesting that technical amines may contain surfactants able to produce the double phase inversion of phases. Figure 52 shows that at 0.036 %, a stable O/W emulsion was observed, i.e. point (4.a). At 0.5 %, this phase inverted to a W/O emulsion at 2.0 %, i.e. point (5.a). Finally, at 4.0 %, the second phase inversion back to an O/W emulsion was observed (the hypothetical point (6)).

This observation is supported by the contact angle curve for solutions of HF (C_{18} - C_{22} aliphatic amines) shown in Figure 2.c. This curve peaks in 120° (value for W/O emulsions) and then slightly descends similarly to that in Figure 18 (for DMAB solutions). It is, therefore, important to bear in mind this hypothetical or apparent **state** (6) in the selection of an extender oil for the flotation of coarse potash ore fractions.

5.4.2.1 Wettability analysis in n-decane

The equilibrium contact angles (*across the aqueous phase*) for solutions of concentration (wt) of 1.000 % of C_{12} , C_{18} , TD, and HTD amines in n-decane are 95°, 109°, >100°, and >100°, respectively, (see Figure 70). It is well documented that solids are wettable by oil above 90°. In this respect, the insets in Figure 33 show that the drops of those solutions spread on KCl surfaces after approximately 50 seconds.

Figures 40.h, 41.h, 42.h, and 43.h demonstrate that n-decane containing 1.000 % (wt) of those amines produced stable W/O emulsions in terms of the final emulsion volume (FEV). According to Schulman and Leja (1954), W/O emulsions are formed and stabilized by the solid powder when the contact angle is slightly larger than 90°. These obtained results link, hence, the measured contact angles to the type of emulsion produced, i.e. water-in-oil (W/O) emulsions.

The equilibrium contact angles (θ_{EQ}) for solutions of 0.050 % of C₁₂, C₁₈, TD, and HTD amines in n-decane are 74°, 94°, 90°, and 95°, respectively, (see Figure 70). Solutions of C₁₂ amine did not produce emulsions (see Figure 40.h), which is in agreement with the measured contact angle of 74°. The other solutions produced stable W/O emulsions in accordance with Schulman and Leja's theory (see section 2.3.1).

The θ_{EQ} for solutions of 0.005 % of C₁₂, C₁₈, TD, and HTD amines in n-decane are 68°, 70°, 85°, and 95°, respectively (see Figure 70). Solutions of HTD formed stable W/O emulsions (see Figure 56.g), which is in agreement with the measured contact angle of 95°. The other solutions did not produce emulsions in time in accordance with Schulman and Leja's theory (see section 2.3.1).

Binks and Lumsdon (2000) claim that the energy with which a particle is held at the oil/water interface, i.e. the energy of attachment, is related to its contact angle at the particle/oil/water three-phase line of contact (see Figure 9). It was expected that stable O/W emulsions were produced for contact angles a little smaller than 90° (see section 2.3.1). The obtained results show, nonetheless, that in those cases no emulsions were formed, indicating that the energy of attachment for contact angles lower than 90° was insufficient to hold KCl particles at the interface. This observation suggests that O/W emulsions occur in a quite narrow range of amine concentrations unlike W/O emulsions. The former and the latter represent, hence, a transition state and equilibrium, respectively. For the sake of illustration, Figure 56 shows that solutions between 0.025 % and 2.0 % of HTD amine in n-decane produced stable W/O emulsions, state (5.a), while, a solution at 0.5 % of TD amine in cyclohexane formed a stable O/W emulsion, state (4.a).

5.4.2.2 Wettability analysis in diesel oil solutions

The equilibrium contact angles (θ_{EQ}) for solutions of 1.000 % (wt) of TD and HTD amines in Diesel oil were higher than 120° (see Figure 70) and higher than those for similar solutions in n-decane (θ_{EQ} >100°), indicating that KCl plates were more wettable for those Diesel oil solutions than for similar solutions in n-decane.

Schulman and Leja (1954) claim that for contact angles much higher than 90°, the particles are completely wetted by oil, thus they remain dispersed in the organic phase and unstable emulsions are formed. Koretsky and Kruglyakov (1971), Tambe and Sharma (1993), Binks et al. (2013), and Hu et al. (2015) agree that stable W/O emulsions would be expected for contact angles in the range 95°-115°, validating the correlation between the measured contact angles (>120°) to the unstable (W/O) emulsions produced (see Figures 42.k-l and 43.k-l). Figure 52 shows another solution of 1.000 % of HTD in Diesel oil, which also formed an unstable W/O emulsion.

The contact angle curve for a solution of 1.000 % (wt) of C_{18} amine in Diesel oil shows θ_{EQ} >100° (see Figure 35.d) similarly to those for 1.000 % of amine in n-decane that produced stable W/O emulsions (see section 5.4.2.1). According to the previous discussions, a contact angle higher than 100° but lower than approximately 115° would be expected to produce stable W/O emulsions, and this is in perfect correlation for that solution of 1.000 % (wt) of C_{18} amine in Diesel oil. Figure 41.1 shows that this solution formed an stable O/W emulsion.

The equilibrium contact angles for solutions of 0.050 % and 1.000 % of C_{12} amine in Diesel oil were about 80°. This result supports the observation that O/W and W/O emulsions are transition and equilibrium states. An initially stable O/W emulsion (θ_{EQ} <90°) may remain stable in the state (4.a), become unstable in the state (4.b), or invert to a W/O emulsion in the state (5.a) unlike W/O emulsions that are stable over a wide range of amine concentrations in state (5.a).

Binks and Rodrigues (2009) and Hu et al. (2015) show that stable O/W emulsions occur over a wide range of surfactant concentrations unlike those produced in this project. The observed instability of O/W emulsions may be, therefore, a inherent characteristic of oil/saturated-brine/KCl systems caused by equilibrium phenomena (see section 5.3).

Figure 35 shows that all contact angle curves for solutions of 0.005 % (wt) of amine in Diesel oil are similar to that of Diesel oil without amine, i.e. a smooth straight line at around 45°. For the same solutions, Figure 38 presents that the interfacial tension curves pass the points (0 s,~22 mN/m) and (20 s,~17 mN/m) similarly to that of Diesel oil without amine (Figure 39). In turn, Figures 40.1, 41.1, 42.1, and 43.1 show that Diesel oil solutions containing 0.005 % (wt) of amine did not form emulsions. All these pieces of evidence together suggest that those solutions behave similarly to that of Diesel oil without amine.

5.4.2.3 Wettability analysis in cyclohexane

The equilibrium contact angles (at 250 seconds) for solutions of 1.000 % of C_{12} , C_{18} , TD, and HTD amines in cyclohexane are 104°, 95°, 140°, and >120°, respectively (see Figure 70), explaining why drops of those solutions spread on KCl surfaces (see Figure 34). All their contact angle curves ascend drastically and then reach a plateau within the first seconds. Interestingly, TD and HTD amines produced stable O/W emulsions despite of their contact angles higher than 120° and C_{12} amine produced unstable W/O emulsions in spite of its contact angle between 100-115°. All these discrepancies could be attributed to the vaporization of cyclohexane over time. Figures 40.d, 42.d, and 43.d show the reduction of practically the entire volume of the organic phase (10 mL) for C_{12} , HTD, and TD amines.

The equilibrium contact angles (θ_{EQ}) for solutions of 0.050 % of C₁₂, C₁₈, TD, and HTD amines in n-decane are 78°, 65°, 117°, and 81°, respectively (see Figure 70). As it was earlier discussed, O/W emulsions may invert to stable W/O emulsions. The contact angle of 117° for the solution of C₁₈ amine suggests that additional mixing is required to reach equilibrium. The contact angle of 81° for the solution of HTD amine suggests, however, that the unstable O/W emulsion produced will remain unstable over time (no inversion is expected). The contact of 65° for the solution of C₁₈ amine is in perfect correlation with no production of emulsions (see Figures 41.d). However, additional mixing could lead to an unstable O/W emulsion for that solution (see Figure 62). Finally, Figures 40.d and 60.g demonstrate the link between no emulsion produced and the contact angle of 78° for the solution of C₁₂ amine.

The θ_{EQ} for solutions of 0.005 % of C₁₂, C₁₈, TD, and HTD amines in n-decane are 80°, 62°, 80°, and 54°, respectively (see Figure 70). All these contact angles are in perfect agreement with the resulting oil/saturated-brine mixtures, i.e. emulsions were not produced for those solutions.

5.4.3 Effect of temperature on emulsion stability

As it was mentioned in section 2.1, ambient temperature fluctuations between summer and winter sessions, which in some locations may be within 15 - 35 °C, affect the sylvite flotation results.

Based on the results of this thesis, phase inversion method is applicable as a lab testing procedure for selection of the oils that could be used as the extender oils in potash ore flotation. In this respect, it is not only important to study the phase inversion as a function of the amine concentration but also as a function of the temperature. The first step in the lab testing is to prepare emulsions at varying amine concentration and at constant temperature. Once the particular amine concentration which yields stable oil-in-water emulsions is known, the second step is to prepare emulsions at varying temperatures and at constant amine concentration in order to study what happens to their stability upon increasing gradually the temperature (see Figures 53-54).

For instance, if cyclohexane containing 1.000 % (wt) octadecylamine emulsified in saturated brine at 35 °C is selected for potash ore flotation, then at 10 °C the behavior of this emulsion may be entirely different. It is to be noted that ambient temperature fluctuations between summer and winter sessions, which in some locations may be within 15 - 35 °C, could cause formation of unstable emulsions and affect the sylvite flotation results (see section 2.1)

These results on temperature are in agreement with Binks and Rocher (2009). These authors indicate that phase inversion can be brought about by changing the temperature of the system because of surfactants arrangements at the oil/water interface changes with temperature and may lead to a progressive increase in sedimentation and coalescence.

5.4.4 Effect of amine concentration on emulsion stability

As it was mentioned in section 2.1, as the amine concentration in oil is increased, the contact angle increases as well and therefore, the oil containing amine solutions can wet KCl surfaces. Dai et al. (1992) measured contact angles with the use of the Axissymmetric Drop Technique for amine in oil solutions at different amine concentrations (see Figure 2). Oils tested in their study included Esso 1156 and Esso 2600 oils. The former is a light gas oil of predominantly aromatic hydrocarbons and is of low viscosity, while the latter is a viscous oil consisting of mostly paraffinic hydrocarbons with a high level of polar compounds (Dai et al., 1992).

Figure 71 shows the effect of HTD amine concentration (wt%) on different hydrocarbons (cyclohexane, decane, Diesel oil, Esso #1156 oil and Esso #2600oil) with or without other additives to oil (Dai et al., 1992). These authors concluded that Esso 2600 oil containing $R_{12}NH_2$ and Esso 1156 containing M210 promoter show the poorest wetting ability because of the high viscosity of these oils, and Esso 1156 oil containing silicone oils exhibits good wetting ability. On the other hand, the three oils tested in this thesis (see section 3.1.3) showed lower contact angles than those tested by Dai et al. (1992) at the lowest HTD amine concentrations except for solutions of 0.050 % and 1.000 % of amine in cyclohexane, which exhibited the highest contact angles.



Figure 71. Contact angle as a function of the Armeen HTD concentration. Solid lines correspond to results of this thesis and dashed lines represent those of Dai and Laskowski (1992).
5.5 Selection of the extender oil for the flotation of coarse potash ore fractions

As the main objective of this thesis is to investigate whether the phase inversion method can be used in testing such extender oil(s), their selection criterion will be only mentioned in this section.

For extender oils selection, the emulsion must be:

- Stable within a time of days.
- The droplets must wet KCl particle in saturated brine.

Therefore, in this project it was assumed that the position (4.a) could be the criterion to select extender oils on the wettability point of view (see Figure 70). At this particular state, the creaming layer reaches its maximum height and reported mostly to the organic (oil) phase. According to Figures 52 and 58, solutions of HTD amine in Diesel at concentration (wt) of 0.036 % and between 0.2 %–0.5 % of TD amine in cyclohexane, respectively, produced stable O/W emulsions within a few days. For the other formulations tested, the amine concentration range in which phase inversion takes place was, nevertheless, found (see Table 2). The study of extender oils in the flotation of coarse fractions of potash ore is well documented (Dai et al., 1992; Laskowski and Dai, 1993; Laskowski, 1994; Laskowski and Wang, 1997; Laskowski et al., 1999; Laskowski et al., 2008), just to mention the main ones. Figures 4 and 5 show the effect of dodecylamine ($R_{12}NH_2$) addition on the flotation performance (recovery, %) of Esso 1156 and Esso 2600 oils.

Phase inversion O/W to W/O emulsions			
Oil	Amine	Amine conc. range (wt%)	
Cyclohexane	C ₁₂	0.500-0.750	
	C ₁₈	0.005-0.01	
	TD	0.500-1.000	
	HTD	0.100-0.200	
n-de cane	C ₁₂	0.050-1.000, >1.000	
	C ₁₈	0.005-0.01	
	TD (*)	0.050-1.000	
	HTD	0.005-0.050	
Diesel oil	C ₁₂	>1.000	
	C ₁₈	0.050-1.000	
	TD	0.050-1.000	
	HTD	0.125-0.5, 2.0-4.0	

Table 2. Range of amine concentrations (wt) at which phase inversion may occur for different amine in oil formulations.

Conclusions

- 1. For a few formulations, which contained several different hydrocarbons "oils" (n-decane, cyclohexane, and Diesel oil) and several amines (dodecylamine, octadecylamine, TD amine and HTD amine), the phase inversion method was tested as a way of selecting the formulation(s) that could be utilized as an extender oil in potash flotation.
- 2. The behavior of oil/saturated-brine/KCl systems is influenced by two equilibration phenomena. A "fast equilibrium" resulting from the diffusion of large amine molecules to the interfaces and a "slow equilibrium" caused by dissolution/recrystallization of mostly NaCl fine crystallites onto KCl surfaces in NaCl-KCl saturated brine.
- 3. A quick and reliable lab testing method for selection of the oils that could be used as the extender in potash ore flotation was developed to study changes in KCl wettability when the KCl surface is contacted with the oil-containing amine.
- 4. Fine KCl particles when in brine are vigorously shaken with the oil-containing amine are able to stabilize emulsions. The determination of the type of formed emulsions was not successful with the use of typical techniques. In these difficult cases, the observation of the system behavior and the patterns that the KCl particles follow with time (seconds) immediately after shaking makes possible to identify the type of the emulsion (using the final emulsion volume). At time zero after shaking, the creaming layer occupies the total volume and then constricted. The solutions of amine in Diesel at 0.005 % amine concentration followed this pattern.
- 5. The amine adsorption modifies the KCl wettability, thereby affecting the emulsion stability, which is quantitatively described by the final emulsion volume. Emulsion stability increase with amine concentration.
- 6. Changes in KCl wettability were sequentially described by eight intermediate states. The latter include the phase inversion from oil-in-water (O/W) to water-in-oil (W/O) emulsions and the observed double inversion of phases, which occurs when KCl particles are already hydrophobic, i.e. from W/O back to O/W emulsions. The sessile drop contact angles and amine concentrations for each state are characteristic of the each particular formulation.
- 7. The observed results show that the W/O emulsions represent the equilibrium and are mostly stable over time. Oppositely, O/W emulsions constitute a transition state and are typically unstable in time. The former and the latter were produced in a wide and narrow range of amine concentrations.
- 8. For solutions at concentrations (wt) of 1.0 % or higher of amine in oil, sessile drop contact angle curves ascended dramatically to around 100° within the first 20-50 seconds and then reached a

plateau. Those contact angles are in perfect agreement with the stable W/O emulsions produced for those solutions.

- 9. Particular solutions at concentrations (wt) between 0.2 % 0.5 % of TD amine in cyclohexane and at 0.036 % of HTD amine in Diesel oil produced stable O/W emulsions within a few days. These formulations could be used as extender oil in potash flotation. For the other formulations the range of amine concentrations containing the possible phase inversion point was determined.
- 10. The tested phase inversion method is able to detect the effect of temperature and additional mixing time on the emulsion stability. The temperature leads to the coalescence phenomena, while the additional mixing may cause inversion of O/W to W/O emulsions.

Potash industry in Saskatchewan operates at very high temperatures in the summer time (up to 35 °C) and at varies cold temperature in the winter (down to 10 °C). The emulsions suggested as extender oils must be stable over this temperature range. The technique recommended for selection of the emulsions must, therefore, be able to investigate the effect of temperature.

As this thesis results indicate (see Figures 53-54), the phase inversion method is able to detect the effect of temperature, but this complicated topic should be further studied. The effect of temperature on solubility of KCl and NaCl is very different and for the system consisting KCl plate immersed in saturated KCl-NaCl brine even a small change in temperature causes dissolution/recrystallization at the KCl crystal/brine interface. This must affect the adsorption of amine at such an interface and its wettability.

This Department was able to acquire Krüss Tensiometer – K11 which is a high accuracy piece of equipment which uses the Wilhelmy plate principle to measure surface/interfacial tension. Much of my time at UBC was spent on modification of this equipment so that it could be used to measure contact angle on solid plates. While this was shown to be possible, the limitations imposed by the modified instrument does not allow to fully use it in the contact angle measurements at the brine/oil interface on the KCl surface. It seems, however, that a new Krüss Tensiometer K100 (if it could be acquired) should be good enough to measure under various conditions contact angles on KCl plates. Again, this could be successful only if both the Phase Inversion Method and contact angle measurements could be carried out strictly at the same temperatures.

As in all surface chemistry measurements, the cleanliness of all the pieces used in the tests is an important issue. However, while it is known how to clean glassware and other water-insoluble lab pieces and mineral specimens it is not clear how to clean KCl plates before their use in the lab experiments. The water-based systems cannot be used because of the KCl solubility. In this thesis KCl plates were cleaned following the procedure suggested by the manufacturer which involved polishing of the KCl plates with cerium oxide in ethanol solution. To avoid doubtful cleaning procedures new KCl plates should always be used (whenever possible).

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APPENDIX A: Glassware cleaning method

Nitric acid and ethanol together form an explosive but highly oxidizing atmosphere that cleanses all organics from glassware. Due to the explosion hazard, mix very small amounts.

Procedure:

- 1. Wear full face shield. Either use good gloves or have wet hands and arms and frequently wash them. Work in a properly ventilated fume hood.
- 2. Pour 2-3 mL of HNO₃ into glassware.
- 3. Add 3-5 drops of ethanol.
- 4. Leave to stand until brown fumes have been generated and completely disappear.
- 5. Rinse glassware well with copious distilled water (avoid the use of soap).

Note: In case of accidental spattering, remove contaminated clothing and rinse affected area thoroughly for 10 minutes. Get medical attention if necessary.

APPENDIX B: KCl weight and shaking mechanism on the phase inversion tests

The shaking mechanism are depicted below where: (a) is a KS 4000 IC shaker, (b) is a Lab-Line shaker, and (c) is a vortex mixer. The numbers in the labels show the weight of KCl where, i.e 1 (1.0 g), 2 (2.0 g), 3 (3.0 g), and 4 (4.0 g), respectively.



Figure 72. Resulting emulsions after shaking with the use of (a) a KS 4000 shaker, (b) a Lab-Line shaker, and (c) a hand.

Figure 13 illustrates that the emulsion stability increases with an increase in the concentration of particles in the system (see section 2.2.5.2 for details). The study of the effect of particle concentration on the emulsion stability is, nonetheless, beyond the objectives of this project. Based on Figure 72, a fixed weight of 1.0 g of fine KCl of about 1 micron (see Appendix E) is used for all the phase inversion tests.

Figure 72 also indicates that a vortex mixer (see Figure 30) is used for the shaking of oil/saturated-brine mixtures.

APPENDIX C: Physical properties of the fluids

The physical properties of the fluids used in this project are tabulated below.

Reagent	Density, ρ	SFT, yao
	(g/cm^3)	(mN/m)
Brine	1.230 ± 0.001	82.57±0.60
Cyclohexane	0.773 ± 0.001	24.87±0.10
Decane	0.724 ± 0.001	23.00±0.03
Diesel	0.826 ± 0.001	23.80±0.32

Table 3. Densities, ρ , and interfacial tensions, γ , of the fluids.

APPENDIX D: Krüss K11 surface tension measurement

Surface tension measurement using the Wilhelmy plate technique (with platinum plate) as reported by the supplier was as follows:

- 1. Clean the measuring probe and place it in the measuring probe holder on the force sensor.
- 2. Lower the sample stage and put 10 ml of oil into the sample vessel.
- 3. Place the sample vessel on the sample stage.
- 4. Position the temperature sensor so that it immerses in the liquid.
- 5. Raise the sample stage so that the surface of the liquid is just below the measuring probe.
- 6. Wait until the required temperature has been reached.
- 7. Start the measurement.

At the air/oil interface, surface tension was measured with the use of a KRÜSS K11 tensiometer as shown in Figure 73. The oil/saturated-brine interfacial tension measurements followed similar experimental procedure but with the addition of oil during the experimental run so that the platinum plate was completely immersed in oil.



Figure 73. Methodology for the surface tension measurement at the air/oil interface with the use of the Wilhelmy plate technique.

At least three measurements were taken for every surface tension (SFT), γ_{AO} , and the standard deviation was calculated, as well. The results are given in Appendix C. The reproducibility in terms of standard deviation was very good, and did not exceed ±0.60 mN/m for all tested samples (see Table 3).

APPENDIX E: Particle size distribution

The particle size distribution for ground KCl particles is shown in Figure 74. The particle size analysis using cyclohexane as solvent.



Figure 74. KCI particle size distribution.