ASH FLOTATION OF DISPERSED OIL DROPLETS - A MODEL SYSTEM FOR BITUMEN FLOTATION FROM TAR SAND

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ASH FLOTATION OF DISPERSED OIL DROPLETS - A MODEL SYSTEM 
FOR BITUMEN FLOTATION FROM TAR SAND

by

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I have read the thesis of Dariusz Lelinski in its final form and have found that (1) its format, citations and bibliographic style are consistent and acceptable; (2) its illustrative materials including figures, tables and charts are in place; and (3) the final manuscript is satisfactory to the supervisory committee and is ready for submission to The Graduate School.

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The recovery of bitumen from tar sand tailings is an important problem that must be solved in order to achieve both economic and environmental benefits. Some bitumen is lost to the tailings as a fine dispersion of bitumen droplets which should be recovered. The recovery of such bitumen droplets from tar sand tailings is, though somewhat complex, a typical example of the general problem of oil separation from water. Air sparged hydrocyclone (ASH) flotation is a promising technology for the recovery of such bitumen. The high capacity, directed fluid flow, and small air bubbles are characteristic of the ASH technology and make it an interesting process alternative.

In order to begin to evaluate the potential of ASH flotation in tar sand processing a simple system containing only dispersed oil, without solids, was examined with respect to both surface chemistry considerations and ASH operation. Two fundamental surface chemistry aspects of the problem were considered:

1. the necessary conditions, with respect to surfactant concentration (sodium dodecyl sulfate, SDS), for oil filming at the air bubble surface; and;
2. the emulsion stability, which was determined by the kinetics of gravity separation of the oil droplets, and correlated with the zeta potential and size distribution of the dispersed oil.
Of particular significance in this phase of the thesis research was the demonstration for the first time that the spreading coefficient for oil at the air/water interface goes through a maximum with respect to the SDS concentration and that both the extent and rate of oil filming is greatest under these conditions. The dispersed oil was floated in the ASH and the effects of additives and flow conditions on the separation efficiency were studied.

Oil recovery from ASH flotation was found to be dependent on the surface chemistry and a maximum in separation efficiency was observed at the best conditions for air bubble filming by oil and at conditions for which the dispersed oil is at its isoelectric point. The appropriate operating conditions for the ASH flotation system were found to be dependent upon the desired quality of the underflow water.
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CHAPTER I

1. INTRODUCTION

1.1 Oil-Water Separation

Advanced oil-water separation techniques have been gaining increasing attention due to more stringent requirements for the treatment of oil polluted water streams. Oil-water emulsions/dispersions are found in water from many sources such as petroleum refineries, washrack and hangar waste water, rolling mills, and chemical processing and manufacturing plants. In some cases the treatment of large amounts of oily water at a high processing rate is required (e.g., ballast and bilge water on ships, washing in shipyards, cooling water from power plants or steel works). In the case of an accidental oil spill, large amounts of water containing bulk and/or dispersed oil must be processed. Many commercial techniques and devices are being developed and marketed for removal of oil from water. However, a simple, economical, and efficient method to treat oil-in-water dispersion with a wide range of droplet size is not yet available. Although methods involving bed separators (coalescers, filters) can be used to produce a clean effluent, their processing capacity per unit volume (i.e., specific capacity) limits their application.

Gravity settlers and plate separators are usually the most
suitable for handling voluminous streams, but they are not easily portable because of their size and weight. The other disadvantage of these techniques is the requirement of a considerably long retention time for separation to occur.\(^{(3)}\) Hydrocyclones have been considered as a possible alternative to gravity and plate separators\(^{(4,5)}\); however, up until now conventional hydrocyclones are used only in the preliminary cleaning stage, because their performance does not meet discharge water quality requirements. Air flotation is widely used to treat oil-bearing effluents from a wide variety of sources.\(^{(6,7)}\) The biggest disadvantage of the conventional flotation technique is the large size of the equipment and small throughput compared to hydrocyclones.

In the last decade, the air-sparged hydrocyclone (ASH) has been found effective for fast flotation of solid particles.\(^{(8)}\) In the present work the application of the ASH has been extended for processing of oil-in-water emulsions. The de-oiling capacity using the ASH was already examined in two early papers.\(^{(9,10)}\) The preliminary results were encouraging, so much so as to warrant further investigation of the surface chemistry and flow conditions, in order to improve the efficiency of oil separation.

1.2 Tar Sand Processing

Bitumen recovery from tar sands by water-based above-ground processing is a type of oil-water separation which is
accomplished in two main stages: digestion and subsequent phase separation.\(^{(11-13)}\) Although digestion requires only 25-30 wt\% of the aqueous phase, the separation stage is carried out with a diluted tar sand suspension to enhance bitumen removal from the slurry. The volume of the tar sand slurry (20 wt\% solids) increases several times with respect to that during digestion which results in increased processing and equipment costs. Thus tar sand processing typifies the separation of heavy hydrocarbons/bitumen droplets from a water emulsion. Two approaches have been adopted for bitumen separation from digested tar sand slurry:

1. In one case, bitumen separation is conducted in a gravity settler followed by flotation of middlings and rejection of coarse sand to the tailings pond, as practiced in both commercial plants in Alberta, Canada. This processing strategy allows a large volume of tailings slurry to be removed immediately after gravity separation.

2. In the second case, bitumen separation is conducted in a gravity cell followed by flotation of the entire tar sand slurry, as proposed for processing of Utah tar sands, in order to maximize bitumen recovery to the concentrate and minimize the loss of bitumen and diluent (if used) with the spent sand.

In order to make the gravity separation successful it has to be assured that bitumen is displaced from the sand grains, forms relatively large droplets, and is of sufficiently lower density than that of the aqueous phase. The latter condition being satisfied by diluent application or air entrapment.

Laboratory experimental results pertaining to U.S. tar
sands\textsuperscript{(13)} indicated that tailings from the gravity cell usually contain more than 1% bitumen. If this bitumen is disposed with the spent sand, the bitumen recovery to the concentrate will remain well below 90% for a lean tar sand (\(< 8\, \text{wt\% bitumen}\)). Water-based processing of tar sands at a moderate temperature (50$^\circ$C) requires addition of diluent prior to digestion.\textsuperscript{(14)} The diluent addition which is in the range of 5 to 30 wt\% (based on bitumen content) may also be lost with bitumen in the tailings.

The hot water extraction process practiced at both commercial plants in Canada (Suncor 110\cdot10^3\, \text{tpd},\textsuperscript{(15)} Syncrude 288\cdot10^3\, \text{tpd}\textsuperscript{(15)}) is usually over 90\% efficient, depending on ore grade. Thus, a considerable amount of unextracted bitumen is discharged into various tailings streams (including unrecovered naphtha used in the extraction of bitumen from the froth).\textsuperscript{(15)} At Syncrude, 0.3 to 0.5 wt\% of the tailings stream is bitumen, over half of which forms bitumen mats upon discharge into the tailings pond. About 10 to 15\% of the bitumen gets trapped in the tailings sand and about 25 to 30\% is dispersed throughout the sludge. The bitumen content in the sludge ranges from 1 to 5 wt\% depending on depth (amount increases with depth). The total amount of unrecovered bitumen, circa 1987, amounted to 7.4\cdot10^6\, \text{t}, 3\cdot10^6\, \text{t} of which was in the pond sand and sludge.\textsuperscript{(16)} Data from a 1979 survey showed the pond sludge contained 4 wt\% bitumen on the average.\textsuperscript{(17)}

Flotation of the digested tar sand slurry, directly
following digestion or preceded by a gravity separation, can reduce the bitumen content in the tailings sand to as little as 0.2% bitumen. However, high investment and operating costs can be expected for conventional flotation devices, due to the amount of processed tar sand slurry. In this regard, the high specific capacity of air-sparged hydrocyclone flotation should exhibit a distinct advantage in scavenging tar sand tailings. Aeration under turbulent shear conditions, as developed in the ASH, should benefit the separation process by disrupting relatively weak mineral-bitumen interactions, according to Hall and Tollefson.

Appreciable effort has been directed to scavenging Athabasca tar sand tailings to recover residual bitumen. Common physical processes that can be used to aid in tailings treatment include filtration, centrifugation, cycloning, and evaporation to separate liquid from solid. One of the simplest proposals for the recovery of residual bitumen is to dilute recovered pond sludge to between 6 and 18% solids, and then allow it to settle for up to 100 hours. Bitumen is recovered as a froth. The middlings fraction (less than 6 to 18% solids) is sent to the retention pond, and sludge (greater than 6 to 18% solids) can be removed for further dewatering. Ashton and Davitt patented a method for recovering residual bitumen from tailings pond in-situ. Pond sludge is pumped to the top of a closed vessel standing in the tailings pond. Bitumen floats to the top where it can be recovered while
sludge flows out through holes near the bottom of the vessel. Bitumen recovery is increased because of agitation of the sludge as it is pumped up to the surface.

There are several patents\(^{(21-29,31)}\) describing various aeration or agitation techniques for recovering bitumen from tailings. Some of these techniques are already in use in some areas. Any form of turbulent shearing motion, whether from tumbling, mixing, aeration, or combinations of these, is useful in dispersing bitumen and bitumen-mineral agglomerates so that the bitumen can rise to the surface as a froth.\(^{(20,23)}\) The recovered froth can be sent to the regular froth treatment plant. An example of a typical aeration/agitation process is outlined in a series of patents by Davitt.\(^{(24-28)}\) In the basic process, pond sludge is simultaneously agitated and aerated and the froth layer that forms is collected and settled in a settling tank. The upper layer that forms in the settling tank is then sent for bitumen recovery. Davitt recovered about half of the residual bitumen using 22 wt% solids pond sludge containing 3 wt% bitumen. The upper layer sent for bitumen recovery contained 40 wt% bitumen, 11.7 wt% solids, and 41.3 wt% water.\(^{(26)}\)

Suncor has used Davitt's patents\(^{(24-28)}\) as the basis for a process to recover bitumen from pond sludge. In this process sludge is pumped from the tailings pond to a mixing tank where the sludge is diluted to 15% solids and then sparged with compressed air. This aeration displaces \(\text{CO}_2\) from solution and
hence increases the pH of the solution from 6.8 to 8.0. The dilute, aerated sludge is sent from the mixing tank through a series of rougher, scavenger, and cleaner flotation tanks to recover the bitumen froth. The froth is sent through an Oleophilic Sieve and the recovered bitumen is then transferred to the centrifugation circuit of the regular froth treatment process. This process recovered about 70% of bitumen from a sludge that originally contained about 6 to 7% bitumen. Half the water used for dilution of the sludge was recovered after 60 days of settling and nearly all was recovered after 6 months.

Baillie and Malmberg(29) patented a process in which chemically flocculated pond sludge was centrifuged to recover usable water for recycle. Flocculation by itself did not work and centrifugation without flocculation took too long. This method removed 37 to 87% of total solids from a 7.1% solids suspension. The efficiency depended upon the extent and speed of the centrifugation. Corti et al.(30,31) emphasized that it was necessary to pretreat the sludge with appropriate conditioners (based on the sludge composition) to destabilize emulsions present. This provided a homogenous feed to the centrifuge and optimized the efficiency of separation. However, this system was designed for smaller oil operations, not the oil sand mines.(30)

ASH flotation may prove to be another viable separation technology for recovery of residual hydrocarbons from tar sand
tailings. The high shear field and small air bubbles produced inside the ASH as well as its high capacity should provide favorable separation conditions if the surface chemistry can be controlled.

1.3 ASH Flotation Technology

Separation and concentration of fine particles by froth flotation is an important unit operation in many industries. The froth flotation separation is generally accomplished in a gravitational field and is not particularly effective for the recovery of fine particles. This poor flotation response results from the low inertia of fine particles. Particle penetration of the bubble film is inhibited, and hence the rate of attachment is low. Further, in conventional flotation, nominal retention times on the order of several minutes are required. The bubble/particle attachment time is frequently on the order of milliseconds, which indicates that the rate of flotation is mostly limited by bubble/particle collision and/or transport. Consideration of these two aspects of conventional flotation technology - limited fine particle recovery and relatively slow flotation rates - led to the concept of air-sparged hydrocyclone flotation. The design was envisioned to establish a controlled high force field by swirl flow in order to increase the inertia of fine particles and to produce a high density of fine air bubbles with a directed motion in order to improve collision
efficiency. The net result is effective fine particle flotation with a flotation rate having retention times which approach intrinsic bubble attachment times. This corresponds to a capacity on the order of 3-20 tpd/m³ of the cyclone volume, at least 100-300 times the capacity of a conventional mechanical or column flotation cell.

In air-sparged hydrocyclone flotation, the slurry is fed tangentially through a conventional cyclone header into a porous tube to develop a swirl flow of a certain thickness in the radial direction (called the swirl-layer thickness). The flow is then discharged through the annular opening created between the tube wall and a froth pedestal which is located on the cylindrical axis at the bottom of the ASH, as shown in Figure 1. Air is sparged through the jacketed porous tube wall and is sheared into numerous small bubbles by the high-velocity swirl flow of the slurry. Hydrophobic particles in the slurry collide with these bubbles, and, after attachment, are transported radially into a froth phase which forms on the cylindrical axis. The froth phase is supported and constrained by the froth pedestal and thus moves towards the vortex finder of the cyclone header, being discharged as an overflow product. Hydrophilic particles generally remain in the slurry phase and are discharged as an underflow product through the annulus between the porous tube wall and the froth pedestal. This preferred design is a result of more than a decade of both fundamental and applied research at the
Figure 1 Schematic of the air-sparged hydrocyclone (ASH)
University of Utah.

With the development of the ASH technology, it has been shown that a high specific capacity not only for the flotation of fine particles but also for intermediate-size particles (60 to 300 μm) is possible. Research at the University of Utah has proved the efficiency of ASH flotation for copper porphyry ore flotation,\(^{(33-35,38)}\) low-grade placer gold and sulfide mineral flotation,\(^{(8,35,36,38)}\) fine coal cleaning,\(^{(8,34,35,37,38)}\) industrial mineral flotation,\(^{(8,38)}\) etc. In these test campaigns, the air-sparged hydrocyclone provided separation efficiencies equivalent to or better than those achieved in conventional flotation.

One of the promising applications has been found to be the use of the ASH for fine coal flotation. As a result of this pioneering research, the effectiveness of the ASH for fine coal flotation has been demonstrated for a number of U.S. and Canadian coals, and plant-site evaluation of large-diameter units is in progress. Testing the first 15-inch air-sparged hydrocyclone (ASH-15C) began in October 1992 at the Homer City Coal Preparation Plant and preliminary results indicate that effective separations will be possible for fine coal cleaning.\(^{(39)}\)

Also during the last few years, attention has been given to applications of air-sparged hydrocyclone flotation technology outside the mineral industry, including the pulp and paper industry and food industry. The most significant
development, however, was the construction in 1991 of a wastepaper recycling pulp mill which uses air-sparged hydrocyclone technology for deinking flotation. The plant, which began operation in June 1992, employs a 3 stage flotation system using twenty 6-inch ASH units to produce 120 ATD/day of recycled market pulp.\(^{(40)}\)

The high processing capacity of the ASH is due to the extremely short retention time, less than one second in a 2-inch system. In this way, optimal control of all the design and operating variables is essential for effective flotation. When compared to conventional flotation, ASH flotation requires a greater degree of control and the flotation performance of the ASH system drops significantly if the levels of the process variables are displaced from optimum conditions.\(^{(38)}\) It is advised that only minus 100 mesh fines should be used for the 2-inch ASH flotation testing due to the strong centrifugal force developed in the 2-inch ASH system. This top size limit can be increased to about 48 mesh when a 6-inch ASH system is utilized. With a 15-inch ASH system, it is anticipated that even coarser feed material can be processed.

1.4 Research Objective

The recovery of bitumen from tailings by ASH flotation is a process which deals with a complex aqueous dispersion of oil and sand, aerated in a high shear field. A simpler system,
which contained dispersed oil (without solids) in water was selected for study for the initial studies. Therefore this research pertains to the surface chemistry and separation technology for oil-in-water emulsions. Two fundamental aspects of the surface chemistry problem are considered:

1. the necessary conditions for oil filming at an air bubble surface, and
2. the stability of the emulsion, as determined by the kinetics of gravity sedimentation, and correlated with both the zeta potential and the droplet size distribution of the oil dispersion.

Finally, ASH flotation of the dispersed oil droplets was studied as a function of additives and operating variables. The results from the surface chemistry study were used to establish conditions for improved separation efficiency.
CHAPTER II

SURFACE CHEMISTRY

Two fundamental surface chemistry aspects of oil flotation were examined before the ASH flotation experiments were initiated. First, the necessary conditions for oil filming at the air-bubble surface were established. Second, the stability of the emulsion was thoroughly investigated.

2.1 Air Bubble Filming by Oil

The encapsulation (or filming) of an air bubble by oil is basically equivalent to spreading phenomenon which can occur at any interface.\(^{(41)}\) Accordingly, the difference between the specific interfacial free energy \(\gamma_{aw}\) of the disappearing interface and the sum \(\gamma_{ow} + \gamma_{ao}\) of the specific interfacial free energies of the spreading phase and the newly formed interface is called the spreading coefficient, \(S\), and this must be positive for spontaneous encapsulation.\(^{(42b)}\)

\[
S = \gamma_{aw} - (\gamma_{ow} + \gamma_{ao}) \tag{1}
\]

Also the spreading process corresponds to the difference between the specific work of adhesion

\[
W_a = \gamma_{aw} + \gamma_{ao} - \gamma_{ow} \tag{2}
\]

and the specific work of cohesion
Consequently, the film formation pressure active in encapsulation of a gas bubble is equal to the difference between \( W_a \) and \( W_c \) and is given by

\[
W_c - 2 \gamma_{ao} \tag{3}
\]

In their study Leja and Bowman\(^{(43)}\) proposed two conditions for oil droplet/air bubble interaction. The first condition, in order for attachment to occur, the following inequality must be satisfied.

\[
\gamma_{aw} + \gamma_{ov} > \gamma_{ao} \tag{5}
\]

This inequality is identical with the description for the conditions for spreading (compare Equation 1).\(^{(42b)}\) However, despite favorable interfacial tensions for a particular system, attachment between the oil droplets and air bubbles may not occur, because of repulsive electrical, long range forces.

In this regard such phenomena play an important role in
the hot water processing of tar sands. First, air bubbles are entrapped in bitumen during digestion enabling recovery of a bitumen concentrate by gravity separation. Second, air is used for the flotation of fine bitumen droplets and bitumen-sand aggregates from liberated sand particles in the tailings. In order to avoid disturbances in process water recycle, and keep the process cost as low as possible, frothers, in general, are not used because surfactants are released from the bitumen during digestion.

Bitumen droplets in a successfully digested tar sand slurry exhibit a broad size distribution with droplets from a few micrometers to 1 mm in size. Large bitumen droplets can be rapidly separated in a gravity cell assuming that they contain a sufficient amount of entrapped air. Fine bitumen droplets and bitumen-sand aggregates are either caught in the fast settling tailings or form the middlings layer, which require flotation for fast and complete recovery. Flotation of negatively charged mineral particles competes with the flotation of negatively charged bitumen droplets resulting in an inferior flotation concentrate quality, when compared to gravity separation. In this regard, efficient separation of small bitumen droplets from sand is expected to be strongly influenced by the sand size distribution.

With respect to the flotation step in hot-water tar sand processing, it has been established that large bitumen drops report to the concentrate due to an air bubble entrapment
mechanism.$^{45}$ The same has been found to be true for separation in a gravity settler. Bubble entrapment can take place only if bitumen droplets are considerably larger than the air bubbles. The encapsulation of air bubbles by bitumen droplets below 0.5 mm still can occur by attachment and filming. The same mechanism generally holds for oil recovery from any oil/water emulsion by flotation.

2.1.1 Experimental Techniques

In order to find the most favorable conditions for air bubble filming by oil, the three interfacial tensions indicated above were determined at different sodium dodecyl sulphate (SDS) concentrations, ranging from 0.3 mg/dm$^3$ ($10^{-6}$M) to 3 g/dm$^3$ ($10^{-2}$M). Several pure hydrocarbons (n-heptane, n-decane, n-dodecane, n-tetradecane, and n-hexadecane) and a bitumen-kerosene blend (two different bitumen/kerosene weight ratios) were used in these experiments. Bitumen was obtained from the gravity concentrate recovered during the Whit-erocks (West-Central deposit) tar sand hot water process. Sand and water present in the gravity concentrate were removed by dilution with kerosene and sedimentation. The bitumen/kerosene blends used in this thesis research contained 0.2% solids and 0.5% water. A detailed description of the concentrate cleaning process as well as solid and water content measurements can be found in reference [46]. The list of suppliers and the grades of chemicals used in the present study are presented in Table
1. The measurements were carried out using the du Noüy ring method, with a Krüss semiautomatic tensiometer, type K10T. The du Noüy ring method is suitable for the surface tension measurements of pure liquids but has not been recommended for solutions of surfactants.\textsuperscript{(47,48)} The adsorption of surfactants from solution may alter the requirement for complete wettability of the platinum ring and lead to low surface tension values. For example, surface tensions of up to 10 mN/m lower can be obtained for sodium laurate solutions at pH=11 after an extended period of time.\textsuperscript{(49)} Nevertheless, the platinum ring technique is acceptable for applied research bearing in mind this possible systematic error.\textsuperscript{(50,51)} It is

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Supplier</th>
<th>Grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-hexane</td>
<td>Sigma Chemical Co.</td>
<td>99%</td>
</tr>
<tr>
<td>n-heptane</td>
<td>Sigma Chemical Co.</td>
<td>99%</td>
</tr>
<tr>
<td>n-decane</td>
<td>Sigma Chemical Co.</td>
<td>99%</td>
</tr>
<tr>
<td>n-dodecane</td>
<td>Sigma Chemical Co.</td>
<td>99%</td>
</tr>
<tr>
<td>n-tetradecane</td>
<td>Sigma Chemical Co.</td>
<td>99%</td>
</tr>
<tr>
<td>n-hexadecane</td>
<td>Sigma Chemical Co.</td>
<td>99%</td>
</tr>
<tr>
<td>sodium dodecyl sulfate</td>
<td>Sigma Chemical Co.</td>
<td>99%</td>
</tr>
<tr>
<td>PERCOL 592</td>
<td>Allied Colloids Inc.</td>
<td>95%*</td>
</tr>
<tr>
<td>sodium chloride</td>
<td>EM Science</td>
<td>technical</td>
</tr>
<tr>
<td>carbon</td>
<td>EM Science</td>
<td>analytical</td>
</tr>
<tr>
<td>tetrachloride</td>
<td>Aldrich Chemicals</td>
<td>99.9% +</td>
</tr>
<tr>
<td>toluene</td>
<td>EM Science</td>
<td>rectification</td>
</tr>
<tr>
<td>acetone</td>
<td>EM Science</td>
<td>spectroscopic</td>
</tr>
<tr>
<td>methanol</td>
<td>EM Science</td>
<td>analytical</td>
</tr>
<tr>
<td>kerosene</td>
<td>gas station</td>
<td>spectroscopic</td>
</tr>
<tr>
<td>bitumen</td>
<td>hot water process**</td>
<td>commercial</td>
</tr>
</tbody>
</table>

*based on total alkyl sulfate content
**produced from Whiterocks tar sand as explained in the text
estimated that the error associated with the data collected for SDS concentrations greater than 30 mg/dm$^3$ ($10^{-4}$M) was ±15%. The relative error for an SDS concentration of 3 mg/dm$^3$ ($10^{-5}$M) is reported to be ±5%.$^{48}$

The bubble filming conditions were estimated and verified experimentally using a Questar 100 long distance microscope coupled with a video camera (SONY RSC-1050). Oil droplets and air bubbles were generated in water (containing varying amounts of SDS) by means of automated microsyringes, and the drainage time needed for the oil droplet to film the bubble was measured. Another simpler technique for the examination of bubble filming by oil involved generation of oil droplets in SDS solution with a syringe. Oil drops were formed at the end of the needle and after an aging period the drops were detached. The distance from the tip of the needle to the surface was kept constant. The drainage times of drops at the interface were determined using a stop-watch (measured as the time elapsed between arrival of a drop at the surface and its coalescence). A minimum of 30 droplets were measured in each experiment. All interfacial tension and filming measurements were carried out at 22°C.

2.1.2 Results and Discussion

2.1.2.1 Oil, Bitumen, and Water Surface Tension

Adsorption of surfactant on the du Noüy ring alters the results of the aqueous phase surface tension and the oil-water
(o/w) interfacial tension.\(^{(47)}\) Additionally, it is known that the equilibrium surface (or interfacial) tension depends upon the surfactant concentration. The time effect extends for more than 10 hr, is most pronounced for dilute solutions (below 3 g/dm\(^3\)), and diminishes markedly for larger concentrations.\(^{(52)}\)

The effect reflects the tendency of the interface to reach equilibrium. In order to make the data reproducible, all the surface and interfacial tension measurements were taken after 30 min of contact time between phases with the platinum ring submerged in the aqueous phase from the very beginning of the experiment. The surface tensions of all liquid phases used in this investigation are presented in Table 2. The experimental

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Surface tension of pure hydrocarbons, bitumen in kerosene blend, and SDS solution in water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>Surface Tension, mN/m</td>
</tr>
<tr>
<td></td>
<td>Measured; 22°C</td>
</tr>
<tr>
<td></td>
<td>Literature; 20°C</td>
</tr>
<tr>
<td>n-heptane</td>
<td>20.9</td>
</tr>
<tr>
<td>n-decane</td>
<td>24.5</td>
</tr>
<tr>
<td>n-dodecane</td>
<td>26.0</td>
</tr>
<tr>
<td>n-tetradecane</td>
<td>27.4</td>
</tr>
<tr>
<td>n-hexadecane</td>
<td>28.8</td>
</tr>
<tr>
<td>kerosene</td>
<td>27.5</td>
</tr>
<tr>
<td>Bitumen solution in kerosene</td>
<td>- 20 wt% bitumen 25.3</td>
</tr>
<tr>
<td></td>
<td>- 40 wt% bitumen 25.6</td>
</tr>
<tr>
<td>C(<em>{12})H(</em>{24})SO(_3)Na solution in water</td>
<td>- 0.3 mg/dm(^3) (10(^{-6})M) 72.1</td>
</tr>
<tr>
<td></td>
<td>- 3 mg/dm(^3) (10(^{-5})M) 71.4</td>
</tr>
<tr>
<td></td>
<td>- 15 mg/dm(^3) (5(^{\cdot})10(^{-5})M) 67.8</td>
</tr>
<tr>
<td></td>
<td>- 30 mg/dm(^3) (10(^{-4})M) 56.1</td>
</tr>
<tr>
<td></td>
<td>- 150 mg/dm(^3) (5(^{\cdot})10(^{-4})M) 44.3</td>
</tr>
<tr>
<td></td>
<td>- 300 mg/dm(^3) (10(^{-3})M) 36.9</td>
</tr>
<tr>
<td></td>
<td>- 3 g/dm(^3) (10(^{-2})M) 34.9</td>
</tr>
<tr>
<td></td>
<td>72.94(^{(42a)})</td>
</tr>
<tr>
<td></td>
<td>20.14(^{(42a)})</td>
</tr>
</tbody>
</table>
data determined with the platinum ring technique corresponds well with the surface tension values available from literature.

2.1.2.2 Oil (Bitumen)-Water Interfacial Tension

Two different approaches were used to determine the o/w interfacial tension variation with time. In the first series of measurements the surfactant solution was equilibrated for a given time with hexadecane and transferred to the tensiometer cell. Next, the ring was submerged in the aqueous phase, the oil was poured on the top, and the measurement was completed after a 30 min time interval (curve (1); Figure 2). The other approach involved equilibration of the oil and surfactant solution in the tensiometer cell. As can be seen in Figure 2, the interfacial tension for the 15 mg/dm$^3$ ($5 \cdot 10^{-5}$M) SDS solution/hexadecane system decreased steadily with time for both oil/water equilibration techniques. Nevertheless, equilibration carried on outside the cell (this procedure involved frequent shaking of the separatory funnel containing both liquids) resulted in a 5 mN/m higher interface tension. Lower interfacial tensions indicated by curve (2) most probably resulted from more extensive surfactant adsorption on the platinum ring. Based on these results, the experimental technique represented by curve (1) was adopted.

The o/w interfacial tensions for pure hydrocarbons (hexane, decane, dodecane and hexadecane) are compared to the
Figure 2 Variations of interfacial tension of aqueous SDS solution (15 mg/dm$^3$) with time for two oil-water equilibration techniques. 
1 - surfactant solution equilibrated for a given time with hexadecane outside the tensiometer cell; 
2 - equilibration of hexadecane and surfactant solution in the cell with platinum ring immersed in the aqueous phase
data reported by other researchers in Figures 3 to 6. Test results obtained in this investigation can almost be superimposed on the data of Gillap et al.\(^{(55,56)}\) who employed the Wilhelmy plate method but the aqueous phase contained 0.1 M NaCl. However, a significant difference can be noticed with respect to the results of Davis and Smith (Wilhelmy plate)\(^{(57)}\) and Rehfeld (drop-volume method)\(^{(58)}\) who used special techniques for equipment preparation and materials purification, especially for the surfactant. It is expected that impurities, small variations in composition, are the main reason for these differences. However in analyzing test results one should bear in mind their intended application. In this work calculated spreading coefficient values will be used for the prediction of flotation pilot plant results and consequently the kind of purification as employed by Davis and Smith,\(^{(57)}\) and Rehfeld\(^{(58)}\) is not warranted. Of course, this same surfactant solution and oil phase were used for all laboratory and pilot plant experiments. Another factor that allows us to use the interfacial tension values of the study to explain the ASH flotation response is that identical procedures were employed for all surface and interfacial tension experiments. Identical errors (if they were made for surface and interfacial tension measurements) cancel out each other during calculation of the spreading coefficient. In this way the final results were associated with a smaller error.

The interfacial tension curves for several pure
Figure 3  
*n*-hexane/water interfacial tension vs. SDS concentration
Figure 4 n-decane/water interfacial tension vs. SDS concentration
Figure 5 n-dodecane/water interfacial tension vs. SDS concentration
This study

Figure 6 n-hexadecane/water interfacial tension vs. SDS concentration

n-Hexadecane

Interfacial Tension [mN/m]

SDS Concentration [mg/dm3]
hydrocarbons are compared in Figure 7. All these hydrocarbons exhibit a similar interfacial tension change with increasing concentration of the surfactant.

The interfacial tensions for kerosene and for the kerosene-tar sand bitumen blend are shown in Figure 8. The kerosene interfacial tension curve is distinctly different from the curves for pure hydrocarbons as is the kerosene/bitumen curve.

2.1.2.3 Spreading Coefficient

The spreading coefficient was calculated from Equation 1. The surface tension of water (with and without SDS) and interfacial tension of o/w (with and without SDS) were taken from experimental results. The surface tension of oil was assumed to be the same for all values of the surfactant concentration. This assumption may be questioned. The surfactants from the water phase could influence the surface tension of oil, despite the fact, that they are not soluble in oil and should not be present at the air/oil interface. A simple experiment was performed to validate this assumption. Hexadecane and water (with different SDS concentrations: 0 mg/dm³, 3 mg/dm³, 30 mg/dm³, 300 mg/dm³, 3 g/dm³) were vigorously shaken for 10 min and equilibrated for 7 days. The hexadecane phase was then separated in a separatory funnel and the surface tension was measured. All measured surface tension values were found to be identical (within the experimental
Figure 7  Pure hydrocarbons/water interfacial tension vs. SDS concentration
Figure 8 Kerosene and bitumen in kerosene blend/water interfacial tension vs. SDS concentration
error), indicating that there was no change in hexadecane surface tension with surfactant concentration in the aqueous phase.

The spreading coefficients were calculated according to Equation 1 and are plotted vs. SDS concentration in Figures 9 and 10. In the case of pure hydrocarbons and kerosene the spreading coefficient reaches a maximum between 15 mg/dm³ (5·10⁻⁵M) and 30 mg/dm³ (10⁻⁴M) SDS concentration. Hexadecane can be distinguished from the other oils because the spreading coefficient is negative at 0.3 mg/dm³ (10⁻⁶M), and even more negative at 300 mg/dm³ (10⁻³M). The most distinct maximum is for kerosene at 28 mN/m.

The maximum for the spreading coefficient vs. SDS concentration function can be discussed in terms of the rates of decrease of \( \gamma_{a/w} \) and \( \gamma_{o/w} \) with respect to the surfactant concentration. Refer to Equation 1. The surface tension of oil \( (\gamma_{a/o}) \) is constant, therefore the spreading coefficient depends only on the change of the surface tension of the aqueous phase \( (\gamma_{a/w}) \) and the o/w interfacial tension \( (\gamma_{o/w}) \). At lower surfactant concentrations the rate of decrease of the o/w interfacial tension has to be greater than that for the air/water interface. The greater the difference between the rates of decrease of \( \gamma_{o/w} \) and \( \gamma_{a/w} \) with respect to SDS concentration, the larger becomes the spreading coefficient. As a consequence, at lower surfactant concentrations, the spreading coefficient increases with an increasing surfactant
Figure 9  Spreading coefficient calculated from Equation 1 vs. SDS concentration for pure hydrocarbons
Figure 10 Spreading coefficient calculated from Equation 1 vs. SDS concentration for kerosene and bitumen/kerosene blend.
concentration.

On the other hand, at higher surfactant concentrations, the decrease in the surface tension for the air/water interface with respect to surfactant concentration can become much greater in comparison to that for the o/w interfacial tension. As a result, at high surfactant concentrations, an increase in the surfactant concentration can actually lower the spreading coefficient. The rate of decrease in these interfacial tensions with respect to surfactant concentration is directly proportional to the surfactant adsorption density as given by the Gibbs equation:

$$\Gamma = -\frac{1}{RT} \left( \frac{da}{d\ln a} \right)$$

where

- $\Gamma$ - surfactant excess concentration [mol/m²]
- $R$ - gas constant [N·m/mol·K]
- $T$ - temperature [K]
- $\gamma$ - interface tension [N/m]
- $a$ - activity of the surfactant (can be approximated by concentration [M])

The results of the adsorption density calculations for the air/water and the hexadecane/water interfaces are presented in Figure 11 (the surface and interfacial tension data were smoothed for calculations). The existence of a maximum in the variation of the spreading coefficient with SDS concentration is evident from these results. The adsorption density of the SDS at the o/w interface is much higher than at the air/water interface. The difference is, of course, the largest for the surfactant concentration at which the maximum spreading coefficient is obtained. The difference in SDS
Figure 11 The interfacial tension (solid line) and adsorption density (dotted line) at air/water and n-hexadecane/water interface vs. SDS concentration.
adsorption density at these interfaces was also observed by other authors,\(^{(55-58)}\) but its influence on spreading coefficient was not examined.

The concentration region of about \(10^{-4}\)M (30 mg/dm\(^3\)) is known as the "saturation adsorption" region at the hydrocarbon/water interface, because plots of the o/w interfacial tension vs. log concentration of SDS are linear in this sector (please note that this concentration is significantly lower than the critical micelle concentration (cmc)).\(^{(55)}\) To explain the adsorption density difference one should remember that the adsorption of surfactant molecules is the result of two different phenomena.\(^{(57)}\) First, the separation of oil molecules as the surfactant penetrates the oil phase, and second, the interaction between the hydrocarbon chains of the surfactant and the molecules of the oil phase. If the oil phase is an alkane hydrocarbon the molecules of the surface active agent will extend into the oil phase and will be aligned as a result of induced dipole and other van der Waals interactions between alkyl chains of oil molecules and surfactant molecules.\(^{(55)}\) At low dilutions of surfactant there will be little or no self-interaction between the alkyl chains of the surfactant molecules. That is, each adsorbed molecule will be surrounded by aligning oil molecules. In the case of the air/water interface there are no such interactions.

The adsorption densities at the cmc as reported in the literature for the hexadecane/water interface are \(3.08 \times 10^{-6}\).
mol/m² \textsuperscript{(57)} and \(3.26 \times 10^{-6}\) mol/m²,\textsuperscript{(58)} whereas for the air/water interface an adsorption density of \(3.78 \times 10^{-6}\) mol/m² is reported.\textsuperscript{(58)} These values are somewhat lower than those obtained in the present investigation. However the higher value of adsorption density at the cmc for the air/water interface and the basic behavior as described above are still valid. The difference in the results obtained in this research may be the result of impurities present in the chemicals used; the SDS surfactant was 95\% grade based on total alkyl sulfate content and the hexadecane was 99\% pure. Because of this, not all added surfactant was SDS, and the adsorption of pure SDS at the interfaces could be inhibited by other components present in the system.

For the bitumen-kerosene blend the spreading coefficient remains strongly positive (26 mN/m) and constant for surfactant concentrations from 0 to 3 mg/dm³ \(\times 10^{-5}\)M), then rapidly decreases reaching a slightly negative value at 300 mg/dm³ \(\times 10^{-3}\)M). Judging from the three interfacial tensions, the tendency of kerosene/bitumen blends to spread at the water surface is most pronounced. The different impact of surfactant concentration on the spreading coefficient for pure hydrocarbons and the bitumen in kerosene blend most probably results from the contribution of natural surfactants present in tar sand bitumen.\textsuperscript{(15)} Compounds dissolved in water during the hot water separation process appear to be carboxylate, sulphate, and sulfonic surfactants produced in the reaction of
precursors present in the bitumen with NaOH.\textsuperscript{(64-66)} Oil sands of higher grades, however, do not require NaOH addition to produce surfactants.\textsuperscript{(66)} The actual amount of soluble surfactant depends on the oil sands grade and the amount of NaOH used in the hot water process. In the case of low-grade oil sand, the fines content is high and the surfactants are adsorbed on the fines. Release of these natural surfactants to the aqueous phase is thus also controlled by adsorption at the surface of the fines.\textsuperscript{(67)}

Schramm and Smith\textsuperscript{(65)} reported that these natural surfactants are vital to the efficiency of the hot water separation process. The carboxylate surfactants control bitumen recovery efficiency in the hot water process when they are present at the optimum concentration of about $1.2 \times 10^{-4}$M. When the concentration of the carboxylate surfactants is too low, the sulphate/sulphonate surfactants control the recovery efficiency. Schramm and Smith\textsuperscript{(65)} concluded from this that the carboxylate surfactants are preferentially adsorbed at the interfaces and are critical for bitumen recovery. All these findings are in excellent agreement with the results presented in this work. The initial concentration of natural surfactants released from bitumen (i.e., $-10^{-4}$M) is equal to the SDS concentration at the maximum spreading coefficient for pure hydrocarbons (see Figure 9). This is the reason for the high spreading coefficient for the bitumen/kerosene blend without surfactant addition. Subsequent increase in the SDS
concentration can only lower the value of the spreading coefficient (this statement is valid only below the cmc).

From the data for foam stability obtained by Wasan et al.\(^{(61)}\) it was stated that surface tension data taken for \(\gamma_{a/w}\) in the absence of oil, or by a technique which disturbs the oil present at the surface, provides larger \(\gamma_{a/w}\) values than the actual value. In conclusion, this may result in a spreading coefficient not only of incorrect magnitude but also of incorrect sign, if the magnitude is close to zero. Nikolow et al. presented a new differential interferometry (DI) technique,\(^{(68)}\) used by Wasan et al., for determining \(\gamma_{a/w}\) and relating the pseudoemulsion film tension to spreading phenomena and to rather complex interactions which exist between the oil droplets and the air/water surface. However, our interfacial tension results (if Wasan’s conclusions are correct - obtained with some relative error) are reliable, because the spreading coefficient is sufficiently positive to overcome the possibility of this error. Thus, the sign (positive or negative) of the spreading coefficient is the main factor necessary to predict the process of filming, not the magnitude of the spreading coefficient.

2.1.2.4 Filming Experiments

Two experimental procedures were used to confirm the dependence of the spreading coefficient on the SDS concentration. In the first filming experiments the Questar
100 long distance microscope coupled with a video camera was used to observe the coalescence of an oil droplet with an air bubble in aqueous SDS solution. Unfortunately, the filming process is very fast and consequently no quantitative results could be obtained from these experiments.

Another simpler technique for the examination of bubble filming by oil involved generation of oil droplets in SDS solution with a syringe (see Figure 12). Oil drops were formed at the end of the needle and after the aging period the drops detached. The behavior of a single oil droplet at the planar air/water interface (instead of air bubble/water interface) will differ from the behavior of droplets dispersed in an aerated emulsion system. However, the data obtained for this basic interaction is indicative of the more complex case. In the past the technique has contributed towards better understanding of the coalescence mechanism and the effects of variables such as the droplet size, the temperature, the added surfactant and the electrolyte.\(^{57,69}\)

The filming experiments have shown that the time which elapses from the moment of oil droplet placement at the o/w surface to oil spreading (i.e., the time of water film drainage) is in excellent correlation with the spreading coefficient calculations. The shortest filming time was found, as expected, for the largest value of the spreading coefficient. These data are presented in Figure 13 (each experimental point represents the mean value for 30 drops, the
Figure 12 Schematic of the experimental set-up for drainage time measurements
Figure 13 Drainage time of oil droplet at air-water interface vs. SDS concentration for pure hydrocarbons, kerosene and bitumen/kerosene blend.
relative error was calculated to be ±20%).

Similar experiments were performed by Warnstedt.\(^{(43)}\) A plate was immersed and fixed in position in a water-filled cell. One or more air bubbles were then applied to the underside of the cover plate. Any desired amount of oil could then be applied to the surface of the air bubble with the second syringe. He examined only one system for which the spreading coefficient was positive (similar to the bitumen/kerosene system used in our experiments). After an initial contact, which led to a transient deformation of the oil drop still adhering to the needle, a spontaneous spreading of the oil over the bubble surface was observed, completely enveloping the bubble.

The explanation for observed minimum for the drainage time is not trivial. The essential part of the filming process is the thinning and rupture of the water film between the oil droplet and air bubble. The stability of this film is commonly ascribed in large measure to the so-called Marangoni effect.\(^{(59)}\) This is the inability of the surfactant molecules to diffuse instantaneously to any locally stretched surface which may be momentarily depleted of surfactant. This produces a local rise in surface tension which opposes the stretching force, thus tending to "heal the wound." A second but somewhat similar mechanism of the system stability is called the Gibbs effect.\(^{(59)}\) This effect involves the possible insufficiency of molecules within the liquid film to recoat the stretched
surface completely, regardless of diffusion rate. A third mechanism, which may be important with some ionic surfactants, is the electrostatic repulsion between the charged parallel surfaces of the film. This repulsion opposes film thinning and hence also opposes the rupture.\(^{(59)}\) Malhotra and Wasan\(^{(60)}\) indicate the effects of many factors on the draining of thin liquid films. These factors include surface or interfacial tension and its gradient (or the Marangoni-Gibbs effect), surface viscosities, drop and film phase viscosities, surfactant transfer onto the interface, surfactant adsorption-desorption kinetics, dispersion forces, interfacial curvature, dimple formation, and film size.

In the current study only the effect of SDS concentration on the spreading coefficient and drainage time behavior is taken under consideration. The SDS surfactant concentration can influence the drainage time either by increasing or decreasing it. The mechanisms of the two effects are quite different. A decrease in drainage time can result from interfacial turbulence (Gibbs-Marangoni effect).\(^{(59)}\) Because of small scale eddies adjacent to the interface, concentration variations of the surfactant may exist, giving rise to local variations in the interfacial tension.\(^{(61)}\) In an attempt to reduce the potential energy of the surface by extension or contraction of the area, the surface undergoes turbulent motion, which may result in disturbances causing premature coalescence between drop and bubble. The likelihood of such
local interfacial tension variations arising in a stagnant system decreases as the concentration of the surfactant approaches chemical equilibrium.\textsuperscript{(62)} Consequently, any decrease in the drainage time would be less likely to occur.

Further, an increase in drainage time can occur after the chemical equilibrium has been established. For example, this increase can be seen in the necessity of an emulsifying agent to produce a stable emulsion and frother to produce a stable froth.\textsuperscript{(42c)} The surfactant first decreases the rate of thinning of the water-phase film mechanically and electrically. Several oriented hydration layers may surround each molecule of surface-active agent, producing a mechanical barrier that must be displaced or removed for coalescence to occur.\textsuperscript{(62)} Surface-active agents tend to prevent the growth of instabilities by damping waves at interfaces in a manner similar to that of viscosity. Surfactants also make the film more elastic by enabling the film to "heal" its own weak spots by changes in the dynamic interfacial tension.\textsuperscript{(59)}

2.2 Zeta Potential of Oil Droplets

Emulsion stability and various physical properties of the emulsion can not be considered separately. Of course, examination of these properties is the best indication of the emulsion stability. Since the stability of an emulsion is a function of the electrical properties of the interface, the measurement of these properties may be of importance (in
conjunction with other measures of stability described in following sections) in the evaluation of emulsions, and in the prediction of their stability. In general, the characteristic feature for the analysis of dispersion stability is the zeta potential.\(^{(70a)}\)

The charging of a surface in a liquid can come about in two ways:\(^{(71)}\)

1. by the ionization or dissociation of surface groups (e.g., the dissociation of protons from surface carboxylic acid groups (-COOH → -COO\(^-\) + H\(^+\)), which leaves behind a negatively charged surface)
2. by the adsorption (binding) of ions from solution onto a previously uncharged surface (e.g., the binding of Ca\(^{2+}\) onto the zwitterionic headgroups of lipid bilayer surfaces, which charges the surface positively). Depending on the ionic conditions, even the air-water and hydrocarbon-water interfaces can be charged this way. The adsorption of ions from solution can also occur onto oppositely charged surface sites, e.g., the adsorption of cationic Ca\(^{2+}\) to anionic COO\(^-\) sites vacated by H\(^+\) or Na\(^+\). This is known as ion exchange.

Irrespective of the charging mechanism, the surface charge is balanced by an equal but oppositely charged number of ions, some of which are transiently bound to the surface within the so-called Stern or Helmholtz layer, whereas other counterions form an atmosphere that is in rapid thermal motion close to the surface and is known as the diffuse electrical double layer.

The variation in the potential across an oil-water
interface is shown in Figure 14. Here $\Delta V$ denotes the surface potential difference between the two phases, and $\chi$ denotes the surface potential jump. If some electrolyte is present, the solubility of the cations and the anions in general will be different in the two phases. Usually the anions will be somewhat more oil soluble than the cations and there should be a net negative charge on the oil droplets, as illustrated in Figure 14b.

The repulsion between oil droplets will be more effective in preventing flocculation the greater the thickness of the diffuse layer and the greater the value of $\Psi_0$, the surface potential. These two quantities depend oppositely on the electrolyte concentration, however. The total surface potential should increase with electrolyte concentration, since the absolute excess of anions over cations in the oil phase should increase. On the other hand, the thickness of the double layer decreases with increasing electrolyte concentration. A plot of emulsion stability versus electrolyte concentration is then expected to go through a maximum.

If an ionic surfactant is present, the potentials should vary as shown in Figure 14c, or perhaps similar to the case 14b with nonsurfactant electrolytes. In addition, however, surfactant adsorption decreases the interfacial tension and thus contributes to the stability of emulsion.$^{(42c)}$

Unfortunately, the surface potential can not be measured experimentally. However, it is possible to calculate this
Figure 14 Variation in potential across an oil-water interface: (a) in the absence of electrolyte, (b) with nonsurfactant electrolyte present, and (c) in the presence of surfactant ions and a large amount of salt.
value from the following equation, if the point of zero charge (pzc) for the system under consideration is known.\(^{(73)}\)

\[
\psi_0 = \frac{RT}{nF} \ln \frac{a_+}{a_0} - \frac{RT}{nF} \ln \frac{a_-}{a_0} \tag{8}
\]

where

- \(R\) - gas constant
- \(T\) - absolute temperature
- \(n\) - valence of the potential determining ion
- \(F\) - Faraday constant
- \(a_+\) and \(a_-\) - activities of potential determining ions at the pzc

Since surface potentials are not measured directly, the electrokinetic behavior of dispersed oil droplets is characterized by zeta potential measurements. Zeta potential \((\zeta)\) is assumed to be the potential difference between a hypothetical plane representing the closest distance of approach of hydrated counter ions to the surface and the bulk solution.\(^{(73)}\) Zeta potential measurements for oil dispersions are made by electrophoresis. During electrophoresis experiments the electrophoretic mobility is measured by tracking the velocity of the particles in the absence of convective flow under a potential gradient. The zeta potential is calculated from the relationship:\(^{(73)}\)

\[
\zeta = 4\pi \frac{\mu}{D} \frac{V}{E} \times 10^{-4} \tag{9}
\]

where

- \(\zeta\) - zeta potential [V]
- \(\mu\) - solution viscosity [Pa]
- \(D\) - dielectric constant
- \(V\) - particle velocity [cm/sec]
- \(E\) - potential gradient [V/cm]
2.2.1 Experimental Techniques

In the following section the influence of flocculant concentration on the zeta potential of oil droplets is reported. As was the case in the filming experiments described in Section 2.1, two kinds of oil phases were selected. In the first kind, which is characterized by hexadecane, the spreading coefficient dependence on surfactant (SDS) concentration (see Figure 9) is typical of pure hydrocarbons. This dependence exhibits very distinct SDS concentration intervals for positive and negative spreading coefficients. In the second kind, which is characterized by a 20% bitumen/kerosene blend, the spreading coefficient variation is different from that of pure hydrocarbons (see Figure 10). Both kinds of oils were examined at two different SDS concentrations. First experiments were performed without surfactant addition second experiments were performed at the SDS concentration which would result in the highest positive spreading coefficient. For hexadecane as an oil phase this concentration was found to be 30 mg/dm³. For the bitumen/kerosene blend the situation is more difficult. The spreading coefficient reaches its largest value from 0 to 3 mg/dm³, decreases slightly at 13 mg/dm³ and rapidly decreases for higher concentrations. To maintain the highest level of the spreading coefficient the experiment should be performed at 0 to 3 mg/dm³ of surfactant. However, the effective operation of the air-sparged hydrocyclone requires a
considerable amount of frother in order to prevent bubble coalescence as well as to ensure the proper froth stability. In this regard, it was observed that the SDS concentration should be maintained above 9 mg/dm$^3$. Consequently, the minimum SDS concentration for the zeta potential measurements was maintained at 9 mg/dm$^3$. The SDS concentration for hexadecane experiments was once again 30 mg/dm$^3$, this concentration was used for bitumen/kerosene, too, so that the emulsion stability of both the oils could be compared at the same concentration of SDS.

A high molecular weight cationic polyelectrolyte (PE), PERCOL 592 (polyacrylamide flocculant), manufactured by Allied Colloids Inc., was selected for charge neutralization.$^{1,74}$

Emulsions were prepared according to the procedure used for ASH flotation tests. Surfactant, if needed, was added to the conditioning tank. The emulsion with and without surfactant addition was equilibrated in the conditioning tank for 15 min. A 2 dm$^3$ sample of the emulsion was taken from the conditioning tank and placed in a glass container which was placed on a magnetic stirrer. Polyelectrolyte was then added in the amount required for the desired concentration. This procedure was repeated for all concentrations of SDS and PE. Each experiment was repeated at least three times.

After equilibration with polyelectrolyte, the zeta potential was measured by the laser-Doppler electrophoretic technique$^{75}$ using a Zetasizer 3 instrument (Malvern...
Instruments, Ltd., London, UK), equipped with the AZ4 standard cell. The schematic of the Zetasizer 3 is presented in Figure 15. Two coherent laser beams of red light produced by splitting the output of a low-power He-Ne laser are focused and made to intersect within the quartz capillary cell holding the oil-in-water emulsion at a point of zero convective flow. As a result, a pattern of interference fringes is formed, and the droplets move across the fringes under the influence of the applied electric field and are tracked by their scattered light. The intensity of the scattered light varies with a frequency which is related to velocity of the particles. A fast photomultiplier together with a digital correlator is used to analyze the signals, and the distribution of droplet velocities (electrophoretic mobilities) and distribution of zeta potentials is thus determined. The sign of zeta potential is determined by referencing the observed Doppler frequency of the light scattered by the droplets moving through the fringes to the modulation frequency applied to one of the laser beams. This apparatus allows for very fast measurements, even for very unstable systems.\(^{(76)}\)

Figure 16 presents a schematic diagram of the AZ4 standard cell used in the present study. This cell consists of a 4 mm diameter quartz capillary. The platinum electrodes are in compartments at each end of the cell. A semipermeable membrane separates the electrodes from the suspension to prevent the contamination of the electrodes by the sample. The
Figure 15 Schematic arrangement of the Zetasizer 3
Figure 16 Schematic diagram of the capillary electrophoresis cell for the Zetasizer 3
electrode chambers are filled with an electrolyte which is at least as conducting as the sample itself. Polarization of the electrodes is prevented by the application of a periodically reversed field. A technique called "duty cycling," which allows the voltage to be switched off for a short time between each cycle, is used to avoid heating of the suspension sample, especially for high conductivity solutions. The problem of electroosmosis is overcome by measuring the velocity of droplets at a point in the cell where the electroosmotic velocity is zero.

2.2.2 Results and Discussion

The zeta potential of hexadecane and the bitumen/kerosene blend are presented in Figure 17 as a function of polyelectrolyte concentration. In both cases the zeta potential values correspond to the data reported by other authors.\textsuperscript{(44,77)} Droplets in both emulsions are negatively charged and the zeta potentials were found to be $\zeta = -43$ mV for hexadecane and $\zeta = -35$ mV for the bitumen/kerosene blend. These results are less negative than these reported in the literature, especially in the case of hexadecane ($\zeta = -63$ mV).\textsuperscript{(76)} It should be noted that for economical reasons, experiments in the current investigation were performed using tap water and 99% hexadecane, taking into account the nature of the subsequent ASH flotation experiments.

The concentration of the polyelectrolyte required to
Figure 17 Zeta potential of oil droplets vs. polyelectrolyte addition
reach the isoelectric point (i.e.p.) is different for different oils and for different surfactant concentrations. The isoelectric point was achieved at 1.5 mg/dm$^3$ and 1.0 mg/dm$^3$ of PERCOL 592 for hexadecane emulsion with and without surfactant, respectively. For the bitumen/kerosene blend emulsion the zeta potential approached zero at 0.3 mg/dm$^3$ with SDS addition - and at 0.1 mg/dm$^3$ without surfactant addition.

The difference in PERCOL 592 concentration needed to establish i.e.p. for a given emulsion with and without surfactant, can be attributed to the reaction between the anionic surfactant and the cationic polyelectrolyte. However, the difference in the isoelectric points for the two different oil phases for a given surfactant concentration, is not that easy to explain. The negative electrical charge of the hexadecane droplets results primarily from preferential adsorption of anions (OH$^-$ and other anions present in tap water). In the case of bitumen/kerosene droplets the negative surface charge is due to the adsorption of ions from the solution and due to the influence of surfactants remaining in the bitumen. Hupka and Miller(44) identified the presence of other surface active agents in bitumen that are more polar than the carboxylate surfactants. The interaction between these surfactants and the polyelectrolyte can lower the PERCOL 592 concentration necessary to approach the i.e.p.

It is necessary to maintain a very low surface charge on the oil droplet during flotation in order to lower the
stability of emulsion and to facilitate attachment between oil
droplets and air bubbles, which are charged negatively. The
zeta potentials of air bubbles with and without addition of
SDS was measured by Okada et al.\(^{(78-80)}\) These measurements were
performed as a function of pH. In surfactant-free water the
zeta potential of air bubbles (diameter 27 \(\mu\)m) was observed to
vary from -44 mV to -53 mV for a pH value between pH = 6 and
pH = 8. In the presence of 10^{-3}\text{mol/dm}^3 SDS the zeta potential
was found to be constant at -59 mV in the pH range from pH = 5 to pH = 10. Unfortunately, these authors performed no
experiments with cationic flocculants. But in another series
of experiments addition of 10^{-3}\text{mol/dm}^3 cationic surfactant
(dodecylamine hydrochloride - DAH) changed the zeta potential
from \(\zeta = +55\) mV at pH = 3 to \(\zeta = -30\) mV at pH = 11, reaching
the i.e.p. at pH = 10.\(^{(80)}\)

Other experiments by Okada et al.\(^{(80)}\) show that the
flotation efficiency of latex particles reaches a maximum when
the zeta potential of bubbles and latex particles attain their
isoelectric points. The effect of the zeta potential of oil
droplets and bubbles on flotation efficiency for the SDS (10^{-4}
M) solution containing NaCl, CaCl\(_2\), and Al\(_2\)(SO\(_4\))\(_3\) has also been
reported.\(^{(79)}\) In the absence of the electrolytes, oil droplets
(heavy oil - B type at concentration 500 mg/dm\(^3\)) and air
bubbles are largely negatively charged. With the addition of
NaCl, both the oil droplets and the air bubbles are still
negatively charged and flotation efficiency remains low. For
CaCl$_2$, flotation efficiency increases with a decrease in the absolute magnitude of the zeta potentials of the oil droplets and the air bubbles. Further, for Al$_2$(SO$_4$)$_3$, the absolute magnitude of the zeta potentials of the oil droplets and the air bubbles becomes even smaller and the bubbles in fact become positively charged. Under these latter circumstances bubbles and droplets are of opposite charge and the flotation efficiency is then at its highest level. These results show that the surface charges of the oil droplets and the air bubbles are dependent on solution composition and the valency of the added electrolyte. Of course, the flotation efficiency is dependent on these changing characteristics which is explained by the fact that when two charged particles approach each other, the interaction force due to the overlap of their electrical double layer acts upon them.

In experiments conducted during this thesis research, polyelectrolyte was added in order to change the zeta potential. Only the zeta potential of oil droplets is known from our experiments. However if this zeta potential is maintained very close to the i.e.p., it is expected from the results of Okada that the zeta potential of the air bubbles should be close to their i.e.p., too. Based on our results (Figure 17) and taking into consideration the findings of Okada et al., polyelectrolyte concentrations of 2 mg/dm$^3$ and 0.5 mg/dm$^3$ respectively were selected for ASH testing of the hexadecane and bitumen/kerosene emulsions.
2.3 Oil Droplet Size Distribution

It is quite uncommon for any emulsion to have uniform droplet size distribution. An emulsion consisting mostly of fine droplets exhibits maximum stability, all other things being equal.\(^{(70a)}\) In this regard, suitable droplet size measurement as well as their description are of critical importance. There are, in general, four different methods by which the droplet size distribution may be determined. These methods include microscopic observation, sedimentation techniques, light-scattering measurements, and instrumental counting.\(^{(70d)}\) It should be noted, however, that some of these methods do not actually yield distributions as such, but only average particle size.

Microscopic measurements have been used extensively for years and are laborious, but most accurate. Observation of the emulsion under the microscope fitted with a micrometer eyepiece permits the tabulation of the numbers of droplets in the various size ranges. From this, a distribution curve may be plotted. Alternatively, a photographic record of the emulsion may be made, from which the droplet sizes can be determined at a later time. In such a way a permanent record of the emulsion is available. In much of the literature relating to the microscopic technique, undue emphasis has been placed on the necessity of counting a large number of droplets in order to get a meaningful size distribution. For example, Fischer and Harkins\(^{(81)}\) made a direct microscopic count of
50,000 particles to obtain size distribution curves. Actually, however, statistically significant counts can be made with as little as 300 droplets. It can be shown\(^{(82)}\) that a count of 300 droplets will result in a distribution in which the error at any size range will be less than 8% within a 95% confidence limit. Reduction of this expected error to 5%, at the same level of confidence, would require counting 2960 droplets. In view of the other sources of error affecting such measurements, such small reduction in error hardly seems worth the tenfold increase in effort.

The second type of measurement is based on sedimentation phenomena. If any emulsion creams at any sort of observable rate, measurement of the amount of creamed material per unit time permits the construction of a size distribution curve. Most methods which depend on this phenomenon measure the change in density.

Droplet size can be also measured, in principle, by optical methods depending either on measurement of the reduction in light transmitted through the solution (turbidimetric or nephelometric methods) or by light scattered at some definite angle (usually 90°) from the optical path. The method employed depends, to some degree, on the type of system being studied, direct transmission methods being more applicable to dispersions of higher turbidity.

Methods depending on the direct counting have been developed recently. A flow counter which also gives particle
size distributions is the Coulter Counter. In this device, the emulsion flows through the narrow orifice surrounded either side by a conductivity electrode. In an oil-in-water emulsion, the conductivity of the dispersed oil droplets is, of course, much lower than that of continuous phase. Consequently, each time a droplet passes through the orifice, a change in conductivity whose magnitude is proportional to the droplet size is recorded.

Since what is determined by most experimental measurements of size distribution is the population of various size ranges, the proper graphical representation of such data is by means of a histogram. For convenient discussion of particle-size data, it may be necessary to simplify matters somewhat by using average quantities. For example, the emulsion may be described in terms of an average particle diameter corresponding to that of a hypothetical monodispersed emulsion. However, this is not as simple a matter as it might seem, for the average diameter may be defined in a number of ways.

If, for example, one defines the total number of droplets in the emulsion as $N$, the total interfacial area as $S$, the volume of dispersed phase as $V$, and the sum of all globule diameters as $D$, six average diameters can be defined as shown below:

$$\bar{d}_{10} = \frac{D}{N} - \frac{\sum d_1 n_i}{\sum n_i} \quad (10)$$
\[ \bar{d}_{20} = \left[ \frac{S}{\pi N} \right]^{1/2} - \left[ \frac{\sum d_i^2 n_i}{\sum n_i} \right]^{1/2} \] (11)

\[ \bar{d}_{30} = \left[ \frac{6 V}{\pi N} \right]^{1/3} - \left[ \frac{\sum d_i^3 n_i}{\sum n_i} \right]^{1/3} \] (12)

\[ \bar{d}_{21} = \frac{S}{\pi D} - \frac{\sum d_i^2 n_i}{\sum n_i} \] (13)

\[ \bar{d}_{31} = \left[ \frac{6 V}{\pi D} \right]^{1/2} - \left[ \frac{\sum d_i^3 n_i}{\sum d_i^2 n_i} \right]^{1/2} \] (14)

\[ \bar{d}_{32} = \frac{6 V}{S} - \frac{\sum d_i^3 n_i}{\sum d_i^2 n_i} \] (15)

where \( n_i \) are the number of globules of diameter \( d_i \). Equation 10 provides a simple arithmetic mean, while equation 15 yields mean volume-surface diameter (often called Sauter diameter). The mean surface or interface area is also an index of the dispersity of the emulsion and is often employed. As indicated above, the most meaningful calculation of this quantity is from the volume-surface diameter.

2.3.1 Experimental Techniques

In this part of the thesis research the droplet size distribution was evaluated. As in the case of filming experiments (described in Section 2.1) and zeta potential measurements (described in Section 2.2) two kinds of oil phases (hexadecane and 20% bitumen/kerosene blend) were employed. Reagents used (surfactant and polyelectrolyte) as well as their concentrations were identical to those in the previous surface chemistry studies. SDS was used as a surfactant and PERCOL 592 was used as a polyelectrolyte. For
both kinds of oil phases four different operating conditions were selected, i.e., no addition of chemicals, only SDS addition, only PERCOL 592 addition, addition of both SDS and PERCOL 592.

Emulsions were prepared following the procedure described in Section 3.1.1. Surfactant and polyelectrolyte, if needed, were added to the conditioning tank. The desired concentration of oil (amount of added during homogenization) was 250 mg/dm³ for each experiment. In each case, with or without chemical additions, the emulsion was equilibrated in the conditioning tank with a recirculating pump for 5 min. Next, chemicals were added (when both SDS and PERCOL 592 were added, SDS was added first) and the emulsion was equilibrated in the conditioning tank for an additional 15 min (when no chemicals were added emulsion was equilibrated in storage tank for the whole 20 min to maintain the identical conditions for each emulsion type). For size distribution experiments, all emulsions were equilibrated for the additional 15 min.

A microscopic technique was adopted to determine the droplet size distribution. A sample of 200 cm³ of emulsion was collected from the conditioning tank and immediately submitted to microscopic analysis. An optical microscope, model AXIOPLAN (ZEISS, Germany) and microscopic slide with master scale (Fein-Optik in Jena, Germany) were used. Photographic records (12 of each sample) were made of each emulsion and the droplet sizes were determined from these photographs. Four hundred
fifty to 500 droplets (5 to 6 photographs were selected for each distribution and every droplet on each photograph was counted) were counted to obtain the size distribution curve. Next, for emulsion the droplet size distribution as well as average diameter were calculated.

2.3.2 Results and Discussion

The droplet size distributions for hexadecane are shown in Figures 18 to 21. The average droplet diameters for these emulsions are presented in Table 3 (formulas for each average diameter are given in Equations 10 to 15).

As can be seen from Figures 18 to 21 there is, essentially, no change in the average droplet size after the addition of chemicals. When the surfactant and polyelectrolyte are added separately, the size distribution becomes narrower and shifts to smaller sizes whereas the average droplet diameters are very similar. The mechanisms by which SDS and

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Average droplet diameter [μm] for hexadecane emulsions with different chemicals added (surfactant, SDS, concentration 30 mg/dm³, polyelectrolyte, PERCOL 592, concentration 2 mg/dm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>no additives</td>
<td>SDS</td>
</tr>
<tr>
<td>( d_{10} )</td>
<td>5.9</td>
</tr>
<tr>
<td>( d_{20} )</td>
<td>6.4</td>
</tr>
<tr>
<td>( d_{30} )</td>
<td>7.5</td>
</tr>
<tr>
<td>( d_{21} )</td>
<td>41.2</td>
</tr>
<tr>
<td>( d_{31} )</td>
<td>3.2</td>
</tr>
<tr>
<td>( d_{32} )</td>
<td>10.2</td>
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</table>
Figure 18 Droplet size distribution for hexadecane as a dispersed phase without the addition of chemicals
Figure 19 Droplet size distribution for hexadecane as a dispersed phase with the addition of 30 mg/dm$^3$ surfactant (SDS)
Figure 20 Droplet size distribution for hexadecane as a dispersed phase with the addition of 2 mg/dm$^3$ polyelectrolyte (PERCOL 592)
Figure 21 Droplet size distribution for hexadecane as a dispersed phase with the addition of 30 mg/dm$^3$ surfactant (SDS) and 2 mg/dm$^3$ polyelectrolyte (PERCOL 592)
PERCOL 592 bring about this small change are quite different from each other. Addition of surfactant to the water increases the susceptibility to emulsification and this makes the droplet diameters shift to smaller sizes. On the contrary, addition of the polyelectrolyte to water causes coalescence and larger droplets form during equilibration time and, as a consequence, an oil layer was observed at the top of the conditioning tank. The evidence for such an explanation can be seen from the change in dispersed oil concentration with time presented in Section 2.4. The oil concentration, especially at the beginning of the experiment, is the highest for the emulsion with the SDS addition, and as expected, the addition of PERCOL 592 decreases the oil concentration. The addition of PERCOL 592 together with SDS gives a broader size distribution and slightly larger average droplet diameter than the addition of PERCOL 592 alone. The addition of SDS and PERCOL 592 makes the emulsion less stable and gravity separation was evident in this case. It must be noted that the flocculation of oil drops may be reversible. Thus, in many cases the aggregates can be easily redispersed by stirring. This action of shearing forces can be enhanced by dilution with a solution of a suitable surface active agent. Furthermore, coagulation of an emulsion is a function not only of the rate of formation of these more or less reversible aggregates, but also of the rate at which the droplets coalesce to form larger droplets.\(^{(70c)}\)

The droplet size distributions for 20% of bitumen in
kerosene blend as an oil phase are shown in Figures 22 to 25. The average droplet diameters for these emulsions are presented in Table 4 (formulas for each average diameter are given in Equations 10 to 15).

Similar to the size distribution results for hexadecane emulsions, there is essentially no change in droplet size distribution for bitumen/kerosene emulsions with the addition of chemicals.

When the basic emulsions without the addition of chemicals were studied, the emulsion of bitumen/kerosene blend as an oil phase was found to have much narrower droplet size distribution range, when compared to the size distribution of hexadecane emulsion. The size distribution difference between these two basic emulsions can be explained by taking into account the origin of the oil phase. Hexadecane is a pure hydrocarbon and emulsion produced with it as an oil phase is a typical model emulsion. Bitumen in kerosene blend is a

<table>
<thead>
<tr>
<th>d_{310}</th>
<th>d_{320}</th>
<th>d_{330}</th>
<th>d_{331}</th>
<th>d_{332}</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2</td>
<td>4.8</td>
<td>5.6</td>
<td>23.5</td>
<td>7.4</td>
</tr>
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<td>1.8</td>
<td>2.0</td>
<td>2.6</td>
<td>4.2</td>
<td>4.0</td>
</tr>
<tr>
<td>2.9</td>
<td>3.6</td>
<td>4.3</td>
<td>12.7</td>
<td>6.1</td>
</tr>
<tr>
<td>3.2</td>
<td>4.2</td>
<td>5.3</td>
<td>17.8</td>
<td>8.4</td>
</tr>
</tbody>
</table>

| Table 4 Average droplet diameter [\mu m] for bitumen/kerosene emulsions with different chemicals added (surfactant, SDS, concentration 9 mg/dm³, polyelectrolyte, PERCOL 592, concentration 0.5 mg/dm³) |

<table>
<thead>
<tr>
<th>no additives</th>
<th>SDS</th>
<th>PE</th>
<th>SDS/PE</th>
</tr>
</thead>
<tbody>
<tr>
<td>d_{310}</td>
<td>4.2</td>
<td>1.8</td>
<td>2.9</td>
</tr>
<tr>
<td>d_{320}</td>
<td>4.8</td>
<td>2.0</td>
<td>3.6</td>
</tr>
<tr>
<td>d_{330}</td>
<td>5.6</td>
<td>2.6</td>
<td>4.3</td>
</tr>
<tr>
<td>d_{331}</td>
<td>23.5</td>
<td>4.2</td>
<td>12.7</td>
</tr>
<tr>
<td>d_{332}</td>
<td>7.4</td>
<td>4.0</td>
<td>6.1</td>
</tr>
<tr>
<td>d_{333}</td>
<td>8.4</td>
<td>4.0</td>
<td>2.9</td>
</tr>
</tbody>
</table>
Figure 22 Droplet size distribution for 20% bitumen/kerosene blend as a dispersed phase without the addition of chemicals
Figure 23 Droplet size distribution for 20% bitumen/kerosene blend as a dispersed phase with the addition of 9 mg/dm$^3$ surfactant (SDS)
Figure 24 Droplet size distribution for 20% bitumen/kerosene blend as a dispersed phase with the addition of 0.5 mg/dm³ polyelectrolyte (PERCOL S92)
Figure 25 Droplet size distribution for 20% bitumen/kerosene blend as a dispersed phase with the addition of 9 mg/dm³ surfactant (SDS) and 0.5 mg/dm³ polyelectrolyte (PERCOL 592)
mixture of many different chemical compounds including the natural surfactants in bitumen. The other element which can have an influence on emulsion formation is the presence of fine particles - emulsion stabilizing agents\(^{(70b)}\) - such as clay and precipitated calcium carbonate\(^{(44)}\) in bitumen. As was pointed out by Becher\(^{(70b)}\) precipitates are, in general, better emulsifiers than substances added to the system and the physical state of the precipitates appears to be a very important factor. Generally, highly gelatinous or highly-dispersed fine precipitates are more efficient than granular ones. If the contact angle between a solid particle and two liquid phases is finite, a stable position for the particle is at the liquid-liquid interface. Coalescence is inhibited because work has to be done to displace the particle from the interface.\(^{(42c)}\)

### 2.4 O/W Emulsion Stability

Emulsions are essentially unstable heterogeneous systems; they are partly dispersions, partly colloids. The properties of emulsions often depend largely on their composition and on their mode of preparation. The physical properties of the emulsions govern the stability of the system.\(^{(70a)}\)

There appear to be two stages in the collapse of emulsions: flocculation, in which some clustering takes place, and coalescence, in which the number of distinct droplets decreases.\(^{(42c)}\) Coalescence rates very likely depend primarily
on the film-film surface chemical repulsion and on the degree of irreversibility of film desorption. However, if emulsions are centrifuged, a compressed polyhedral structure similar to that of foams results and coalescence may now take place by mechanisms more related to those operative in the thinning of foams. Flocculation, on the other hand, should be sensitive to long range forces as droplets approach closer.

It should be noted that in a process consisting of two consecutive reactions, the overall reaction rate is determined by the slower of the two. For a very dilute oil-in-water emulsion the rate of flocculation can be made much smaller than the rate of coalescence. As a consequence, the stability of emulsion will be affected by the factors that affect the rate of flocculation. On the other hand, increasing the concentration of the oil phase in the emulsion will result in a slowly increasing rate of coalescence and a much faster increasing rate of flocculation. Thus, in highly concentrated emulsions, the coalescence can be rate-determining.

In a certain range of concentrations these two reaction rates can be roughly equivalent. Becher\(^{(70c)}\) has pointed out that even in very diluted emulsions, it is possible to make coalescence the rate determining by the addition of surface active agents which may have little or no effect on the rate of flocculation while inhibiting coalescence.

In addition to the manner in which the droplet sizes are distributed in an emulsion, the total amount of the dispersed
phase present would be expected to be important. However, the best and most direct indication of the stability of an emulsion is to measure the change in the dispersed phase concentration as a function of time under stagnant conditions. The results of this measurement can be presented as weight percent, weight fraction, volume percent, volume fraction or molarity. In the present work the units of mg/dm$^3$ are used which are almost identical to ppm (parts per million) when the density of water is assumed as 1 kg/m$^3$. The change in the emulsion density after the addition of oil and chemicals is negligible.

Generally, the oil phase sedimentation from o/w emulsions follows first order kinetics.\textsuperscript{(1,84-86)} The sedimentation coefficient ($k_s$) as calculated from the following equation can be used as an indicator of emulsion stability.\textsuperscript{(1)}

$$\ln \frac{c}{c_0} = -k_s t$$

(16)

where $c_0$ - initial concentration
c - concentration after time $t$
$k_s$ - sedimentation coefficient [1/s]
t - time [s]

The value of the sedimentation coefficient for very stable emulsions is smaller than $3 \cdot 10^{-7}$s$^{-1}$ and for unstable emulsion, $k_s$ is larger than $5.6 \cdot 10^{-4}$s$^{-1}$.
2.4.1 Experimental Techniques

In this part of the thesis research, the decrease of dispersed oil concentration with time was evaluated under stagnant conditions during sedimentation in a gravity field. Oil phases, added chemicals and their concentrations as well as the procedure of emulsion preparation and the addition of chemicals were identical to those described in Section 2.3.1. Equilibration in the conditioning tank was done for 20 min.

After equilibration, a sample of 3.5 dm³ of emulsion was taken from the conditioning tank. Next, the sample was left under quiescent conditions to allow gravity separation to occur. Samples of the emulsion were taken at various time intervals from the bottom of the container without disturbing the quiescent conditions of sedimentation. The time interval between successive sampling was set at 15 min at the beginning and was increased to 12 hr toward the end of each experiment. Concentration of dispersed oil phase was measured using HORIBA OCMA-220 oil-in-water analyzer, as described in Section 3.1.1.

2.3.2 Results and Discussion

The results from the measurements of dispersed oil concentration as a function of time for hexadecane and bitumen/kerosene blend are presented in Figures 26 and 27 respectively. As can be seen, both oils exhibit similar trends. The emulsions are most concentrated when surfactant is added. A continuous reduction in oil concentration is evident.
Figure 26 Dispersed oil concentration vs. time for hexadecane as an oil phase with chemicals addition
Figure 27 Dispersed oil concentration vs. time for 20% bitumen/kerosene blend as an oil phase with chemicals addition
during the course of the experiment. The emulsions with the addition of polyelectrolyte (with and without surfactant) are less stable than the emulsions with no additives. This could be observed at the very beginning of all experiments. The initial concentration is much smaller than the anticipated value. All emulsions were prepared using exactly the same amount of oil. The initial concentration difference comes from the gravity separation during equilibration in the conditioning tank. Especially in the case of the hexadecane emulsion with addition of SDS and PERCOL 592, a froth layer in the conditioning tank was observed. In other cases with only PERCOL 592 addition, a thin oil layer at the surface was also observed.

In spite of the similar effects of the chemical additives, the two kinds of emulsion produced from different oil phases can be easily distinguished from each other. The emulsion made from the bitumen/kerosene blend is more stable (i.e., higher oil concentration after a given period of time). The values of the sedimentation coefficient presented in Table 5 are calculated from Equation 16. Two distinct stages of sedimentation can be distinguished in Figures 26 and 27. Consequently, data for the two periods of time before and after 60 min of sedimentation were taken for calculations. Each stage can be approximated as a first order rate process. In the first stage, the rate of sedimentation is about an order of magnitude greater than after 60 min. This finding is
Table 5  Sedimentation coefficient calculated from the first order sedimentation rate equation for hexadecane and bitumen/kerosene emulsions with different chemicals added

<table>
<thead>
<tr>
<th>Additives</th>
<th>Sedimentation Coefficient [s⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hexadecane ≤60 min</td>
</tr>
<tr>
<td>no additives</td>
<td>4.3·10⁻⁴</td>
</tr>
<tr>
<td>SDS</td>
<td>1.9·10⁻⁴</td>
</tr>
<tr>
<td>PE</td>
<td>4.2·10⁻⁴</td>
</tr>
<tr>
<td>SDS + PE</td>
<td>3.2·10⁻⁴</td>
</tr>
</tbody>
</table>

very important because in the separation process the first period of 60 min is the most significant period of time, during which the emulsion is processed.

It can be concluded from the sedimentation coefficient calculations, that the bitumen/kerosene emulsion is more stable than the hexadecane emulsion (the smaller sedimentation coefficient, the more the stable emulsion). This can be seen especially for the first 60 min of sedimentation. When comparing the less stable emulsions (addition of SDS as well as SDS and PERCOL 592) with each other and with the more stable emulsions, the time of the conditioning process (30 min in tank before sampling) has to be taken into consideration. The initial concentration was not the same in all cases. Especially with the addition of SDS and PERCOL 592 the initial concentration was much lower than that anticipated (250 mg/dm³); for hexadecane 149 mg/dm³, for bitumen/kerosene 185 mg/dm³. As a consequence, such an emulsion (with addition of SDS and PERCOL 592) is less stable than it can be concluded
from data presented in Table 5. For the period of time over 60 min, all emulsions examined (with and without chemical additions) have similar stability.

The reason for the higher stability of the bitumen/kerosene than hexadecane emulsion is the presence of natural surfactants and fine particles as was discussed in Section 2.3.2. Addition of surfactant makes the bitumen/kerosene emulsion more stable than hexadecane emulsion. On the other hand, the addition of polyelectrolyte reduces the stability of bitumen emulsion. In the case of the hexadecane emulsion the reduction in stability due to PERCOL 592 addition is less evident.

2.5 Summary

As discussed in the literature, there appear to be two stages in the collapse of emulsions: flocculation, in which some clustering takes place, and coalescence, in which the number of distinct droplets decreases. The same analysis can be adopted for the removal of dispersed oil from emulsions during flotation where coalescence also involves air bubbles and includes filming phenomena.

Flocculation is sensitive to long range forces between the droplets and bubbles as they approach each other. The flocculation or air bubble/oil droplet attachment can be controlled by adjusting the zeta potential of droplets and bubbles. The zeta potential should be adjusted so that the
The surface charge of bubble and droplet are opposite in sign which leads to attraction and attachment. Also, the zeta potential of a bubble and a droplet (or two droplets) should be close to the isoelectric point such that repulsion is weak. Satisfaction of either one of the above described conditions enhances flocculation. In filming experiments (Section 2.1.2.3) neither of the above described conditions was satisfied (there was no polyelectrolyte added), but the buoyancy effect (the density difference between the continuous and the dispersed phases) stimulated oil droplet to rise to the surface. Since conditions were identical for each experiment, (the same droplet diameter and distance to the surface) the results obtained provided clear indication for the probability of the filming process.

The coalescence and/or filming rates depend on the thermodynamic properties of the interfacial films and on the degree of irreversibility of film desorption. The possibility of filming can be estimated by calculation of the spreading coefficient for the system. A positive spreading coefficient is necessary for filming process to occur. To calculate the spreading coefficient, interfacial tensions of air/water, air/oil, and water/oil were used as described in Section 2.1.2.3. From these calculations, the existence of a maximum in the variation of the spreading coefficient within SDS concentration can be observed. The reason for the existence of this maximum is that the adsorption density of the SDS at the
oil/water interface is much higher than at the air/water interface. The difference is, of course, the largest for the surfactant concentration at which the maximum spreading coefficient is obtained.

Results from surface chemistry experiments identified the best conditions for dispersed oil flotation from emulsions. For hexadecane as the oil phase, the addition of 30 mg/dm$^3$ of surfactant (SDS) and 2 mg/dm$^3$ of polyelectrolyte (PERCOL 592) satisfies the conditions for filming and thus flotation. For the 20% kerosene/bitumen blend as the oil phase, the addition of 0.5 mg/dm$^3$ of polyelectrolyte (PERCOL 592) without added surfactant satisfied the conditions for effective filming. However, to maintain the optimal working conditions for ASH flotation, the addition of 9 mg/dm$^3$ of surfactant (SDS) is necessary for froth stability. The spreading coefficient for this system decreases from 26.5 mN/m to 24.0 mN/m with this SDS addition, so it can be assumed that the designed conditions for filming are still maintained.

The difference in properties between these two emulsions results from the presence of natural surfactants and fine particles such as clays and precipitated carbonates in the bitumen.
Various separation techniques for oily water treatment have been proposed in recent years. These methods are frequently characterized by the drop size that can be separated. For example in the case of gravity and parallel plate separators the drop size is limited to about 30 μm, whereas for a coalescer/filter separation drops as small as 5-10 μm can be separated.\(^{[84]}\) The treatment of oily water consisting of oil droplets of diameter smaller than 10 μm can be enhanced by chemical destabilization of the emulsion, filtration with an agglomerating medium, and biological treatment. Air flotation has been recommended for separation of emulsified oil and extensive investigations have been reported.\(^{[6,10,15,18,31,74]}\)

There are essentially five different types of flotation systems, their classification being based on the method of bubble generation:\(^{[6]}\)

1. dissolved air - air precipitates from a supersaturated solution as a result of a sudden reduction in pressure
2. induced (dispersed) air - the air and liquid are mechanically mixed to induce bubble formation in the liquid
3. sparged air - the air is directly injected into fluid by means of a sparger
4. electrolytic - the bubbles are generated by electrolysis of water
5. vacuum release - air is released from a saturated solution by a negative pressure

However, of the five systems, only the first four are used industrially for oil flotation.

There are two major flotation systems currently being used on an industrial scale:

1. dispersed air flotation; in which air bubbles are introduced into the waste stream using high speed impellers
2. dissolved air flotation; in which air is dissolved in the waste water under pressure and is released to the solution when the pressure is dropped. As a result of the pressurization/depressurization, very small air bubbles are formed which subsequently rise to the surface along with attached oil and hydrophobic particles.

Principal differences between the two types of air flotation are the bubble size and the mixing conditions. In dissolved air flotation, the bubbles are about 50 to 60 μm in diameter,(83) whereas in induced-air flotation bubbles are an order of magnitude larger. Dissolved air flotation units operate under fairly quiescent conditions and the liquid phase approximates plug flow. For dispersed air flotation, the submerged rotor imparts enough energy to the liquid so that the tank contents are well mixed.(83)

The industrial use of dispersed air flotation for oily waste water treatment went into full-scale production in 1969.(83) The application has sine grown rapidly, aided by
"Wemco" who is selling more flotation cells for application on oil platforms than to all mineral industries together. Although dispersed air flotation equipment is simple, the fluid mechanics of the process are not simple; and the arrangement of the turbine, sleeve, and perforations have been determined essentially by trial-and-error experimentation with small-scale units.

Dissolved air flotation has been practiced for almost 90 years. Francis E. Elmore patented a "vacuum process for flotation" in 1904. In spite of the early beginnings of dissolved air flotation during the first two decades of this century, it has not found extensive industrial use until the advent of large scale water and waste treatment applications. These applications are now growing at a rapid rate.\(^{(87)}\)

The removal of emulsified oil from oily waters involves the complex effects of several variables. With the rise of the fine bubbles, the oil emulsion begins a complicated motion. The emulsified oil is transported to the top of the bubble layer and removal of the emulsified oil is achieved by the energy due to the fluid flow and the collapse of the bubbles. As a result, an oil layer is formed at the top of the bubble layer. In this regard the removal of the emulsified oil is very similar to the froth flotation practiced in mineral processing operations.\(^{(84)}\) Generally, the kinetics of emulsified oil flotation have been found to follow a first order kinetics model, especially in column flotation, as
reported by various authors.\textsuperscript{(84-86)}

In the hot water process, as applied in commercial plants in Canada and proposed for Utah tar sands, flotation is used for bitumen recovery after gravity separation. In Canada, flotation cells, both roughers and scavengers, are used to recover bitumen from the middlings stream of the primary separation vessel.\textsuperscript{(88)} The froth in such cells is normally shallow and unstable and contains a considerable amount of solids. Separation of bitumen in the froth stream of a flotation cell is normally carried out by centrifuging. The load on the centrifuge and thus the cost of centrifugation is directly related to the amount of solids present in the feed stream. An alternative approach\textsuperscript{(88)} in order to reduce solids recovery in the flotation process is to use flotation columns instead of conventional cells. The major innovation of such columns is the addition of wash water at the top of the froth. This wash water percolates downward through the froth zone of a flotation column and provides an efficient cleaning action thereby suppressing the solids recovery in the froth.\textsuperscript{(89)} For Utah tar sand processing, a Denver flotation machine has been used for flotation of the entire tar sand slurry after the gravity separation.\textsuperscript{(18)} The recirculation of process water from the flotation cell decreases the solids content in the concentrate by a factor of one half.\textsuperscript{(90)} Recent preliminary studies using either a flotation column and an air-sparged hydrocyclone provided encouraging results.\textsuperscript{(91)}
The air-sparged hydrocyclone is a promising alternative to conventional air flotation for oil recovery. The first published work in this regard was by Misra et al.\( ^{(92)} \) for kerogen recovery from oil shales. The quality of separation achieved was comparable to that of conventional batch flotation experiments. A recovery of 70\% of the kerogen to the concentrate with a concentrate grade of 21\% was obtained with the ASH at a retention time of less than 0.8 sec. With a conventional flotation cell it took more than 2 min. to achieve 70\% kerogen recovery and 20\% grade.

Other experiments were performed by Miller and Hupka\( ^{(9)} \) for the removal of dispersed oil from water using a modified design of the 5 cm dia. ASH. This design (see ref. [9] for complete description) allows for the separation of oil and water without the addition of frother, contrary to the original design of the ASH, which requires a dense froth phase to carry oil to the overflow. In this modified design, the emulsion was fed from the bottom and the formation of a uniform swirl flow layer at the porous cylinder wall was achieved when the water flowrate was maintained above 25 dm\(^3\)/min. Mechanically produced emulsion used for feed to the modified ASH contained 10 g/dm\(^3\) of oil with a droplet size between 50 \(\mu\)m and 5 mm. The modified ASH used in these experiments had the highest efficiency for an effluent split of 3/10, the air-to-water ratio of 11/10, and no surfactant addition. However, the underflow stream showed only 40\%
reduction of oil content, making the process uncompetitive with other oil/water separation techniques.

The most recent ASH application in the oil/water separation field was presented by Beeby and Nicol.\(^{(10)}\) In this work the ASH, as originally designed and now marketed by APT, was used. A chemically stabilized o/w emulsion (addition of sodium hydroxide to water and oleic acid to the mineral oil) was prepared by continuous treatment through a high shear pump for 5 hr. The final emulsion concentration was 440 mg/dm\(^3\) and the droplet size distribution was 90\% by volume less than 10 \(\mu\)m in diameter. The effect of flocculant and frothing agents was investigated using a high molecular weight cationic flocculant and an anionic surfactant (unfortunately specific compositional details of the chemicals were not provided). The flocculant concentration was varied from 2 to 6 mg/dm\(^3\), while the surfactant concentration were varied from 2 to 60 mg/dm\(^3\). It was possible to remove 96\% of the turbidity (which was assumed to be directly proportional to the oil content) from the underflow when the feed oil concentration was 440 mg/dm\(^3\). Maximum turbidity removal was achieved when the froth pedestal was fully elevated, small annular underflow opening, but the underflow flowrate was then only 50\% of the total flowrate. It was concluded that a viable method of operating the ASH would be with the pedestal in the fully lowered position, provided that secondary treatment of the underflow follows. The flowrate of the underflow was 88-94\% of the feed flowrate, but
the oil concentration of the underflow stream was reduced to only about 50 mg/dm³.

The difference between the previous work⁹ and that described by Beeby and Nicol¹⁰ was that the previous study was performed on a mechanical emulsion, whereas the latter work pertained to a chemically stabilized emulsion. Chemically stabilized oil droplets behave more like solid particles than mechanically stabilized droplets because of the higher charge density on the droplet surface and its smaller size. The previous study with the modified ASH⁹ also considered that a change in diameter/height ratio to 1/1 would improve oil separation by inducing quiescent separation conditions. This may also improve the separation of chemically stabilized emulsion. However, if operated in the turbulent regime where optimum oil removal can be achieved by high air flow/water flow values and where surfactant is used, the change in the dimensions may not be beneficial.

3.1 Emulsion Stability Control in the Conditioning Tank

ASH flotation experiments were initiated with hexadecane as an o/w emulsion. The results obtained from the surface chemistry experiments were used as a basis for the selection of appropriate ASH flotation conditions (see Chapter 2, page 14). Such an oil phase selection provides a satisfactory representation of the spreading coefficient dependency on
sodium dodecyl sulfate concentration for the standard single component hydrocarbon case. The spreading coefficient behavior for hexadecane is characteristic of all hydrocarbons examined (see Figure 9) and shows a distinct maximum at an SDS concentration of 30 mg/dm$^3$ ($10^{-4}$M) with negative values for a wide range of concentrations (below 3 mg/dm$^3$ ($10^{-5}$M) and above 300 mg/dm$^3$ ($10^{-3}$M)). The change in the susceptibility to filming occurs at distinct SDS concentrations which makes the selection of the examined concentrations easy. Concentrations of 0, 15, 30, and 50 mg/dm$^3$ SDS were selected for the ASH flotation study.

From the zeta potential measurements, the influence of the high molecular weight cationic polyelectrolyte (PERCOL 592) on the droplet charge were established, please see Figure 17. The i.e.p. for hexadecane emulsion was found at 1.5 mg/dm$^3$ and 1.0 mg/dm$^3$ PERCOL 592 concentration with and without surfactant, respectively. Flotation experiments were performed at PERCOL 592 concentrations of 0, 1.0, 2.0, and 5.0 mg/dm$^3$.

3.1.1 Experimental Techniques

The oil samples were emulsified in 5 dm$^3$ of water using the SILVERSON L4R homogenizer (5 min, 7200 rpm) and then diluted in 200 dm$^3$ conditioning tank. Since air flotation devices work best with feed streams having oil concentrations of 300 mg/dm$^3$ or less, air flotation should be preceded by a gravity separation to remove free oil. Typical oily waste
water, according to Bennett,\(^6\) leaving API separators has oil droplets less than 30 µm in diameter and oil concentrations less than 200 mg/dm\(^3\). The concentration of oil, during ASH flotation tests, after dilution was approximately 200 mg/dm\(^3\) in most experiments, unless stated differently. The temperature was maintained at 25°C (note that the solidification of hexadecane occurs at 18°C). The average droplet size changed with the addition of chemicals as discussed in Section 2.3. The measurements of the oil concentration were performed using the HORIBA OCMA-220 oil-in-water analyzer. For concentrations which were expected to be greater than 200 mg/dm\(^3\), extraction was performed in a separatory funnel with 1:1 CCl\(_4\)/H\(_2\)O vol. ratio. The extract, diluted by the addition of a known amount of CCl\(_4\) was measured in the HORIBA analyzer. Such a method of oil content determination has been shown to be sufficiently accurate for these experiments.\(^{77}\)

A 5 cm dia. and 47 cm long (two sections: 16 and 31 cm) ASH unit (the ASH-2C) with separate, adjustable air supply to both sections was used in all experiments. The operating variables were the flowrates of emulsion and air (expressed as \(Q^*\) - the dimensionless flowrate ratio) and the underflow and the overflow opening areas, the underflow area was controlled by changing the position of the pedestal (see Figure 1), (expressed as \(A^*\) - dimensionless OF/UF area ratio).

The schematic representation of the experimental set-up
is presented in Figure 28. Both chemicals were added directly to the emulsion in the conditioning tank and conditioned for about 30 min. Samples were taken after 30 s of ASH operation in order to establish steady state conditions. The feed, the underflow (UF), and the overflow (OF) were sampled in each experiment for oil concentration and the UF and OF volumes were also determined to establish the UF/OF split.

3.1.2 Results and Discussion

3.1.2.1 Single Pass Experiments

First, the ASH working conditions were evaluated. The emulsion flowrate was changed from 30 to 80 dm³/min and the air flowrate from 30 to 280 dm³/min (which corresponds to a range of $Q^*$ from 0.5 to 5). The preliminary results obtained indicate that the best separation was obtained when the emulsion flowrate was maintained at 55 dm³/min and the air flowrate at 200 dm³/min which correspond to the dimensionless flowrate ratio $Q^* = 3.5$.

In the first series of experiments both chemicals were added to the conditioning tank and equilibrated. The ASH flotation results for the hexadecane emulsion are presented in Figures 29 and 30. Generally, it was observed that oil recovery increases with an increase of the water split to the overflow which is controlled by the variation of the underflow opening and thus $A'$. As was expected, the highest oil recovery to the overflow was obtained for 30 mg/dm³ of SDS and 2 mg/dm³
1. homogenizer
2. conditioning tank
3. pump
4. air-sparged hydrocyclone (ASH)
5. receiving tanks

Figure 28 Schematic representation of the experimental set-up used for the ASH flotation
Figure 29 ASH flotation of hexadecane as a function of UF/OF split; 30 mg/dm³ SDS
Figure 30 ASH flotation of hexadecane as a function of UF/OF split; 2 mg/dm$^3$ PERCOL 592
of PE for each tested overflow/underflow split. The worst result was obtained without the addition of flocculant the presence of which is necessary to neutralize the charge on the oil droplets and allow for bubble attachment. The effect of polyelectrolyte addition on hexadecane recovery is shown in Figure 29 for a constant surfactant concentration of 30 mg/dm$^3$. The lower oil recovery obtained for 5 mg/dm$^3$ PERCOL 592 as compared to that for 1 mg/dm$^3$ PERCOL 592 is attributed to the zeta potential change of the oil droplets and air bubbles. The higher polyelectrolyte concentration causes the zeta potential to be more positive in both cases which generates droplet/ bubble repulsion and consequently, the probability of droplet/ bubble contact is significantly lowered.

The effect of surfactant addition on hexadecane recovery is shown in Figure 30 for a constant polyelectrolyte concentration of 2 mg/dm$^3$. The value of the spreading coefficient does not change for 15 and 50 mg/dm$^3$ SDS added to the emulsion and the difference in oil recovery can be explained by the SDS influence on the bubble size. The average bubble size produced in the ASH decreases with the addition of surfactant,$^{(93)}$ which increases the efficiency of ASH flotation. It is evident that the recovery goes through a maximum at approximately 30 mg/dm$^3$ SDS and 2 mg/dm$^3$ PE which corresponds to the best conditions for filming (see Figure 9) and to the i.e.p. for the system (see Figure 17).
3.2.2.2 Recirculation Experiments

ASH flotation of hexadecane from the o/w emulsion was also tested for emulsion recirculation. Because of the difficulties associated with maintaining the oil concentration at sufficiently high concentration with both chemicals added to the conditioning tank (after addition of flocculant and surfactant gravity separation occurs and a top layer of oil forms in the tank, which, of course, changes the oil concentration in the feed), this experiment was performed at an initial concentration of 86 mg/dm³ of hexadecane. The flowrate conditions were identical to the single pass experiments and the split to the overflow was 6% at all times. The underflow was returned to the conditioning tank. The results are presented in Table 6.

Satisfactory results (14 mg/dm³ concentration in the UF) were obtained after 3 min of recirculation. In the case of emulsion recirculation with a higher oil concentration, the process should be performed in three stages. First, chemicals should be added and the equilibration of the system should be reached. Second, the top layer of oil should be collected after gravity separation. Third, ASH flotation should follow

<table>
<thead>
<tr>
<th>Time [sec]</th>
<th>0</th>
<th>5</th>
<th>30</th>
<th>60</th>
<th>180</th>
<th>420</th>
<th>900</th>
<th>1320</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed [mg/dm³]</td>
<td>86</td>
<td>-</td>
<td>65</td>
<td>38</td>
<td>14</td>
<td>13</td>
<td>9</td>
<td>11</td>
</tr>
<tr>
<td>OF [mg/dm³]</td>
<td>225</td>
<td>139</td>
<td>-</td>
<td>66</td>
<td>52</td>
<td>73</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
with underflow recirculation.

3.2 Emulsion Stability Control in the Feed Pipe

Two different oil phases hexadecane and a 20% bitumen/kerosene blend were examined. The results obtained from the surface chemistry experiments and ASH hexadecane flotation with emulsion stability control in the conditioning tank provided the basis for the selection of appropriate ASH flotation conditions.

Such an oil phases selection provides a satisfactory representation of the spreading coefficient dependency on SDS concentration. The spreading coefficient change for hexadecane was described earlier. The 20% bitumen/kerosene blend shows a different dependence of the spreading coefficient on the SDS concentration (see Figure 10). In this case, the spreading coefficient is strongly positive and constant for the SDS concentration from 0 to 3 mg/dm$^3$ ($10^{-5}$M) and reaches a slightly negative value at 300 mg/dm$^3$ ($10^{-3}$M).

From the zeta potential measurements, the influence of the high molecular weight cationic polyelectrolyte (PERCOL 592) on the droplet surface charge is determined. For the bitumen/kerosene blend emulsion, the zeta potential approached zero at 0.1 mg/dm$^3$ without SDS addition and at 0.3 mg/dm$^3$ with surfactant addition.
3.2.1 Experimental Techniques

The addition of surfactant and polyelectrolyte was done by two different methods. In the first experiments (described earlier, Section 3.1) both chemicals were added directly to the emulsion in the conditioning tank. In the second set of experiments these chemicals were added to the slurry feed pipe as indicated in Figure 28. This change in the experimental set-up arose from the difficulty encountered in maintaining the required oil concentration in the feed due to the gravity separation of oil in the conditioning tank after addition of chemicals (see Section 2.4, page 76). This change should improve the oil recovery because part of the oil phase which was separated during conditioning in the tank will be found as a part of the oil phase reporting to the overflow stream during ASH flotation.

All other experimental arrangements including emulsion preparation, air-sparged hydrocyclone set-up, sampling and oil content measurements were described in Section 3.1.1.

3.2.2 Results and Discussion

3.2.2.1 Hexadecane O/W Emulsion

The operating conditions evaluated earlier for the ASH flotation are employed for emulsion stability control in the feed pipe. The emulsion flowrate was maintained at 55 dm$^3$/min and the air flowrate at 200 dm$^3$/min which corresponds to the dimensionless flowrate ratio $Q'$ = 3.5.
In this series of experiments both chemicals (30 mg/dm$^3$ SDS and 2 mg/dm$^3$ PERCOL 592) were added by a peristaltic pump directly to the feed line as shown schematically in Figure 28.

As shown in Figure 31 the results from these experiments show improvement in hexadecane recovery to the overflow by 20% when compared to previous experiments where the reagents were added to the conditioning tank. The concentration of hexadecane in the feed was 240 mg/dm$^3$ and was lowered to about 60 mg/dm$^3$ after a single pass through the ASH-2C as presented in Table 7 (each result is the average of from three to five replicate experiments).

The difference in the results obtained for these two different experimental procedures for emulsion stability control is due to the oil separation by gravity in the conditioning tank. The emulsion stability control in the feed pipe has an advantage over control in the conditioning tank because the emulsion is treated in a single step operation when the chemicals are added to the feed pipe. The efficiency

<table>
<thead>
<tr>
<th>Split to OF [%]</th>
<th>Oil Concentration in UF [mg/dm$^3$]</th>
<th>Oil Concentration in OF [mg/dm$^3$]</th>
<th>Recovery to OF [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.9</td>
<td>72</td>
<td>5876</td>
<td>71</td>
</tr>
<tr>
<td>4.8</td>
<td>68</td>
<td>3650</td>
<td>73</td>
</tr>
<tr>
<td>12.0</td>
<td>65</td>
<td>1520</td>
<td>76</td>
</tr>
<tr>
<td>23.0</td>
<td>50</td>
<td>876</td>
<td>84</td>
</tr>
</tbody>
</table>
Figure 31 ASH flotation of hexadecane as a function of UF/OF split; 30 mg/dm³ SDS, 2 mg/dm³ PERCOL 592
of ASH flotation in both cases is expected to be the same. However, when chemicals were added to the feed pipe, the entire oil present in the emulsion is fed to the hydrocyclone including larger drops which could have been removed by gravity separation.

3.2.2.2 Bitumen/Kerosene O/W Emulsion

In this section, the ASH flotation results for the bitumen/kerosene blend emulsion are presented. The experiments with the bitumen emulsion were performed by the continuous addition of chemicals to the ASH feed pipe since this practice yielded more favorable results in the case of the hexadecane system. The experimental results are presented in Figure 32. The recovery of oil to the overflow was greater for preferred surfactant and polyelectrolyte doses as established in the surface chemistry experiments (see Section 2.1 and 2.2), namely 9 mg/dm$^3$ SDS and 0.5 mg/dm$^3$ PERCOL 592. The initial concentration of oil in the feed was 240 mg/dm$^3$ and after a single pass through the ASH the oil content was reduced to as low as 34 mg/dm$^3$ as shown in Table 8 (each result is the average from three to five replicate experiments).

An increase in the surfactant and the polyelectrolyte concentration to 30 mg/dm$^3$ and 2.0 mg/dm$^3$ respectively, lowers the recovery of oil to the overflow because under these circumstances the spreading coefficient becomes less positive (see Figure 10). Recall from Figure 10 that the best condition
Figure 32 ASH flotation of bitumen/kerosene as a function of UF/OF split
Table 8  ASH flotation of bitumen/kerosene emulsion from a feed concentration 240 mg/dm$^3$, with 9 mg/dm$^3$ SDS and 0.5 mg/dm$^3$ PE

<table>
<thead>
<tr>
<th>Split to OF [%]</th>
<th>Oil Concentration in UF [mg/dm$^3$]</th>
<th>Oil Concentration in OF [mg/dm$^3$]</th>
<th>Recovery to OF [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5</td>
<td>65</td>
<td>5074</td>
<td>74</td>
</tr>
<tr>
<td>9.5</td>
<td>58</td>
<td>1970</td>
<td>78</td>
</tr>
<tr>
<td>17.0</td>
<td>38</td>
<td>1228</td>
<td>87</td>
</tr>
<tr>
<td>22.0</td>
<td>34</td>
<td>971</td>
<td>89</td>
</tr>
</tbody>
</table>

for filming is the in absence of surfactant. However, a certain amount of frother (e.g., 9 mg/dm$^3$) is required to produce smaller bubbles and provide a suitable froth phase with sufficient stability to carry the oil droplets.

The difference in the flotation response of the hexadecane and the bitumen/kerosene emulsions is a result of three different factors. First, the magnitude of the spreading coefficient is three times larger for the bitumen emulsion. However this effect may be related to the larger amount of surfactant added to the system in the hexadecane case which results in finer bubbles and therefore a better recovery. The second factor pertains to the polyelectrolyte addition. As was experimentally determined, the quantity of PERCOL 592 needed to reach the i.e.p. or a slightly positive zeta potential is four times less for the bitumen emulsion than the amount of PERCOL 592 needed for the hexadecane emulsion. As was presented earlier, the addition of PERCOL 592 effects both the oil droplets and the air bubbles. The addition of PERCOL 592
probably reduces the negative zeta potential for bubbles proportional to its concentration. In the case of the bitumen droplets, the charge on bubbles can still be slightly negative thus the attraction between a droplet and a bubble increases. The third important difference between these two systems is the presence of fine solids in the bitumen/kerosene blend. As reported in the literature,\(^{(41)}\) the presence of fine solid particles in the dispersed oil increases the oil recovery during flotation. The combination of these three effects results in slightly higher oil recovery from the bitumen/kerosene emulsion than from the hexadecane emulsion.

**3.3 SUMMARY**

Dispersed oil flotation from o/w emulsions in an air-sparged hydrocyclone requires the control of two groups of process variables:

1. the surface chemistry conditions at the oil/water and the air/water interfaces as controlled by the addition of surfactant and polyelectrolyte
2. the ASH operating conditions (air and water flowrates as well as the size of overflow and underflow openings)

Due to the complexity of the emulsion - surfactant system, optimum conditions must be determined experimentally. The amount of surfactant should be established based on the evaluation of the spreading coefficient, bearing in mind the requirements for the ASH flotation. The appropriate concentration of the polyelectrolyte can be determined by zeta
potential measurements. After these surface chemistry experiments the best conditions for ASH flotation can be established. It was shown that the performance of the ASH system for dispersed oil flotation is dependent on the tendency of oil to film at the air bubble surface.

The change in the location of reagent addition to the emulsion allows for a single stage process instead of two stages (i.e., gravity separation and flotation) without a decrease in the overall recovery efficiency (probably this arrangement allows for a higher overall recovery).

The results from this phase of the thesis research have been very promising. Oil recovery values comparable to the conventional dispersed air flotation were obtained (in the case of conventional dispersed air flotation the average effluent contains 15-50 mg/dm$^3$ of oil, with the addition of chemicals and recycle the average effluent contains 5-10 md/dm$^3$ of oil$^{(6)}$). Of course, the residence time in the ASH is significantly lower (0.8 s) when compared to the residence time (5 min) in conventional dispersed air flotation. The operating conditions of the ASH flotation system depend on the desired quality of the underflow water.
CHAPTER IV

SUMMARY AND CONCLUSIONS

It is imperative to recover as much bitumen as possible during the hot water process of tar sand resources. Currently Syncrude and Suncor recover approximately 90% of the bitumen, with the largest loss (at Syncrude) being the sand tailings from the primary separation vessel. Syncrude lost approximately $0.7 \times 10^6$ t of bitumen in 1986\(^{(16)}\) and these losses are likely to increase as the ore quality decreases (percentage of bitumen in the oil sands declines). Thus in turn will result in a decrease in separation efficiency and speaks for the need to develop more efficient technology for bitumen recovery, and in particular recovery of bitumen from tailings.

As was emphasized by Hall and Tollefson,\(^{(20,23)}\) any form of turbulent shearing motion whether originating from tumbling, mixing, aeration, or combinations of these, is useful in dispersing bitumen and bitumen-mineral agglomerates so that the bitumen can be separated by flotation. The air-sparged hydrocyclone appears to be ideal for this application. The design of the ASH was envisioned to establish a controlled high force field by swirl flow in order to increase the inertia of fine particles and to produce a high density of
fine air bubbles with a directed motion to improve collision efficiency. The net result is effective fine particle flotation with a flotation rate having retention time which approach intrinsic bubble attachment times.\(^{(8)}\)

### 4.1 Surface Chemistry

The recovery of bitumen from tar sand tailings involves a complex system of oil, sand and natural surfactants with many compositional features and detailed surface chemistry interactions still unknown. In this thesis research it was decided to first use a simpler system containing only dispersed oil (i.e., no solids) in water and to focus on the chemical and physical properties of the emulsion with emphasis placed on two fundamental aspects of the surface chemistry problem, namely the stability of emulsion and the necessary conditions for oil filming at the air bubble surface.

Three system features were considered in order to study the emulsion stability: the zeta potential (especially the necessary conditions under which the electrophoretic mobility of oil droplets in the emulsion is significantly reduced - the zeta potential approaches zero), the droplet size distribution and dispersed oil phase concentration in the emulsion as a function of time. There appear to be two stages in the collapse of emulsions flocculation and coalescence. The same mechanism can be adopted for the removal of the oil phase from emulsions during flotation, where coalescence is considered to
include bubble filming.

Flocculation is sensitive to long range forces as it involves the first stage of the interaction of droplets and bubbles. The possibility of flocculation or air bubble-oil droplet attachment can be controlled by the zeta potential measurements of droplets and bubbles. The zeta potential should be adjusted in one of two ways; first conditions can be established where bubble and droplet are of opposite surface charge, which leads to attraction and attachment; second conditions can be established where the zeta potentials of the bubble and the droplet (or two droplets) should approach their respective isoelectric points, in which case repulsive forces are weak. Satisfaction of either one of the above described conditions will enhance flocculation.

The coalescence and/or filming rates very likely depend on the interfacial film repulsion and on the degree of irreversibility of film desorption. It was shown for the first time that the possibility of filming can be estimated by calculation of the spreading coefficient for the system. A positive spreading coefficient is necessary for filming to occur. In order to calculate the spreading coefficient three interfacial tensions are needed: air/water, air/oil, and water/oil. These interfacial tensions were measured for several different systems.

It was found that the air/oil surface tension does not change for a broad range of aqueous surfactant concentrations.
However, the air/water and oil/water interfacial tensions decrease with the addition of surfactant to the aqueous phase. The rate of this decrease with respect to SDS concentration has a very pronounced effect on the sign and magnitude of the spreading coefficient. In the case of pure hydrocarbons and kerosene the spreading coefficient reaches a maximum at an SDS concentration of 30 mg/dm$^3$ ($10^{-4}$M), identical for all systems. The existence of these maxima is better understood after the analysis of the adsorption density of SDS at the air/water and oil/water interfaces. The adsorption density of SDS at the oil/water interface was found to be much higher ($3.2 \cdot 10^{-6}$ mol/m$^2$) than at the air/water interface ($1.45 \cdot 10^{-6}$ mol/m$^2$). The difference is most pronounced for the surfactant concentration at which the maximum spreading coefficient value is obtained. This higher adsorption density at the oil/water interface can be explained by the interaction between the hydrocarbon chains of the surfactant and the molecules of the oil phase.

For the bitumen/kerosene blend the spreading coefficient remains strongly positive and constant for the SDS surfactant concentrations from 0 to 3 mg/dm$^3$ ($10^{-5}$M), then rapidly decreases. Judging from the three interfacial tensions, the tendency of the bitumen/kerosene blends to spread at the water surface is most pronounced.

The difference in behavior between these two oil phases results from the presence of natural surfactants and fine particles in tar sand bitumen. Compounds dissolved in water
during the hot water process appear to be the carboxylate, sulphate, and sulfonic surfactants produced in the alkaline 
environment during the hot water separation process, with the precursors present in the bitumen phase. The concentration of 
natural surfactants present in bitumen corresponds to the SDS concentration at which the spreading coefficient reaches 
maximum for the hydrocarbons studied. Thus, as a consequence, a high spreading coefficient is observed for the bitumen/ 
kerosene blend at low SDS concentrations.

4.2 ASH Flotation

Based on surface the chemistry results, the ASH flotation of dispersed oil droplets was studied and the effect of 
additives and flow conditions on the flotation response was examined. As was expected, the highest oil recovery (89%) to 
the OF was obtained for the best surface chemistry conditions, maximum spreading coefficient, regardless of the OF/UF split.

The change in the procedure for reagent addition from the addition to conditioning tank with 30 min conditioning time to 
addition to the feed line with essentially no conditioning time, improved the hexadecane recovery to the overflow by 20%. 
The concentration of the oil phase in the feed was 240 mg/dm³ and after a single pass through the ASH-2C the dispersed oil 
concentration was lowered to about 60 mg/dm³ for hexadecane as the oil phase. In the case of the 20% bitumen/kerosene blend 
as the oil phase the oil concentration was reduced to as low
as 34 mg/dm³. The difference in results obtained for this two different procedures for emulsion stability control results from including in the overflow stream the oil being separated by gravity in the conditioning tank. The emulsion stability control in the feed pipe has the advantage over control in the conditioning tank that the emulsion is treated and oil is recovered in a single step operation.

The difference in flotation response between the two kinds of emulsions (hexadecane and bitumen/kerosene) is a result of a three factors. First, the magnitude of the spreading coefficient is three times larger for the bitumen emulsion. The second factor pertains to the polyelectrolyte addition. As was experimentally determined, the quantity of PERCOL 592 needed to reach the i.e.p. or a slightly positive zeta potential is four times less for the bitumen emulsion than the amount of PERCOL 592 needed for the hexadecane emulsion. As was presented earlier, the addition of PERCOL 592 affects both the oil droplets and the air bubbles. The addition of PERCOL 592 probably reduces the negative zeta potential for bubbles proportional to its concentration. In the case of the bitumen droplets, the charge on bubbles can still be slightly negative, thus the attraction between a droplet and a bubble increases. The third important difference between these two systems is the presence of fine solids in the bitumen/kerosene blend. As reported in the literature, the presence of fine solid particles in the dispersed oil
increases the oil recovery during flotation. The combination of these three effects results in slightly higher oil recovery from the bitumen/ kerosene emulsion than from the hexadecane emulsion.

Air-sparged hydrocyclone flotation was found to be a very promising method for the recovery of oil from o/w emulsions and it is expected that similar separation of bitumen from tar sand tailings can be achieved with proper surface chemistry control. Nevertheless future research work with sand in the system is required. In addition, other variables such as type of surfactant and flocculant as well as the influence of other ASH design parameters and operating variables need to be studied. Future research may lead to the use of ASH flotation as one of the most effective methods for oil recovery from many different o/w emulsions including the recovery of bitumen from tar sand tailings.
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