

THE MECHANISM OF
SOLUBLE SALT FLOTATION

by

Ronald J. Roman

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A thesis respectfully submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Doctor of Science.

Signed:

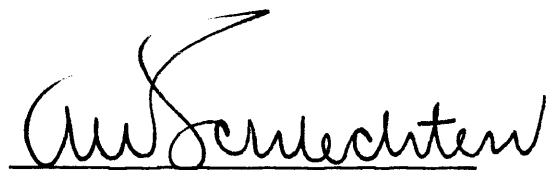

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ABSTRACT

Micro-flotation studies with NaCl and KCl together with solubility determinations of collector salts were undertaken to elucidate the mechanism of soluble salt flotation. The existence of a surface charge on the alkali halide salts is revealed, and a flotation mechanism involving surface charge and collector solubility is developed. This mechanism is expanded to explain the effects of activating ions, temperature, and pH on the flotation behavior of the alkali halide salts.

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INTRODUCTION

There is no substitute for potassium as a plant nutrient in agricultural fertilizers; it is essential to the maintenance and expansion of food production. In the United States the consumption of potassium compounds as fertilizer, 2.9 million tons of K_2O in 1963, was up 13 percent over the previous year (1). Potash would have been in limited supply if imports had not been received from Canada.

Although potassium occurs in many minerals, commercial sources are limited to its soluble salts in salt deposits and brines. The Carlsbad, New Mexico, deposit supplies over 80 percent of the potash produced in the United States. The average grade of ore mined in 1963 from this deposit was 18.78 percent K_2O or 29.75 percent KCl (2). At this grade the ore must be concentrated before it can be sold as a fertilizer. Fertilizer consumes 95 percent of the U. S. potash production. If the minimum ore grade could be lowered to 5 percent K_2O , the New Mexico deposits could be worked for another 1,000 years at the present rate of production (3).

Before deposits of this quality can be worked, understanding of the mechanisms involved in soluble salt flotation will have to be attained. At the present time, the mechanisms of collector adsorption are not understood.

However, four major hypotheses have been developed to describe the mechanism of soluble salt flotation. Each is entirely different, and each fails to explain certain phenomena in the behavior of sylvite or halite flotation. In 1961 Singewald (4) commented on the lack of basic data in salt flotation:

Many effects which contribute to selectivity cannot be elucidated yet, and there are as yet not even any starting points to work from.

Existing Mechanisms

Ion Exchange Mechanisms

Gaudin (5) has suggested that the difference in floatability of halite (NaCl) and sylvite (KCl) with primary amines is due to the ionic size of the RNH_3^+ , K^+ , and Na^+ ions.

In the case of amine flotation, the cation would attach itself to the chloride. I have speculation there, which I cannot prove, that the ammonium group, that is the NH_3 group in the amine, floats potassium chloride because the dimensions of this group as it has been measured in other compounds is almost identical to dimensions of the potassium ion, quite different from the sodium ion, and so fits where the potassium had been in place of it and not attached to it.

In 1955 Fuerstenau and Fuerstenau (6) expanded this hypothesis to include all of the alkali halide salts. Their results are summarized in Figure 1. It can

Ion (radius, Å)	F ⁻ (1.36)	Cl ⁻ (1.81)	Br ⁻ (1.95)	I ⁻ (2.16)
Li ⁺ (0.60)	No flotation			
Na ⁺ (0.95)				
K ⁺ (1.33)	Flotation			
Rb ⁺ (1.48)				
Cs ⁺ (1.69)				

Experimental →

Theoretical ↗

Figure 1 - Ion-exchange mechanism applied to the alkali-halide salts.

be seen that, with the exception of NaI, all of the salts containing cations smaller than the amine ion (Na and Li salts) are not floated, whereas those salts containing cations larger than the amine ion (K, Rb, and Ca salts) are floated.

Several exceptions to this hypothesis are known. That is, this model does not explain why salts containing the same cation nor why salts of different degrees of hydration respond differently to flotation. For example, NaI will float with an amine, whereas $\text{NaI} \cdot 2\text{H}_2\text{O}$ will not (7).

The ion exchange mechanism does not explain anionic flotation such as the use of sulfonates to float NaCl. No correlation between ionic size and flotation can be made in anionic flotation. Further, the ion exchange hypothesis does not explain the effect of magnesium or lead activation, nor does it offer any explanation of the role of temperature in salt flotation. According to this hypothesis, and all the others to be discussed, NaCl cannot be floated with an amine. However, this is not always the case, in that if a short chain amine is used, NaCl will float (8).

Ion Hydration Mechanism

Rogers and Schulman (9) and (10), realizing some of the inadequacies of the ion exchange mechanism, proposed another mechanism based on the heat of solution of the salts. They concluded that salts which have a heat of solution more negative than 3 kcal per mole can be floated with amines and sulfonates, that salts which have a heat of solution between zero and -3 kcal per mole can be

floated with fatty acids, and that salts which have a positive heat of solution cannot be floated at all. Their work was not limited to the alkali halide salts alone but included also the alkaline earth halides.

This mechanism has taken precedence over the ion exchange mechanism even though it offers little more in the way of general explanation of soluble salt flotation. Although Rogers states that the heat of hydration, and not ionic size, is the controlling factor in salt flotation, it has been shown (11) that the heat of hydration (L) can be related to the ionic radius (r) as shown by these equations:

$$\frac{87.5}{r} = L$$

for the alkali cations and

$$\frac{167.5}{r} = L$$

for the halide anions.

A second criticism of this mechanism is that the values used for the heats of solution are the heats of solution at infinite dilution and may be vastly different from those of the salts in their saturated solution. Unfortunately, the heats of solution of many of the salts in their saturated solutions have not yet been determined.

Figure 2 summarizes their results for the alkali halide salts. Rogers arbitrarily chose the distinction between the different degrees of hydration as a convenience to conform to experimental flotation data.

	F ⁻	Cl ⁻	Br ⁻	I ⁻
Li ⁺	No flotation			
Na ⁺	Flotation with fatty acid		Flotation with amine and sulfonates	
K ⁺	No flotation			
Rb ⁺				
Cs ⁺				

Figure 2 - Ion hydration mechanism applied to the alkali-halide salts.

Figure 3 summarizes the mechanism of flotation as suggested by Rogers for NaCl and KCl with three different collectors. It would be thought, that if a fatty acid is reactive (polar) enough to replace water on the surface of NaCl but is not sufficiently reactive to replace potassium on the surface of KCl, then a sulfonate, which is reactive enough to replace chloride on the surface of KCl, should also be able to replace water on the surface of NaCl. However, this is not the case; therefore, other factors probably control the adsorption of collector.

This mechanism, as well as the ion exchange mechanism, fails to explain the role of lead ion in the flotation of NaCl with a sulfate or sulfonate, and the reason why NaCl may be floated by an amine under the proper conditions. For these reasons the ion hydration theory presented by Rogers and Schulman cannot be accepted as a general mechanism for salt flotation.

Other Proposed Mechanisms

The ion exchange and the ion hydration mechanisms have received the most widespread acceptance of all of the mechanisms of salt flotation. However, two other attempts to explain salt flotation will be mentioned here briefly.

As a result of observations by Halbligh (12), a mechanism has been developed that involves the formation of an insoluble product by mutual neutralization of collector and alkali metal ions. Halbligh concludes that sodium salts are floated with fatty acids, while potassium salts are not, because sodium carboxylates are more insoluble than potassium carboxylates. On the other hand, potassium salts

are floated with sulfonates, but sodium salts are not, because potassium sulfonate is more insoluble than sodium sulfonate.

In another study Bachmann (13) attributed the selective flotation of KCl from NaCl with amines to the fact that there are structural similarities between the dimensions of the KCl lattice and the quasi-crystalline structure of the amine collector; however, there is no structural similarity between the amine collector and the NaCl lattice. This premise is quite similar to the ion exchange model if the chloride ion on the surface of the KCl is thought of as belonging to the collector molecule.

Neither of these hypotheses has received widespread acceptance due to the numerous exceptions noted in salt flotation.

Purpose of this Investigation

The mechanisms described all show some correlation between the flotation characteristics of a salt and some physical or chemical property of the salt. In each case the proposed mechanism fails in several instances, and not one of the mechanisms explains the puzzling effects of lead, magnesium, and temperature on flotation response. For these reasons, it can be concluded that these hypotheses do not delineate the mechanisms involved. The purpose of this investigation is to learn the mechanism of soluble salt flotation.

Scope of this Investigation

Although the aim of this investigation is to develop a general theory of salt flotation, the experimental work will be limited to a study of the flotation characteristics of KCl and NaCl with primary alkyl amines, alkyl carboxylates or fatty acids, and alkyl sulfonates as collectors. The effects of magnesium and lead will be studied to determine their role as activators in the flotation of NaCl. The effect of slimes and impurities will not be studied because this is a problem peculiar to each ore deposit and the effect of slimes and impurities is not part of a general mechanism.

EXPERIMENTAL MATERIALS
AND PROCEDURES

Reagents

The potassium and sodium chlorides used in all of the experiments were analyzed reagent grade. The collectors used had the following purity as reported by the supplier:

<u>Reagent</u>	<u>Purity (percent)</u>		<u>Supplier</u>
Dodecyl amine chloride	99+		Armour Chemical Corporation
Tetradecyl amine chloride	99+		Armour Chemical Corporation
Hexadecyl amine chloride	99+		Armour Chemical Corporation
Caprylic acid	99+		Hormel Institute
Sodium octyl-sulfonate	87.22*	96.4**	Marathon Oil Company
Sodium decyl-sulfonate	96.99*	99.4**	Marathon Oil Company

* carbon analysis

** I. R. analysis

The principal impurity in the sulfonate was sodium sulfate. The magnesium chloride used in the preparation of the magnesium-fatty acid compounds and in the flotation experiments was also of reagent grade.

The water used in all of the experimental work was conductivity water which was prepared by passing distilled water through an ion exchange column. This water had an average measured conductivity of 1 micromho.

Apparatus

Flotation Cell

A 100-ml micro-flotation cell was used for all of the flotation experiments. The cell was constructed by removing the stem from a 150-ml Buchner funnel (60 micron glass frit) and replacing it with another stem parallel to the frit for gas introduction. A lip was bent at the rim of the funnel to facilitate collection of the froth and to give a cell volume of 100 ml. The cell contents were stirred by a teflon coated magnetic stir-bar. A glass microscope slide was placed radially and vertically in the cell to act as a baffle. Figures 4 and 5 show the flotation cell and the complete flotation apparatus. Nitrogen gas was passed through a bottle of Ascarite to remove any carbon dioxide. In each flotation experiment, 100 ml of gas was passed through the flotation cell at a pressure of about 3 feet of water.

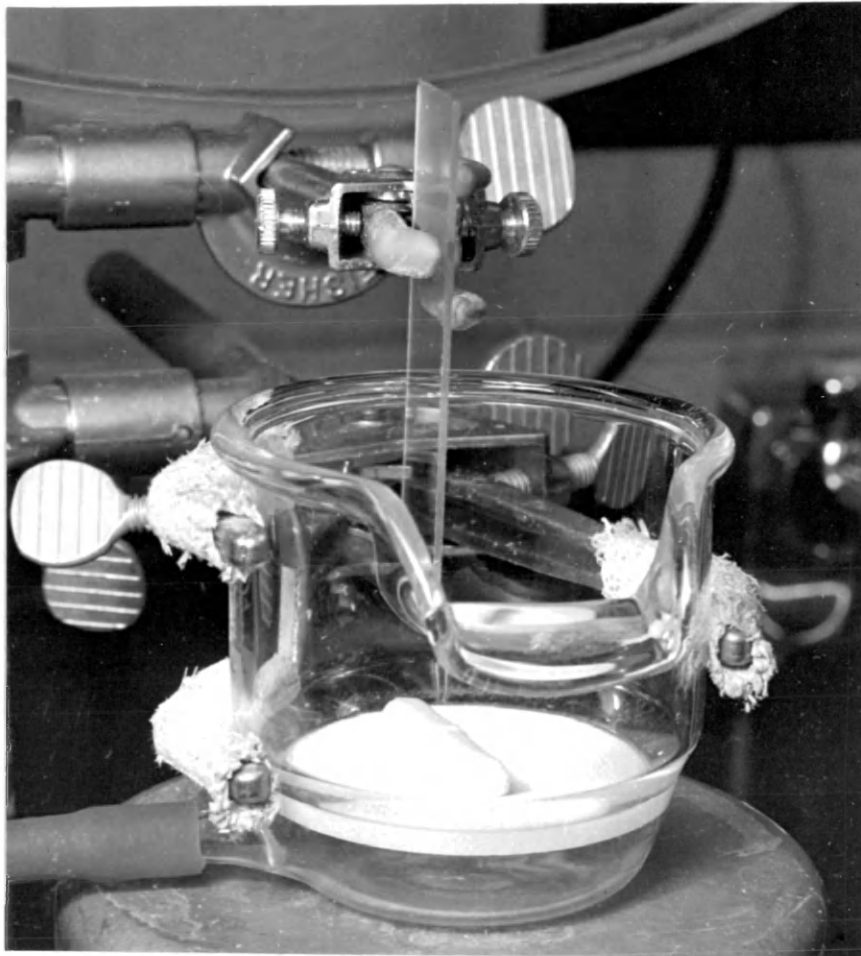


Figure 4 - Micro-flotation cell.

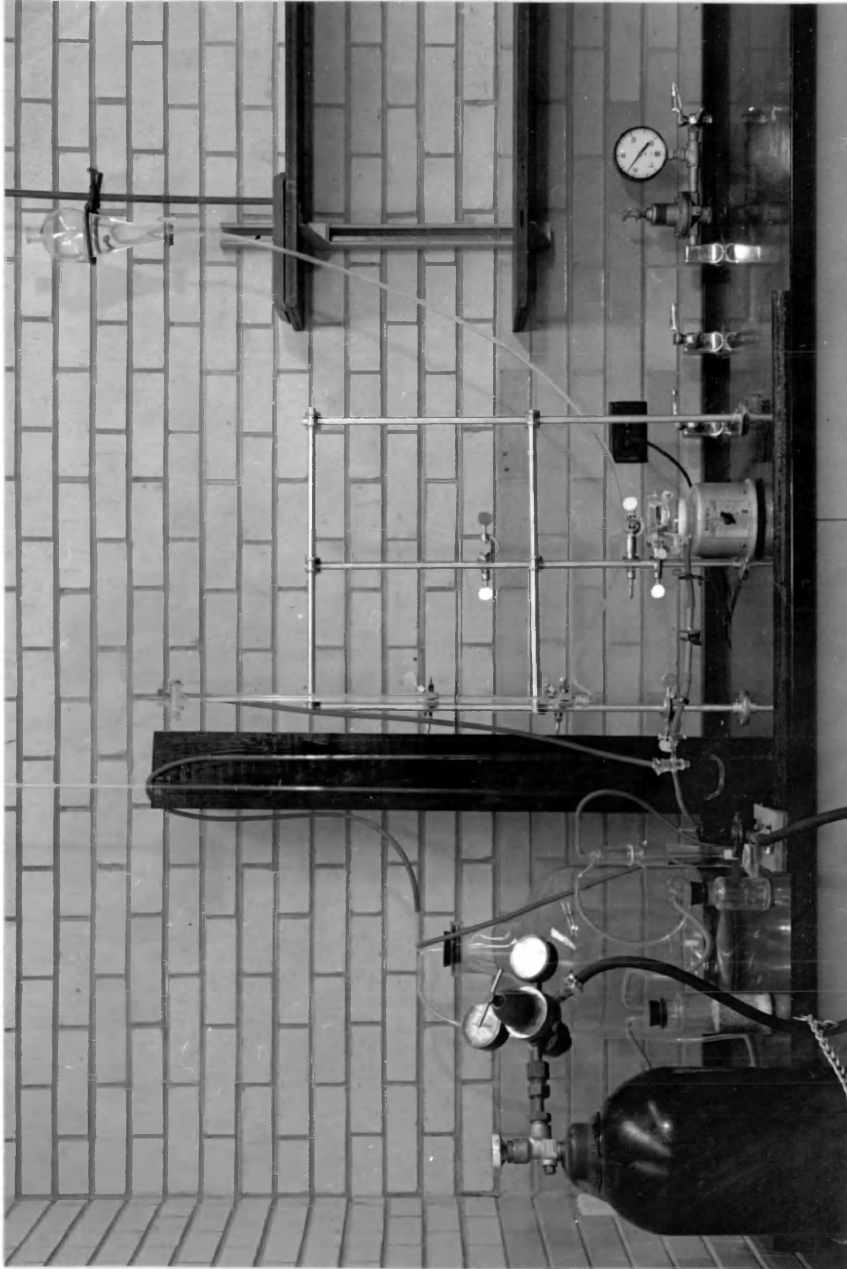


Figure 5 - Micro-flotation apparatus.

Nephelometer

A nephelometer was used in all of the solubility determinations. The sample cell was a 250-ml beaker suspended inside a 400-ml beaker, which acted as a water jacket. The 400-ml beaker was fitted with an inlet tube near the bottom, and an outlet tube near the top so that water at a constant temperature could be circulated from between the two beakers to a constant temperature bath. The 400-ml beaker was completely wrapped with black tape, with the exception of two windows, which were at right angles to each other, in a horizontal plane. A light source was secured in front of one window, and a photocell was placed in front of the other window. The photocell was connected to an amplifier, and the amplifier was connected to a strip chart recorder. Figures 6 and 7 show a schematic diagram of the sample cell and the assembled nephelometer.

Experimental Procedures

Flotation Experiments

All of the flotation experiments were conducted at room temperature (23°C) according to the following procedure:

- (1) The desired amount of collector in water solution was placed into a 250-ml beaker, and the amount of salt necessary to saturate this solution was added to the beaker.

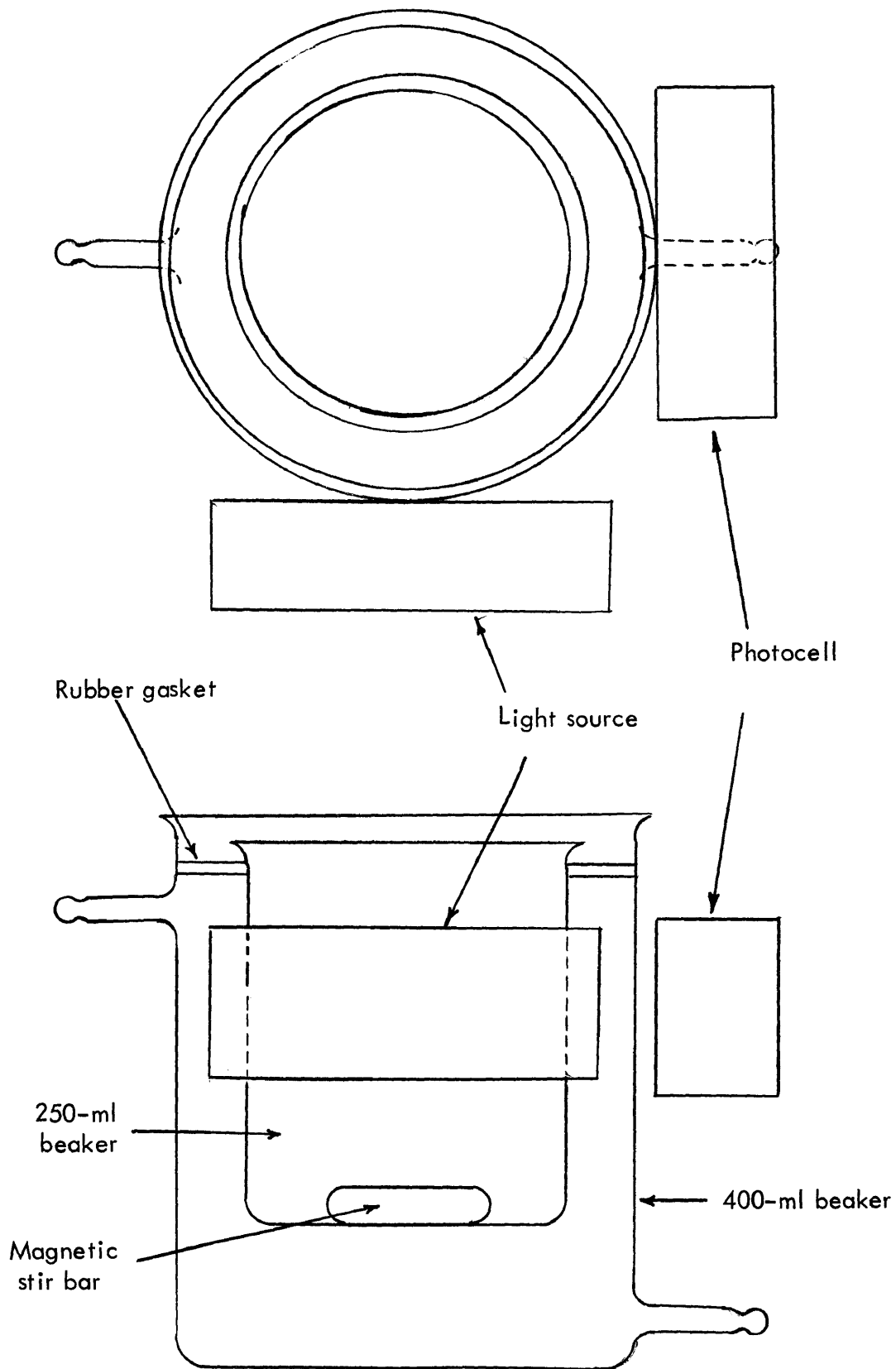


Figure 6 - Nephelometer sample cell
(not to scale)

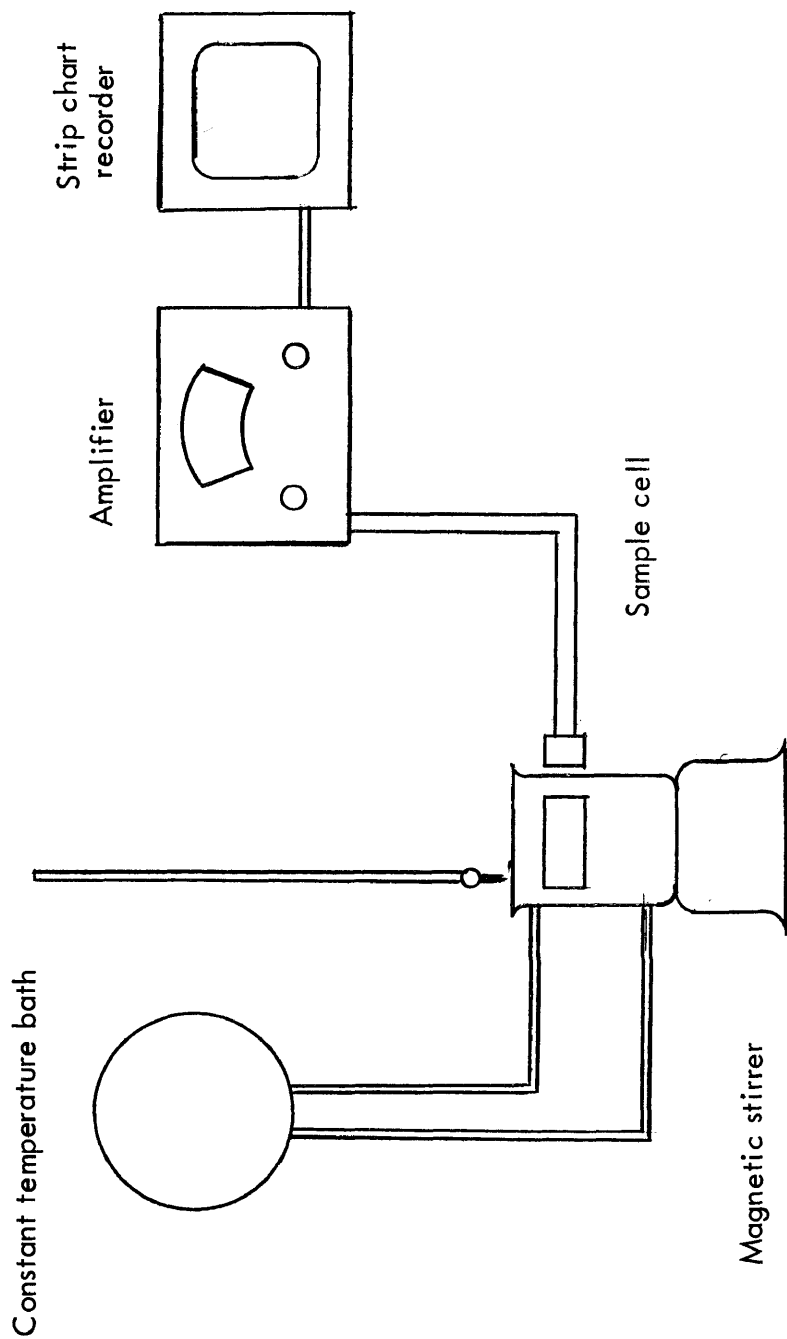


Figure 7 - Nephelometer

- (2) This solution was diluted to 100 ml total volume with a saturated salt solution and transferred to the flotation cell.
- (3) Five gm of 65 x 150 mesh of the desired salt was added to this solution.
- (4) Two drops of a solution containing 20 parts water to 1 part iso-amyl alcohol by volume were added as frother.
- (5) The pulp was allowed to condition for 3 minutes in the flotation cell.
- (6) 100 ml of nitrogen gas were passed through the cell, and the froth was collected as the concentrate.

All of the flotation experiments were conducted in solutions saturated with the salt being floated. In the experiments in which magnesium was used as an activator, the magnesium chloride was added in solid form before the solution was diluted to the 100-ml volume.

Solubility Determinations

The solubilities of several collectors were determined with the following procedure:

- (1) A predetermined volume of an alkali halide salt solution of known concentration was transferred to the 250-ml beaker, which acted as the sample cell in the nephelometer.
- (2) A measured volume of conductivity water was then added if the salt solution was saturated to prevent interference due to salt precipitation.

- (3) The solution was then brought to the desired temperature by connecting the water-jacket to the constant temperature bath.
- (4) The collector solution of known concentration was added to the sample cell with a burette.
- (5) At pre-selected collector addition levels, after the solution had been given sufficient time to reach equilibrium, a reading was taken on the nephelometer.
- (6) The temperature of the solution was measured at intervals throughout the experiment.

Nephelometer readings were plotted as a function of collector addition on a rectangular plot. (The point at which a precipitate first forms is evidenced by a change in the slope of this plot, and the concentrations of the salt and collector can be calculated.) A solubility product was calculated after the salt concentration was converted to activity. However, the collector concentration was used in place of the activity of the collector.

EXPERIMENTAL RESULTS

The initial work on this thesis was directed toward determining quantitatively the amount of amine adsorbed on the KCl surface; an infrared technique was developed for this purpose. Finely ground KCl was conditioned with the collector solution, filtered, and pelletized. The pellet was used as the infrared sample. Results showed only slight adsorption until high concentrations (10^{-4} mole per liter) of amine were used, and under these conditions the amine retained by the KCl was equivalent to several monolayers on the KCl surface. It was noted that the amine precipitated in this amine-KCl system, and that the precipitated amine remained with the solid KCl. No method could be developed for differentiating between the amine adsorbed on KCl and that which was precipitated; therefore, no quantitative measurements could be made. For this reason this experimental technique was abandoned in favor of other approaches.

Flotation Experiments

The results of the flotation experiments can best be shown by three separate figures in which the salt recovery is plotted as a function of collector addition.

Figure 8 shows the effect of dodecylamine and tetradecylamine additions on the recovery of KCl. It can be seen that essentially no KCl is floated until an addition of 10^{-6} mole per liter tetradecylamine or 5×10^{-5} mole per liter dodecylamine is used. (In all of the flotation experiments, a recovery of 10 percent was considered nominal.)

The effect of octyl sulfonate and decyl sulfonate on the recovery of KCl is shown in Figure 9. In this case recovery increases gradually until the collector addition exceeds 2×10^{-5} and 10^{-4} mole per liter, decyl and octyl sulfonate, respectively. At these additions the recovery increases at a high rate.

Figure 10 shows the flotation response of NaCl as a function of caprylic acid addition. Again, nominal recovery is obtained until the collector addition exceeds 6×10^{-4} mole per liter.

Several additional flotation experiments were conducted to determine the role of metal ion activation in salt flotation. Magnesium, lead, and barium chlorides were added to NaCl systems containing sulfonate or nonylate at various values of pH. The results of this series of experiments are listed in Table 1.

The results shown in Table 1 supplement work by previous investigators in salt flotation. The results of two tests were unexpected. First, a C-12 sulfate

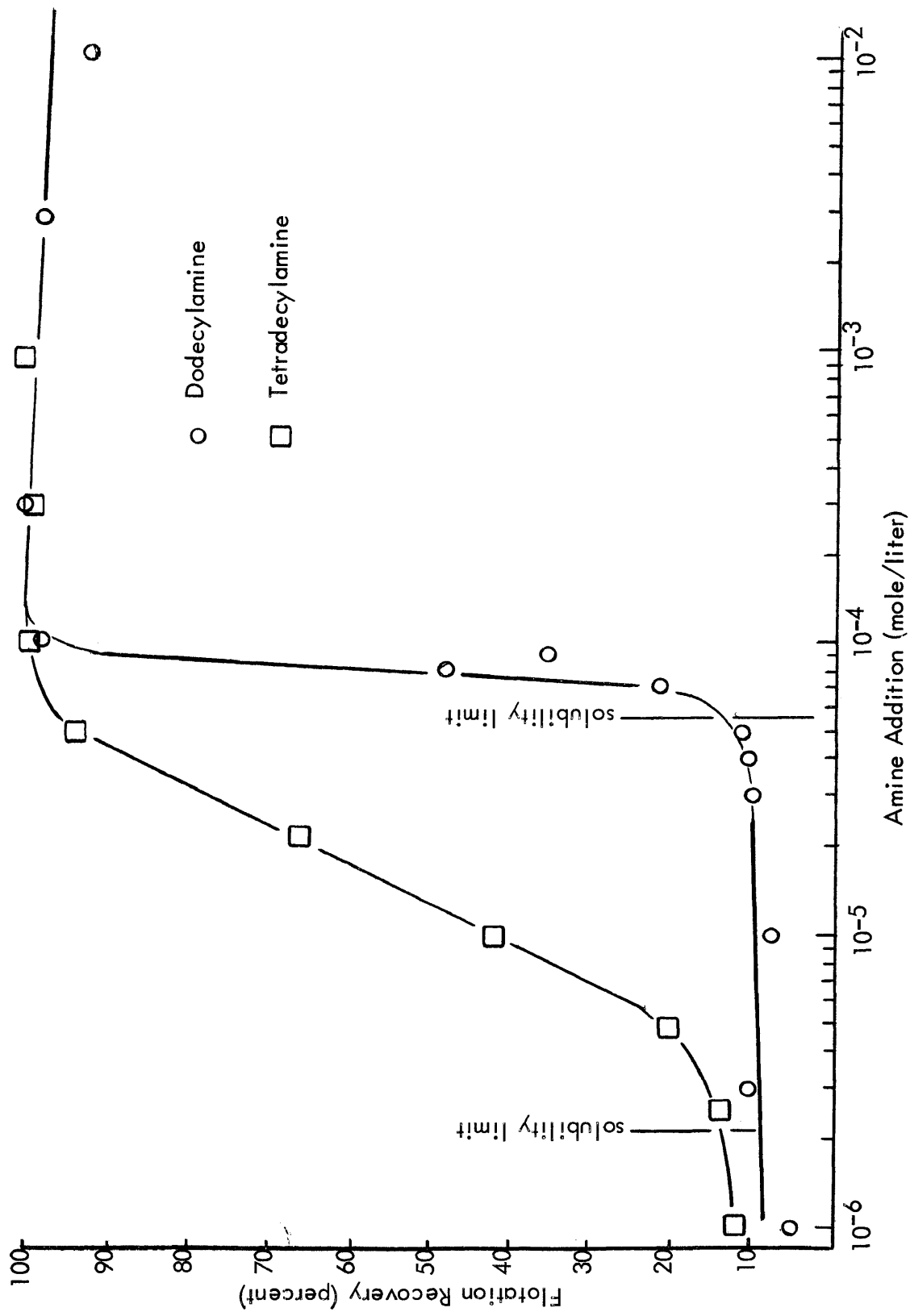


Figure 8 - Relationship between recovery of KCl and amine addition.

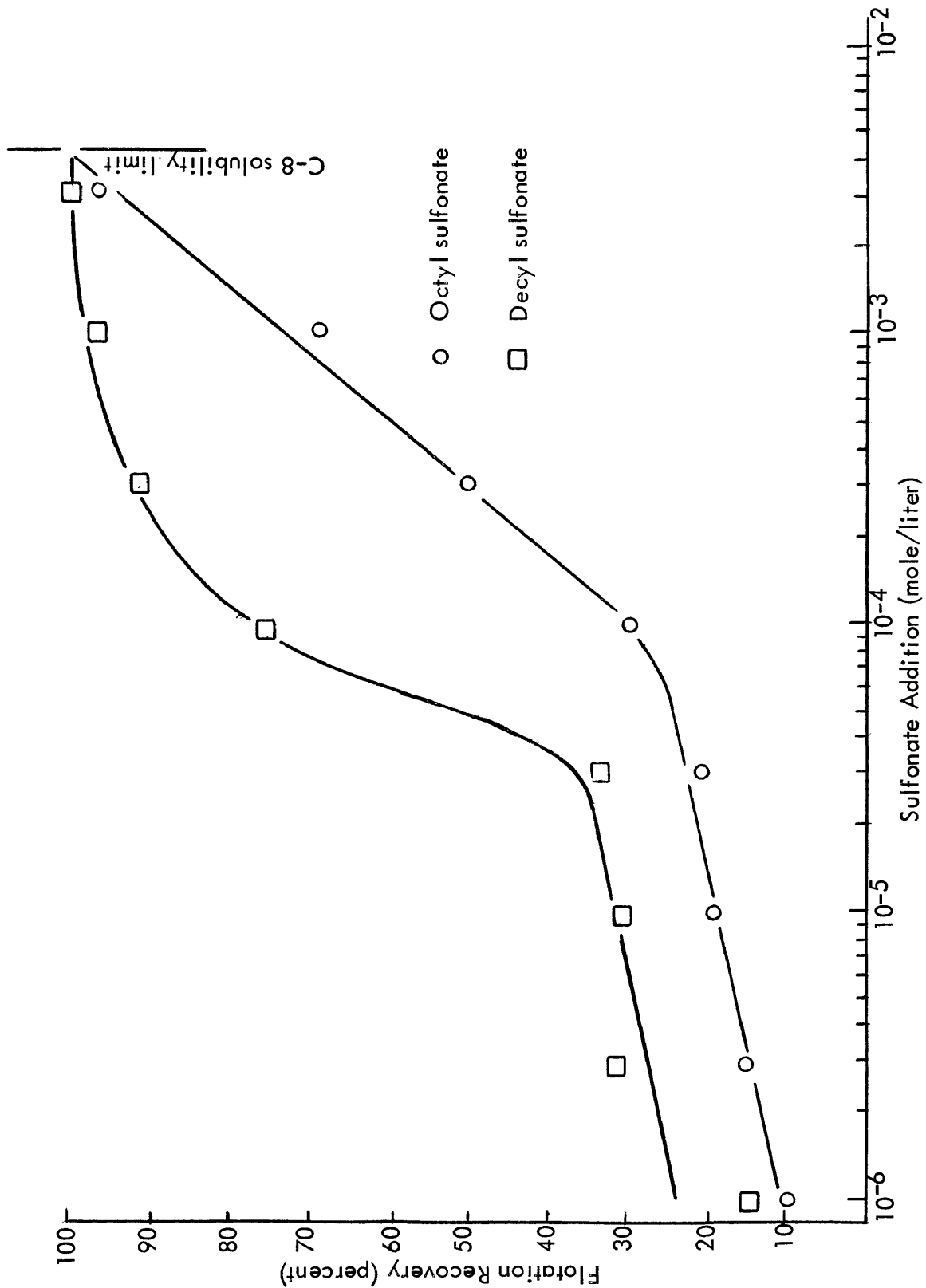


Figure 9 - Relationship between recovery of KCl and sulfonate addition.

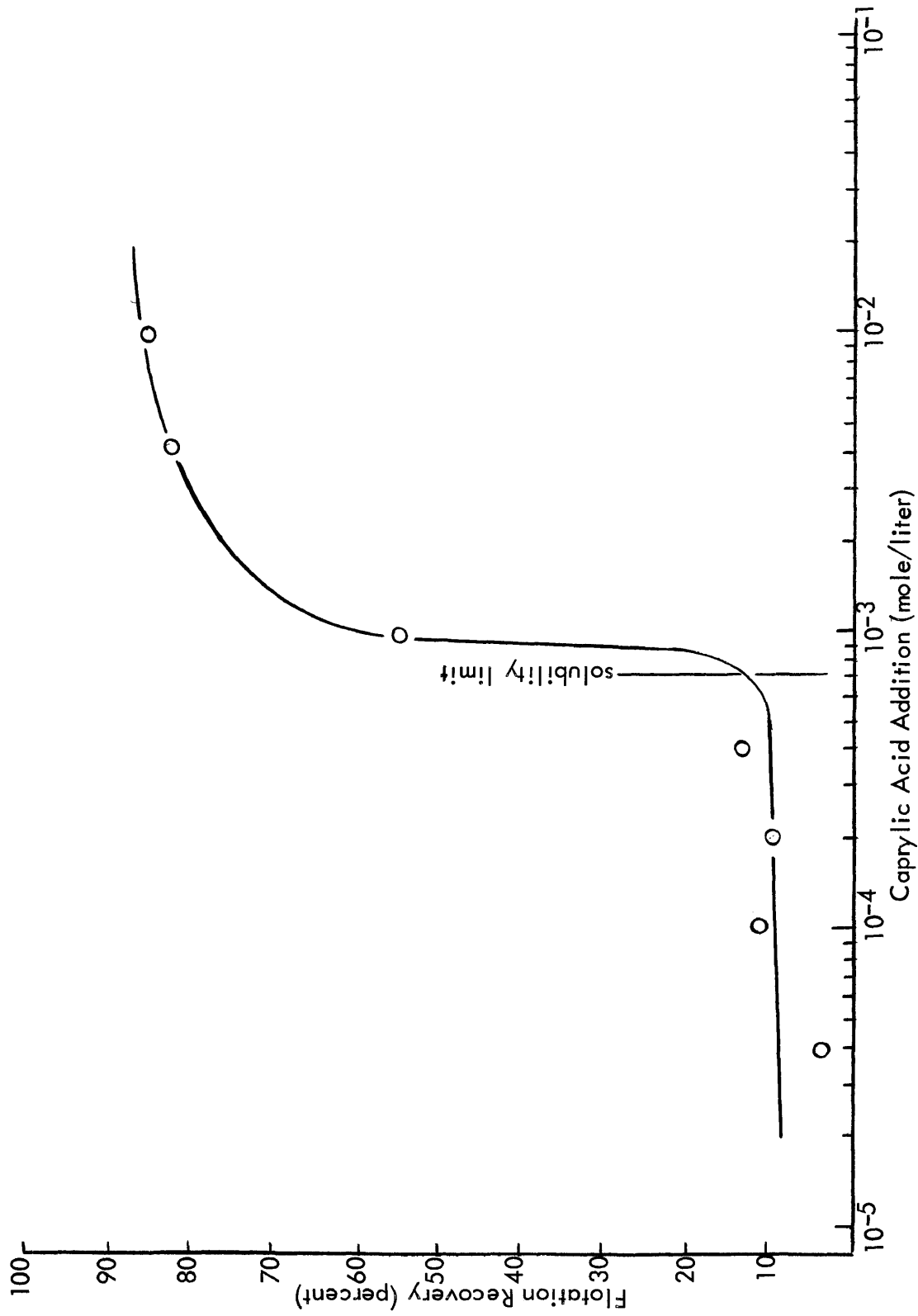


Figure 10 - Relationship between recovery of NaCl and caprylic acid addition.

TABLE 1 - Results of flotation experiments to determine the role of metal ion activation in salt flotation.

<u>Test</u>	<u>Collector</u>	<u>Collector Addition (mole/liter)</u>	<u>Activator</u>	<u>Activator Addition (mole/liter)</u>	<u>pH</u>	<u>Flotation Response</u>
1	C-14 sulfonate	10^{-4}	Pb^{+2}	1.0×10^{-2}	6.5	No flotation
2	C-9 fatty acid	2×10^{-4}	Mg^{+2}	0.34	5.5	No flotation
3	C-9 fatty acid	2×10^{-4}	Mg^{+2}	0.34	8.5	Flotation
4	C-10 sulfonate	10^{-4}	Ba^{+2}	1.2×10^{-2}	6.5	No flotation

will float NaCl when the NaCl is activated with lead, but a C-14 sulfonate will not. Second, magnesium will depress NaCl in a fatty acid float at a pH of 5.5 but not at a pH of 8.5.

Surface Charge Determination

A standard experimental approach to the measurement of surface charge of minerals is complicated by the high solubility of the salts under investigation in this thesis.

A Zeta-Meter cannot be used to determine surface charge in soluble salt systems because of the difficulty of obtaining colloidal-size particles of these salts and also because of the high conductivity of the solutions; however, it was thought that the streaming potential apparatus might be used to give some information as to the sign of the surface charge on the salts. A sample of 48 x 65-mesh KCl was placed in the sample holder of the apparatus, and the reservoirs were filled with saturated KCl solution. As the saturated solution flowed through the KCl sample, the direction of the current flow was noted. The solution flow was then reversed. The current direction did not reverse as it should have; it continued in the same direction. This unexpected phenomenon has also been noted when pyrex glass beads are placed in the sample cell.

Since these techniques could not be used to determine a surface charge, it was decided that observing the salts in their saturated solutions under a micro-

scope would be useful in predicting the presence or absence of a surface charge on the salt. Photographs of the three systems studied appear in Figures 11, 12, 13, and 14. In Figure 11, showing KCl in a saturated solution, it can be noted that the particles are relatively dispersed. Figure 12 shows NaCl in a saturated solution; again the particles are dispersed. Figure 13, however, shows the flocculated condition which exists when both KCl and NaCl are present in a saturated brine. For determination as to whether the flocs were concentrations of NaCl or KCl or a combination of both, a photograph of the system was taken in which all of the NaCl was present as 65-mesh particles and all of the KCl as 15-micron particles. This is shown in Figure 14 and the adherence of the fine KCl particles on the NaCl particles is striking.

Solubility Determinations

The data needed for the solubility determinations are listed in Appendix I. The solubilities of dodecyl-, tetradecyl-, and hexadecylamine chlorides in concentrated KCl solutions were determined at various temperatures. The amine together with its formula and the temperatures of the determinations are listed below.

<u>Amine Chloride</u>	<u>Formula</u>	<u>Temperature (°C)</u>
dodecyl	$\text{CH}_3(\text{CH}_2)_{11}\text{NH}_3\text{Cl}$	25.0, 30.3, 37.3
tetradecyl	$\text{CH}_3(\text{CH}_2)_{13}\text{NH}_3\text{Cl}$	29.7, 25.2
hexadecyl	$\text{CH}_3(\text{CH}_2)_{15}\text{NH}_3\text{Cl}$	29.8

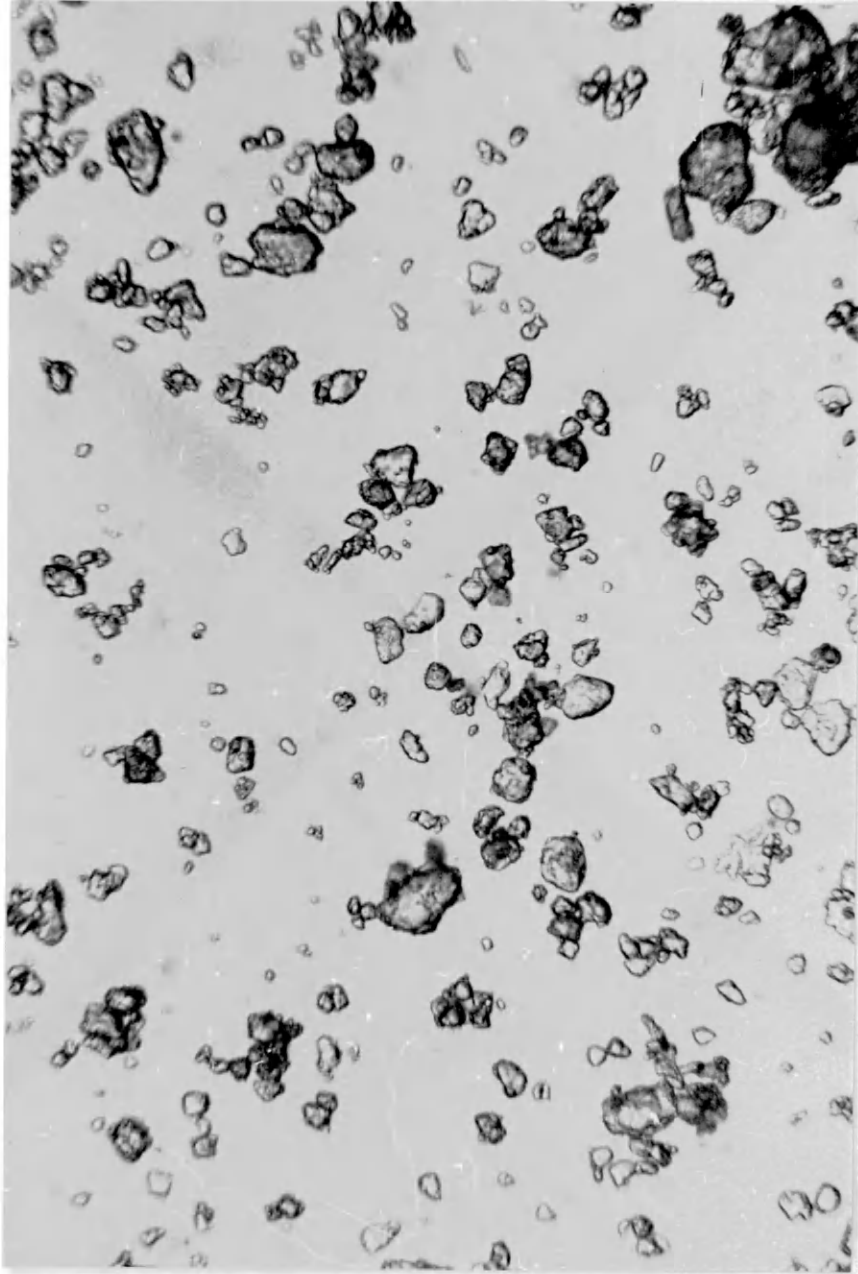


Figure 11 - KCl (15μ) in a saturated solution.

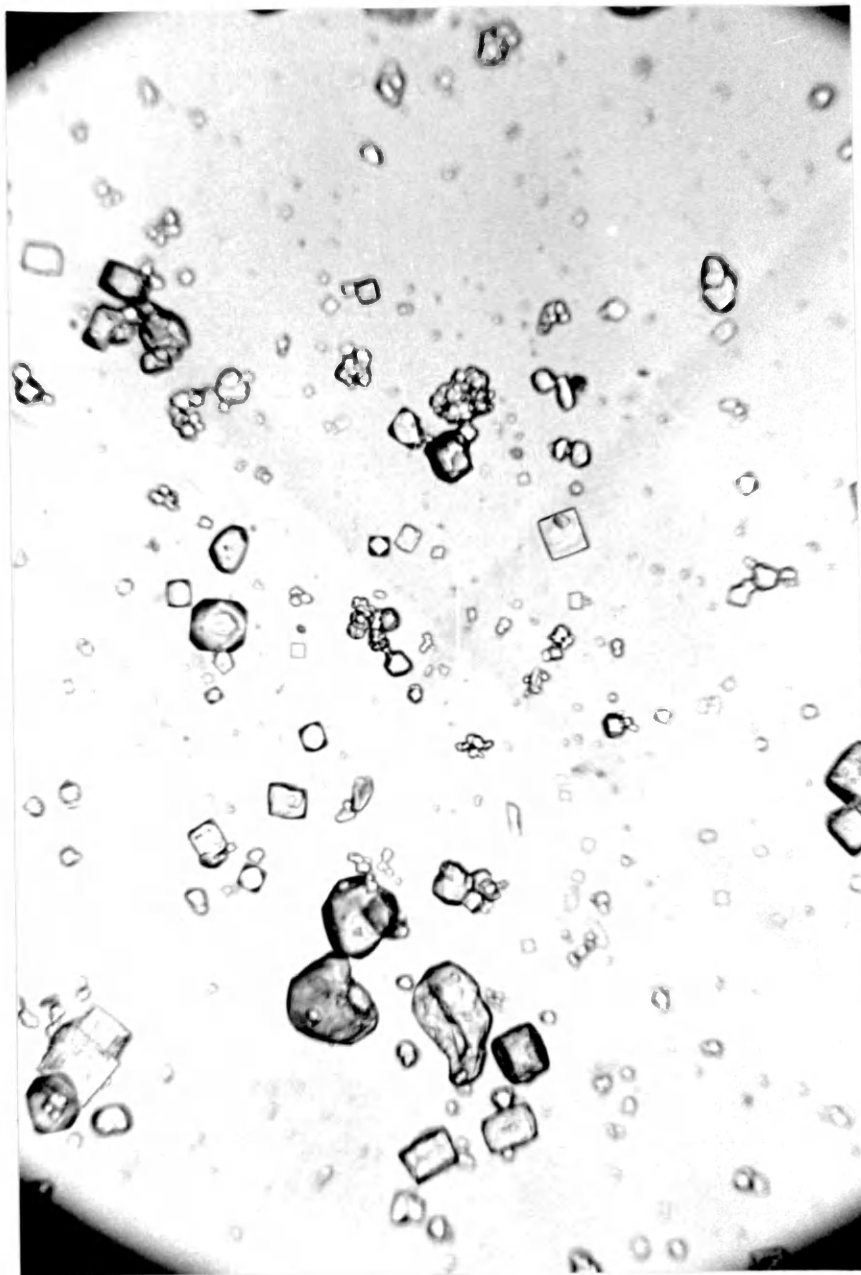
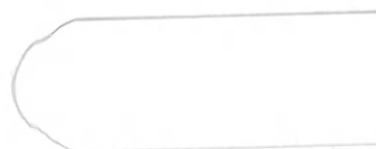


Figure 12 - NaCl (-325 mesh) in a saturated solution.



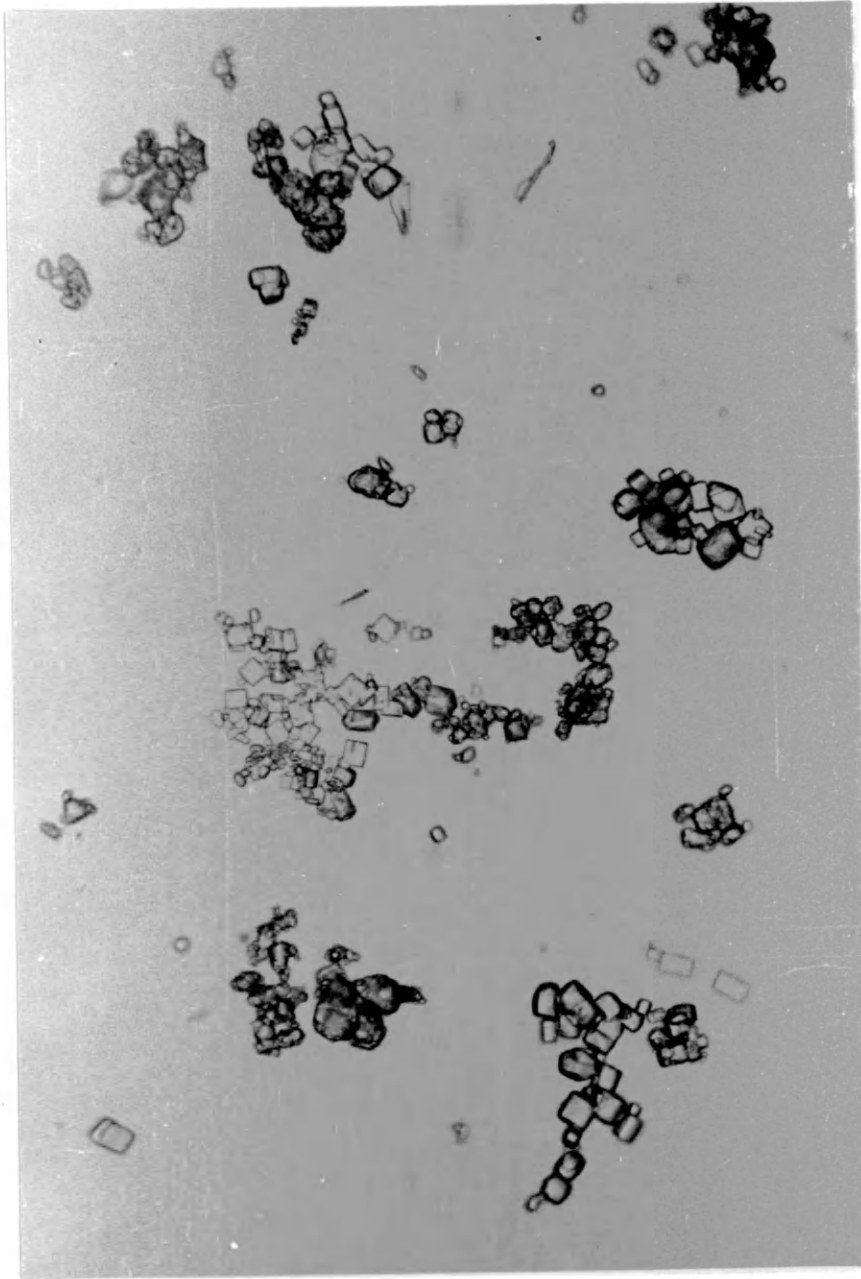


Figure 13 - NaCl and KCl (approximately $15\ \mu$) in saturated brine.

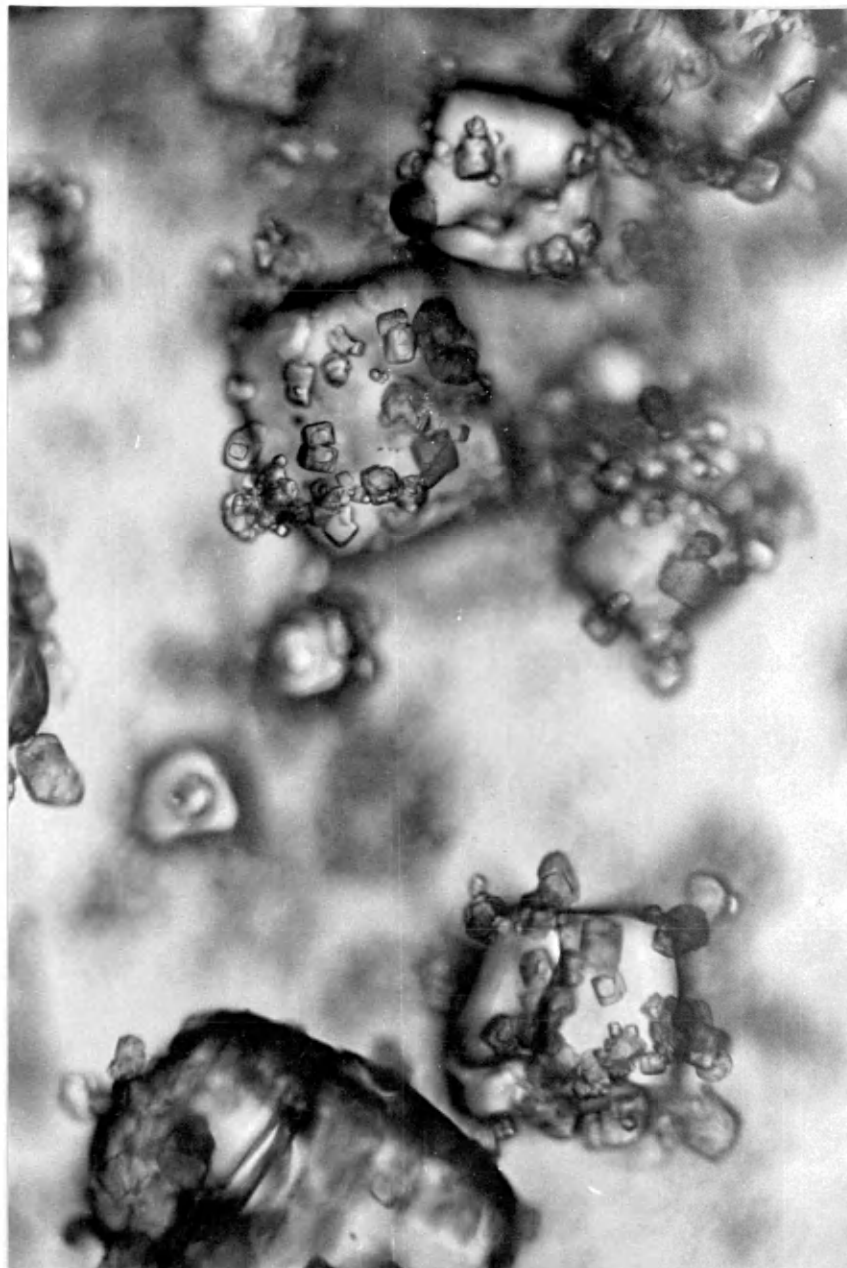


Figure 14-a - 65 mesh NaCl and 15 μ KCl in a saturated brine.

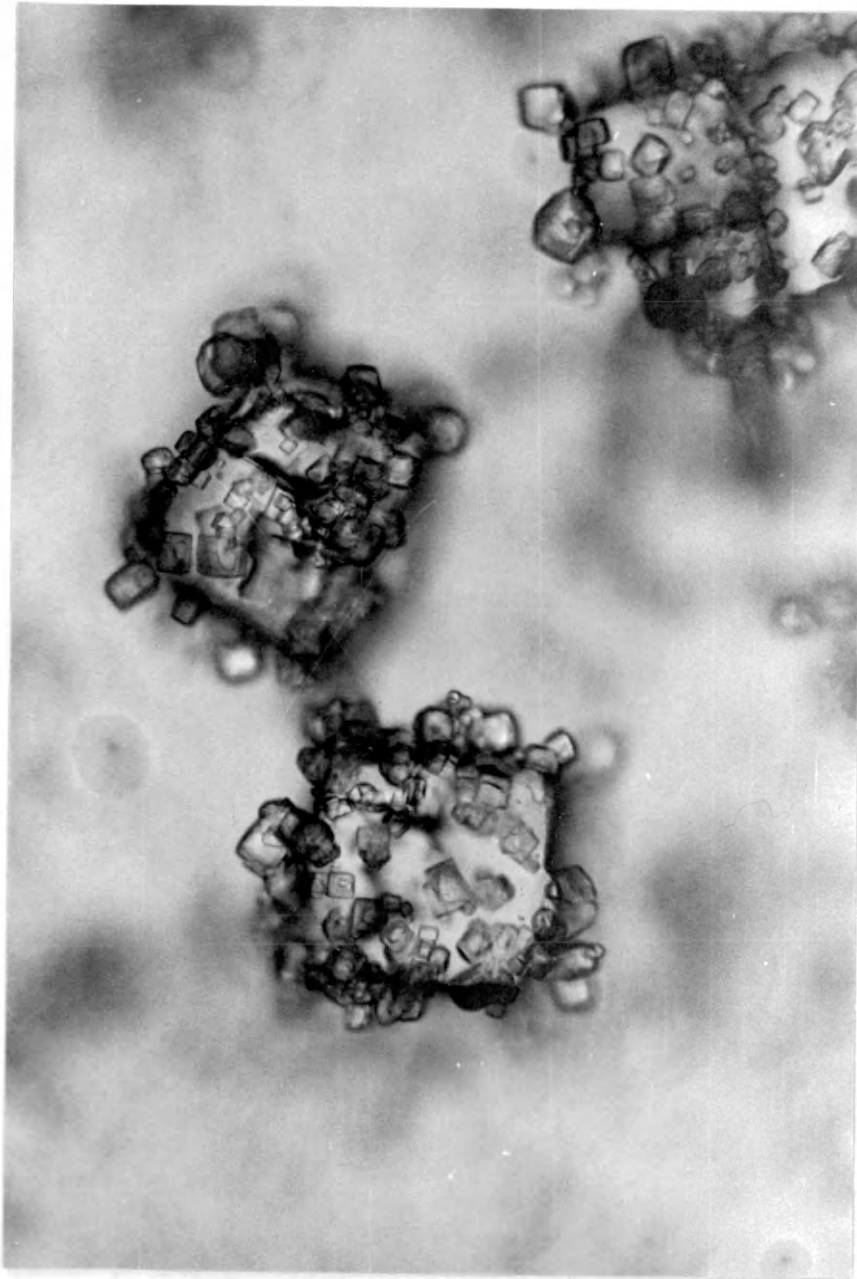


Figure 14-b - 65 mesh NaCl and 15 μ KCl in a saturated brine (same as Figure 14-a but different field).

Figures 15 and 16 show the relation of the solubility product of the amine chlorides to temperature and hydrocarbon chain length. Figure 15 is a plot of the van't Hoff equation

$$\log K_{sp} = - \frac{\Delta H^{\circ}}{2.303 R} \left[\frac{1}{T} \right]$$

A plot of $\log K_{sp}$ versus $1/T$ will give a straight line of slope $-\Delta H^{\circ}/2.303R$ where ΔH° is the sum of the heat contents of the products less the heat content of the dissolving collector salt when each is at its standard state. R is the gas constant. If the products of dissolution remain the same over the temperature range studied, the line should have a constant slope. Ignoring entropy effects, ΔH° is a measure of the strength of the bond being broken during dissolution of the collector salt. This bond strength will not change to any large degree as the carbon-chain length increases from 12 to 16; therefore, the lines for the 12, 14, and 16 carbon amines should be parallel.

In general, a plot of $\log K_{sp}$ versus the number of carbon atoms in an alkyl compound will be a straight line. This phenomenon is observed in the case of the amine chlorides over the range studied as shown in Figure 16. From Figures 15 and 16 the solubility product may be estimated for the alkyl amine chlorides containing from 10 to 18 carbon atoms per molecule and between 5 and 45°C.

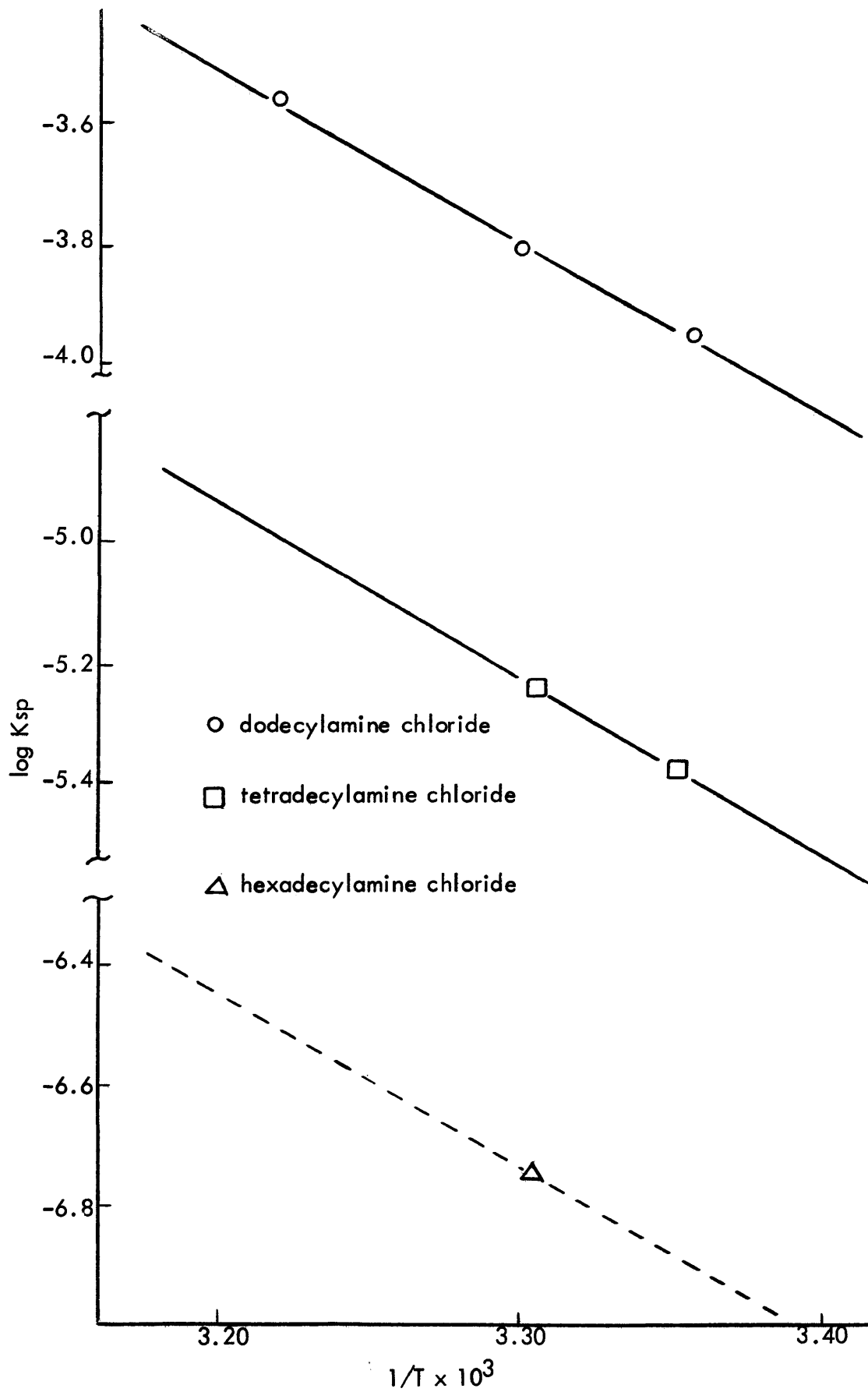


Figure 15 - Relationship between solubility and temperature for various amine chlorides.

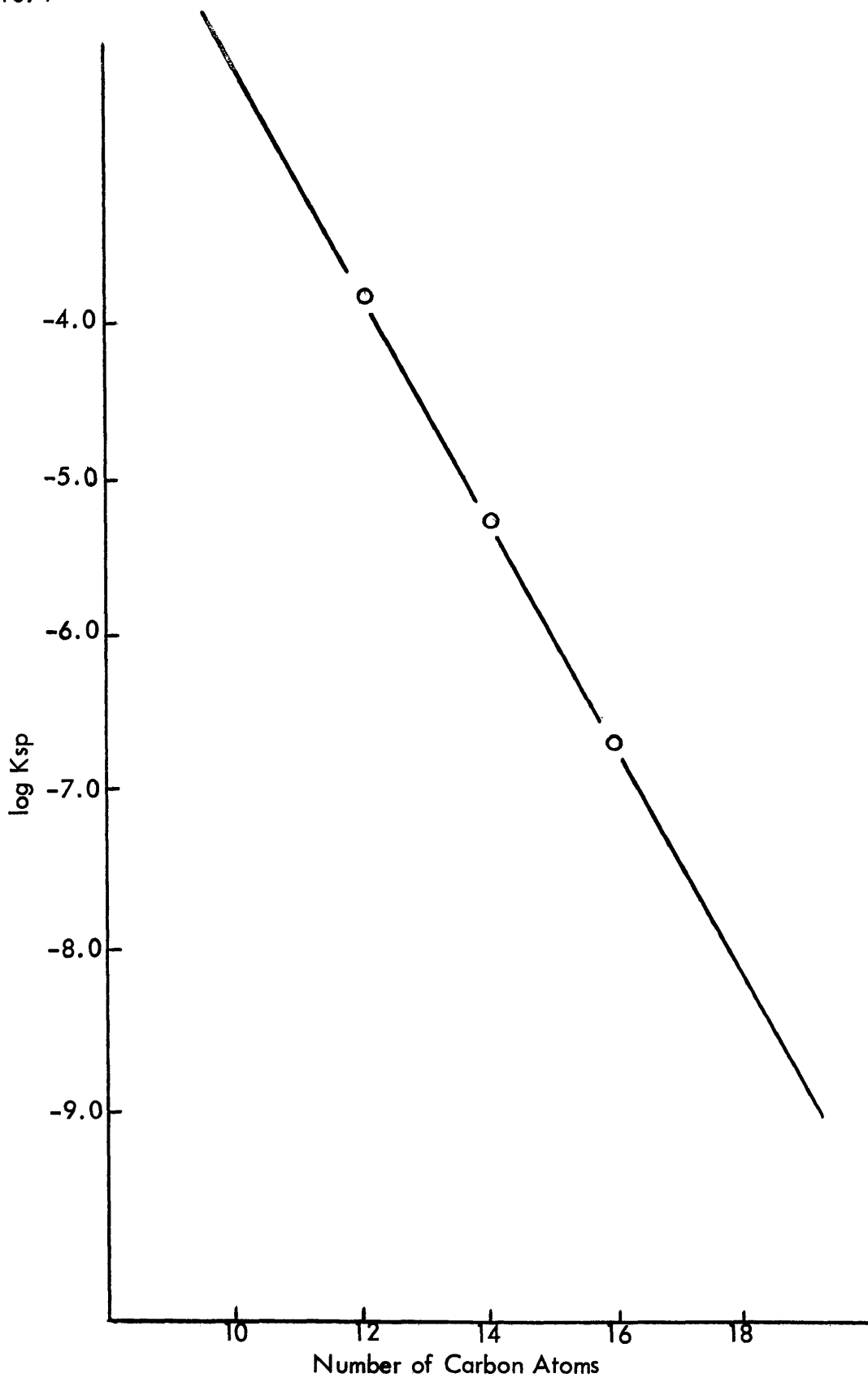


Figure .16 - Relationship between solubility at $30 \pm 0.3^\circ\text{C}$ and number of carbon atoms in the amine.

In addition to the amine chloride solubilities, the solubility of several other collector salts were determined. The results are listed in Table II.

TABLE II - Solubilities of various collector salt compounds

<u>Collector Salt</u>	<u>Temperature (°C)</u>	<u>K_{sp}</u>
CH ₃ (CH ₂) ₆ COONa	25	7.0 × 10 ⁻⁴
CH ₃ (CH ₂) ₁₁ NH ₃ F	32	3.9 × 10 ⁻⁴
CH ₃ (CH ₂) ₁₁ NH ₃ Br	28	2.0 × 10 ⁻⁴
CH ₃ (CH ₂) ₁₁ NH ₃ I	27	9.9 × 10 ⁻⁵
CH ₃ (CH ₂) ₇ SO ₃ K	24	9.2 × 10 ⁻³

Precipitate Analysis

To obtain a sample of the collector precipitate formed in the presence of magnesium approximately 10 grams of MgCl₂·6H₂O were dissolved in 100 ml of conductivity water; and approximately one gram of CH₃(CH₂)₈COOK, dissolved in conductivity water, was added. The precipitate that formed was centrifuged, but because only about 1/4 of the precipitate was heavier than the solution, 3/4 of the precipitate collected in a layer on the top of the solution. These two products (sink and float) were kept separate and dried at 300°C to remove all of the water, weighed, and ignited to 600°C to decompose the organic material, and reweighed. From the weight of the residue, which was taken to be MgO, the MgO content of the dried precipitate was calculated. The results of this

determination are shown in Table III. Duplicate analyses were conducted on each product.

If the precipitates are $\text{Mg}(\text{CH}_3(\text{CH}_2)_8\text{COO})_2$ and $\text{Mg}(\text{OH})\text{CH}_3(\text{CH}_2)_8\text{COO}$ as might be expected, the weight loss would be 87.5 and 81.2 percent, respectively. This outcome agrees fairly well with the experimental results.

Samples of these compounds were also prepared individually at pH 5.5 and 8.7 to produce either a predominance of $\text{Mg}(\text{CH}_3(\text{CH}_2)_8\text{COO})_2$ or $\text{Mg}(\text{OH})\text{CH}_3(\text{CH}_2)_8\text{COO}$ for infrared analysis. A portion of the spectra of these two compounds is given in Figure 17.

TABLE III - MgO determinations of the precipitated collector

	Float		Sink	
	1	2	1	2
Crucible wt	10.0765	9.72999	9.94690	9.93772
Crucible and sample at 300°	10.17868	9.84365	9.99298	9.96678
Weight of dried ppt	0.10803	0.11366	0.04068	0.02906
Crucible and sample at 600°	10.08365	9.74612	9.95664	9.94300
Weight loss 300-600°	0.09503	0.09753	0.03634	0.02378
Percent wt loss	87.5	86.7	78.8	81.6
Average	87.1		80.2	
Percent MgO	12.9		19.8	

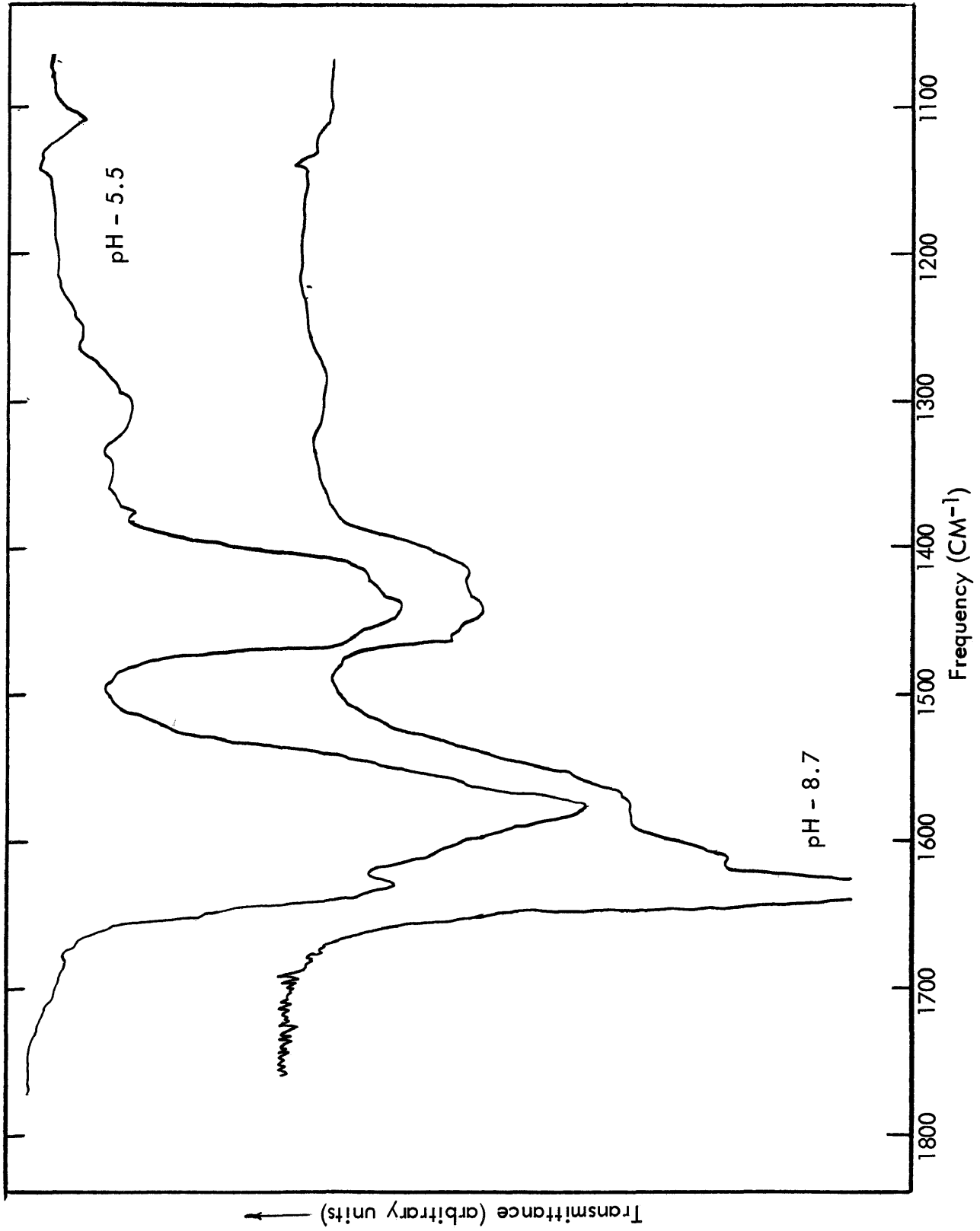


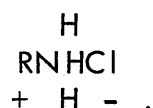
Figure 17 - IR spectra for magnesium fatty acid precipitates at pH 5.5 and 8.7.

DISCUSSION OF RESULTS
AND
DEVELOPMENT OF A MECHANISM

The data contained in Figures 8, 9, and 10 show that KCl is floated with amines and that NaCl is floated with a fatty acid only after the precipitation of the collector. Further, in the absence of polyvalent metal ions such as Pb^{++} and Mg^{++} , flotation of KCl occurs with sulfonate before precipitation of the sulfonate salt. No flotation of NaCl occurs with sulfonate under these conditions. When sulfonate is used, the anion RSO_3^- is functioning as the collector for KCl. In the case of amine flotation of KCl and fatty acid flotation of NaCl, either the precipitates $RNH_3Cl(s)$ and $RCOONa(s)$ or some species in equilibrium with these solids, such as $RNH_3Cl(aq)$ and $RCOONa(aq)$, are functioning as collectors in the KCl and NaCl systems, respectively. It will be shown later in this discussion that the aqueous species are probably the active species responsible for flotation.

If it is assumed that $RNH_3Cl(aq)$ is the species of amine adsorbed on the KCl and also that RSO_3^- is the active sulfonate species, then it can be suggested that the collector in this system is negatively charged. That is, RSO_3^- is obviously

negative and $\text{RNH}_3\text{Cl}(\text{aq})$ is a polar molecule, the negative end of which adsorbs on the salt surface. The configuration of $\text{RNH}_3\text{Cl}(\text{aq})$ suggests asymmetry of electrical charge because of the lack of symmetry of the molecule. Further, the negative end of the dipole is towards the chloride end, or



By the same reasoning, in NaCl flotation with sodium carboxylate, the collector can be suggested to be $\text{RCOONa}(\text{aq})$; however, in this case the end of the dipole, which can adsorb on the salt, is positively charged.

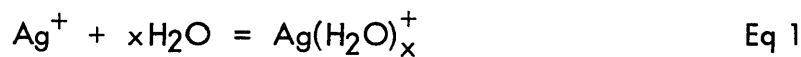
This correlation strongly suggests an electrical mechanism of adsorption if it is assumed that the surface of the NaCl has a negative charge and that the surface of the KCl has a positive charge.

Unfortunately, present equipment used for determining surface charge is not applicable to salts as soluble as NaCl and KCl. However, Figures 11, 12, 13, and 14 indicate that NaCl and KCl are oppositely charged. At first it might be thought that the surface of NaCl and KCl are uncharged in these high ionic strength solutions and that flocculation observed in Figures 13 and 14 is due to van der Waals attraction. However, if this were the case, the systems shown in Figures 11 and 12 would also be flocculated. In view of these facts, it appears that flocculation is produced by attraction of oppositely charged particles.

Although no experimental method exists for proving the existence of surface charges on NaCl and KCl, a theoretical approach may be developed. On noting that AgI has a surface charge in its saturated solution, de Bruyn and Agar (14) have stated:

This asymmetry in the ZPC (a ZPC at $pAg = 8$ would be symmetrical with respect to ion concentration, $K_{sp} = 10^{-16}$ for AgI) is related to the difference in degree of hydration of the cation and anion.

This fact becomes obvious when the dissolution of AgI in water is considered. Surface Ag^+ and I^- ions, after reacting with water molecules or hydrating, are removed from the surface. This reaction can be written as,



The extent of each reaction is a function of the free energy of reaction, or in this case the free energy of hydration. Therefore, if reaction (1) has a greater negative free energy than reaction (2), the solid surface will lose more Ag^+ ions than I^- ions and thus acquire a net negative charge. Conversely if reaction (2) has the greater negative free energy, the solid will acquire a positive surface charge. From the free energy data available, it should be possible, therefore, to predict the surface charge of a mineral in its saturated solution. With the use of the silver halide system as an example, surface charges which have been predicted are listed in Table IV together with experimentally determined charges.

TABLE IV - Silver halide surface charges

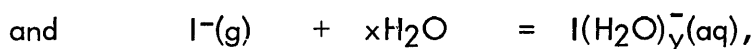
Salt	$-\Delta G_{-}^{\circ}$ (Kcal/mole)	$-\Delta G_{+}^{\circ}$ (Kcal/mole)	Charge	
			Theoretical	Experimental(15)
AgCl	84.2	87	negative	negative
AgBr	78.0	87	negative	negative
AgI	70.0	87	negative	negative

ΔG_{-}° = standard free energy of hydration of the anion (16).

ΔG_{+}° = standard free energy of hydration of the cation (17).

It can be seen that there is excellent agreement between theoretical and experimental results.

Some care, though, must be exercised in the use of the free energy data available. The standard state for the values given is the gaseous ion and the one molar solution. Therefore, the free energy listed is for reactions of the type



and not for the reactions from the solid salt. Therefore, these data can be used only when the bond energy of the salt is evenly divided between the cation and the anion. Such is not the case for salts like BaCl_2 , Na_2SO_4 , or hydrated salts such as $\text{NaBr} \cdot 2\text{H}_2\text{O}$.

With these precautions in mind Table V was developed to show the relation between floatability of the 20 alkali halide salts, surface charge, and solu-

TABLE V - Application of the surface charge - collector solubility hypothesis to the alkali halide salts.

Salt	$-\Delta G_{+}^{\circ}$ (Kcal./mole)	$-\Delta G_{-}^{\circ}$ (Kcal./mole)	Surface charge	Does amine halide ppt	Flotation Results	
					Experimental	Theoretical
LiF	114.6	113.6	?	No	No flotation	--
NaF	89.7	113.6	+	No	No flotation	No flotation
KF	73.5	113.6	+	Yes	No data	Flotation
RbF	67.5	113.6	+	Yes	No data	Flotation
CsF	60.8	113.6	+	Yes	No data	Flotation
LiCl	114.6	84.2	-	Yes	No data	No flotation
NaCl	89.7	84.2	-	Yes	No flotation	No flotation
KCl	73.5	84.2	+	Yes	Flotation	Flotation
RbCl	67.5	84.2	+	Yes	Flotation	Flotation
CsCl	60.8	84.2	+	Yes	Flotation	Flotation
LiBr	114.6	78.0	-	Yes	No data	No flotation
NaBr	89.7	78.0	-	Yes	No flotation	No flotation
KBr	73.5	78.0	+	Yes	Flotation	Flotation
RbBr	67.5	78.0	+	Yes	Flotation	Flotation
CaBr	60.8	78.0	+	Yes	Flotation	Flotation
LiI	114.6	70.0	-	Yes	No data	No flotation
NaI	89.7	70.0	-	Yes	No flotation	No flotation
KI	73.5	70.0	-	Yes	No flotation	No flotation
RbI	67.5	70.0	+	Yes	No flotation	No flotation
CsI	60.8	70.0	+	Yes	Flotation	Flotation

bility of the dodecylamine halide. If an error of ± 1 kcal is assumed in the values for the free energy of hydration, the surface charge of LiF is questionable. Of the remaining 19 alkali halides there is no flotation data available for the non-hydrated forms of KF, RbF, CsF, LiCl, LiBr, and LiI. The flotation data for NaI shows that the non-hydrated form floats, but the hydrated form does not. Of the remaining 13 salts, all those which have a positive surface charge, with the exception of NaF, float with amine. Solubility data for the amine halides show that in the saturated solution, 12 of the 13 salts precipitate the amine if 10^{-4} mole per liter of amine is added. The exception is again the NaF system. In each case, the amine halide molecule forms a dipole, the negative end of which can adsorb on the positive surface of the salt. In the case of NaF, however, the positive surface would repel the positive aminium, RNH_3^+ , ion; therefore, the salt would not float.

Of the salts which possess a negative surface charge, not one can be floated with the precipitated amine. This fact indicates that the negative surface repels the negative end of the amine dipole. This is in excellent agreement with the electrical mechanism proposed. Figures 18, 19, and 20, respectively, show surface models for salts with a positive surface and the amine aqueous species, NaF and the ionic amine solution, and salts with a negative surface charge and the amine aqueous species.

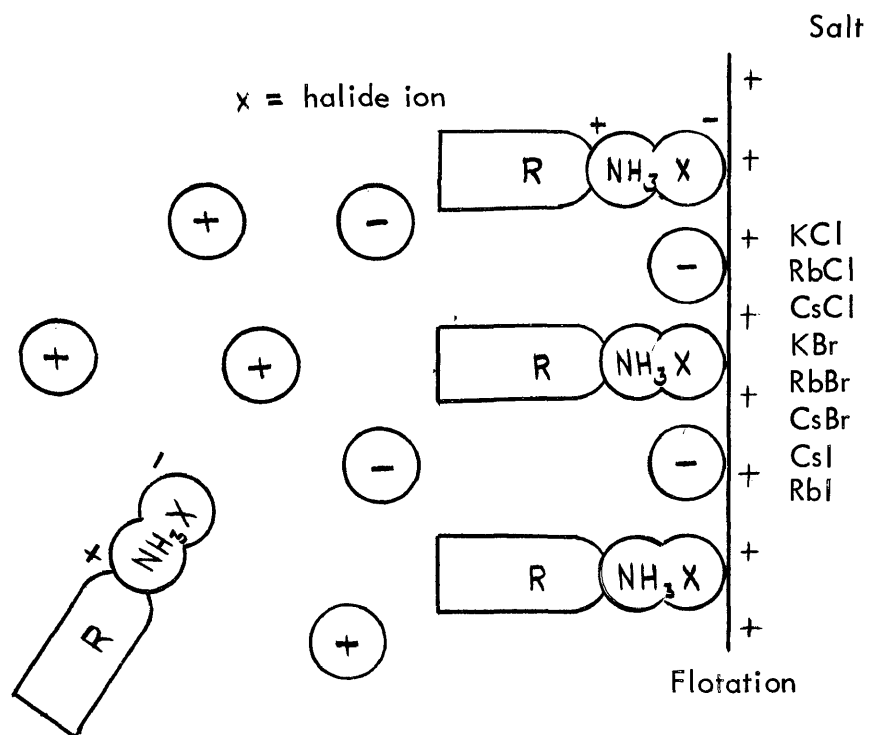


Figure 18 - Surface model of positive salt and dodecylamine.

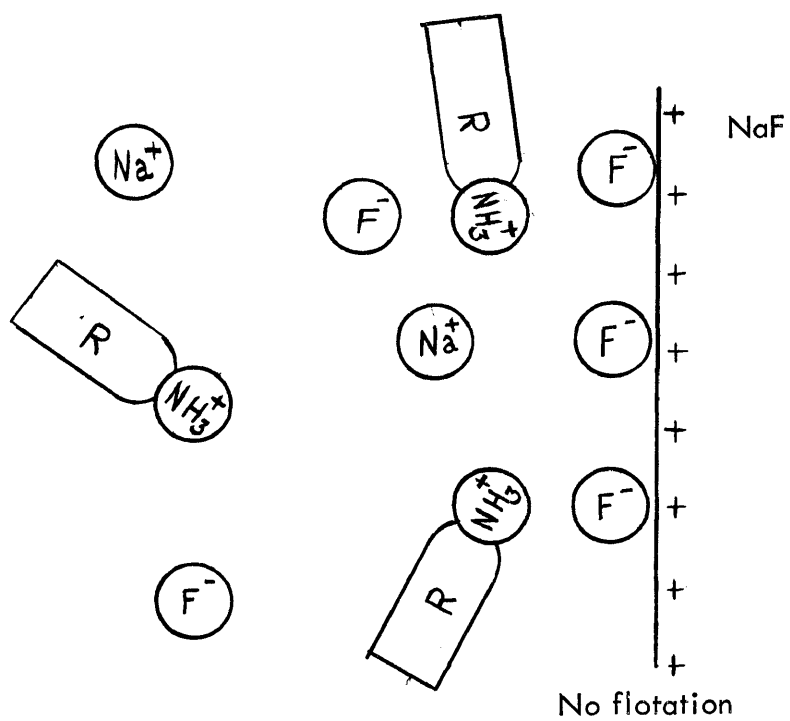


Figure 19 - Surface model of NaF in the presence of dodecylamine.

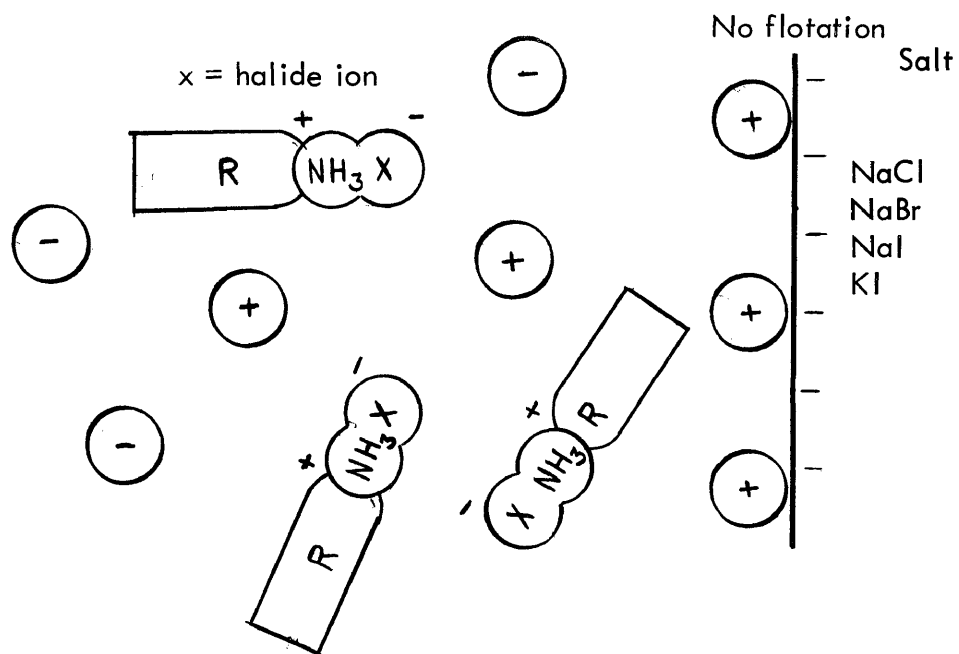


Figure 20 - Surface model of negative salt and dodecylamine.

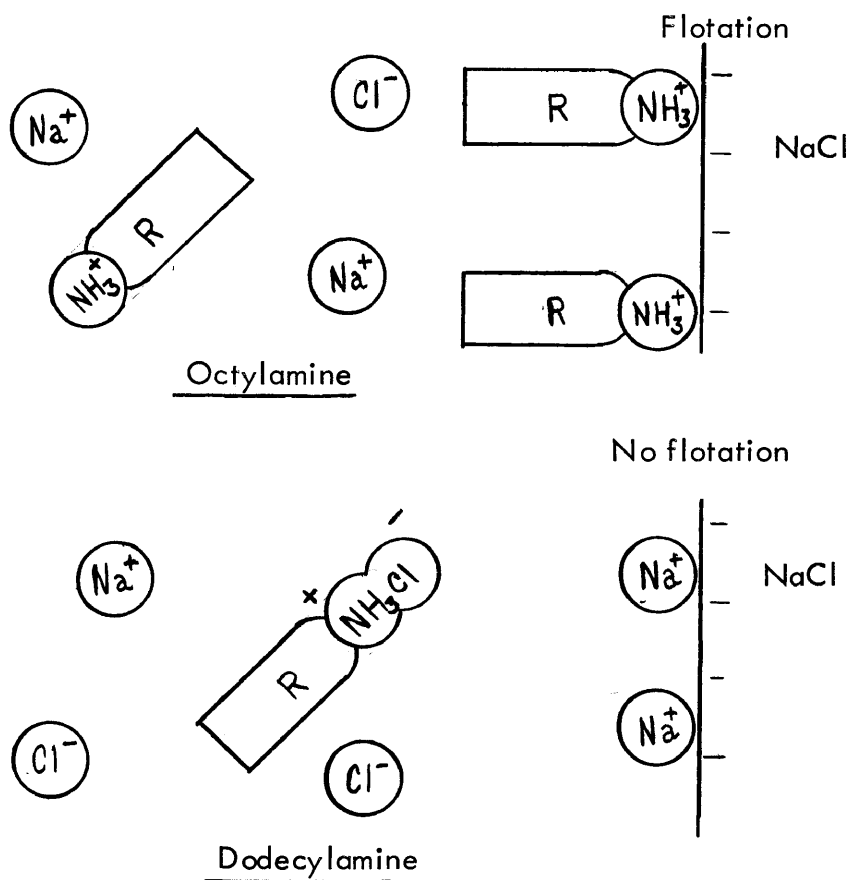


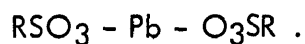
Figure 21 - Surface model of NaCl in the presence of octyl- and dodecylamine.

Work by Singewald (8) has shown that NaCl may be floated by octylamine. This is readily explained by the fact that octylamine chloride has not precipitated under these flotation conditions and the positive RNH_3^+ ion adsorbs on the negative surface. When dodecylamine is involved, however, precipitation of this collector occurs at fairly low concentrations, and the aqueous complex, having a negative active end, is repelled by the negative NaCl surface. A surface model of this system is shown in Figure 21.

This mechanism of flotation based on surface charge and collector solubility can be extended to explain the role that lead ions assume in depressing KCl and activating NaCl in sulfonate flotation, and the role of magnesium ions in depressing NaCl and activating KCl in fatty acid flotation.

Two observations are noteworthy in lead depression and activation. First, the concentration of lead added to the pulp is high, above 10^{-2} mole per liter (18), and secondly, in the absence of lead, lauryl sulfate will float KCl and not NaCl; whereas in the presence of lead, NaCl is floated and KCl is not (19). The pH of the pulp has been found to be critical in lead activation of NaCl with an optimum at about pH 7. At this pH the lead is present essentially as PbOH^+ , and since Pb(OH)RSO_3 or Pb(OH)RSO_4 is relatively insoluble, it will precipitate under these conditions. Again, as in the case of fatty acid flotation of NaCl where the positive end of the RCOONa dipole adsorbs on the negative NaCl surface, the positive (Pb) end of the lead hydroxysulfonate dipole can adsorb

on the NaCl surface. If the pH is lowered, the predominant lead species is no longer PbOH^+ but is now Pb^{+2} , and the precipitate formed will be $\text{Pb}(\text{RSO}_3)_2$, its aqueous species may be represented as



This configuration would not be polar as was that of the lead hydroxysulfonate and thus would show no attraction for the charged salt surface. At higher values of pH, $\text{Pb}(\text{OH})_2$ or $\text{Pb}(\text{OH})_3^-$ would be more stable than lead hydroxysulfonate; as a result, depression of the system occurs. Figures 22, 23, and 24 show schematically the system of NaCl, lead, and sulfonate at a pH below 7, at a pH near 7, and at a pH above 7.

The role of magnesium ions is similar to that of lead; however, requirements of a higher pH for hydrolysis account for the different results produced. When no magnesium is present in a brine, NaCl is floated in preference to KCl but both minerals are floated. On addition of magnesium salts, however, NaCl is depressed but KCl is still floated. At 7 grams magnesium per liter, both NaCl and KCl float equally as well. If the magnesium addition is increased above 7 grams per liter, NaCl is further depressed, and KCl continues to float (20). At the natural pH of a brine (pH 6.5) the magnesium is present as Mg^{+2} ions, and magnesium carboxylate precipitates. Its aqueous species may be represented as



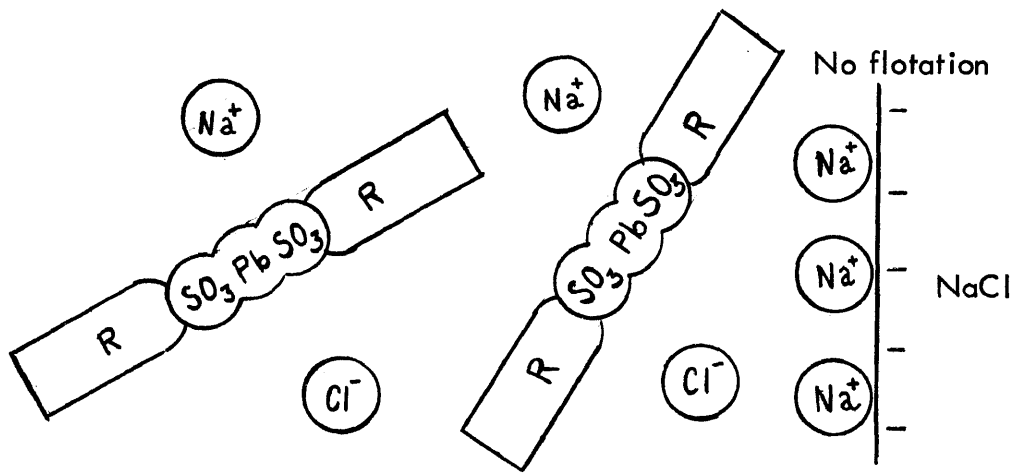


Figure 22 - Surface model of lead-NaCl-sulfonate system below pH 7.

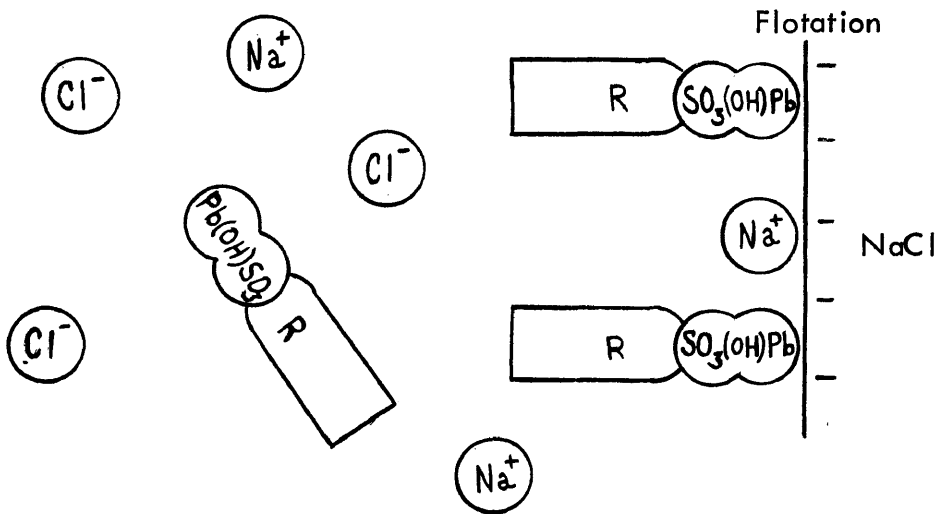


Figure 23 - Surface model of NaCl-lead-sulfonate system at pH near 7.

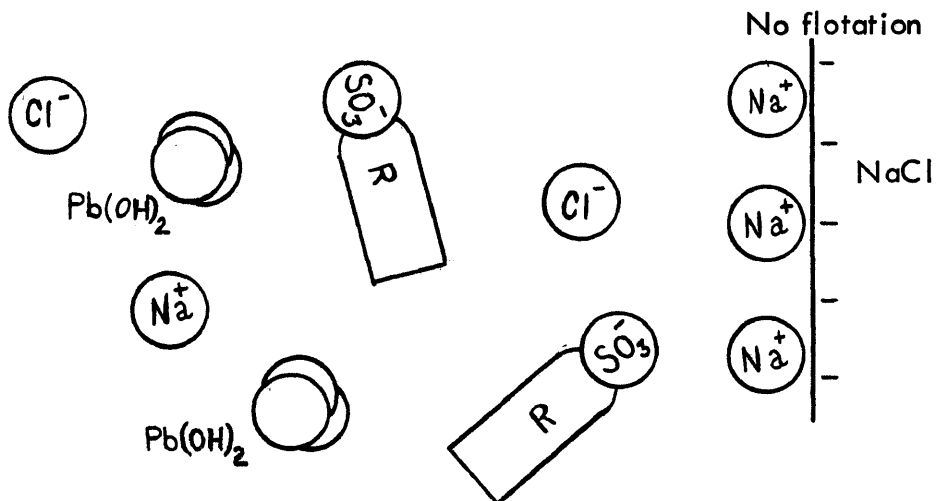
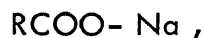


Figure 24 - Surface model of NaCl-lead-sulfonate system above pH 7.

Again, as in the case of lead at low values of pH, the compound that precipitates is probably not polar due to the symmetrical structure of the molecule. The magnesium precipitate will be more insoluble than its sodium counterpart,



which is also polar and can adsorb on the negatively charged NaCl. Thus the collector for NaCl, RCOONa , is removed from the system and is replaced by an inert precipitate $\text{Mg}(\text{RCOO})_2$. However, the residual RCOO^- ion is still present at a sufficiently high concentration to produce good flotation of KCl. This mechanism is demonstrated in experiments 2 and 3 of Table I. It can be seen that by raising the pH to about 8.7, where MgOH^+ is apparently the predominant form of magnesium, the precipitate formed will be $\text{Mg}(\text{OH})\text{RCOO}$. $\text{Mg}(\text{OH})\text{RCOO}$ (aq), which is polar, is then present and can adsorb on the negative NaCl. Figures 25 and 26 show a model of the surface of NaCl in a magnesium-fatty acid system at two different values of pH.

The effect of magnesium on salt flotation suggests an alternative to the lead activation process; however, selectivity might be reduced because the magnesium hydroxycarboxylate is probably more soluble than the lead hydroxysulfonate, and the high residual RCOO^- concentration might be sufficient to float KCl.

The effect of barium (Table I) is similar to that of lead and of magnesium at lower values of pH.

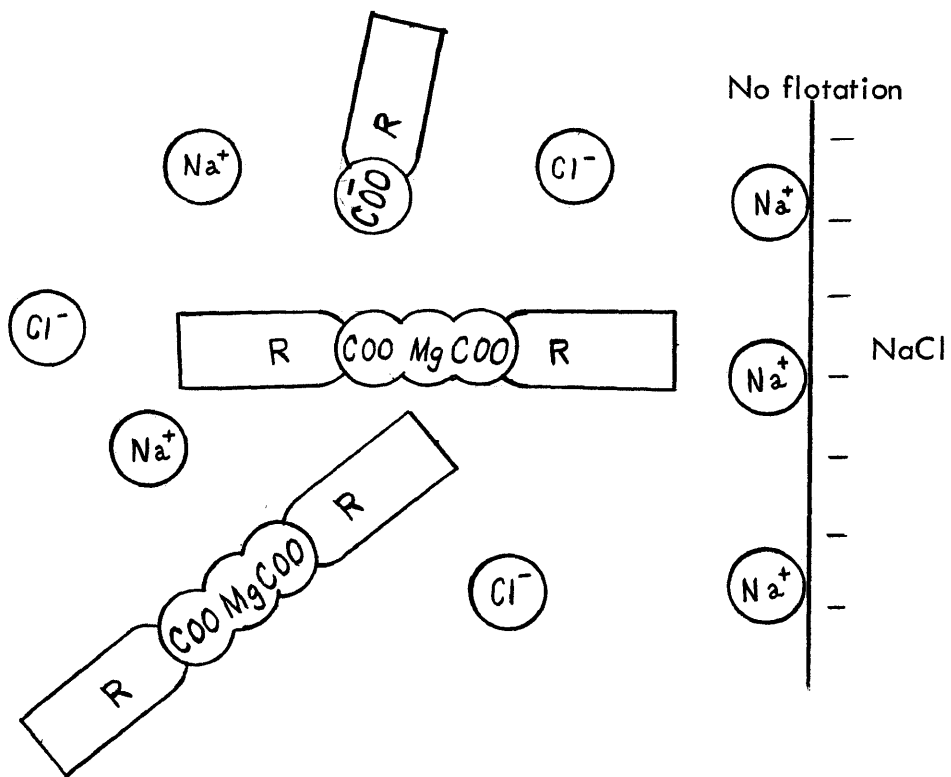


Figure 25 - Surface model of NaCl-magnesium-fatty acid system at pH 5.5.

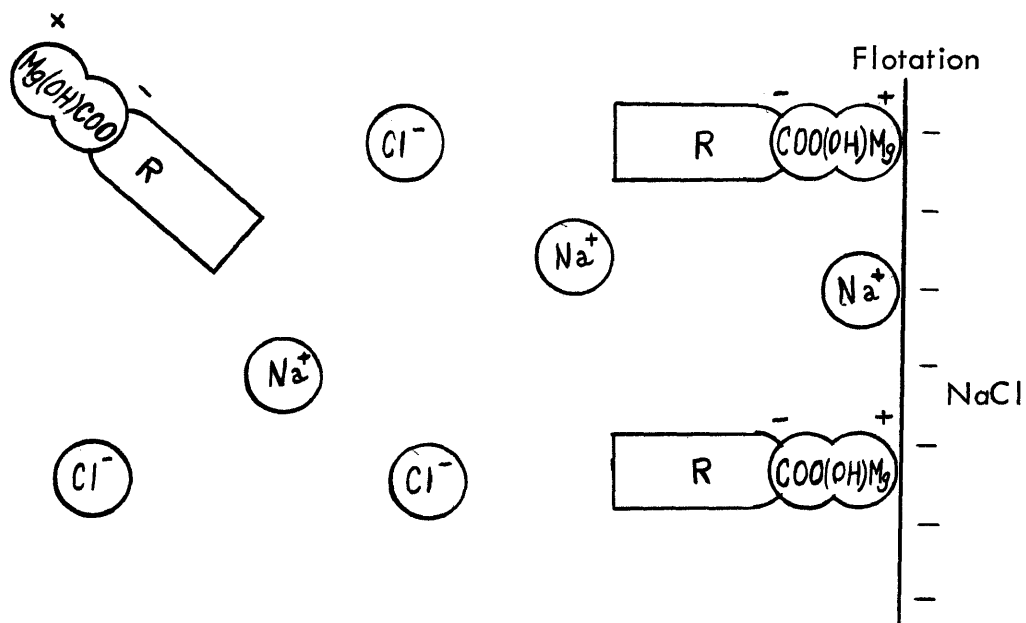


Figure 26 - Surface model of NaCl-magnesium-fatty acid system at pH 8.7.

The premise that the various aqueous species, such as RNH_3Cl (aq), RCOONa (aq) and $\text{Pb}(\text{OH})\text{RSO}_3$ (aq) are functioning as the collectors in salt systems is supported by the data determined with tetradecyl sulfonate. As shown in Table I, no flotation of NaCl is obtained in the presence of lead ions as would be predicted from work with lauryl sulfate. This behavior is probably due to the lower solubility of the C-14 basic lead sulfonate. If the precipitate itself were functioning as the collector, good flotation would be expected. However, if the aqueous species is the active collector, lower solubility resulting in lower concentrations of the aqueous species would lead to a decrease in recovery.

Several investigators have noted the effect of temperature on the recovery of KCl with amine. One Carlsbad potash producer uses dodecylamine in the winter when the pulp is cold and changes to hexadecylamine in the summer when the pulp is 15 to 20°C warmer. The effect of temperature becomes obvious from Figures 14 and 15 and the solubility data of NaCl and KCl . Any change in temperature will result in a change of collector solubility, which can be compensated for by altering the collector concentration or by changing the collector chain length. A change in surface charge will also accompany a change in temperature due to the free energy of hydration varying with temperature. Both of these effects will be evidenced by a change in flotation recovery due to an increase or decrease in the amount of collector adsorbed on the salt surface. If it is assumed that only a small change in surface charge occurs with a change in temperature,

the increase or decrease in flotation recovery may be attributed to an increase or decrease in collector solubility. As the temperature rises the collector becomes more soluble, and produces more of the aqueous complex. However, at some point the aqueous complex will decompose more rapidly with an increase in temperature than it is produced from the precipitate. At this point the recovery of the salt being floated will be decreased.

CONCLUSIONS

The mechanism of soluble salt flotation has never been understood previously, although attempts have been made by several investigators. The mechanism developed in this thesis explains the role of surface charge and collector solubility in soluble salt flotation. The following conclusions may be drawn from this investigation:

- (1) The mechanism of soluble salt flotation is one of electrical attraction of the collector, either an ion or a neutral aqueous dipole, to the charged salt surface.
- (2) The surface charge of a salt can be determined by the relative free energy of hydration of its anion and cation. If the cation has a larger negative free energy of hydration than the anion, then the surface of the salt will be negative. If the anion has the larger negative free energy of hydration, the surface of the salt will be positive.

- (3) With certain collectors, precipitates of the collector must be present to yield a sufficient amount of aqueous polar species for flotation to result.
- (4) KCl can be floated either by the RNH_3Cl (aq) molecule or the RSO_3^- ion.
- (5) NaCl can be floated by the RNH_3^+ ion, and the aqueous molecules $\text{Pb}(\text{OH})\text{RSO}_3(\text{aq})$, $\text{NaRCOO}(\text{aq})$, and $\text{Mg}(\text{OH})\text{RSO}_3(\text{aq})$.
- (6) If the aqueous molecule is the active collector, the precipitate with which it is in equilibrium must have a solubility high enough to produce a sufficient concentration of the aqueous molecule to effect flotation.
- (7) The role of temperature is simply to alter the collector solubility and thus increase or decrease the amount of active collector available for adsorption.
- (8) Activators such as magnesium and lead regulate the amount of collector ions in solution, and concentration of the aqueous molecule in the system, or the form, either polar or non-polar.
- (9) The pH influences recovery by controlling the equilibrium between the various collector species such as $\text{Mg}(\text{RCOO})_2$ and $\text{Mg}(\text{OH})\text{RCOO}$, and $\text{Pb}(\text{RSO}_3)_2$ and $\text{Pb}(\text{OH})\text{RSO}_3$.

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APPENDIX

APPENDIX 1 - Data required for the calculation of the solubility product of the various collector salts.

TABLE 1-A -- Solubility of NaCl and KCl at various temperatures (21).

Temperature (°C)	0	10	20	30	40	50
NaCl (gm/100 gm H ₂ O)	35.7	35.8	36.0	36.3	36.6	37.0
KCl (gm/100 gm H ₂ O)	27.6	31.0	34.0	37.0	40.0	42.6

TABLE 2-A -- Specific gravity of saturated solutions (22).

Salt	NaCl	KCl
Specific Gravity	1.1978	1.1783
Temperature (°C)	25	25

TABLE 3-A -- Activity coefficients of KCl at various concentrations and at 25°C (23).

Concentration (m/l)	1.0	1.5	2.0	3.0	4.0	5.0
γ_{\pm}	0.603	0.582	0.572	0.568	0.576	0.590

APPENDIX 1 continued

TABLE 4-A -- ΔB values for various salt solutions (24).

$$\log \gamma_{\pm} = \log \gamma_{KCl} + m \Delta B$$

Concentration (m/l)	NaCl	KF	KBr	KI
0.1	0.049	0.03	0.01	0.045
0.5	0.043	0.028	0.011	0.035
1.0	0.0365	0.028	0.009	0.029
2.0	0.0335	0.030	0.0075	0.023
3.0	0.0330	0.031	0.0065	0.0197
4.0	0.0332	0.0326	0.0057	0.0167
5.0	0.034	--	0.0050	0.0139