Design and Development of Mineral Structure Specific Collectors in Flotation

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Summary

The success of mineral flotation processes depends on the hydrophobization of the surface for the desired mineral particles whilst keeping, or making, all other minerals hydrophilic. This is achieved by adding several reagents to the flotation pulp to adsorb selectively at the mineral/water interface. The reagents (surface active agents) which selectively adsorb on minerals to be floated are called collectors. It is realized that many of these commonly used reagents are highly toxic and often potential threats to the environment. Use of many of these conventional chemicals will therefore be restricted soon and must eventually be stopped. An immediate effort is necessary to develop alternative eco-friendly reagents in order to continue to extract valuable minerals from ores. In addition, with the steady depletion of high grade, relatively easy to process ores, the mineral industry is confronted with a challenging task of finding more efficient techniques so as to exploit low grade, complex and disseminated type of ore deposits and old tailing dumps. The development of new selective and environmentally acceptable substances containing almost tailor-made reagents is thus inevitable for sustainability. Several known chelating agents have been appropriately modified to make those behave as selective flotation collectors with some degree of success. The problem is that almost all of the chelating groups form complexes with almost all of the transition and many non-transition metals. As a consequence, absolute selectivity does not exist. Besides being unsatisfactory from a scientific viewpoint, it assumes that the metal ion specificity observed for a functional group in bulk aqueous system would remain valid during surface chelation at the interface, while in actual practice, the specificity based on metal ion is neither valid nor useful where the cations participating in the complexation reactions are the same, for example separation among the calcium minerals.

It is clear that a selective reagent should be based on the reagent interactions not merely with the metal ion on the surface, but with the whole surface. It is more appropriate to design reagents having functional groups so spaced that those are compatible with the relative positions of the metal ion sites available on the surface, that is, to design not just metal-specific but structure-specific reagents.

The understandings of molecular interactions involved in the recognition of surfaces by organic molecules in biomineralization process suggest the possibility of reagents specific to the crystal structure. These understandings have been successfully applied to the rational design and synthesis of molecules either for the control of crystal morphology or to inhibit crystal growth processes through the recognition of specific crystal surfaces. The idea of molecules consisting of two groups having appropriate spacing between them to achieve structural compatibility during interaction with surface exhibit structure-specificity is of direct relevance to the reagents selectivity in flotation processes.

The present investigation aims to develop and distinguish mineral specific reagents with two functional groups for use in flotation of calcium containing minerals. For this purpose, a series of dicarboxylate-based surfactants with varying spacing between the carboxylate groups (one, two or three methylene groups) were synthesized. As reference, a surfactant with the same alkyl chain length but with only one carboxylate group in the polar part was synthesized. The adsorption behavior of these new reagents on pure apatite, calcite and fluorite mineral surfaces was studied using Hallimond tube flotation, ζ-potential and FTIR
measurements. The relation between the adsorption behavior of a given surfactant on a specific mineral surface and its molecular structure over a range of concentration and pH values, as well as the region of maximum recovery were established. It was found that one of the reagents, with a specific distance between the carboxylate groups, was much more selective for a particular mineral surface than the other homologues synthesized. This selective adsorption of a given surfactant to a particular mineral surface relative to other mineral surfaces as evidenced in flotation studies is substantiated by ζ-potential and infrared spectroscopy data. Our investigation revealed that it is possible to design and develop mineral specific reagents in flotation.
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List of papers

This thesis is based on the following papers

I  Design and development of novel mineral-specific collectors for flotation
    Anuttam Patra, Tommy Karlkvist, Kota Hanumantha Rao, Andreas Fredriksson,
    Romain Bordes, Krister Holmberg
    In: Proc. International Mineral Processing Congress, 20-24 October, Santiago, Chile -
    In press

II Molecular recognition in mineral flotation: selectivity in apatite-calcite system
    Tommy Karlkvist, Anuttam Patra, Kota Hanumantha Rao, Romain Bordes, Krister
    Holmberg, Andreas Fredriksson
    In press

III Selective Flotation of Calcite and Fluorite Minerals
    Tommy Karlkvist, Anuttam Patra, Kota Hanumantha Rao, Romain Bordes, Krister
    Holmberg
    Manuscript

Other papers (not included)

    Revisiting sulphide mineral (bio) processing: a few priorities and directions
    Kota, H. R., Javadi, A., Karlkvist, T., Patra, A., Vilinska, A. & Chernyshova, I. V.
    (2013), Powder Metallurgy & Mining. 2, 4
# Contents

Summary ................................................................................................................................... iii  
Acknowledgments ...................................................................................................................... v  
List of papers ............................................................................................................................ vii  
Introduction ................................................................................................................................ 1  
  Objectives ................................................................................................................................... 1  
  Significance .................................................................................................................................. 1  
  Background ................................................................................................................................. 2  
  Mechanisms of molecular recognition in biomineralization ......................................................... 4  
  Short analysis of flotation literature of calcium containing minerals ............................................ 7  
Theory of experimental methods .................................................................................................. 9  
  Flotation ....................................................................................................................................... 9  
  ζ-potential .................................................................................................................................. 10  
  IR/DRIFTS ................................................................................................................................... 11  
  NMR Spectroscopy ....................................................................................................................... 11  
  Quartz Crystal Microbalance ......................................................................................................... 12  
Experimental ............................................................................................................................... 13  
  Materials ..................................................................................................................................... 13  
  Reagents ...................................................................................................................................... 13  
  Synthesis of collectors ................................................................................................................... 14  
  Hallimond tube flotation studies .................................................................................................... 16  
  ζ-potential studies ......................................................................................................................... 16  
  Diffuse reflectance FTIR spectroscopy studies ................................................................................. 17  
Results and discussion .................................................................................................................. 19  
  Hallimond tube flotation studies .................................................................................................... 19  
    Apatite ....................................................................................................................................... 19  
    Calcite ....................................................................................................................................... 21  
    Fluorite ...................................................................................................................................... 22  
  ζ-potential studies ......................................................................................................................... 23  
    Apatite ....................................................................................................................................... 23  
    Calcite ....................................................................................................................................... 24  
    Fluorite ...................................................................................................................................... 26
DRIFT studies ....................................................................................................................... 28
Apatite ................................................................................................................................ 28
Calcite .................................................................................................................................. 28
Fluorite ............................................................................................................................... 29
Conclusions .............................................................................................................................. 31
Future work .............................................................................................................................. 33
References ................................................................................................................................ 35
Introduction

Objectives
The main goal of this Licentiate Thesis is to distinguish and develop mineral specific reagents for use in flotation processes based on the molecular recognition mechanisms at the inorganic-organic interface seen in biomineralization. The general understanding and concepts of molecular recognition mechanisms of simultaneously satisfying the geometric, stereochemical and electrostatic requirements at inorganic/organic interface was used for the development of new reagents with two functional groups with varying spacing between them.

The aim for this PhD project is to develop a new reagent scheme for effective dephosphorisation of magnetite fines and apatite recovery from the flotation tailings containing carbonate, silicate and iron minerals. As an initiating first step in the project, a systematic study on the mineral-reagent interactions in the flotation separation of apatite-calcite and calcite-fluorite systems using alkyl di-carboxylic acid derivatives with varying spacing between the two functional groups that were synthesized in this research program has been investigated.

Significance
The magnetite ore at LKAB in Kiruna contains about 1 wt% phosphorous which is detrimental to blast-furnace technology. Dephosphorization is carried out by floating phosphate gangue from magnetite fines with a fatty acid based collector (Atrac). The level of phosphorous content in magnetite fines should be below 0.025 wt% and this is achieved at a collector dosage of about 30-70 g/t. The concentrated magnetite fines are then treated in a pelletizing plant. The green balls produced during the green pelletization step are found to be less strong than similar balls derived from the treatment of non-floated magnetite fines. Studies showed that the surface contamination of magnetite by chemicals adsorbed during the flotation step was responsible for this behavior. Thus there is an economically urgent need either to strip the adsorbed collector from magnetite fines or to develop new reagent scheme which is very specific to apatite mineral.

Furthermore, there used to be production of phosphate from the flotation tailings of dephosphorization. Since 1989, phosphate production has been discontinued due to varying phosphorous content with associated carbonate gangue mine leading to problems in the flotation circuit. The processing of phosphate containing carbonate gangue requires highly selective reagents. The phosphate containing material at LKAB can be classified into:

i) Tailings of crushed magnetite rock material from the magnetic separation process
ii) Floated gangue material from magnetite fines from the dephosphorisation process
iii) Accumulated flotation tailings over the years

Considering the fact of dwindling phosphate resources, high price of phosphate raw material and adverse effect of tailings on environment, LKAB management have been investigating the possibility to initiate the production of phosphate concentrate once again from the tailing materials. Hence it is essential to treat the tailings and produce phosphate concentrate fulfilling the industry requirements.
**Background**

The efficiency of a mineral flotation process depends on making the desired mineral particles hydrophobic while at the same time keeping, or making, all unwanted particles hydrophilic. To make the mineral surface hydrophobic a collector is added to the flotation pulp. Currently there is no satisfactory scientific theory describing the collector selectivity for mineral surfaces and most of the reagents presently used were discovered by empirical and/or trial and error methods. Several known chelating agents have been appropriately modified to make them act as selective flotation collectors with some degree of success. The problem is that almost all of the chelating groups form complexes with almost all of the transition and many non-transition metals. Hence, absolute selectivity does not exist, especially where the cations participating in the complexation reactions are the same.

As the easy to access and high grade ores are steadily depleting, it is becoming more and more urgent to find efficient techniques to exploit low-grade, complex and disseminated type of ore deposits and old tailings dumps. The development of new selective reagents (collectors) by correlating the chemical structure of a surface-active molecule directly to the physico-chemical activity of a mineral is vital for this purpose. The minerals studied have been chosen due to their importance in LKAB industry. These minerals all contain calcium in surface sites, a factor which is believed to determine the differences in their interaction with surfactants having two functional groups with varying spacing between them.

Much research has been performed on the adsorption of fatty acid collectors to the calcium minerals surface and comprehensive reviews have previously been published in the literature. Despite this, there is still no solution for their separation processes on an industrial level. This is partially due to the complexity of the minerals themselves and in part due to the high reactivity of the collectors employed for this purpose. The traditional collectors have a low selectivity with depression of unwanted minerals being the way to selectively separate calcium minerals with limited success.

It would be more efficient to design a selective collector based on interactions with the whole surface and not only on a single constituent, i.e. designing a collector that recognizes the surface of a mineral and takes into account the differences in the crystal structure of the mineral surfaces. To investigate this, reagents having two functional groups so spaced that they are compatible with the relative positions of the metal ion sites available on the surface were synthesized to design not only metal-specific but also structure-specific reagents, illustrated in Figure 1.

![Figure 1. Collector with two negative functional groups interacting with the positive sites on a simplified metal oxide surface, where R is the hydrophobic tail of the collector, Fn is the negatively charged functional group, M is the positive metal ion and O is the negatively charged oxide.](image-url)
A scientific approach to designing mineral separation reagents involves two important surface chemical aspects:

i. Selection of the appropriate functional group

ii. Design of the corresponding molecular architecture depending on its end use

The discoveries in biomineralization that molecules with the same functional groups but different distances in between will interact differently with the inorganic surface suggest the possibility of designing crystal structure specific reagents. The same influence with reagents having only one functional group was not observed indicating that the distance between functional groups is an important factor in selectivity for crystal growth inhibition. These concepts have been successfully applied to the rational design and synthesis of molecules either for the control of crystal morphology or to inhibit crystal growth processes through the recognition of specific crystal surfaces.

The structure specificity in mineral-reagent interactions, even though not specifically stated, can be noticed in the flotation of calcium minerals. Among calcium minerals, the dominant flotation of fluorite using conventional fatty acid collectors has been attributed to the better templating effects at the fluorite surface. The different flotation response of chloro- and fluoro-apatites using fatty acids has been attributed to their different crystal structures. Amino-carboxylic fatty acids have been found to be effective in fluorite-calcite separation. Diphosphonic acid collectors with varying link lengths exhibited different flotation response for apatite and calcite. The selectivity of these reagents can be attributed to their geometrical match and compatibility at the mineral surfaces.
Mechanisms of molecular recognition in biomineralization

One of the most fundamental characteristic properties of biochemical systems is recognition. Several researchers have studied biomineralization systems indicating that nucleation and growth of crystals is affected by specific molecular interactions at the inorganic-organic interface. If there is a geometric compatibility between lattice spacing of the crystal structure and distances between ion-binding sites on the organic surface, nucleation on a specific crystal face can occur.

By exposing growing calcite crystals to different α,ω-dicarboxylates it was showed that only one of them (a malonate containing compound) severely inhibited crystal growth perpendicular to the c-axis, especially the prismatic face $\{110\}$. This indicates the preferred interaction with one face over the others. The authors reported that the distances in the dicarboxylate groups in the malonate compound which severely inhibits crystal growth is close to 4 Å. This is close to that of carbonates between adjacent anion layers in the $\{110\}$ and $\{110\}$ faces of calcite (Figure 2). The other longer chains had only minimal effect on growth. It was therefore believed that the malonate compound interact with the crystal surface using both carboxylate groups, which is not possible for the other longer chained compounds.

**Figure 2.** A calcite cell projection parallel to the [110] axis; where A and B are the binding sites for malonate in the (100) face.
Other studies with growth of barium sulphate (BaSO$_4$)$^{12,21}$ and calcium fluoride (CaF$_2$)$^{10}$ in aqueous solutions in the presence of inhibiting surfactants show matching conclusions confirming the geometric, stereochemical and electrostatic match of organic molecules with the crystal lattice. In the barium sulphate studies (Figure 3) the most successful inhibitor was amino-dimethylene diphosphonates (DMD), with a distance of 5.7 Å between the phosphonate groups.

**Figure 3.** A projection of the BaSO$_4$ structure normal to the (011) sulfate layer showing diphosphonate ions replacing sulfate ions$^{12}$. 

![Figure 3](image_url)
This matches well with the 5.6 Å S-S atoms in the crystal surface making substitution possible and reduces crystal growth. The calcium fluoride studies used several dicarboxylic acids (oxalic, malonic, malic, tartaric, succinic and glycolic acid) where oxalic acid was found to be the most active inhibitor. The authors also reported that it was even better to use two carboxyl group and one hydroxyl group in α-position which fits well with the Ca-Ca distancing within the unit cell of CaF₂ (Figure 4)\textsuperscript{10}.

**Figure 4.** Interaction between dicarboxylic acids and a unit cell of fluorite depending on the distance between the functional groups\textsuperscript{10}.

Based on the above and other studies\textsuperscript{22-25}, the process of molecular recognition is considered to be determined by electrostatic binding or association, geometric matching, and stereochemical complementarity at the inorganic-organic interface.
Short analysis of flotation literature of calcium containing minerals

There has been a substantial amount of research effort devoted to the physicochemical aspects of flotation in sparingly soluble minerals using a variety of flotation collectors over the years\textsuperscript{2, 4, 14, 26}. The higher aqueous solubility of these minerals is of great importance since it increases the mineral-reagent interactions. The minerals themselves affect the nature of the aqueous environment and the environment determining the nature of the interfacial reaction. This added complexity of the flotation system could contribute to the difficulty explaining the selectivity issues within the separation process. The order of selectivity for a few common collectors used in calcium mineral flotation is summarized in Table 1.

\begin{table}[h]
\centering
\begin{tabular}{|l|l|}
\hline
Reagent & Order of Selectivity  \\
\hline\hline
Sodium oleate & Fluorite > Fluorapatite > Calcite  \\
Potassium Octadecano hydroxamate & Calcite > Fluorite  \\
\textit{n}-octyl imino-bismethylene phosphonic acid & Fluorite > Calcite > Apatite  \\
Flotol-7,9-(1-hydroxyalkyl-idene-1,1-diphosphonic acid) & Fluorite > Apatite > Calcite  \\
Oleoylsarcosine (\textit{N}-oleoyl-\textit{N}-methylamine acetic acid) & Fluorite > Calcite  \\
\hline
\end{tabular}
\caption{Flotation selectivity order as observed in single mineral flotation tests}
\end{table}

Using fatty acids as collectors, the order of selectivity shows that fluorite is the most floatable of all calcium minerals. There have been several attempts to explain oleates higher affinity for fluorite, which has been attributed to the higher density of Ca on the fluorite surface (12.8 Å\textsuperscript{2}/Ca-atom)\textsuperscript{2, 14, 27, 28} than on calcite (20 Å\textsuperscript{2}/Ca-atom)\textsuperscript{2}. This explanation is not considered to be entirely satisfactory as hydration of the mineral surfaces should be considered\textsuperscript{29, 30}. Fluorite is significantly more strongly hydrated than calcite, which in turn should make it much less favorable for collector adsorption. One explanation could be the crosslinking of adsorbed oleate molecules via ether bonds which stabilize the layer and makes it significantly more hydrophobic\textsuperscript{3}. Studies using molecular modeling indicate the fluorite surface to be more favorable for this crosslinking than calcite\textsuperscript{11}. It has been shown that oleoylsarcosine (\textit{N}-oleoyl-\textit{N}-methylamine acetic acid) can be effective in separating a calcite-fluorite system in Hallimond tube flotation where four times less reagent is required for fluorite flotation compared to calcite flotation\textsuperscript{15}. Collectors based on phosphonic acid has been tested for calcium mineral flotation by different groups\textsuperscript{16, 17}. Collectors with the same functional groups but different molecular structure have shown different selectivity for apatite and calcite. These examples from the literature support that the stereochemical compatibility between the binding sites on the surface and the molecular architecture of the collector may determine the selectivity of the adsorption process.
**Theory of experimental methods**

**Flotation**

Flotation is one of the most important and widely used methods in mineral processing to separate minerals from gangue material. The method aggregates air bubbles and mineral in an aqueous solution with the aggregates then follow the flow of air bubbles to the surface. Whether or not the mineral particle attaches to the air bubble is determined by thermodynamics. If the work of adhesion ($W_{AD}$) between the water molecules and the mineral surface is lower than the work of cohesion ($W_{CO}$) between water molecules, the mineral-water interaction will strive to be as low as possible. This is related to what degree of wettability the surfaces of the mineral particles have. Wettability is essentially how much a drop of a certain liquid will spread on a surface in the presence of air. Assuming the surface is flat and rigid the equation for surface tension is simplified to the Young equation (1).

\[
\gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cos \theta
\]  

where $\gamma_{SG}$ is the surface tension between the solid phase and the gas phase, $\gamma_{SL}$ is the surface tension between the solid and liquid phase, $\gamma_{LG}$ is the surface tension between the liquid and gas phase and $\theta$ is the contact angle of the drop at the boundary point.

Thus the contact angle describes the wettability of a surface (Figure 5) where a $\theta$ larger than 90° correspond to a hydrophobic surface, from greek *hydro*, meaning water and *phobic*, meaning fear. A $\theta$ smaller than 90° corresponds to a hydrophilic surface, from greek *philia*, meaning love. As can be seen from the figure, a high wettability results in less interaction with the gas phase and more with the water phase, with water spreading itself over the surface. A low wettability results in more interaction with the gas phase and low water phase interaction, with water taking on more of a drop shape to reduce water-solid interaction.

![Figure 5. Wettability of a drop of water on a solid surface](image)
When a surface active reagent (collector) adsorbs to the mineral, it shields the surface from the water molecules and the water interacts with the collector instead of the mineral. If the collector is sufficiently hydrophobic, it will increase $\gamma_{SG}$ enough to promote the collector-mineral complex to attach to air bubbles and follow them to the surface where they can be skimmed off. To only add collector is usually not enough. Other reagents may have to be added for improved recovery or control of the process for example depressants, to prevent unwanted minerals or gangue to float, frothers to stabilize the froth so that the bubbles do not burst and release the minerals before they have been skimmed off, and activators to facilitate the collector-mineral adsorption. The mineral recovery can be calculated according to equation (2)

$$Recovery = \frac{m_f}{m_{tot}} \times 100$$

(2)

Where $m_f$ is the mass of floated mineral and $m_{tot}$ is the total mass of mineral used in the experiment.

The common way to develop new collector reagents for flotation has been by trial and error. This is then quantified by empirical means to determine which collectors are useful and which are not. As the demands on the mineral industry has increased over the years with steady depletion of high grade, relatively easy to process ores as well as government pressure for a more environmentally friendly process; new reagents have to be discovered. Tailor-made reagents with two functional groups instead of one can be a solution. These novel collector must coordinate both their groups in such a way that they can adsorb on the mineral surface. As every mineral surface is different, the difference in distance between suitable places of adsorption on the mineral surface as well as differences in distance between the two functional groups of the tailor-made collectors will severely limit the possibility of adsorption.

ζ-potential

ζ-potential is the electric potential difference between the shear plane of a moving particle and the stationary liquid the particle is dispersed in. The most common way to calculate the ζ-potential is by experimentally determining the electrophoretic mobility by electrophoresis. The electrophoretic mobility is then calculated using the Smoluchowski equation (3)

$$\zeta = \frac{\mu_E \times \eta}{\varepsilon}$$

(3)

where $\mu_E$ is the particles electrophoretic mobility, $\eta$ viscosity of the solution, $\varepsilon$ is the permittivity of the dielectric and $\zeta$ is the ζ-potential.

When a charged particle is in contact with an aqueous solution, the free ions in the solution will cover the charged particle with an immobile stationary layer of ions of opposite charge (counter ions) to that of the particle called the stern layer or compact layer. Outside of this layer a second mobile layer of counter ions called the diffuse layer will form. These two layers, the diffuse and the stern layer, are called the electrical double layer, or simply the double layer. The ζ-potential is the electrostatic potential at the boundary between these two layers.

By placing aqueous particles in an electric field and measuring their mobility, the ζ-potential can be calculated. This is an important parameter for the understanding of several chemical and biological processes, agglomeration stability of fine particles for instance. In this thesis however, ζ-potential is used to monitor the mineral surface. By examining the ζ-potential, we can see if the mineral particle surface is changed when for different pH or collector concentration, which can indicate collector adsorption or affinity for the mineral surface.
**IR/DRIFTS**

Infrared (IR) spectrometry uses light in the infrared region and is split in three groups, near infrared (NIR) 14000-4000 cm⁻¹, mid infrared (MIR) 4000-400 cm⁻¹ and far infrared (FIR) 400-10 cm⁻¹. In this thesis MIR has been used for all experiments which is mostly used to study fundamental vibrations. Light in the infrared region has the right frequency to excite atoms in molecules, making them move to release the energy absorbed. As the IR-beam passes through a sample with molecules, energy is absorbed. Different bonds will absorb energy from different frequencies. A detector on the opposite side of the sample will then measures the beam that has passed through and calculates and absorbance spectra. IR spectroscopy has a very wide array of applications and several different methods have been developed over the years. One such method is Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS). It is a method that has been developed specifically for powder samples. The infrared beam is directed towards the sample where the beam is then partially absorbed as it refracts, diffracts and reflects before exiting the sample. The fraction of the incident beam that escapes the sample is called the *diffusely refracted* beam and is recorded. The recorded spectra is then ratioed against a nonabsorbing reference spectra (normally KBr) to get the reflectance spectra \( R(v) \). The reference spectra must be converted to be linear towards concentration using the Kabelka-Munk theory.

**NMR Spectroscopy**

Nuclear magnetic resonance (NMR) is a phenomenon which occurs when the nuclei of certain atoms are immersed in a static magnetic field and exposed to a second oscillating magnetic field. Some nuclei experience this phenomenon, and others do not, depending on the presence or absence of spin in the nuclei. Nuclear magnetic resonance spectroscopy uses the NMR phenomenon to study physical, chemical, and biological properties of matter. There are two major interactions within NMR spectroscopy: chemical shift and spin-spin coupling.

First, chemical shift: When an atom is placed in a magnetic field, its electrons circulate about the direction of the applied magnetic field. This circulation causes a small magnetic field at the nucleus, which opposes the externally applied field. The magnetic field at the nucleus (the effective field) is therefore generally less than the applied field by a fraction \( \sigma \):

\[
B = B_0(1 - \sigma)
\]

where \( B \) is the magnetic field interacting with the sample, \( B_0 \) is the external magnetic field and \( \sigma \) is the shielding constant.

The electron density around each nucleus in a molecule varies according to the types of nuclei and bonds in the molecule. The opposing field and therefore the effective field at each nucleus will vary. This is called the chemical shift phenomenon. The chemical shift is a precise measurement of the chemical environment around a nucleus.

Spin-Spin Coupling: Nuclei experiencing the same chemical environment or chemical shift are called equivalent. Those nuclei experiencing different environments or having different chemical shifts are nonequivalent. Nuclei which are close to one another exert an influence on each other's effective magnetic field. This effect shows up in the NMR spectrum when the nuclei are nonequivalent. If the distance between non-equivalent nuclei is less than or equal to three bond lengths, this effect is observable. This effect is called spin-spin or \( J \) coupling.
**Quartz Crystal Microbalance**

The Quartz crystal microbalance (QCM) is an instrument that determines a mass per unit area by measuring the change in frequency of a quartz crystal resonator. When mass is added to or removed from the surface, the resonance frequency of the crystal changes. It is possible to determine mass densities down to a level of ng/m², as frequency measurements are easily made to high precision. If the mass is deposited on one side of the electrodes the change in resonant frequency is proportion to the mass deposited according to the Sauerbrey equation (5):

\[ \Delta f = -\frac{2f_0^2}{A\sqrt{\rho_q\mu_q}} \times \Delta m = -S \times \Delta m \]  

(5)

where \( S \) is the Sauerbrey constant for a given crystal, \( \Delta f \) is the measured frequency shift, \( f_0 \) is the resonant frequency of the fundamental mode of the crystal, \( \Delta m \) is the mass change per unit area, \( A \) is the piezo-electrically active area, \( \rho_q \) is the density of quartz and \( \mu_q \) is the shear modulus of quartz.
**Experimental**

**Materials**

Pure natural apatite, calcite and fluorite mineral crystals were procured from Gregory, Bottley & Lloyd Ltd., United Kingdom. These crystals were crushed in a jaw crus-her and further reduced in size using a stainless-steel rod mill. The fine particles were sieved to collect the -150+38 µm size fraction. Some material was further comminuted to produce a size fraction of -5 µm for ζ-potential measurement and FTIR experiments using a Fritsch Pulverisette 2 mortar grinder. The particles were sieved using a 5 µm filter cloth screen in an ultrasonic bath.

The solubility measurements by NMR were made using acetonitrile as a reference (5µL for 1 ml of surfactant solution). The samples of surfactants were prepared in D2O, and the required amount of a concentrated CaCl2 solution or HCl was added. The samples were then stirred for 6 hours. All the samples (1H and 13C) were recorded on a 200 MHz Varian Gemini Fourier Transform NMR spectrometer. MestReNova Lite software (version 5.2.5-4119) was used to process and analyze of 1D (1H & 13C) NMR data sets. All spectra were acquired using deuterated water (D2O) as the solvent containing a 0.1% tetramethylsilane (TMS) as internal standard. The latter was used to scale the spectra to 0 ppm. 1H-NMR spectra were collected with a minimum number of transients of 16. 13C-NMR spectra were collected with a minimum number of transients of 1024.

Quartz Crystal Microbalance with monitoring of the dissipation (QCM-D) was used to evaluate the specificity of adsorption of some of the collectors on apatite-like surfaces. A QCM-D instrument (model D300) from Q-Sense (Gothenburg, Sweden) was employed. In order to avoid crystal perturbations during the shear oscillation of the crystals, the measurements were carried out under non-flowing conditions. Q-Sense supplied hydroxypatite coated crystals. The surfaces were cleaned prior to use by a simple UV-ozone treatment. The mass adsorbed were determined by applying the Sauerbrey relationship including a correction for the bulk contribution. More information can be found elsewhere.

**Reagents**

Hydrochloric acid (HCl) and sodium hydroxide (NaOH) was used as pH regulators for all experiments. In the ζ-potential measurement sodium chloride (NaCl) was used as the background electrolyte.

Lauroyl chloride, l-aspartic acid, l-glutamic acid, aminomalonic acid diethyl ester hydrochloride, l-glycine ethyl ester, lithium aluminum hydride, calcium chloride anhydrous were purchased from Sigma–Aldrich, USA. Dodecylamine, bromoacetic acid, bromopropionic acid, bromoacetic acid methyl ester, bromopropionic acid methyl ester, carbon disulfide were purchased from Alfa-Aesar, UK. Sodium hydroxide, hydrochloric acid 37%, ethanol, tetrahydrofuran (THF) anhydrous were purchased from VWR, Sweden. All these chemicals were used as purchased. Pyridine (Aldrich, 99%) was used freshly distilled in vacuum and stored over potassium hydroxide (KOH).
**Synthesis of collectors**

The carboxylate-terminated collectors with different spacing between the functional groups used in this thesis, Figure 6, were synthesized both at Chalmers University of Technology (CTH), left column, and at Luleå University of Technology (LTU), right column. The synthesis scheme for the CTH compounds is outlined in Figure 7. The malonate and glycine based surfactants have been prepared via an ester protected route while the aspartate and the glutamate were prepared by the Schotten-Baumann reaction.

**Figure 6.** Collector molecules synthesized and used for apatite and calcite flotation.

Chalmers University of Technology, Gothenburg, Sweden
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**Figure 7.** Schematic diagram of synthesis of calcium-mineral specific (carboxylic acid terminated) collectors carried out at CTH.
C12MalNa2: The diethyl ester of the malonate amino acid (47 mmol) was dissolved in pyridine (100 mL) in a round-bottomed flask. Lauroyl chloride (47 mmol) in THF (100 mL) was added under stirring at room temperature. A precipitate appeared and the suspension was stirred for 18 hours. The mixture was then poured into aqueous hydrochloric acid (1.5 L, 1 M). After 2 hours of stirring, the suspension was filtered. The solid diethyl ester of the dicarboxylate surfactant was filtered, washed with water and dissolved in ethanol (150 mL) in a round-bottomed flask. Sodium hydroxide (2 M, 2 eqv.) in ethanol (30 mL) was then added, leading to a white precipitate, which was isolated by filtration. Yield: 95%. 1H NMR (D2O, δ 0.85 (t, 3 protons), δ 1.26 (m, 16 protons), δ 1.58 (m, 2 protons), δ 2.30 (t, 2 protons), δ 3.33 (s, 1 proton)), 13C NMR (D2O, δ 13.96, 17.07, 17.08, 22.68, 29.35, 29.86, 36.07, 49.11, 57.62, 62.19, 174.39, 175.62).

C12AspNa2 and C12GluNa2: A suspension of amino acid (310 mmol) was prepared in a mixture of water/acetone (210 mL/150 mL) in a round-bottomed flask. pH was set to 12 with an automatic titrator filled with a solution of sodium hydroxide (2.5 M). Lauroyl chloride was added drop-wise under stirring at 5°C and stirring was continued for 90 minutes. The mixture was then cooled to 0°C and stirred for 2 hours while the pH was kept at 12. The solution was warmed to room temperature and then acidified to pH 2. A white precipitate appeared which was collected by filtration and washed with water. The product was recrystallized three times in toluene. The product was dissolved in ethanol, and a solution of sodium hydroxide was added (2 M, 2 eq.) leading to a precipitate, which was isolated by filtration. Yield: 74%. C12AspNa2: 1H NMR (D2O, δ 0.85 (t, 3 protons), δ 1.26 (m, 16 protons), δ 1.56 (m, 2 protons), δ 2.24 (t, 2 protons), δ 2.56 (d, 2 protons), δ 4.38 (t, 1 proton)), 13C NMR (D2O, δ 14.02, 22.71, 25.67, 29.28, 29.36, 29.42, 29.61, 29.71, 31.99, 36.25, 40.16, 52.97, 176.08, 178.98, 179.10). C12GluNa2: 1H NMR (D2O, δ 0.83 (t, 3 protons), δ 1.24 (m, 16 protons), δ 1.56 (m, 2 protons), δ 1.85 (m, 1 proton), δ 2.02 (m, 1 proton), δ 2.23 (m, 4 protons), δ 4.12 (m, 1 proton)), 13C NMR (D2O, δ 13.98, 22.65, 25.72, 29.15, 31.90, 34.40, 36.16, 55.42, 176.39, 179.16, 182.36).

C12GlyNa: l-glycine ethyl ester (10 g) was dissolved in pyridine (20 mL) in a round-bottomed flask under reflux. Dodecyl chloride (15.7 g) was added drop-wise under stirring, leading to a white precipitate. The solvent was evaporated. The product was dispersed in water, stirred and then filtered and recrystallized from ethanol. The N-dodecyl ester formed was dissolved in ethanol (100 mL) and aqueous sodium hydroxide (2 M, 35 mL) was added drop-wise under stirring, leading to a white precipitate of the sodium salt of the surfactant. Yield: 46%. 1H NMR (D2O, δ 0.83 (t, 3 protons), δ 1.25 (m, 16 protons), δ 1.57 (m, 2 protons), δ 2.26 (t, 2 protons), δ 3.70 (s, 2 protons)), 13C NMR (D2O, δ 13.84, 22.58, 25.67, 29.07, 29.24, 29.46, 29.56, 31.84, 36.09, 43.44, 176.49, 176.91). The compounds synthesized in house at LTU, see the right column in Figure 6, were synthesized using the scheme shown in Figure 8.

Figure 8. Schematic diagram of synthesis of calcium-mineral specific (carboxylic acid terminated) collectors carried out at LTU.
C12sp1Na: Dodecylamine (10 g, 54 mmol, 2 eq.) was dissolved in ethanol (50 mL) in a round-bottomed flask. Bromoacetic acid (3.75 g, 27 mmol, 1 eq.) was added drop-wise under stirring, leading to a white precipitate. The mixture was set for reflux, at which point the precipitate dissolved. The reflux condition was maintained for 24 hours. The solvent was evaporated. The product was purified by repeated crystallization in ethanol. Yield: 76%. 1H NMR (D2O, 360 MHz): δ 3.2 (s, 2H), 2.6 (t, 2H), 1.5 (br t, 2H), 1.3 (br m, 18H), 0.9 (t, 3H). 13C NMR (D2O, 90 MHz): δ 182.2, 56.2, 52.3, 36.7-28.5, 26.0, 17.3.

C12sp11Na2: C12sp1Na (1.33 g, 5 mmol, 1 eq.) was dissolved in ethanol (20 mL) in a round-bottomed flask. Bromoacetic acid (0.70 g, 5 mmol, 1 eq.) was added drop-wise under stirring, leading to a white precipitate. The mixture was set for reflux and the precipitate dissolved. The reflux condition was maintained for 24 hours. The solvent was evaporated. The product was purified by repeated recrystallization in ethanol. Yield: 62%. 1H NMR (D2O, 360 MHz): δ 3.2 (s, 4H), 2.6 (t, 2H), 1.5 (br t, 2H), 1.3 (br m, 18H), 0.9 (t, 3H). 13C NMR (D2O, 90 MHz): δ 182.3, 62.6, 59.3, 36.7-28.5, 26.0, 17.3.

C12sp12Na2: C12sp1Na (1.33 g, 5 mmol, 1 eq.) was dissolved in ethanol (20 mL) in a round-bottomed flask. Bromopropionic acid (0.77 g, 5 mmol, 1 eq.) was added drop-wise under stirring, leading to a white precipitate. The mixture was set for reflux and the precipitate dissolved. The reflux condition was maintained for 24 hours. The solvent was evaporated. The product was purified by repeated crystallization in ethanol. Yield: 41%. 1H NMR (D2O, 360 MHz): δ 3.2 (s, 2H), 2.9 (t, 4H), 2.6 (t, 2H), 2.4 (t, 2H), 1.5 (br t, 2H), 1.3 (br m, 18H), 0.9 (t, 3H). 13C NMR (CDCl3, 90 MHz): δ 184.2, 181.3, 60.7, 57.5, 54.0, 37.4, 36.3-27.6, 25.7, 17.0.

C12sp22Na2: The synthesis was performed using a similar scheme as for the preparation of C12sp11Na2, but using bromopropionic acid instead of bromoacetic acid for both the steps. Stoichiometry remained unchanged. Yield: 28%. 1H NMR (D2O, 360 MHz): δ 2.9 (t, 4H), 2.6 (t, 2H), 2.4 (t, 4H), 1.5 (br t, 2H), 1.3 (br m, 18H), 0.9 (t, 3H). 13C NMR (CDCl3, 90 MHz): δ 184.0, 56.6, 53.0, 37.1, 36.7-28.5, 26.0, 17.3.

Hallimond tube flotation studies
The flotation of the mineral samples was performed in a 100 ml Hallimond tube flotation cell with an aqueous suspension of 1 g of pure mineral in the size fraction -150+38 μm. The suspension of mineral in deionized water and collector was conditioned for 10 minutes, transferred to the Hallimond cell and floated for 1 minute at ambient temperature. The flotation recovery was calculated as the ratio of the recovered floated particle weight and the total weight of mineral particles taken as shown in equation (2)

ζ potential studies
ζ-potential measurements were performed using a ZetaCompact instrument (CAD instruments) with NaCl as a background electrolyte in a concentration of 1 × 10^-2 mol/dm^3. The solid concentration of the samples was 0.50 g/dm^3. Each sample was equilibrated for 10 minutes on a shaking table before being measured. The results were calculated using Zeta4 software® with the Smoluchowski equation using an average of three repeated measurements.
**Diffuse reflectance FTIR spectroscopy studies**

Diffuse Reflectance Infrared Fourier-Transformed Spectroscopy (DRIFTS) measurements were performed using a Bruker IFS 66 v/S instrument with a deuterated triglycine sulfate (DTGS) detector. The -5 μm fractions were conditioned for 10 minutes, at different pH and concentration. The samples were then washed three times with deionized water and filtered to remove any molecules not chemically adhered to the surface. Furthermore, the samples were air-dried overnight at room temperature. The dry samples were mixed with potassium bromide to give a 13 wt% concentration. The spectra were recorded using 128 scans at a resolution of 4 cm\(^{-1}\).
Results and discussion

Hallimond tube flotation studies

Apatite

The recovery of apatite was performed with a constant collector concentration of $2 \times 10^{-4}$ mol/dm$^3$ while varying the pH in the range 2-12 (Figure 9) as well as using a constant pH of 10.5 with the collector concentration ranging from $5 \times 10^{-6}$ mol/dm$^3$ to $1 \times 10^{-3}$ mol/dm$^3$ (Figure 10). In the pH experiments (Figure 9) it is shown that all collectors except C12GlyNa can recover apatite in the low pH range. C12GlyNa reaches a peak recovery at pH 7.2. After this peak the recovery stabilizes in the low recovery region for the rest of the pH range. It is however noticeable that at higher pH, among all the four collectors used in this study; only C12MalNa$_2$ has significant flotation recovery of apatite.

Figure 9. Hallimond tube flotation experiments of apatite performed with a constant collector concentration of $2 \times 10^{-4}$ mol/dm$^3$ in the 2-12 pH range.

This holds true for the concentration experiments at high pH as well (Figure 10). Even though C12GlyNa can recover apatite at this pH, it does so at a higher concentration than C12MalNa$_2$ and with much lower recovery. The remaining two collectors, C12GluNa$_2$ and C12AspNa$_2$, show no significant recovery at this pH.
Figure 10. Hallimond tube flotation experiments of apatite using a constant pH of 10.5 with the collector concentration ranging from $5 \times 10^{-6}$ mol/dm$^3$ to $1 \times 10^{-3}$ mol/dm$^3$. 
Calcite
Calcite recovery was performed using a constant collector concentration of $2 \times 10^{-4}$ mol/dm$^3$ with pH ranging from 6 to 12 (due to the alkaline nature of CaCO$_3$) (Figure 11) and with a constant pH of 10.5 and with collector concentrations varying from $5 \times 10^{-6}$ mol/dm$^3$ to $1 \times 10^{-3}$ mol/dm$^3$ (Figure 12). With a constant concentration (Figure 11), all collectors except C12MalNa$_2$ can float calcite to some degree in the lower pH range (pH 6-8). C12GluNa$_2$ shows the highest recovery at the lowest pH, decreasing to very low or basically no flotation at all with increasing pH. C12GlyNa on the other hand was found to be an excellent collector for calcite in the entire pH range with especially good recovery between pH 9.6 and 9.8.

Figure 11. Hallimond tube flotation experiments of calcite performed with a constant collector concentration of $2 \times 10^{-4}$ mol/dm$^3$ in the 6-12 pH range.

With a constant pH of 10.5 (Figure 12) and collector concentrations varying from $5 \times 10^{-6}$ mol/dm$^3$ to $1 \times 10^{-3}$ mol/dm$^3$, it can be clearly seen that C12GlyNa is the only collector that can recover calcite at this high pH, but only at concentrations higher than $1 \times 10^{-4}$ mol/dm$^3$.

Figure 12. Hallimond tube flotation experiments of calcite using a constant pH of 10.5 with the collector concentration ranging from $5 \times 10^{-6}$ mol/dm$^3$ to $1 \times 10^{-3}$ mol/dm$^3$. 
Fluorite
The fluorite Hallimond tube flotation experiments were performed using a constant collector concentration of $2 \times 10^{-4}$ mol/dm$^3$ in the pH range 2-12 (Figure 13) as well as using a constant pH of 10.5 (Figure 14) and at natural pH (Figure 15) using collector concentrations in intervals from $5 \times 10^{-6}$ mol/dm$^3$ to $1 \times 10^{-3}$ mol/dm$^3$. In Figure 13 it can be seen that at pH 2, all collectors can successfully recover fluorite with C12GlyNa having the lowest recovery of approximately 30%. As the pH increases so does the recovery to above 80% for all collectors except C12MalNa$_2$. Although C12MalNa$_2$ initially has at a relatively high collector recovery at pH 2, it decrease from 65% to 40% when reaching pH 7 keeping relatively stable at this recovery until, or close, to reaching pH 10, where all collectors drop below 40% recovery.

![Figure 13. Hallimond tube flotation experiments of fluorite performed with a constant collector concentration of $2 \times 10^{-4}$ mol/dm$^3$ in the 6-12 pH range.](image)

In the experiment conducted at pH 10.5 (Figure 14) it can be seen that only two collectors, C12GlyNa and C12MalNa$_2$, have any significant flotation recovery at $2 \times 10^{-4}$ mol/dm$^3$. At the highest concentrations used in this study, it was possible for minor flotation of fluorite using the other two collectors.

![Figure 14. Hallimond tube flotation experiments of fluorite using a constant pH of 10.5 with the collector concentration ranging from $5 \times 10^{-6}$ mol/dm$^3$ to $1 \times 10^{-3}$ mol/dm$^3$.](image)
With natural pH (Figure 15), it is evident that all collectors are capable of floating fluorite and at high recovery, with C12GluNa$_2$ having an excellent recovery even at minimal concentrations.

**ζ-potential studies**

**Apatite**

The ζ-potential measurements were performed with pH ranging from 2 to 12 using a constant collector concentration of $2 \times 10^{-4}$ mol/dm$^3$ as well as in the absence of collector to get values for the pure mineral (Figure 16) and using a constant pH of 10.5 with collector concentrations ranging from $5 \times 10^{-6}$ mol/dm$^3$ and $1 \times 10^{-3}$ mol/dm$^3$ (Figure 17). In constant collector concentration study (Figure 16) the behavior is similar to the one seen in the flotation experiments, especially in the higher pH region where the flotation using all collectors decreases from high to low or nonexistent. This is especially the case for C12GluNa$_2$, C12GlyNa and C12AspNa$_2$ where the measured ζ-potential follows the same pattern as the pure apatite mineral with no collector, indicating that little or no adsorption takes place at these conditions. At pH 5, where the flotation of C12GluNa$_2$ and C12AspNa$_2$ show high flotation recovery, the measured values for ζ-potential are markedly different from that of the pure apatite mineral indicating the possibility of strong adsorption. Comparing the ζ-potential values for these two collectors with C12MalNa$_2$ shows that the malonate derivative has a higher change in ζ-potential than the others. This is in accordance with the flotation data indicating that C12MalNa$_2$ is the best collector reagent out of the four tested collectors. Comparing the iso-electric points (IEP), the pure apatite mineral without collector is slightly lower than pH 4 while the IEP for apatite mineral surface in the presence of C12GlyNa and C12GluNa$_2$ is found below pH 3. The IEP for apatite mineral surfaces in the presence of C12MalNa$_2$ or C12AspNa$_2$ were not observed in the pH region examined in this experiment.
Figure 16. ζ-potential measurements of apatite with pH ranging from 2 to 12 using a constant collector concentration of $2 \times 10^{-4}$ mol/dm$^3$ as well as of the pure fluorite surface.

With a constant collector concentration (Figure 17), the graphs follow the same trend and are in good agreement with the Hallimond tube flotation experiments. At pH 10.5 we can see a decrease in the ζ-potential for C12MalNa2 at concentrations higher than $2 \times 10^{-5}$ mol/dm$^3$, indicating adsorption at the mineral surface. It is also at this concentration that the recovery starts to increase in the flotation studies. The same can be seen for C12GluNa2, which had moderate flotation recovery at relatively high concentrations. When reaching concentrations above $6 \times 10^{-4}$ mol/dm$^3$ the ζ-potential starts to decrease, indicating collector adsorption on the surface in agreement with the flotation response.

Figure 17. ζ-potential measurements of apatite using a constant pH of 10.5 with collector concentrations ranging from $5 \times 10^{-6}$ mol/dm$^3$ to $1 \times 10^{-3}$ mol/dm$^3$.

Calcite

Calcite ζ-potential measurements were performed using a constant collector concentration of $2 \times 10^{-4}$ mol/dm$^3$ at different pH ranging from pH 6 to 12, except for the pure calcite mineral where no collector was present (Figure 18) and at pH 10.5, with collector concentrations varying from $5 \times 10^{-6}$ mol/dm$^3$ to $1 \times 10^{-3}$ mol/dm$^3$ (Figure 19). Examining the curves of two collectors, C12AspNa2 and C12GluNa2 at a constant concentration but varying pH (Figure 18), they show a fairly similar trend to that of calcite with no collector present, indicating that little or no collector-mineral adsorption takes place. C12GlyNa on the other hand shows a different trend compared to the pure mineral indicating that adsorption takes place. This is in good agreement with the calcite recovery seen in the Hallimond tube experiment. C12MalNa2 shows a drastic decrease in ζ-potential, just as in the apatite experiment, while virtually no calcite is recovered in the flotation experiment. This might indicate that the collector is
adsorbed on the surface, but in a less favorable position giving a less hydrophobic layer. The IEP for C12AspNa2 and C12GluNa2 were found close to neutral pH, while for C12GlyNa the IEP was found in the alkaline region, above pH 11.5. The IEP for the pure calcite mineral without collector as well as for calcite mineral in the presence of C12MalNa2 was not observed in this experiment, although extrapolation of the studies using C12MalNa2 indicates a possible IEP slightly below pH 7.

Figure 18. ζ-potential measurements of calcite with pH ranging from 6 to 12 using a constant collector concentration of $2 \times 10^{-4}$ mol/dm$^3$ as well as of the pure fluorite surface.

The measurements at a constant pH of 10.5 (Figure 19) follow a similar trend as that of the flotation data. The ζ-potential of the mineral surface decreases with increasing collector concentration. At pH 10.5 both C12AspNa2 and C12GluNa2 have essentially constant ζ-potential values until reaching high collector concentrations. This is in accordance with the flotation data, as no significant recovery was observed. C12GlyNa and C12MalNa2 on the other hand show a decrease in the ζ-potential at lower collector concentrations compared to the two previous collectors. The ζ-potential graph for C12GlyNa show similar behavior compared to the flotation recovery data, where recovery is only possible at higher collector concentrations. C12MalNa2 decreases the ζ-potential of the calcite mineral even at lower collector concentrations; still it does not assist flotation at any concentration.

Figure 19. ζ-potential measurements of calcite using a constant pH of 10.5 with collector concentrations ranging from $5 \times 10^{-6}$ mol/dm$^3$ to $1 \times 10^{-3}$ mol/dm$^3$. 

25
Fluorite
The fluorite \( \zeta \)-potential were performed with a constant collector concentration of \( 2 \times 10^{-4} \) mol/dm\(^3\) in the pH range 2 to 12 (Figure 20) as well as using a constant pH of 10.5 (Figure 21) and at natural pH (Figure 22) with collector concentrations in intervals from \( 5 \times 10^{-6} \) mol/dm\(^3\) and \( 1 \times 10^{-3} \) mol/dm\(^3\). With a constant collector concentration (Figure 20), the mineral surface in the presence of C12GlyNa has the same trend as the fluorite without collector but the \( \zeta \)-potential is distinctly lower, indicating some adsorption in the low pH region before approaching the \( \zeta \)-potential of the pure fluorite mineral. The same trend can be seen for the mineral surface in the presence of collectors C12AspNa\(_2\) and C12GluNa\(_2\), but with an even larger difference in \( \zeta \)-potential in the low pH region, indicating stronger adsorption below pH 6. The \( \zeta \)-potential for the mineral surface in the presence of C12MalNa\(_2\) on the other hand, shows adsorption over the entire pH region. Comparing this with the flotation recovery data, it seems likely that it even slightly suppresses the natural recovery of fluorite. The pure fluorite mineral was found to have its IEP slightly below pH 6.6 while the fluorite mineral surface in the presence of C12GlyNa is suspected to have its IEP between pH 3 and 6. No IEP was found for fluorite mineral surface in the presence of the other three collectors.

![Figure 20](image_url)

**Figure 20.** \( \zeta \)-potential measurements of fluorite with pH ranging from 2 to 12 using a constant collector concentration of \( 2 \times 10^{-4} \) mol/dm\(^3\) as well as of the pure fluorite surface.

At a constant pH of 10.5 (Figure 21), the fluorite surface becomes negatively charged even at low concentrations using either C12GlyNa or C12MalNa\(_2\). This gets even more prominent with concentrations higher than \( 1 \times 10^{-3} \) mol/dm\(^3\); which is in good agreement with the flotation results as both collectors increase the fluorite recovery noticeably above this concentration. In the presence of both C12GluNa\(_2\) and C12GAspNa\(_2\) the drop in \( \zeta \)-potential starts at concentrations above \( 6 \times 10^{-4} \) mol/dm\(^3\), which is the same concentration range as the moderate flotation recovery seen in the Hallimond tube flotation. For pH 10.5 no IEP could be found for the mineral surface in presence of any collector.
Figure 21. ζ-potential measurements of fluorite using a constant pH of 10.5 with collector concentrations ranging from $5 \times 10^{-6}$ mol/dm$^3$ to $1 \times 10^{-3}$ mol/dm$^3$.

At natural pH (Figure 22), a sharp decrease in ζ-potential for the mineral surface in the presence of collector with increasing concentration can be seen. In the presence of either C12MalNa$_2$, C12GluNa$_2$ or C12AspNa$_2$ the mineral surface reaches a plateau around $2 \times 10^{-5}$ mol/dm$^3$; this is the same concentration where the flotation recovery reaches its maximum. The ζ-potential curve of fluorite in the presence of C12GlyNa reaches its plateau at $1 \times 10^{-4}$ mol/dm$^3$, which is in good agreement with the maximum Hallimond flotation recovery. The plateaus might indicate maximum surface collector coverage at these conditions. At natural pH the IEP for fluorite mineral surface in the presence of C12GlyNa or C12GluNa$_2$ can be found at $1 \times 10^{-5}$ mol/dm$^3$ and $5 \times 10^{-6}$ mol/dm$^3$ respectively. No specific IEP was observed for the mineral surface in the presence of any of the remaining two collectors at these conditions.

Figure 22. ζ-potential measurements of fluorite using a constant pH of 10.5 with collector concentrations ranging from $5 \times 10^{-6}$ mol/dm$^3$ to $1 \times 10^{-3}$ mol/dm$^3$. 
**DRIFT studies**

**Apatite**

In the apatite DRIFTS spectra (Figure 23), C12MalNa₂ is predominantly adsorbed while the other three collectors show insignificant adsorption on the apatite mineral surface. Of the three insignificantly adsorbed collectors, C12GlyNa show slightly stronger absorbance than the other two. Comparing these results to the previous flotation results it can be seen that only C12GlyNa and C12MalNa₂ can recover apatite at these conditions. The other two collectors, C12AspNa₂ and C12GluNa, are not capable of recovering apatite, likely due to the low surface coverage. It is possible that only one of the carboxylate functional groups in C12AspNa₂ and C12GluNa is adsorbing on the mineral surface, while the other groups are facing away from the surface, interacting with water and thereby creating strong hydrophilic islands at the surface. There is also the possibility that both functional groups adsorb, but due to steric reasons the molecule is not able to orient in the required fashion to generate the hydrophobicity required to float.

![Figure 23](image.png)

**Figure 23.** DRIFTS spectra of apatite at pH 10.5 and a collector concentration of $6 \times 10^{-4}$ mol/dm$^3$.

**Calcite**

The calcite DRIFTS spectra (Figure 24) is slightly more complicated to interpret than the other mineral spectra as calcite itself absorbs in the region examined. However, it can be determined that both C12GlyNa and C12MalNa₂ adsorbs on the calcite mineral surface, although only C12GlyNa assist in the flotation recovery of calcite. Even though C12MalNa₂ does not assist flotation of calcite at any concentration used in this experiment, the DRIFT spectrum shows the presence of large amounts of the collector at the calcite interface and this is in accordance with data from the ζ-potential measurements. It is possible that the adsorption does not occur in such a way that a stable hydrophobic layer can be formed. The two other collectors, C12GluNa and C12AspNa₂, show little or no absorbance, indicating no significant collector concentration at the mineral surface, which is in line with the insignificant flotation recovery.
Figure 24. DRIFTS spectra of calcite at pH 10.5 and a collector concentration of $6 \times 10^{-4}$ mol/dm$^3$.

**Fluorite**

In the fluorite DRIFTS spectra (Figure 25), we can see that all collectors adsorb at the mineral interface to some extent, which is in line with the Hallimond tube flotation experiment results as well as the $\zeta$-potential measurements. As with the previous DRIFT experiments, C12MalNa2 shows considerably higher mineral adsorption than the other three collectors. Interestingly, C12GlyNa which has the smallest peak area still show significant flotation recovery.

Figure 25. DRIFTS spectra of fluorite at pH 10.5 and a collector concentration of $6 \times 10^{-4}$ mol/dm$^3$. 
Conclusions

• Several conclusions can be made from the results shown in this thesis. Most importantly, the collector C12MalNa₂ was found to be an apatite specific collector, while C12GlyNa was found to be more specific to calcite than apatite. The results indicate that by controlling pH and concentration, the separation of calcite from apatite using C12GlyNa would be possible. Furthermore, by carefully controlling the concentration of C12MalNa₂ and the pH it should be possible to selectively separate apatite from calcite. Unfortunately, as both collectors are able to recover fluorite, albeit with low recovery at high pH, the selective separation of all three minerals cannot be successful by using only these two collectors.

• Using careful control of both pH and concentration, separation of apatite, calcite and fluorite could be possible. For example by using C12MalNa₂ at pH 10.5 apatite and fluorite could be separated from calcite. At natural pH, C12GluNa₂ assist recovery of fluorite, but not calcite or apatite recovery; making it possible to separate fluorite from apatite or calcite. This shows that by carefully managing the flotation conditions, separation between calcium minerals could be feasible.

• Collectors containing two or more carbons in between the functional groups, C12AspNa₂ and C12GluNa₂, do not have a significant flotation recovery at high pH (pH 10.5) unless the concentration is very high. The same can be stated for natural pH, except for fluorite which has significant flotation recovery using these collectors even at low concentrations. In the low pH range however, there was significant flotation (pH 2-4 for apatite and fluorite, pH 6-8.5 for calcite). This coincides with the low solubility of the collectors at these conditions; possibly there is adsorption of collector aggregates on the mineral surface thereby making the surface hydrophobic.

• When comparing all the experimental conditions, fluorite shows an overall higher recovery compared to apatite and calcite. Calcite on the other hand, has the lowest recovery amongst the three minerals studied. Moderate recovery can be achieved using most of the collectors.

• The ζ-potential curves usually follow the same trend as the flotation recovery curves. There was a discrepancy with calcite mineral using C12MalNa₂ as a collector. Even though there was no significant flotation, there was a large change in the ζ-potential indicating collector adsorption on the mineral surface.
• The best specific collector adsorption was found at high pH. At natural pH, most collectors adsorb on the minerals at one concentration or another. Hence no mineral specific collector was found at natural pH.

• The DRIFTS data indicate that for flotation to occur maximum surface coverage is not required when using a collector with only one functional group. C12GlyNa with high apatite recovery showed only slightly more surface adsorption compared to C12AspNa₂ and C12GluNa₂, which do not facilitated apatite. Similarly, even though we only see slight adsorption we can still see significant flotation recovery of both calcite and fluorite using C12GlyNa.

• The results unambiguously show that it is possible to design and develop tailor-made selective collectors for a specific mineral separation in flotation systems.
Future work

- Solution chemistry studies of the newly synthesized reagents, for example, solubility, surface tension, critical micelle concentration (CMC), pK-values, frothing characteristics, etc.

- It would be interesting to model the mineral-collector interaction to further understand the interaction, as well as predict other possible collector targets for important mineral systems.

- Combining minerals in one study to see the selectivity of a collector in the presence of other minerals.

- Test reagents on iron oxides, like hematite, magnetite or goethite, to see the possibility of using these collectors in the reverse flotation process used in iron oxide concentration.

- Scale up the test towards bench scale flotation and use real mineral systems. This would show the possibility of using the collectors in conventional industrial scale flotation processes.

- Develop and test a new batch of collectors for different mineral systems.
References


Design and development of novel mineral-specific collectors for flotation
Design and development of novel mineral-specific collectors for flotation

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ABSTRACT
Almost all of the flotation reagents used today were discovered by continued application of empirical methods and/or trial and error experimentation. Moreover, with the metal-ion specific approach used so far, it is difficult to separate the minerals containing the same constituent metal ion. A critical assessment of molecular recognition processes involved in biomineralization suggested the possibility of using reagents which are surface specific. The concept that the molecules consisting of two or more functional groups having appropriate spacing between those so as to achieve structural/stereochemical compatibility during interaction with the mineral surface exhibit structure-specificity, is thought to be extended to the design of specific collectors in flotation processes. In the present study, for the first time, a rational design of surface active molecules, and thereby the recognition of crystal faces (of minerals) by these molecules through structural and stereochemical matching is being utilized successfully to selectively float various minerals. For this purpose, carboxylate- and hydroxamate-based collectors (for mineral specific flotation of calcium minerals) as well as xanthate-based collectors (for mineral specific flotation of sulphide minerals) with a fixed alkyl chain length but having two functional groups with varying geometrical distances (separated by a spacer of one, two and three carbon atoms) between them have been synthesized. In this article, we have discussed the design, synthesis, purification of these novel mineral specific collectors as well as their important solution parameters in relation to flotation processes.
INTRODUCTION

The success of mineral flotation processes depends on the hydrophobization of the surface for the desired mineral particles whilst keeping, or making, all other minerals hydrophilic. This is achieved by adding several reagents to the flotation pulp to adsorb selectively at the mineral/water interface. The reagents (surface active agents) which have selectivity for minerals to be floated are called collectors. Several known chelating agents have been appropriately modified to make those behave as selective flotation collectors with some degree of success. The problem is that almost all of the chelating groups form complexes with almost all of the transition and many non-transition metals. As a consequence, absolute selectivity does not exist, (because this approach suffers from a major drawback). Besides being unsatisfactory from a scientific viewpoint, it assumes that the metal ion specificity observed for a functional group in bulk aqueous system would remain valid during surface chelation at the interface, while in actual practice, the specificity based on metal ion is neither valid nor useful where the cations participating in the complexation reactions are the same.

It is clear that a selective reagent should be based on the reagent interactions not merely with the metal ion on the surface, but with the whole surface. Is it possible to design reagents which can recognize the surface structure of the substrate? Should the reagent design not take into account the differences in the crystal structure of the mineral surfaces? If possible, it would be more appropriate to design reagents having functional groups so spaced that those are compatible with the relative positions of the metal ion sites available on the surface, that is, to design not just metal-specific but structure-specific reagents (Rao and Forssberg 1995).

A scientific approach of designing mineral separation reagents involves two important surface-chemical aspects, i) selection of the appropriate functional group, and ii) design of the corresponding molecular architecture depending on its end use.

The understandings of molecular interactions involved in the recognition of surfaces by organic molecules in biomineralization process (Mann 1988; Mann 1993) suggest the possibility of reagents specific to the crystal structure. The influence of organic additives on crystal growth processes suggest that molecules having at least two groups can influence either the morphology of surfaces or inhibit crystal growth whereas no marked changes have been observed with molecules containing one functional group (Heywood and Mann 1992; Grases et al. 1991; Mann et al. 1990). The spacing between the functional groups is found to be an important factor in the efficacy of crystal growth inhibition. These concepts have been successfully applied to the rational design and synthesis of molecules either for the control of crystal morphology or to inhibit crystal growth processes through the recognition of specific crystal surfaces (Davey et al. 1991). The concept of molecules consisting of two groups having appropriate spacing between those so as to achieve structural compatibility during interaction with surface exhibit structure-specificity is of direct relevance to the reagents selectivity in flotation processes.

In the present study, for the first time, a rational design of surface active molecules, and thereby the recognition of crystal faces (of minerals) by these molecules through structural and stereochemical matching is being utilized successfully to selectively float various minerals. As mentioned earlier, carboxylate-terminated collectors (for mineral specific flotation of calcium minerals, Fig. 1) as well as...
The natural text is as follows:

Xanthate-based collectors (for mineral specific flotation of sulfide minerals, Fig. 2) with a fixed alkyl chain length but having two functional groups with varying geometrical distances (separated by a spacer of one, two and three carbon atoms) between those have been synthesized. In this article, we have discussed the design, synthesis, purification of these novel mineral specific collectors. Most of these novel reagents were prepared in our own synthesis laboratory at Luleå University of Technology (LTU), however some amino-acid based carboxy-terminated surfactants (Bordes and Holmberg 2011) (Fig. 1, left column) were kindly provided by Prof. Krister Holmberg, Chalmers University, Sweden. Synthesis methods of these molecules were also provided in this article. In order to evaluate the mineral-specific interaction of the collectors, we have trialed these novel collectors with different calcium minerals, viz., apatite, calcite and fluorite. In this article, the differential flotation behavior of these calcium minerals with these novel mineral-specific collectors (surfactant homologues) are described as an example of mineral specific interaction of two functional group collectors.

Fig. 1. Collector molecules (for calcium mineral flotation) in the left column are synthesized (Bordes and Holmberg 2011) at the Chalmers University while the molecules in right column are synthesized at LTU.
EXPERIMENTAL

Materials

The solubility measurements by NMR were made using acetonitrile as a reference (5µL for 1 ml of surfactant solution). The samples of surfactant were prepared in D2O, and the required amount of a concentrated CaCl2 solution or HCl was added. The samples were then stirred for 6 hours.

Quartz Crystal Microbalance with monitoring of the dissipation (QCM-D) was used to evaluate the specificity of adsorption of some of the collectors on apatite like surfaces. A QCM-D instrument (model D300) from Q-Sense (Göteborg, Sweden) was employed. In order to avoid crystal perturbations during the shear oscillation of the crystals, the measurements were carried out under non-flowing conditions. Q-Sense supplied hydroxyapatite coated crystals. The surfaces were cleaned prior to use by a simple UV-ozone treatment. The mass adsorbed were determined by applying the Sauerbrey relationship including a correction for the bulk contribution. More information can be found elsewhere (Bordes, Tropsch, and Holmberg 2010).

Reagents

Lauroyl chloride, l-aspartic acid, l-glutamic acid, aminomalonic acid diethyl ester hydrochloride, l-glycine ethyl ester, lithium aluminum hydride, calcium chloride anhydrous were purchased from Sigma–Aldrich, USA. Dodecylamine, bromanilic acid, bromopropionic acid, bromoacetic acid methyl ester, bromopropionic acid methyl ester, carbon disulfide were purchased from Alfa–Aesar, UK. Sodium hydroxide, hydrochloric acid 37%, ethanol, tetrahydrofuran (THF) anhydrous were purchased from VWR, Sweden. All these chemicals were used as purchased. Pyridine (Aldrich, 99%) was used freshly distilled in vacuo and stored over potassium hydroxide (KOH).

Fig. 2. Collector molecules synthesized and used for sulfide mineral flotation. Molecules shown are at present being synthesized at LTU (project sponsored by Boliden AB)

Synthesis of Collectors

The structures of the molecules synthesized are shown in Fig. 1, left column (Bordes and Holmberg 2011). The synthesis scheme is outlined in Fig. 3. The malonate and glycine based surfactants have been prepared via an ester protected route while the aspartate and the glutamate were prepared by
the Schotten-Baumann reaction.

C12MalNa2: The diethyl ester of the amino acid (47 mmol) was dissolved in pyridine (100 mL) in a round-bottomed flask. Lauroyl chloride (47 mmol) in THF (100 mL) was added under stirring at room temperature. A precipitate appears and the suspension was stirred for 18 hours. The mixture was then poured into aqueous hydrochloric acid (1.5 L, 1 M). After 2 hours stirring the suspension was filtered. The solid diethyl ester of the dicarboxylate surfactant was filtered, washed with water and dissolved in ethanol (150 mL) in a round-bottomed flask. Sodium hydroxide (2 M, 2 eqv.) in ethanol (30 mL) was then added, leading to a white precipitate, which is isolated by filtration. Yields: 95%.

1H NMR (D2O, δ 0.85 (t, 3 protons), δ 1.26 (m, 16 protons), δ 1.58 (m, 2 protons), δ 2.30 (t, 2 protons), δ 3.33 (s, 1 proton)), 13C NMR (D2O, δ 13.96, 17.07, 22.68, 29.35, 29.68, 29.71, 31.99, 36.07, 49.11, 57.62, 62.19, 174.39, 175.62).

C12AspNa2 and C12GluNa2: A suspension of amino acid (310 mmol) was prepared in a mixture of water/acetone (210 mL/150 mL) in a round-bottomed flask. pH is set to 12 with an automatic titrator filled with a solution of sodium hydroxide at 2.5 M. Lauroyl chloride was added drop-wise under stirring at 5°C and stirring was continued for 90 minutes. The mixture was then cooled to 0°C and stirred for 2 hours while the pH is kept at 12. The solution was warmed to room temperature and then acidified to pH 2. A white precipitate appeared which was collected by filtration and washed with water. The product was recrystallized three times from toluene. The product was dissolved in ethanol, and a solution of sodium hydroxide is added (2 M, 2 eq.) leading to a precipitate which was isolated by filtration. Yield: 74%.

1H NMR (D2O, δ 0.85 (t, 3 protons), δ 1.26 (m, 16 protons), δ 1.56 (m, 2 protons), δ 1.85 (m, 1 proton), δ 2.24 (t, 2 protons), δ 2.56 (d, 2 protons), δ 4.38 (t, 1 proton)), 13C NMR (D2O, δ 13.96, 17.07, 22.68, 29.35, 29.68, 29.71, 31.99, 36.07, 49.11, 57.62, 62.19, 174.39, 175.62).

C12GluNa2: 1H NMR (D2O, δ 0.83 (t, 3 protons), δ 1.24 (m, 16 protons), δ 1.56 (m, 2 protons), δ 1.85 (m, 1
proton), δ 2.02 (m, 1 proton), δ 2.23 (m, 4 protons), δ 4.12 (m, 1 proton)). \(^{13}\)C NMR (D\(_2\)O, δ 13.98, 22.65, 25.72, 29.15, 31.90, 34.40, 36.16, 55.42, 176.39, 179.16, 182.36).

C12GlyNa: L-glycine ethyl ester (10 g) was dissolved in pyridine (20 mL) in a round-bottomed flask under reflux. Dodecyl chloride (15.7 g) was added drop-wise under stirring, leading to a white precipitate. The solvent was evaporated. The product was dispersed in water, stirred and then filtered and recrystallized from ethanol. The N-dodecyl ester formed was dissolved in ethanol (100 mL) and aqueous sodium hydroxide (2 M, 35 mL) was added drop-wise under stirring, leading to a white precipitate of the sodium salt of the surfactant. Yield: 46%. \(^1\)H NMR (D\(_2\)O, δ 0.83 (t, 3 protons), δ 1.25 (m, 16 protons), δ 1.57 (m, 2 protons), δ 2.26 (t, 2 protons), δ 3.70 (s, 2 protons)). \(^{13}\)C NMR (D\(_2\)O, δ 13.84, 22.58, 25.67, 29.07, 29.24, 29.46, 29.56, 31.84, 36.09, 43.44, 176.49, 176.91).

B The structures of the molecules synthesized are shown in Fig. 1, right column. The synthesis scheme is outlined in Fig. 4.

C12sp1Na: Dodecylamine (10 g, 54 mmol, 2 eq.) was dissolved in ethanol (50 mL) in a round-bottomed flask. Bromoacetic acid (3.75 g, 27 mmol, 1 eq.) was added drop-wise under stirring, leading to a white precipitate. The mixture was set for reflux, at which point the precipitate dissolved. The reflux condition was maintained for 24 hours. The solvent was evaporated. The product was purified by repeated crystallization from ethanol (Haldar et al. 2004). Yield: 76%. \(^1\)H NMR (D\(_2\)O, 360 MHz): δ 3.2 (s, 2H), 2.6 (t, 2H), 1.5 (br t, 2H), 1.3 (br m, 18H), 0.9 (t, 3H). \(^{13}\)C NMR (D\(_2\)O, 90 MHz): δ 182.2, 56.2, 59.3, 36.7–28.5, 26.0, 17.3.

C12sp11Na\(_2\): C12sp1Na (1.33 g, 5 mmol, 1 eq.) was dissolved in ethanol (20 mL) in a round-bottomed flask. Bromoacetic acid (0.70 g, 5 mmol, 1 eq.) was added drop-wise under stirring, leading to a white precipitate. The mixture was set for reflux, when the precipitate dissolved. The reflux condition was maintained for 24 hours. The solvent was evaporated. The product was purified by repeated crystallization from ethanol. Yield: 62%. \(^1\)H NMR (D\(_2\)O, 360 MHz): δ 3.2 (s, 4H), 2.6 (t, 2H), 1.5 (br t, 2H), 1.3 (br m, 18H), 0.9 (t, 3H). \(^{13}\)C NMR (D\(_2\)O, 90 MHz): δ 182.3, 62.6, 59.3, 36.7–28.5, 26.0, 17.3.

C12sp12Na\(_2\): C12sp1Na (1.33 g, 5 mmol, 1 eq.) was dissolved in ethanol (20 mL) in a round-bottomed flask. Bromopropanoic acid (0.77 g, 5 mmol, 1 eq.) was added drop-wise under stirring, leading to a white precipitate. The mixture was set for reflux, when the precipitate dissolved. The reflux condition was maintained for 24 hours. The solvent was evaporated. The product was purified by repeated crystallization from ethanol. Yield: 41%. \(^1\)H NMR (D\(_2\)O, 360 MHz): δ 3.2 (s, 2H), 2.9 (t, 2H), 2.6 (t, 2H), 2.4
(t, 2H), 1.5 (br t, 2H), 1.3 (br m, 18H), 0.9 (t, 3H). 13C NMR (CDCl₃, 90 MHz): δ 184.2, 181.3, 60.7, 57.5, 54.0, 37.4, 36.3-27.6, 25.7, 17.0.

C12sp₂Na₂: It was done using a similar scheme for preparation of C12sp₁₁Na₂, but using bromopropanoic acid instead of bromoacetic acid for both the steps. Stoechiometry remained unchanged. Yield: 28%. 1H NMR (D₂O, 360 MHz): δ 2.9 (t, 4H), 2.6 (t, 2H), 2.4 (t, 4H), 1.5 (br t, 2H), 1.3 (br m, 18H), 0.9 (t, 3H). 13C NMR (CDCl₃, 90 MHz): δ 184.0, 56.6, 53.0, 37.1, 36.7-28.5, 26.0, 17.3.

C The structures of the molecules synthesized are shown in Fig. 2. The synthesis scheme is outlined in Fig. 5

Step I and Step II: It was done using a similar scheme for preparation as mentioned above (section B), but using bromoacetic acid methyl ester and bromopropanoic acid methyl ester and instead of free acid derivatives used earlier.

Step III: To a stirred suspension of 2 g of lithium aluminum hydride in 50 mL of tetrahydrofuran (distilled over lithium aluminum hydride) was added slowly a solution of 4 g of step II product in 50 mL of tetrahydrofuran and the mixture was refluxed for 2 hours (Shapiro, Flowers, and Hecht 1957). After cooling in an ice bath, 3 mL of water was added followed by 3 mL of 20% sodium hydroxide and 6 mL of water. The precipitated inorganic salts were filtered off and washed with ether. The combined filtrates were washed with saturated sodium chloride solution and dried over sodium sulfate.

Step IV: Sodium wire was added to step III product (1 eq.) and when the initial reaction moderated, the mixture was gently boiled until all the sodium had reacted. The solution was chilled, and carbon disulfide (1 eq.) added precisely; yielding of the pale yellow, odourless xanthate crystals (Bulmer and Mann 1945).

Fig. 5. Schematic diagram of synthesis of sulfide-mineral specific (xanthate-terminated) collectors carried out at LTU.
RESULTS

Calcium interaction study

NMR was used to determine quantitatively the amount of surfactant remaining in solution as the CaCl₂ concentration was increased. The result, shown in Figure 6, confirms that the glutamate surfactant is more calcium tolerant than the two other surfactants. The surfactants investigated were the disodium salts of N-dodecylaminomalonic acid (C12MalNa₂), N-dodecylaspartic acid (C12AspNa₂) and N-dodecylglutamic acid (C12GluNa₂). Measurements were made at 25°C and at concentration of 100 mM, 146 mM and 148 mM respectively.

![Figure 6. Relative amount of dissolved surfactant as a function of molar ratio of added CaCl₂ to surfactant.](image)

A tentative explanation for the difference is the following. The aminomalate and the aspartate surfactants have one and two carbon atoms, respectively, separating the carboxyl groups. These surfactants should be capable of forming intramolecular chelates with the divalent calcium ion, leading to six- and seven-membered rings. The glutamate surfactant has a three carbon spacer and would form an eight-membered ring with the calcium ion, which is less favourable. The concept is shown in Figure 7 for calcium ion binding to C12MalNa₂ and to C12GluNa₂.

![Figure 7. Intramolecular complexes between calcium ion and (left) an aminomalate surfactant and (right) a glutamate surfactant.](image)
Precipitation seems to be favoured by the intramolecular binding of calcium ions, which is not surprising since calcium soaps of divalent acids are known to precipitate readily. The intramolecular chelating of calcium ions may be assisted by interaction between the carbonyl oxygen of the amide bond and the cation. Such interactions have been observed before for similar chelating agents and divalent cations (Chan et al. 1997).

In parallel to the bulk behavior study, the adsorption of the three dicarboxylate surfactants C12MalNa2, C12AspNa2 and C12GluNa2 was studied by quartz crystal microbalance with dissipation monitoring (QCM-D). QCM is a versatile technique that allows the use of many different surfaces such as mineral surfaces. Figure 8 shows QCM-D curves for adsorption of the three dicarboxylic surfactants on a thin layer of hydroxyapatite applied on a gold coated quartz crystal, normalized to the CMC of the surfactants. CMCs are 50 mM, 73 mM and 74 mM for C12MalNa2, C12AspNa2 and C12GluNa2, respectively.

The adsorption of the dicarboxylic surfactants at hydroxyapatite is as follows C12AspNa2 > C12MalNa2 > C12GluNa2. As discussed above, the distance between the two carboxyl groups in the series of dicarboxylic amino acid-based surfactants, i.e., the length of the spacer unit, plays a crucial role for the interaction of the headgroup with divalent cations in solution, and should match the topology of the hydroxyapatite surface. The weak adsorption of the glutamate surfactant on the hydroxyapatite surface can most likely be explained by the same argument as used above to explain the good tolerance to calcium ions for this surfactant compared to the aminomalonate and the aspartate surfactants: its inability to form strong intramolecular complexes due to a too long spacer between the carboxyl groups. It is then reasonable that C12GluNa2 is not efficient in chelating calcium from the crystal lattice. Following this way of reasoning, the stronger adsorption of C12AspNa2 compared to C12MalNa2 can be assumed to be due to better complexing of the aspartate surfactant with lattice calcium. These results can serve as a basis for the rationalization of the flotation work.
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Molecular recognition in mineral flotation: selectivity in apatite-calcite system
Molecular recognition in mineral flotation: selectivity in apatite-calcite system

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ABSTRACT

The present investigation aims to develop and distinguish mineral specific reagents with two functional groups for use in flotation of calcium containing minerals. For this purpose, a series of dicarboxylate-based surfactants with varying length between the carboxylate groups (one, two or three methylene groups) were synthesized. As reference, a surfactant with the same alkyl chain length but with only one carboxylate group in the polar part was synthesized. The adsorption behavior of these new reagents on pure apatite and calcite mineral surfaces was studied using Hallimond tube flotation, FTIR and \( \zeta \) potential measurements. The relation between the adsorption behavior of a given surfactant on a specific mineral surface and its molecular structure over a range of concentration and pH values, as well as the region of maximum recovery were established. It was found that one of the reagents, with a specific distance between the carboxylate groups, was much more selective for a particular mineral surface than the other homologues synthesized. This selective adsorption of a given surfactant to a particular mineral surface relative to other mineral surfaces as evidenced in flotation studies is substantiated by \( \zeta \) potential and infra-red spectroscopy data.
INTRODUCTION

Design, development and selection of reagents, or industrial performance chemicals e.g. surfactants, dispersants, flocculants, are important in many industrial fields, including mineral processing. Most of the currently used commercial reagents have been discovered in a trial and error method based on rules of thumb and past experience. This way of discovery is time and resource consuming and the design of an acceptable reagent combination for a particular application is therefore prohibitively expensive. Furthermore, using past experience as a basis for discovery limits the selection of new reagents to already known families of surfactants and polymers.

Much research effort has been devoted on the physico-chemical aspects of flotation of sparingly soluble calcium minerals using a variety of flotation collectors. Calcium minerals are characterized by their higher aqueous solubility compared to oxide and silicate minerals. Separation amongst some of these minerals, possessing highly similar surface properties (such as scheelite-fluorite, fluorite-calcite, apatite-calcite and fluorite-barite), is a challenging task. Fatty acids have been fairly standard collectors for calcium mineral separation and their mechanism of adsorption has been widely studied. Their separation has not been solved on an industrial level, however; this is due to the high reactivity and low selectivity of the collectors employed. As a remediation, differential depression became the most common way to use these collectors and often yielding limited selective flotation of many complex ores. Nowadays these difficulties are increased, especially with the declining of high grade and relatively easy to process ores. The separation methods have therefore to be even more efficient to enable the recovery of low grade, complex and disseminated type of ore deposits as well as old tailing dumps economical. The development of new selective and environmentally acceptable reagents and almost tailor-made reagents is vital for this purpose.

Collector reagents are normally lipophilic aliphatic chains with a hydrophilic polar head group, also known as surfactants. Almost all collectors employed to date consist of only one polar functional group. When choosing (Grases et al. 1991; Heywood and Mann 1992; Mann et al. 1990) the functional group the primary need is its complexation/chelation ability with the metal ions present at the mineral surface. This way of choosing groups cannot be used in a system where the minerals have similar surface metal ion such as Ca²⁺ at the surfaces of calcium minerals. This makes it evident that to find a collector that is specific for a given surface one cannot look only on its chelation chemistry with the surface metal ion but its interaction with the whole surface (Rao and Forssberg 1995). Understanding the molecular interactions involved in biominalization processes hints at the possibility of designing reagents specific to given crystal structure (Pradip et al. 2002; Mann 1993; Mann et al. 1988). By looking at the influences of organic aids on crystal growth processes it can be hinted that using more than one functional group will affect either the morphology of the surface or inhibit the crystal growth, while no marked changes has been seen for molecules with only one functional group. Multiple functional groups also make it possible to have different spacing between the groups, and this spacing has been found to be an important factor in the efficacy of crystal growth inhibition. The concept itself has been successfully applied to control
crystal morphology or inhibit crystal growth processes and based on this we have synthesized collector molecule (Bordes and Holmberg 2011) with two functional groups to be used for achieving mineral specificity in flotation separation of calcium minerals (Davey et al. 1991).

The influence of the surface structure in mineral-reagent-interactions can be noticed in the flotation of calcium minerals, even if it is not fully understood. When looking at fluorite flotation with fatty acid collectors, the higher collector affinity is thought to be due to the better templating effects at the fluorite surface (Arad et al. 1993). From chloro- and fluoro-apatite flotation using fatty acids the difference in flotation response has been attributed to the differences in crystal structures. The use of amino-carboxylic fatty acids to separate fluorite appears to be effective while diphosphonic acid collectors of different link lengths have had different flotation responses for apatite and calcite (Kotlyarevsky et al. 1984; Collins, Wright, and Watson 1984). The selectivity of these different reagents can be attributed to their geometrical match and compatibility at the mineral surface, even if this is not clearly stated in the literature.

In the present study, we have examined novel anionic surfactants containing two carboxylic acids with varying spacing between the functional groups. Previous study (Bordes and Holmberg 2011) of these surfactants have revealed that a strong role of the spacer in the interaction with calcium ions. By finding mineral-specific interaction of the collector as discussed above, we aim at designing ‘smart’ collectors capable of identifying and attaching to specific mineral surface to achieve preferential floatation.

EXPERIMENTAL

Materials

Pure apatite and calcite minerals used in this paper were purchased from Gregory, Bottley & Lloyd Ltd., United Kingdom. The minerals were received as large 500 g blocks, crushed in a jaw crusher. The minerals were further reduced in size using a stainless-steel rod mill and screened to collect the -150+38 μm size fraction. To produce the -5 μm size fraction (for ζ potential measurements and FTIR experiments) a Fritch Pulverisette 2 mortar grinder was used and screened with a 5 μm filter cloth screen in an ultrasonic bath.

Reagents

All pH regulations were done using hydrochloric acid (HCl) and sodium hydroxide (NaOH). For the ζ potential measurements sodium chloride (NaCl) was used as the background electrolyte.

The double-headed surfactants in Figure 1 were synthesized in-house (Bordes and Holmberg 2011) and used as mineral-specific collector.

Sodium hydroxide (Fluka, ≥98%) and hydrochloric acid (Rüdel de Haën, 37%) were used as purchased.
ζ potential measurements

ζ potential measurements were performed using a ZetaCompact (CAD instruments) instrument. 1 × 10^{-2} mol/dm^3 NaCl was used as background electrolyte and the solid concentration of the samples was 0.50 g/dm^3. Each sample was equilibrated for 10 minutes on a shaking table. The results were calculated using Zeta4 software® with the Smoluchowski equation and are an average of three repeated measurements.

Hallimond flotation test

The flotation of the mineral samples was performed in a 100 ml Hallimond tube flotation cell using 1 g of pure mineral in the size fraction -150+38 μm at the desired pH. The suspension of mineral in deionized water and collector was conditioned for 10 minutes, transferred to the Hallimond cell and floated for 1 minute at ambient temperature. The flotation recovery was calculated as the ratio of the recovered floated particle and the total amount of mineral particles taken.

Diffuse reflectance FTIR spectroscopy

Diffuse Reflectance Infrared Fourier-Transformed Spectroscopy (DRIFTS) measurements were performed using a Bruker IFS 66 v/S instrument with a deuterated triglycine sulfate (DTGS) detector. The -5 μm fractions were conditioned for 10 minutes, at the different pH and concentration used in the report. The samples were then washed three times with deionized water and filtered to remove any molecules not chemically adhered to the surface. The samples were then dried overnight at room temperature. The dried samples were mixed with potassium bromide to a 13 wt% concentration and recorded with 128 scans at a resolution of 4 cm^{-1}.

Figure 1 Collector molecules synthesized and used for apatite and calcite flotation (Bordes and Holmberg 2011)
RESULTS AND DISCUSSIONS

Hallimond flotation test and ζ potential measurement - Effect of pH

**Flotation recovery**

Flotation recovery of apatite in the entire pH range 2-12 were measured with a constant collector concentration of $2 \times 10^{-4}$ mol/dm$^3$ and the data obtained were presented in Figure 2a. At low pH (~5) all tested collectors except C12GlyNa can recover apatite, while C12GlyNa has peak recovery at pH 7.2 before stabilizing at 20% recovery for the rest of the pH range. However, it is noticeable that at higher pH, among all the four collectors used in this study, only C12MalNa$_2$ has significant flotation recovery of apatite.

Flotation recovery of calcite in the pH range 6-12 were measured (due to the alkaline nature of CaCO$_3$, it was not possible to measure at pH lower than 6) with a constant collector concentration of $2 \times 10^{-4}$ mol/dm$^3$ and the data obtained are presented in Figure 2b. From the figure it can be seen that C12AspNa$_2$ and C12GluNa$_2$ can float calcite only at certain low pH (~6 or slightly higher), while at higher pH flotation recovery is extremely poor. C12MalNa$_2$ does not float calcite at any pH. On the other hand, single-headed collector C12GlyNa was found to be an excellent collector for calcite and it can recover the mineral successfully within the whole pH range studied, especially around pH 9.6-9.8.

**ζ potential measurement**

The apatite $ζ$ potential measurements at different pH with a constant collector concentration of $2 \times 10^{-4}$ mol/dm$^3$, as well as in the absence of a collector can be seen in Figure 3a. The behavior is similar to the one observed for the flotation measurement. The curves for C12GluNa$_2$, C12AspNa$_2$ and C12GlyNa almost follow (especially at higher pH where flotation recovery is in the lower side) the curve for ‘apatite without any flotation collector’ – indicating that little or virtually no adsorption at these conditions occurs. However, at low pH (~2-3) where C12GluNa$_2$ and C12AspNa$_2$ show high flotation recovery, the sharp changes in $ζ$ potential are also noticeable, possibly indicating significant adsorption at these conditions. In comparison, the measured change in $ζ$ potential using collector C12MalNa$_2$ is much higher, which is in support to the data obtained showing the best apatite flotation recovery using this collector. In the absence of any flotation collector the apatite used in these experiments show an iso-electric point slightly below pH 4. With a collector concentration of $2 \times 10^{-4}$ mol/dm$^3$ of either C12GluNa$_2$ or C12GlyNa the iso-electric point is shifted to below pH 3. In the presence of collectors C12MalNa$_2$ and C12AspNa$_2$ the iso-electric point is not observed in the pH range examined and the surface remained negatively charged throughout the whole pH range studied.

Calcite $ζ$ potential measurements using constant collector concentration of $2 \times 10^{-4}$ mol/dm$^3$, as well as in the absence of a collector, as a function of pH can be seen in Figure 3b. The curves for C12AspNa$_2$ and C12GluNa$_2$ almost follow the curve for ‘calcite without any flotation collector’ – indicating little or virtually no adsorption at this conditions. In this graph we can see a decrease in $ζ$.
potential for C12GlyNa with increasing pH, which is in support to the data obtained showing the excellent calcite flotation recovery using this collector. However, it is interesting to note that the change in ζ potential is even higher using the collector C12MalNa₂, just as we saw in apatite case that the change in ζ potential is very high using this mineral. However, though there is a big change in ζ potential in both the cases, flotation recovery of calcite using collector C12MalNa₂ is very low, in contrast to the high flotation recovery of apatite using the same collector.

Both C12AspNa₂ and C12GluNa₂ coated calcite surfaces change from negative to positive ζ potential between pH 7 and pH 8, while C12GlyNa changes from positive to negative potential.
around the pH 11.7. For calcite without any flotation collector and using C12MalNa₂ there was no specific iso-electric point; the former remained positive at all the pH while C12MalNa₂ coated surface were negatively charged in the entire pH range studied.

Hallimond flotation test and ζ potential measurement of apatite and calcite mineral - Effect of concentration

Apatite flotation
Flotation experiments using apatite at constant pH 10.5, with a varying collector concentration ranging from $5 \times 10^{-6}$ mol/dm$^3$ to $1 \times 10^{-3}$ mol/dm$^3$ can be seen in Figure 4a. At the pH 10.5, apatite mineral is floated significantly (90%) with the collector C12MalNa₂ only. The collector C12GlyNa also floats this mineral moderately (50%) at this pH, but only at concentration higher than $1 \times 10^{-4}$ mol/dm$^3$. Collectors C12AspNa₂ and C12GluNa₂ do not float apatite at pH 10.5 at all.

Apatite ζ potential measurement
Figure 5a show that the ζ potential curves essentially mimic the flotation results. For example, at pH 10.5, using collector C12MalNa₂ (which gives the best flotation recovery at this condition) we can see a sharp decrease in the ζ potential with increasing collector concentration, indicating strong adsorption at the mineral interface (please also see corresponding FTIR data). In a similar way, the ζ potential decreases slightly with the collector C12GlyNa (in which case we have noticed moderate mineral recovery by flotation) with a collector concentration more than $6 \times 10^{-4}$ mol/dm$^3$, while for collector C12AspNa₂ and C12GluNa₂ the ζ potential values virtually remained unchanged (where we have found no improvement in flotation recovery by adding collector) at any collector concentration indicating little or almost no adsorption of these collectors on the apatite interfaces.

Calcite flotation
Again, flotation behavior of calcite mineral both at constant pH 10.5, with a varying collector concentration from $5 \times 10^{-6}$ mol/dm$^3$ to $1 \times 10^{-3}$ mol/dm$^3$ can be seen in Figure 4b. It is clearly noticed that only single head group collector C12GlyNa can recover calcite very efficiently. At a higher pH like 10.5, collector concentrations more than $1 \times 10^{-4}$ mol/dm$^3$ are required to get significant flotation recovery. Double-headed collectors C12MalNa₂, C12AspNa₂ and C12GluNa₂ cannot recover the mineral at all at pH 10.5.

Calcite ζ potential measurement
As previously observed, we have found that the ζ potential curves follow the same trend as flotation data obtained, as shown in the Figure 5b. In this figure it can be seen that the ζ potential is decreasing with increasing collector concentration. At pH 10.5, applying C12AspNa₂ and C12GluNa₂ does not make calcite surface negative until reaching the maximum collector concentration used in this experiment (i.e., around millimolar concentration). In this case, we have
hardly seen any flotation.

Figure 4 Flotation recovery of apatite and calcite at pH 10.5 using different collector concentrations ranging from $5 \times 10^{-6}$ mol/dm$^3$ to $1 \times 10^{-3}$ mol/dm$^3$. (a) apatite (b) calcite;

Figure 5 ζ potential measurement of apatite and calcite at pH 10.5 using different collector concentrations ranging from $5 \times 10^{-6}$ mol/dm$^3$ to $1 \times 10^{-3}$ mol/dm$^3$. (a) apatite (b) calcite

Applying C12GlyNa and C12MalNa$_2$ collectors, calcite surface becomes negative at lower collector concentrations, nearly $3 \times 10^{-4}$ mol/dm$^3$ and $3 \times 10^{-5}$ mol/dm$^3$ respectively at pH 10.5. It must be noted again, as we have seen in Figure 3b, the change in ζ potential of calcite mineral is very high using the collector C12MalNa$_2$. However, this collector does not assist flotation of calcite mineral at all at any pH, as we have seen earlier in Figure 2b. On the other hand, the ζ potential measurements performed correlate the much higher recoverability of calcite mineral using C12GlyNa collector. This is also supported by the corresponding FTIR data, see discussion below.
**Diffuse reflectance FTIR spectroscopy**

The alkyl chain absorbance band region for the DRIFTS experiments performed for apatite with the C12MalNa2 collector (the best collector for apatite flotation as found earlier) concentration from $5 \times 10^{-6}$ mol/dm$^3$ to $1 \times 10^{-3}$ mol/dm$^3$ and at pH 10.5 are shown in Figure 6a. It can be seen that significant collector adsorption on the mineral interface is occurring when collector concentration is $1 \times 10^{-4}$ mol/dm$^3$ or more.

The absorbance values of the alkyl chain band region measured by DRIFTS experiments performed for calcite with the C12GlyNa collector (the best collector for calcite flotation as found earlier) at different concentrations from $5 \times 10^{-6}$ mol/dm$^3$ to $1 \times 10^{-3}$ mol/dm$^3$ and at pH 10.5 are shown in Figure 6b. It can be noticed that significant collector adsorption on the mineral interface is occurring when collector concentration is $3 \times 10^{-4}$ mol/dm$^3$ or more.

These values are very close to the information obtained from the flotation studies and ζ potential measurements, as seen earlier in this article.

For the absorbance spectra for C12GlyNa collector on calcite, it is difficult to see the collector absorbance, as calcite itself has two bands overlapping with the CH$_2$-band absorption region. A spectra obtained for pure (freshly ground) calcite is subtracted from the original spectra (of collector-coated calcite) to find the spectra for the adsorbed collector only.

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**CONCLUSION**

Several important remarks can be made from the results obtained:

1. It was observed that the dicarboxylate collector C12MalNa2 (with the carboxylate groups separated by one methylene group) is an apatite specific reagent while the single carboxylate collector C12GlyNa is a calcite specific collector. Interaction of the C12GlyNa
reagent with the calcite surface and of the C12MalNa₂ reagent with the apatite surface brings about a pronounced difference in flotation behavior, indicating a strong adsorption at the mineral surfaces, thus making the surface hydrophobic enough for flotation to occur. By carefully controlling both the concentration of the collector used and the pH of the solution, it should be possible to use these collectors to elegantly separate the two minerals from each other.

2. Dicarboxylic collectors with two or three methylene groups as spacer (C12AspNa₂ and C12GluNa₂, respectively) do not assist flotation at pH 10.5. However, significant flotation was observed when the collectors were used at lower pH (2.0-4.5 with apatite and 6.0-8.5 with calcite), where the collectors have poor solubility in water. It is possible that collector aggregates become adsorbed on the mineral surface at this pH, making the interface hydrophobic and promoting flotation.

3. The \( \zeta \) potential curves followed the flotation curves well. The only discrepancy was observed with calcite mineral using C12MalNa₂ as collector. In this case, a rapid decrease of the \( \zeta \) potential with increasing collector concentration was seen, possibly indicating a fairly good amount of collector adsorption on the solid surface; however, hardly any flotation was observed.

4. Interestingly, DRIFT spectra support the flotation results and the \( \zeta \) potential data. Not only do the DRIFT spectra show that on the apatite surface there is significant C12MalNa₂ adsorption (Figure 6a) at a collector concentration of more than \( 1 \times 10^{-4} \text{ mol/dm}^3 \), but the spectra also show that on the calcite surface significant C12GlyNa adsorption occurs (Figure 6b) at a collector concentration of more than \( 3 \times 10^{-4} \text{ mol/dm}^3 \). Both these values correspond well with the flotation results and with the \( \zeta \) potential curves (Figures 4a/5a and 4b/5b, respectively).

To summarize, this work shows the potential of using dicarboxylic collectors for specific mineral recovery in complex systems. This opens for the very interesting possibility of using tailor-made double-headed collectors for specific separation processes.

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Selective Flotation of Calcite and Fluorite Minerals
Selective Flotation of Calcite and Fluorite Minerals

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ABSTRACT

A series of amino acid-based surfactants with a fixed alkyl chain length but having two carboxyl groups with varying geometrical distances (separated by a spacer of one, two and three carbon atoms) between those have been synthesized. To compare the adsorption behavior, another amino acid-based surfactant, containing only one carboxyl group, was also synthesized. Adsorption behaviors of these new reagents on calcite and fluorite were studied using Hallimond tube flotation, in order to understand mineral specific behavior of the novel collectors. The results demonstrate that only one of the reagents with a specified geometric distance between the anchoring groups is more selective for a particular mineral surface than other homologues synthesized. This selective adsorption of a given surfactant to a particular mineral surface relative to other mineral surfaces as evidenced in flotation studies is supported by ζ potential and infra-red spectroscopy data. Relation between adsorption behavior of a given surfactant on a specific mineral surface and its molecular structure over a range of concentration and pH values, and region of maximum recovery were established. All the results together showed the potential of using as specific mineral recovery in complex systems.

1 Introduction

The success of mineral flotation processes depends on the hydrophobization of the surface for the desired mineral particles whilst keeping, or making, all other minerals
This is achieved by adding several reagents to the flotation pulp to adsorb selectively at the mineral/water interface. The reagents (surface active agents) which have selectivity for minerals to be floated are called collectors. Several known chelating agents have been appropriately modified to make those behave as selective flotation collectors with some degree of success. The problem is that almost all of the chelating groups form complexes with almost all of the transition and many non-transition metals. As a consequence, absolute selectivity does not exist, (because this approach suffers from a major drawback). Besides being unsatisfactory from a scientific viewpoint, it assumes that the metal ion specificity observed for a functional group in bulk aqueous system would remain valid during surface chelation at the interface, while in actual practice, the specificity based on metal ion is neither valid nor useful where the cations participating in the complexation reactions are the same.

It is clear that a selective reagent should be based on the reagent interactions not merely with the metal ion on the surface, but with the whole surface. Is it possible to design reagents which can recognize the surface structure of the substrate? Should the reagent design not take into account the differences in the crystal structure of the mineral surfaces? If possible, it would be more appropriate to design reagents having functional groups so spaced that those are compatible with the relative positions of the metal ion sites available on the surface, that is, to design not just metal-specific but structure-specific reagents.

A scientific approach of designing mineral separation reagents involves two important surface-chemical aspects, i) selection of the appropriate functional group, and ii) design of the corresponding molecular architecture depending on its end use.

The understandings of molecular interactions involved in the recognition of surfaces by organic molecules in biominalization process suggest the possibility of reagents specific to the crystal structure. The influence of organic additives on crystal growth processes suggest that molecules having at least two groups can influence either the morphology of surfaces or inhibit crystal growth whereas no marked changes have been observed with molecules containing one functional group. The spacing between the functional groups is found to be an important factor in the efficacy of crystal growth inhibition. These concepts have been successfully applied to the rational design and synthesis of molecules either for the control of crystal morphology or to inhibit crystal growth processes through the recognition of specific crystal surfaces. The concept of
molecules consisting of two groups having appropriate spacing between those so as to achieve structural compatibility during interaction with surface exhibit structure-specificity is of direct relevance to the reagents selectivity in flotation processes.

Considerable amount of research efforts has been devoted for the last several decades on the physico-chemical aspects of flotation of sparingly soluble calcium minerals using a variety of flotation collectors. These minerals are characterized by their higher aqueous solubility than oxide and silicate minerals. The semi-soluble characteristics of these minerals increase the complexity of the mineral-reagent interactions: the minerals themselves contribute towards the nature of the aqueous environment which in turn, controls the nature of interfacial reactions. Separation amongst some of these minerals, possessing highly similar surface properties (such as scheelite-fluorite, fluorite-calcite, apatite-calcite and fluorite-barite), thus becomes a challenging task. Generally, fatty acids are used as collectors for these mineral systems. However, separation of these minerals from each other has not been solved on an industrial level. The complexity of selective flotation of these minerals is due to the high reactivity of the collectors employed for this purpose, whether of the anionic or of the cationic type. The low selectivity of these collectors is a well-known fact. Consequently, the role of differential depression became the option and being practiced in selective flotation of many complex ores, namely, calcite-fluorite-scheelite, calcite-fluorite, barite-fluorite, calcite-apatite and other ores but with limited success.

In the present study, instead, we have examined four amino-acid based anionic surfactants containing two functional groups with varying spacing between those. In order to evaluate the mineral-specific interaction of the collector, we have trialed these novel collectors with calcium minerals, calcite and fluorite. In this article, the differential flotation behavior of these calcium minerals with these novel mineral-specific collectors (surfactant homologues) are described.
2 Experimental

2.1 Materials

Pure apatite and calcite minerals used in this paper were purchased from Gregory, Bottley & Lloyd Ltd., United Kingdom. The minerals were received as large 500 g blocks, crushed in a jaw crusher. The minerals were further reduced in size using a stainless-steel rod mill and screened to collect the \(-150+38\) μm size fraction. To produce the \(-5\) μm size fraction (for ζ potential measurements and FTIR experiments) a Fritch Pulverisette 2 mortar grinder was used and screened with a 5 μm filter cloth screen in an ultrasonic bath.

2.2 Reagents

All pH regulations were done using hydrochloric acid (HCl) and sodium hydroxide (NaOH). For the ζ potential measurements sodium chloride (NaCl) was used as a background electrolyte.

Lauroyl chloride, L-aspartic acid, L-glutamic acid, aminomalonic acid diethyl ester hydrochloride, L-glycine ethyl ester, lithium aluminum hydride, calcium chloride anhydrous were purchased from Sigma–Aldrich, USA. Dodecylamine, bromoacetic acid, bromopropionic acid, bromopropionic acid methyl ester, carbon disulfide were purchased from Alfa-Aesar, UK. Sodium hydroxide, hydrochloric acid 37%, ethanol, tetrahydrofuran (THF) anhydrous were purchased from VWR, Sweden. All these chemicals were used as purchased. Pyridine (Aldrich, 99%) was used freshly distilled in vacuo and stored over potassium hydroxide (KOH).
2.2.1 Synthesis of Collectors

The molecules synthesized are shown in figure 1.

2.3 \( \zeta \) potential measurements

\( \zeta \) potential measurements were performed using a ZetaCompact (CAD instruments) instrument. \( 1 \times 10^{-2} \) M NaCl was used as background electrolyte and the solid concentration of the samples was 0.50 g/dm\(^3\). Each sample was equilibrated for 10 minutes on a shaking table. The results were calculated using Zeta4 software\(^\circ\) with the Smoluchowski equation and are an average of three repeated measurements.

2.4 Hallimond flotation test

The flotation of the mineral samples was performed in a 100 ml Hallimond tube flotation cell using 1 g of pure mineral in the size fraction -150+38 \( \mu m \) at the desired pH. The suspension of mineral in deionized water and collector was conditioned for 10 minutes, transferred to the Hallimond cell and floated for 1 minute at ambient temperature. The flotation recovery was calculated as the ratio of the recovered floated particle and the total amount of mineral particles taken.

2.5 Diffuse reflectance FTIR spectroscopy

Diffuse Reflectance Infrared Fourier-Transformed Spectroscopy (DRIFTS) measurements were performed using a Bruker IFS 66 v/S instrument with a deuterated triglycine sulfate (DTGS) detector. The -5 \( \mu m \) fractions were conditioned for 10 minutes, at the different pH and concentration used in the report. The samples were then washed three times with deionized water and filtered to remove any molecules not chemically adhered to the surface. The samples were then dried overnight at room temperature. The dried samples were mixed with potassium bromide to a 13 wt% concentration and recorded with 128 scans at a resolution of 4 cm\(^{-1}\).
3 Results and Discussions

3.1 Hallimond flotation test and ζ potential measurement - Effect of pH

3.1.1 Flotation recovery

Flotation recovery of calcite in the pH range 6-12 were measured (due to the alkaline nature of CaCO₃, it was not possible to measure at pH less than 6) with a constant collector concentration of $2 \times 10^{-4}$ M and the data obtained are presented in Figure 2a. From the figure it can be seen that C₁₂AspNa₂ and C₁₂GluNa₂ can float calcite only at certain low pH (~6 or slightly higher), while at higher pH flotation recovery is extremely poor. C₁₂MalNa₂ does not float calcite at any pH. On the other hand, monodentate ligand C₁₂GlyNa was found to be an excellent collector for calcite, and it can recover the mineral successfully at within the whole pH range studied.

Flotation recovery of fluorite in the entire pH range 2-12 were measured with a constant collector concentration of $2 \times 10^{-4}$ M and the data obtained were presented in Figure 2b. It can be seen that there are moderate or high flotation recovery with any of the collectors. Especially within the pH range 4-10, the flotation recovery is high for C₁₂GlyNa, C₁₂AspNa₂ and C₁₂GluNa₂. C₁₂MalNa₂ can recover the mineral with moderate success at this intermediate the pH range 4-10. However above pH 10, none of the collector is able bring significant flotation recovery. At low pH (~2), collectors C₁₂MalNa₂, C₁₂AspNa₂ and C₁₂GluNa₂ can assist high flotation recovery, while C₁₂GlyNa assist only moderate (35%) fluorite flotation at this pH.

3.1.2 Calcite ζ potential measurement

Calcite ζ potential measurements using constant collector concentration of $2 \times 10^{-4}$ M, as well as in the absence of a collector, as a function of pH can be seen in Figure 2c. The curves for C₁₂AspNa₂ and C₁₂GluNa₂ almost follow the curve for ‘calcite without any flotation collector’ – indicating little or virtually no adsorption at this conditions. In this graph we can see a decrease in calcite ζ potential using C₁₂GlyNa collector with increasing pH, which is in support to the data obtained showing the excellent calcite flotation recovery using this collector in that range. However, it is interesting to note that the change in ζ potential is even higher using the collector C₁₂MalNa₂, just as we saw in apatite case that the change in ζ potential is very high using this mineral. However, though there is a big change in ζ potential in both the cases, flotation recovery
of calcite using collector C12MalNa$_2$ is very low, in contrast to the high flotation recovery of apatite using the same collector.

Both C12AspNa$_2$ and C12GluNa$_2$ coated calcite surfaces change from negative to positive potential between pH 7 and pH 8, while C12GlyNa changes from positive to negative potential around the pH 11.7. For calcite without any flotation collector and using C12MalNa$_2$ there was no specific iso-electric point; the former remained positive at all the pH while C12MalNa$_2$ coated surface were negatively charged in the entire pH range studied.

3.1.3 Fluorite $\zeta$ potential measurement

Fluorite $\zeta$ potential measurements at different pH with a constant collector concentration of $2 \times 10^{-4}$ M, as plotted in figure 2d. In the absence of any flotation collector the fluorite used in these experiments show an iso-electric point slightly below pH 6.6. The curve for C12GlyNa almost follow the trend of the curve for ‘fluorite without any flotation collector’. Though the measured change in $\zeta$ potential using collector C12MalNa$_2$ is relatively higher compared to other collectors used, flotation recovery of fluorite using collector C12MalNa$_2$ is only moderate, and we saw in figure 2c, this collector actually assist flotation of fluorite in much lesser extent than the other three collectors used. It is interesting to note that, the $\zeta$ potential vs. pH curves for this mineral, both in the presence or absence of any collector, pass through a minima ~pH 4, and again through a maxima ~pH 5-6. In the presence of collectors C12MalNa$_2$, C12AspNa$_2$ and C12GluNa$_2$ no specific iso-electric point was observed in the pH range examined, while it can be interpreted that the C12GlyNa coated surface is almost neutral in the pH range 3-6.
3.2  Hallimond flotation test and ζ potential measurement of calcite mineral - Effect of concentration

3.2.1  Calcite flotation

Flotation behavior of calcite mineral both at constant pH 10.5 and natural pH, with a varying collector concentration from $5 \times 10^{-6}$ M to $1 \times 10^{-3}$ M can be seen in Figure 3(a-b). It is clearly noticed that only single head group collector C12GlyNa can recover calcite very efficiently. At a higher pH like 10.5, collector concentrations more than $1 \times 10^{-4}$ M are required to get significant flotation recovery. However with this collector, at the natural pH, flotation starts even at one order less collector concentration ($1 \times 10^{-5}$ M). At natural pH, C12AspNa2 and C12GluNa2 can also recover the mineral moderately around millimolar concentrations, but not at all at pH 10.5. C12MalNa2 does not assist flotation of calcite at any pH or concentration.

3.2.2  Calcite ζ potential measurement

As previously observed, we have found that the ζ potential curves for collector-coated calcite follow the same trend as flotation data obtained, as shown in the Figure 3(c-d). In this figure it can be seen that the ζ potential is decreasing with increasing collector concentration. At pH 10.5, applying C12AspNa2 and C12GluNa2 does not make calcite surface negative until reaching the maximum collector concentration used in this experiment (i.e., around millimolar concentration). In this case, we have hardly seen any flotation. At the natural pH, however, the ζ potential curves (especially C12GluNa2) shows a strong decrease with increasing concentration with these collectors, which supports the flotation data obtained in Fig. 4b.

Applying C12GlyNa and C12MalNa2 collectors, calcite surface becomes negative at lower collector concentrations, nearly $3 \times 10^{-4}$ M and $3 \times 10^{-5}$ M respectively, both at pH 10.5 and natural pH. It must be noted again, as we have seen in Figure 2d, the change in ζ potential of calcite mineral is very high using the collector C12MalNa2. However, this collector does not assist flotation of calcite mineral at all at any pH, as we have seen earlier in Figure 2b. On the other hand, the ζ potential measurements performed correlate the much higher recoverability of calcite mineral using C12GlyNa collector. This is also supported by the corresponding FTIR data, see discussion below.
3.3 Hallimond flotation test and ζ potential measurement of fluorite mineral - Effect of concentration

3.3.1 Fluorite flotation

Again, flotation behavior of fluorite mineral both at constant pH 10.5 and natural pH, with a varying collector concentration from $5 \times 10^{-6} \text{ M}$ to $1 \times 10^{-3} \text{ M}$ can be seen in figure 4(a-b). At a higher pH like 10.5, it is clearly noticed that C12GlyNa and C12MalNa$_2$ can recover fluorite significantly, especially at collector concentrations higher than $2 \times 10^{-4} \text{ M}$. C12AspNa$_2$ and C12GluNa$_2$ hardly recover the mineral at pH 10.5, however at concentration more than $6 \times 10^{-4} \text{ M}$, moderate flotation recovery were observed. On the other hand, at the natural pH, all the collectors can assist fluorite flotation, especially at concentrations higher than $2 \times 10^{-4} \text{ M}$.

3.3.2 Fluorite ζ potential measurement

Figure 4(c-d) show that the ζ potential curves essentially mimic the flotation results in figure 4(a-b). For example, at pH 10.5, fluorite surface can become negative even at very low concentrations of both the collectors C12GlyNa and C12MalNa$_2$, and these effects become more prominent at concentration more than $1 \times 10^{-4} \text{ M}$, i.e., in the same concentration range where both these collectors cause high flotation recovery of fluorite. Again at pH 10.5, using C12AspNa$_2$ and C12GluNa$_2$ collectors the slight decrease in ζ potential are noticed only at concentration greater than $6 \times 10^{-4} \text{ M}$, i.e., in the same range where we found moderate flotation using these collectors. However, it must be noted that, in the presence of all the individual collectors used in this study, no specific iso-electric point was observed, and the surface remained negatively charged in the entire concentration range examined.

Again, at the natural pH, there is a sharp decrease in ζ potential with increasing concentration of all the collectors. The general trend is that all these curves (except C12GlyNa) reach a plateau around $2 \times 10^{-5} \text{ M}$ concentration, i.e., at the same concentration where the respective flotation curves reached the maxima. The ζ potential curves involving C12GlyNa reaches the plateau value at the $1 \times 10^{-4} \text{ M}$ concentration, again at the same value where flotation curves reaches the maxima. These possibly indicate complete surface coverage with the respective collector used at this condition of pH and concentration. Moreover, at the natural pH, applying C12GlyNa and
C12GluNa2 collectors, calcite surface becomes negative at very low collector concentrations, $1 \times 10^{-5}$ M and $5 \times 10^{-6}$ M respectively. In the presence of collectors C12MalNa2 and C12AspNa2 no specific iso-electric point was observed, both remained negatively charged in the entire concentration range examined.

3.4 Diffuse Reflectance FTIR Spectroscopy (DRIFTS)

The alkyl chain absorbance band region from the DRIFTS experiments performed for apatite, calcite and fluorite with a collector concentration of $6 \times 10^{-4}$ M and at pH 10.5 are shown in figure 5.

Calcite: The CH$_2$-band region for the calcite DRIFTS experiments at $6 \times 10^{-4}$ M collector concentration and pH 10.5 are shown in figure 5(a). In this picture it is more difficult to see the collector absorbance, given that calcite itself has two bands in this region. From this figure it is possible to determine that there are collectors adsorbed in both C12GlyNa and C12MalNa2, while only the former assisted flotation of calcite. Though C12MalNa2 does not help calcite flotation at any concentration, the DRIFT spectrum shows that presence of large amount of the collector on calcite interface, which is in support to the data obtained by $\zeta$ potential measurements as shown in figure 3(b) – that calcite interface is able to adsorb C12MalNa2 but this phenomenon does not lead to any improved flotation recovery. While the other two collectors C12AspNa2 and C12GluNa2 do not appear to have a large enough surface collector concentration, and as a consequence, do not assist flotation.

Fluorite: The CH$_2$-band region for the fluorite DRIFTS experiments at $6 \times 10^{-4}$ M collector concentration and pH 10.5 are shown in figure 5(b), where we can see that all the four collectors, more or less, is adsorbed at the fluorite mineral surface with this collector concentration and pH, as we have seen with $\zeta$ potential measurements and as it was evidenced in flotation studies as well. Again, collector C12MalNa2 is adsorbed more on this surface compared to the other collectors. Of the three less adsorbed collectors C12GlyNa has the lowest peak area, though it can float fluorite very well. We have seen earlier in figure 4(a), C12MalNa2 and C12GlyNa can float fluorite better than the other two collectors at this concentration and pH.
4 Conclusion

Several important remarks can be drawn from the results obtained-

1. It was observed that single headed collector C12GlyNa is calcite mineral specific collector. On the other hand, the fluorite mineral can be floated using single headed collector C12GlyNa as well as double headed collector C12MalNa₂ (separated by a single spacer group).

2. Collectors with 2 or 3 carbon spacers (C12AspNa₂ and C12GluNa₂ respectively) do not much assist flotation at pH 10.5 with the minerals studied. At natural pH, these collectors are able to float fluorite, even at concentration as low as $1 \times 10^{-3}$ M.

3. In general, fluorite has better flotation recovery than calcite mineral, i.e., if floats with, at least moderately, with most of the collectors.

4. With all the minerals, significant flotation was observed using these two collectors with 2 or 3 carbon spacers (C12AspNa₂ and C12GluNa₂ respectively) at lower pH (2.0-4.5 for fluorite, while 6.0-8.5 with calcite), where the collectors have poor solubility in water. Possibly some collectors aggregates gets adsorbed on the mineral interface at this pH, making the interface hydrophobic and promoting flotation.

5. The $\zeta$ potential curves usually follow the flotation curves well. The only discrepancy was observed with calcite mineral and C12MalNa₂ collector. In this case, rapid decrease of $\zeta$ potential with increasing collector concentration possibly indicates fairly good amount of collector adsorption on the solid interface, while there was hardly any flotation was observed.

6. It was noticed that specific pairing between a given mineral and a given collector occurs better at higher pH like 10.5 than at natural pH. At the natural pH, almost all collectors get adsorbed on various mineral interfaces, more or less. Thereby, any distinct mineral specific adsorption is not observed at this pH.

7. FTIR study indicated that even if the surface is slightly covered with single-headed C12GlyNa ligand, significant flotation recovery is possible. For example, in fig 5(b) and 5(c), we can see excellent flotation recovery of both calcite and fluorite using C12GlyNa collector, though the adsorption is only moderate in both the minerals.
To summarize, the collectors examined in this work show the potential of using bidentate collectors for specific mineral recovery in complex systems. This opens up the very interesting possibility of use of tailor made collectors – depending on the specific separation process they are to be used in.

5 Acknowledgement

Financial support from the Hjalmar Lundbohm Research Centre (HLRC) and Luossavaara-Kiirunavaara AB (LKAB) is gratefully acknowledged. Helpful discussions with Assoc. Prof. Allan Holmgren and Assoc. Prof. Mattias Grahn are greatly appreciated.
Figure 1. Collector molecules synthesized and used for calcite and fluorite flotation.
Figure 2. Flotation recovery and ζ potential measurement of calcite and fluorite as a function of pH, in the presence of 2 × 10^{-4} M collector concentration. (a) flotation recovery of calcite; (b) flotation recovery of fluorite; (c) ζ potential measurement of calcite; (d) ζ potential measurement of fluorite.
Figure 3. Flotation recovery and ζ potential measurement of calcite using different collector concentrations ranging from $5 \times 10^{-6}$ M to $1 \times 10^{-3}$ M. (a) flotation recovery at pH 10.5; (b) flotation recovery at natural pH; (c) ζ potential measurement at pH 10.5; (d) ζ potential measurement at natural pH.
Figure 4. Flotation recovery and $\zeta$ potential measurement of fluorite using different collector concentrations ranging from $5 \times 10^{-6}$ M to $1 \times 10^{-3}$ M. (a) flotation recovery at pH 10.5; (b) flotation recovery at natural pH; (c) $\zeta$ potential measurement at pH 10.5; (d) $\zeta$ potential measurement natural pH.
Figure 5. DRIFTS spectra at 6 × 10^{-4} M collector concentration and pH 10.5. (a) calcite, (b) fluorite.
6 References


