

AN INVESTIGATION OF THE FLOTATION
OF THE SOLUBLE SALTS,
 NaNO_3 , KNO_3 , and K_2SO_4

by

Ramon S. Pizarro

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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 Master of Science.

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ABSTRACT

Microflotation experiments with pure salts (NaNO_3 , KNO_3 , and K_2SO_4) together with solubility determinations of collector-salt compounds were carried out to study the mechanisms of soluble salt flotation.

Experimental results show that sodium nitrate floats well with octyl sulfonate, moderately well with caprylic acid, and negligibly with longer-chain fatty acids and amines.

Potassium nitrate floats well with octyl sulfonate and the 8-, 12-, and 14- carbon amines but only moderately with relatively high additions of fatty acids.

Potassium sulfate floats well with amines, octyl sulfonate, and longer-chain fatty acids.

In some cases flotation occurs only after precipitation of the collector has occurred. Aqueous complexes, such as $\text{RNH}_3\text{NO}_3(\text{aq})$ and $\text{RCOOK}(\text{aq})$, are the species that

are probably responsible for flotation under these conditions. Mechanisms of adsorption of these species are presented.

CONTENTS

	<u>Page</u>
INTRODUCTION.....	1
Purpose and Scope of this Investigation.....	3
EXPERIMENTAL MATERIALS AND PROCEDURES.....	4
Reagents.....	4
Microflotation Apparatus.....	5
Solubility Apparatus.....	5
Flotation Experiments.....	8
Solubility Determinations.....	11
EXPERIMENTAL RESULTS.....	13
Flotation Experiments.....	13
Solubility Product Determinations.....	25
DISCUSSION OF RESULTS.....	29
Summary of Current Theories.....	29
CONCLUSIONS.....	37
BIBLIOGRAPHY.....	39

ILLUSTRATIONS

<u>Figure</u>		<u>Page</u>
1.	Schematic diagram of micro flotation cell..	6
2.	Schematic diagram of micro flotation apparatus.....	7
3.	Schematic view of sample cell.....	9
4.	Schematic diagram of solubility apparatus..	10
5.	Solubility limit determination.....	12
6.	NaNO_3 recovery as a function of carboxylic acid ³ additions.....	14
7.	NaNO_3 recovery as a function of amine additions.....	16
8.	K_2SO_4 , NaNO_3 , and KNO_3 recoveries as a function of ³ sodium octyl sulfonate.....	17
9.	KNO_3 recovery as a function of caprylic and ³ capric acid additions.....	18
10.	KNO_3 recovery as a function of lauric and oleic acid additions.....	20
11.	KNO_3 recovery as a function of amine additions.....	21

<u>Figure</u>	<u>Page</u>
12. K_2SO_4 recovery as a function of carboxylic acid additions.....	22
13. K_2SO_4 recovery as a function of amine additions.....	24

TABLES

<u>Table</u>		<u>Page</u>
I	Nitrogen statistics.....	1
II	Mean activity coefficients of 1-1 electrolytes at 25°C.....	26
III	Mean activity coefficients of potassium sulfate at 25°C.....	26
IV	Solubility products of various collector salt compounds.....	28

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INTRODUCTION

World demands for nitrogen are continuously increasing at a very high rate, as shown in the table below. (1)

TABLE I - Nitrogen statistics

(Thousand short tons of contained nitrogen)

	<u>1956-60</u>	<u>1961</u>	<u>1962</u>	<u>1963</u>	<u>1964</u>	<u>1965</u>
U. S. Production	3521	4429	4920	5656	6447	7252
World Production	11956	15403	16320	18864	21213	23401

The U. S. domestic production of ammonia has now doubled that of ten years ago. The construction of large plants, over 1000 tons per day, has contributed to lower unit costs and consequently to the higher rates of production now obtained.

But this bright picture is not applicable to the saltpeter industry in Chile, once the only nitrogen supplier in the world. Thirty years ago, natural sodium nitrate supplied the world requirements of nitrogen as a fertilizer agent. More than thirty thousand people were

engaged in this industry, and the installed plant capacities reached as high as five million tons of finished product per year. In fact, the saltpeter industry was the most important mining activity in Chile.

Now the situation is quite different. The competition of synthetic ammonium nitrate has severely affected the Chilean industry to such an extent that it produces at only twenty percent of its rated capacity. Chilean exports of sodium nitrate in 1965 reached about one million tons of finished product. Two facts have contributed to this situation. First, the synthetic ammonium nitrate has a higher nitrogen content per unit weight than does the natural sodium nitrate. Second, and this is a very important reason, the production costs are higher for the saltpeter.

It is believed that if the Chilean industry could substantially reduce its production costs, it could favorably compete with the ammonium nitrate industry. This would require a drastic change in the present operating procedures, which involve dissolution of the "caliche" and fractional crystallization.

One approach could be the concentration of sodium nitrate by flotation. This is quite reasonable, since the flotation of other soluble salts such as sylvite (KCl)

from halite (NaCl) is a gratifying reality in the potash industry.

Purpose and Scope of this Investigation

The purpose of this investigation is two-fold:

(1) to contribute to the understanding of the mechanisms involved in soluble salt flotation and (2) to show on the basis of work with pure salt systems whether it might be possible to concentrate Chilean saltpeter deposits by flotation.

The experimental work covered the areas of flotation response to amines, fatty acids, and sulfonates as collectors together with the determination of collector solubility in saturated salt solutions.

EXPERIMENTAL MATERIALS
AND PROCEDURES

Reagents

The sodium and potassium salts (NaNO_3 , KNO_3 , and K_2SO_4) used in this investigation were analyzed reagent grade compounds.

The collectors used had the following reported purity:

<u>Name</u>	<u>Formula</u>	<u>Purity (percent)</u>
Caprylic acid	$\text{CH}_3 - (\text{CH}_2)_6 - \text{COOH}$	+99
Capric acid	$\text{CH}_3 - (\text{CH}_2)_8 - \text{COOH}$	+99
Oleic acid	$\text{C}_{17}\text{H}_{33}\text{COOH}$	+99
Octyl amine	$\text{C}_8\text{H}_{17}\text{NH}_2$	+99
Dodecyl amine	$\text{C}_{12}\text{H}_{25}\text{NH}_2$	+99
Tetradecyl amine	$\text{C}_{14}\text{H}_{29}\text{NH}_2$	+99
Sodium octyl sulfonate	$\text{C}_8\text{H}_{17}\text{SO}_3\text{Na}$	+96
Sodium nonyl sulfonate	$\text{C}_9\text{H}_{19}\text{SO}_3\text{Na}$	+96

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 one micro-mho.

Microflotation Apparatus

A microflotation apparatus was used in all of the flotation experiments (See Figures 1 and 2). The microflotation cell had a fritted glass bottom (60-micron, average pore size) for gas introduction. Agitation of the pulp was obtained with a variable-speed magnetic stirrer and a Teflon-coated stirring bar. Commercial nitrogen was used for flotation; carbon dioxide was removed from the gas prior to flotation by passing the nitrogen through an aqueous sodium hydroxide solution and a column of Ascarite.

Apparatus for Solubility Determinations

The apparatus used for solubility determinations consisted of a 250-ml beaker suspended inside a 400-ml beaker, which functioned as a water jacket. Water at constant temperature entered through an inlet near the top of the beaker. The 400-ml beaker was carefully wrapped with black tape, with the exception of two small windows, displaced 180° from each other, in a horizontal plane. A light source of constant intensity was directed through one of the windows, and a photocell was placed in front of the other window.

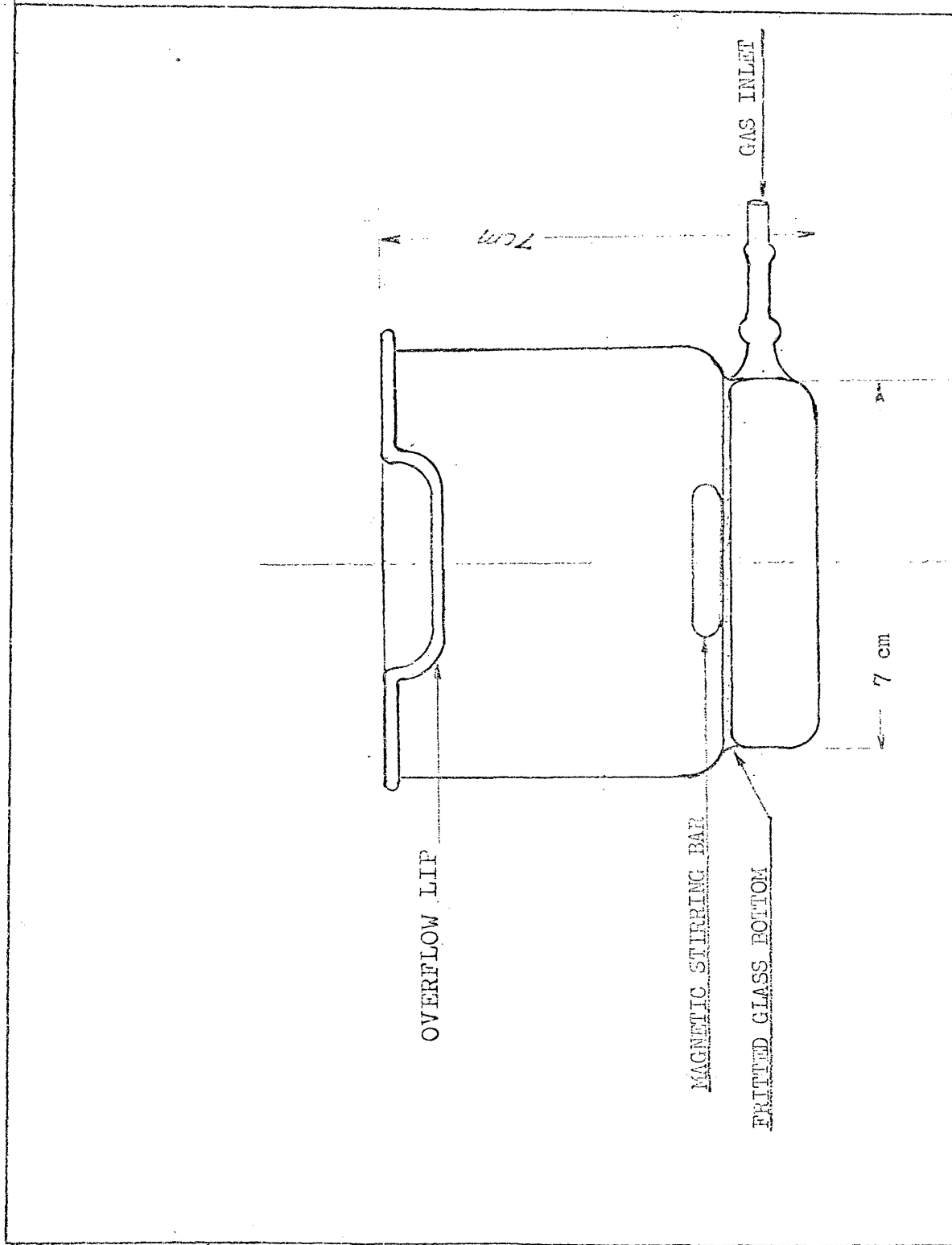


Figure 1. Schematic diagram of micro-flotation cell.

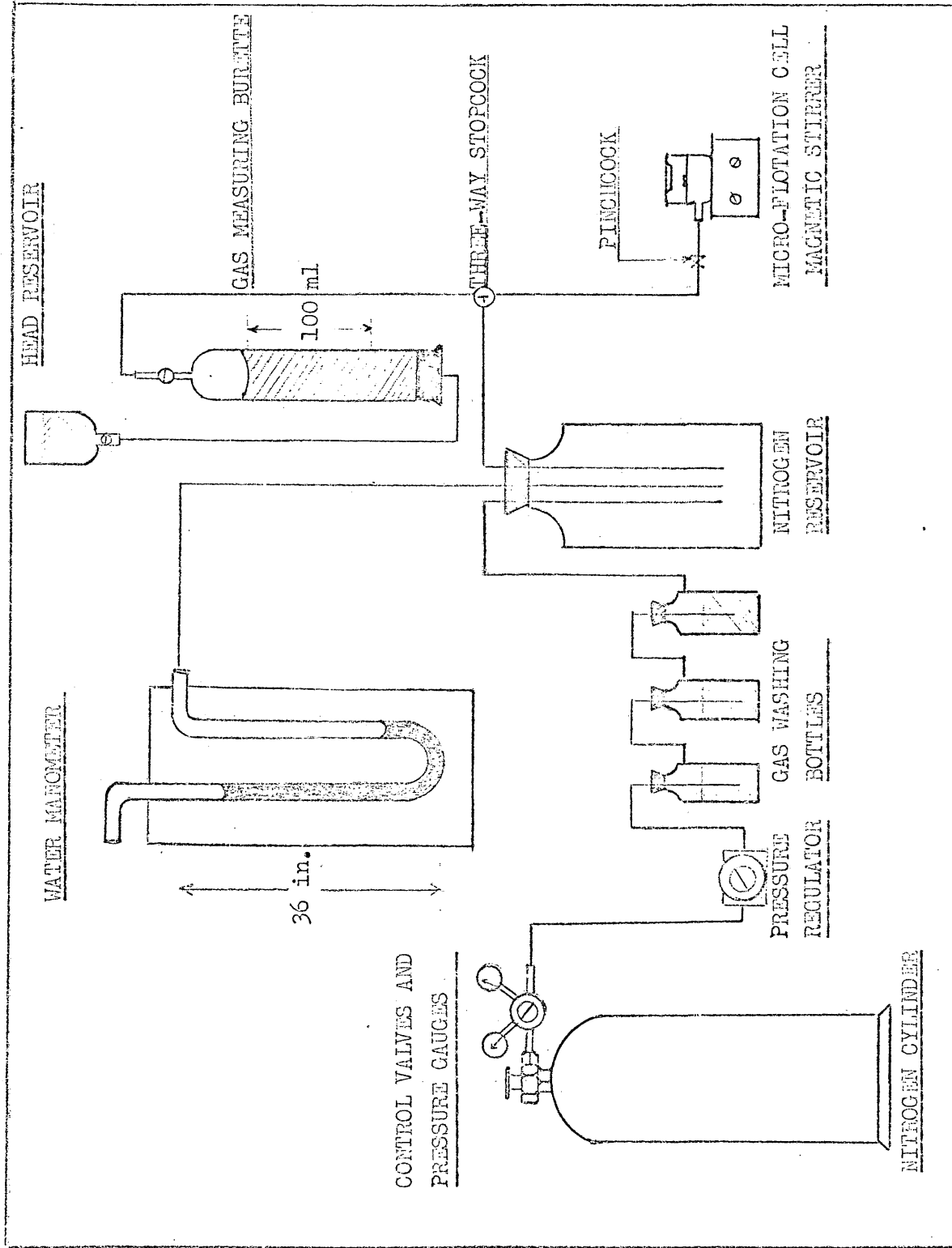


Figure 2. Schematic diagram of micro-flotation apparatus.

Figures 3 and 4 show a schematic diagram of the instruments used.

Flotation Experiments

All of the flotation experiments were carried out at ambient temperature (23°C) with the following procedure:

1. A measured amount of saturated solution was transferred to the microflotation cell.
2. A five-gram sample, 65 x 150 mesh, was added to this solution.
3. 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.
4. The collector solution was added to the cell and allowed to condition for three minutes.
5. Two drops of a solution containing 20 parts of water to 1 part of Dowfroth 250 were added as frother.
6. 100 ml of nitrogen gas were passed through the cell, the froth being collected as the concentrate.
7. Flotation recoveries were calculated from the relationship:

$$\text{Percent recovery} = \frac{\text{Weight of Concentrate} \times 100}{\text{Weight of Concentrate} + \text{Tail}}$$

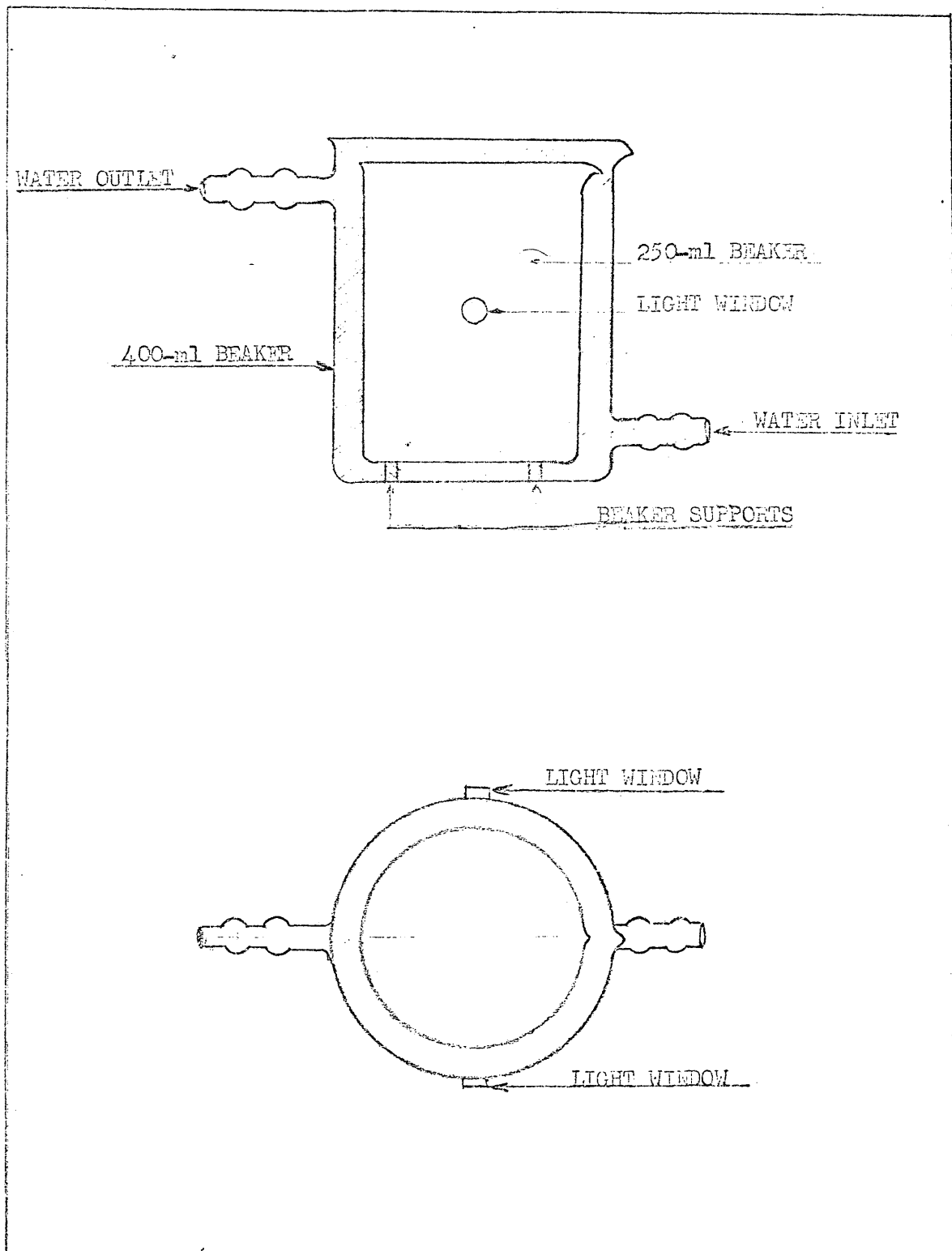


Figure 3. Schematic view of cell used in solubility determinations.

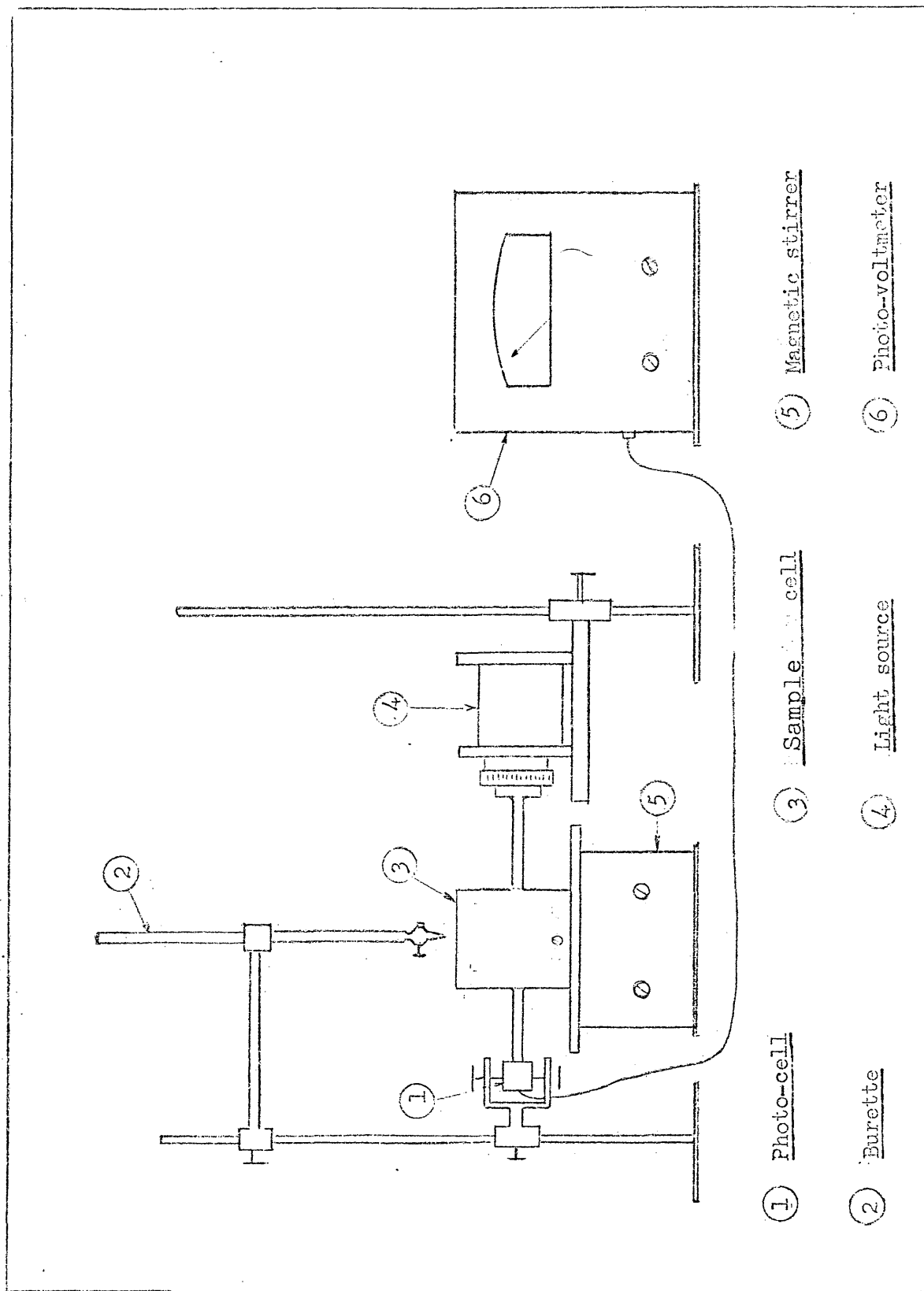


Figure 4. Schematic diagram of complete apparatus used in solubility determinations.

Solubility Determinations

The solubility products of several collectors were determined with the following procedure:

1. 150-ml of a salt solution of known concentration were transferred to a 250-ml beaker, which acted as the sample cell.
2. The collector solution of known concentration was added to the sample cell with a burette.
3. After each collector addition, the solution was agitated with a magnetic stirrer for two minutes. After this time a reading was taken in the photocell amplifier. Transmitted light readings were plotted as a function of collector additions on a rectilinear plot. The formation of a precipitate causes a sudden change in the slope of this plot, and the concentrations of salt and collector may thus be calculated. A plot of typical data obtained with this technique is given in Figure 5.

A solubility product was calculated after the salt concentration was converted to activity. However, the collector concentration was used instead of the collector activity.

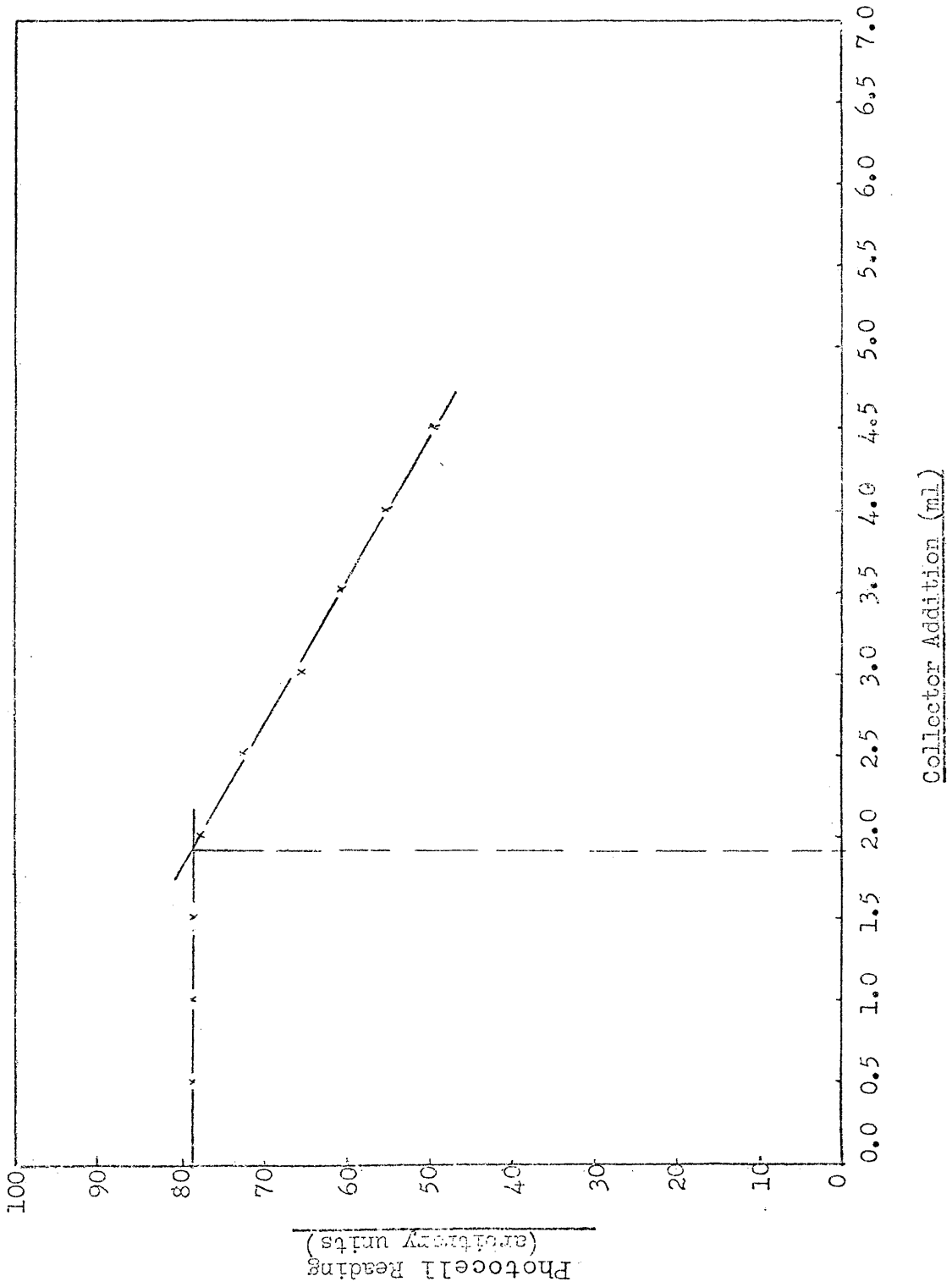


Figure 5. Solubility Limit Determination. K_2SO_4 -Oleic Acid.

EXPERIMENTAL RESULTS

The experimental work can be separated conveniently into two categories:

- a. Determination of flotation response to anionic collectors (carboxylic acids and sulfonates) and to cationic collectors (amines).
- b. Determination of collector solubility in various saturated solutions.

Flotation Experiments

The first salt examined was NaNO_3 , and the recovery obtained in the presence of various fatty acids is presented in Figure 6. It can be observed that flotation was obtained only with caprylic acid, and only with a rather high addition of collector, i. e. 6×10^{-3} mole per liter. The solubility limit of sodium caprylate could not be determined with the solubility apparatus technique because of its high solubility. However, the solubility limit is greater than 5×10^{-2} mole per liter caprylate.

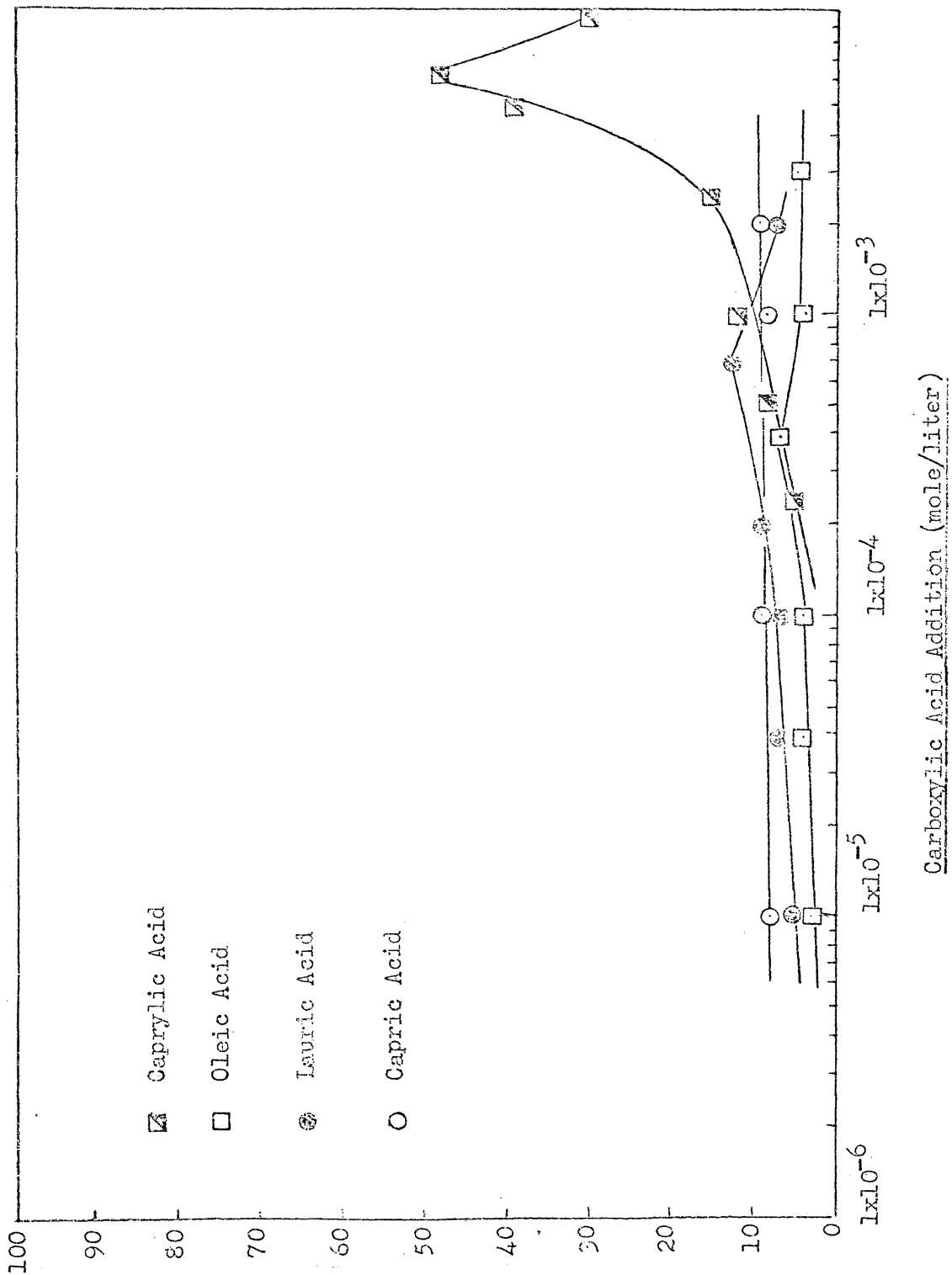


Figure 6. NaNO_3 recovery as a function of carboxylic acid additions.

In all flotation experiments, a recovery of 10 percent was considered nominal.

An interesting point is the effect of temperature on the flotation of sodium nitrate. Small changes of temperature, two or three degrees, affected the recovery substantially because of the extreme solubility of the sodium nitrate. Very careful control of the temperature was a requisite for obtaining consistent results.

Figure 7 shows NaNO_3 flotation recoveries as a function of amine addition. The recoveries obtained ranged from 20 to 30 percent with higher collector additions. No substantial differences were found in the recoveries obtained with dodecyl amine and tetradecyl amine. Recoveries obtained with octyl amine were lower at all collector additions.

The flotation recovery of NaNO_3 is plotted as a function of sodium octyl sulfonate addition in Figure 8. As shown, a recovery of about 80 percent was obtained with 1×10^{-3} mole per liter. The solubility limit was measured at 9×10^{-4} mole per liter octyl sulfonate. No precipitation of collector was observed with either KNO_3 or K_2SO_4 under these conditions.

The next salt examined was KNO_3 , and its flotation response to various fatty acids is given in Figures 9

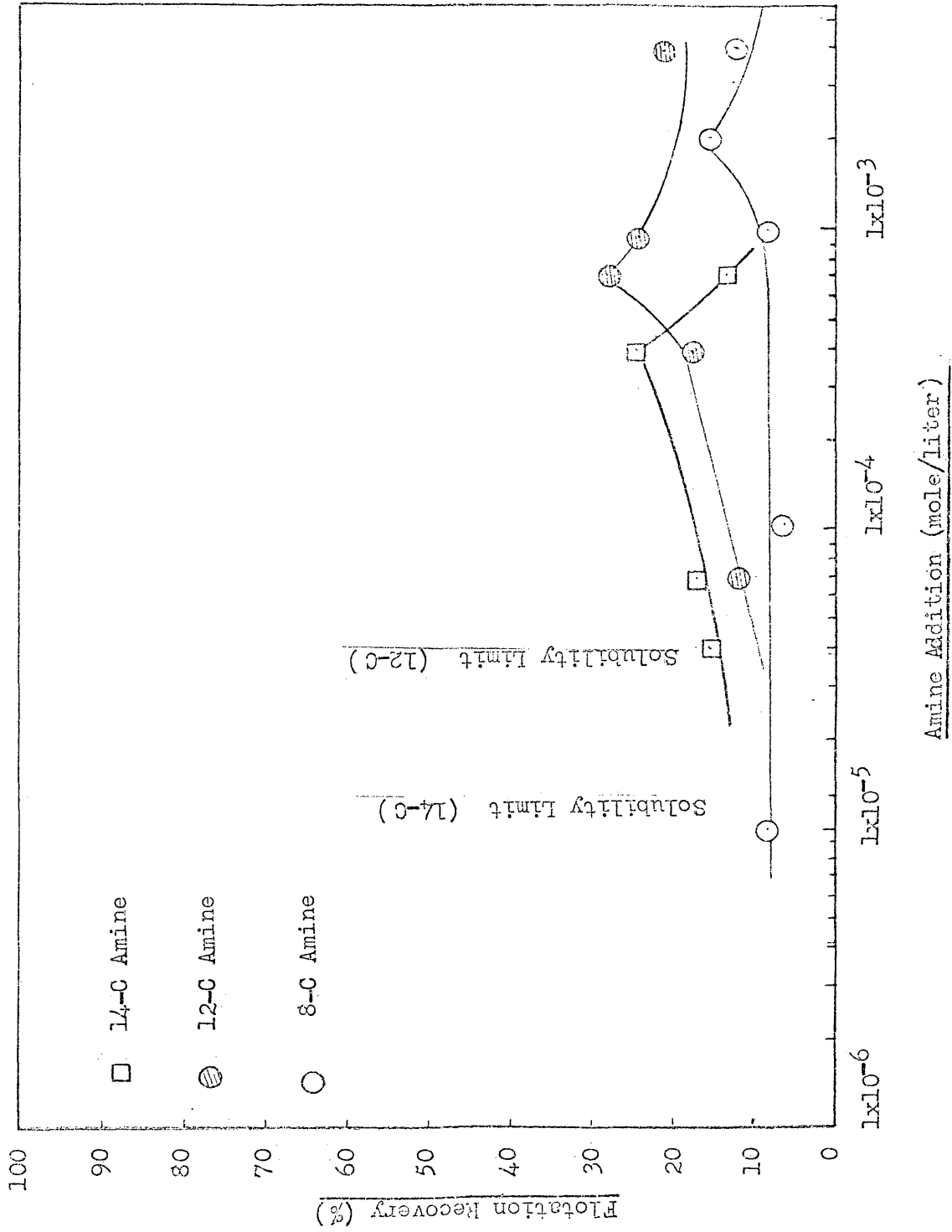


Figure 7. NaNO_3 recovery as a function of amine additions.

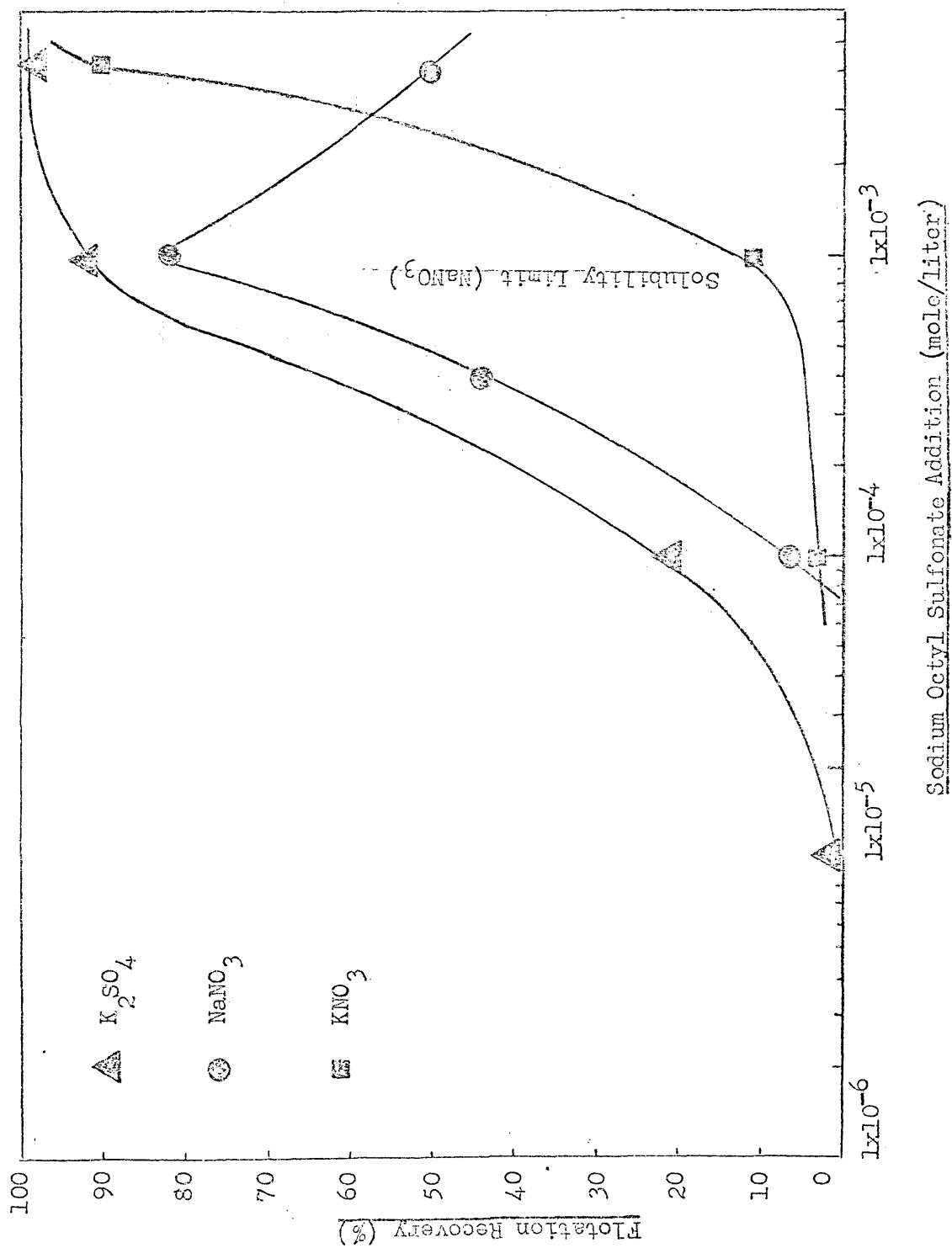


Figure 8. K_2SO_4 , $NaNO_3$, and KNO_3 recoveries as a function of sodium octyl sulfonate additions.

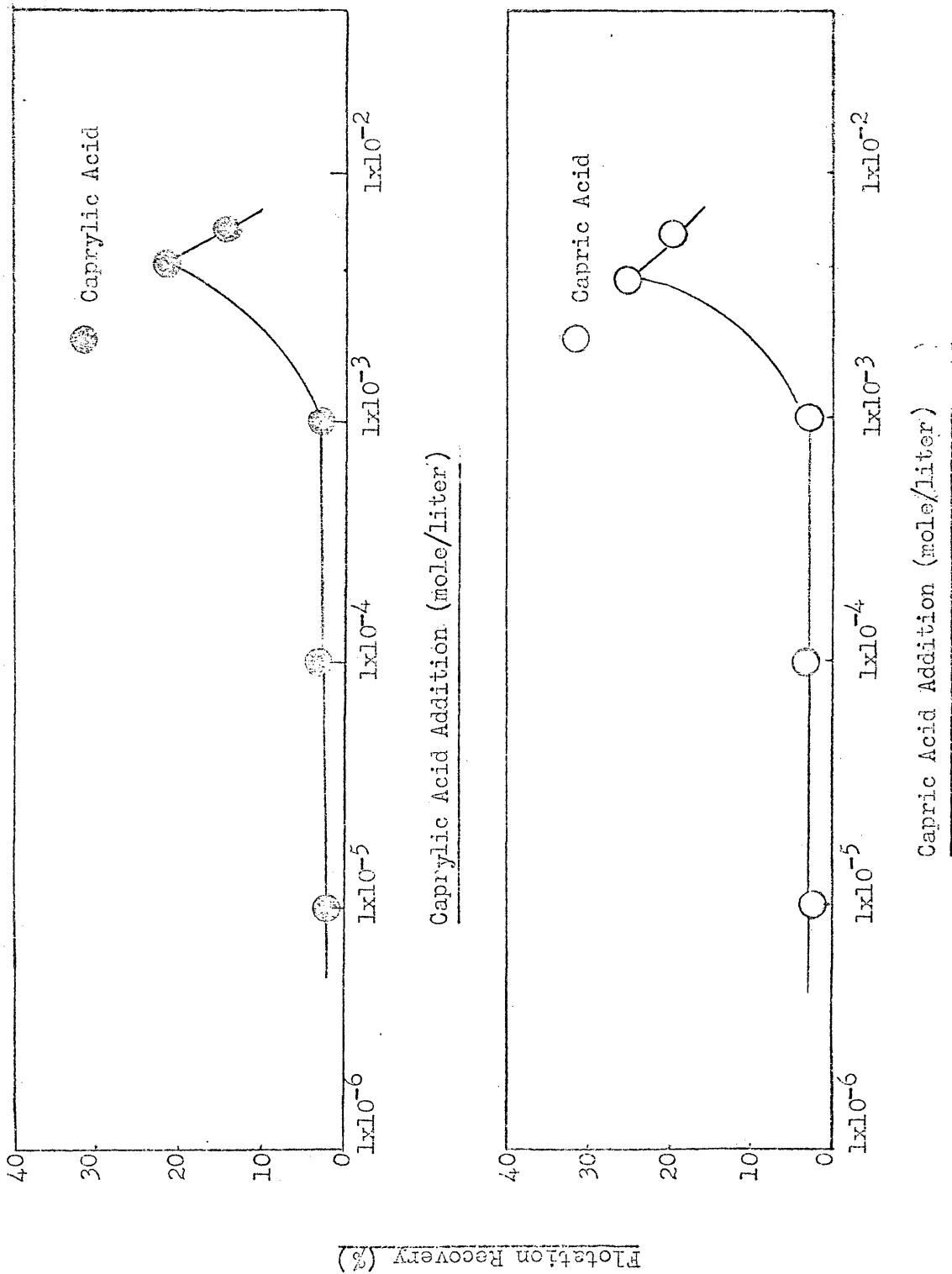


Figure 9. KNO_3 recovery as a function of caprylic and capric acid additions.

and 10. Low flotation recoveries were obtained, even at high collector additions (4×10^{-3} mole per liter).

As shown in Figure 11, flotation of KNO_3 occurred only after precipitation of amine nitrate had occurred in solution when dodecyl and tetradecyl amines were used. On the other hand, essentially complete flotation was obtained with octyl sulfonate before precipitation of potassium octyl sulfonate (Figure 8).

Figure 12 shows the effect of carboxylic acid additions on the flotation recovery of K_2SO_4 . As can be seen, a recovery of almost 100 percent was obtained with oleic acid. No flotation was obtained with collector additions lower than 5×10^{-6} mole per liter. A recovery of about 90 percent with 7×10^{-4} mole per liter was obtained and remained constant at this level up to 4×10^{-4} mole per liter. Recovery dropped rapidly at higher collector additions, that is at 4×10^{-3} mole per liter, the recovery was only 22 percent. The solubility limit of potassium oleate is shown to be 1.8×10^{-6} mole per liter.

The lower molecular weight carboxylic acids such as caprylic, capric and lauric acids, yielded relatively small flotation recoveries of K_2SO_4 , the maximum being obtained with lauric acid (48 percent) at 1×10^{-3} mole per liter. The solubility limit of potassium laurate was

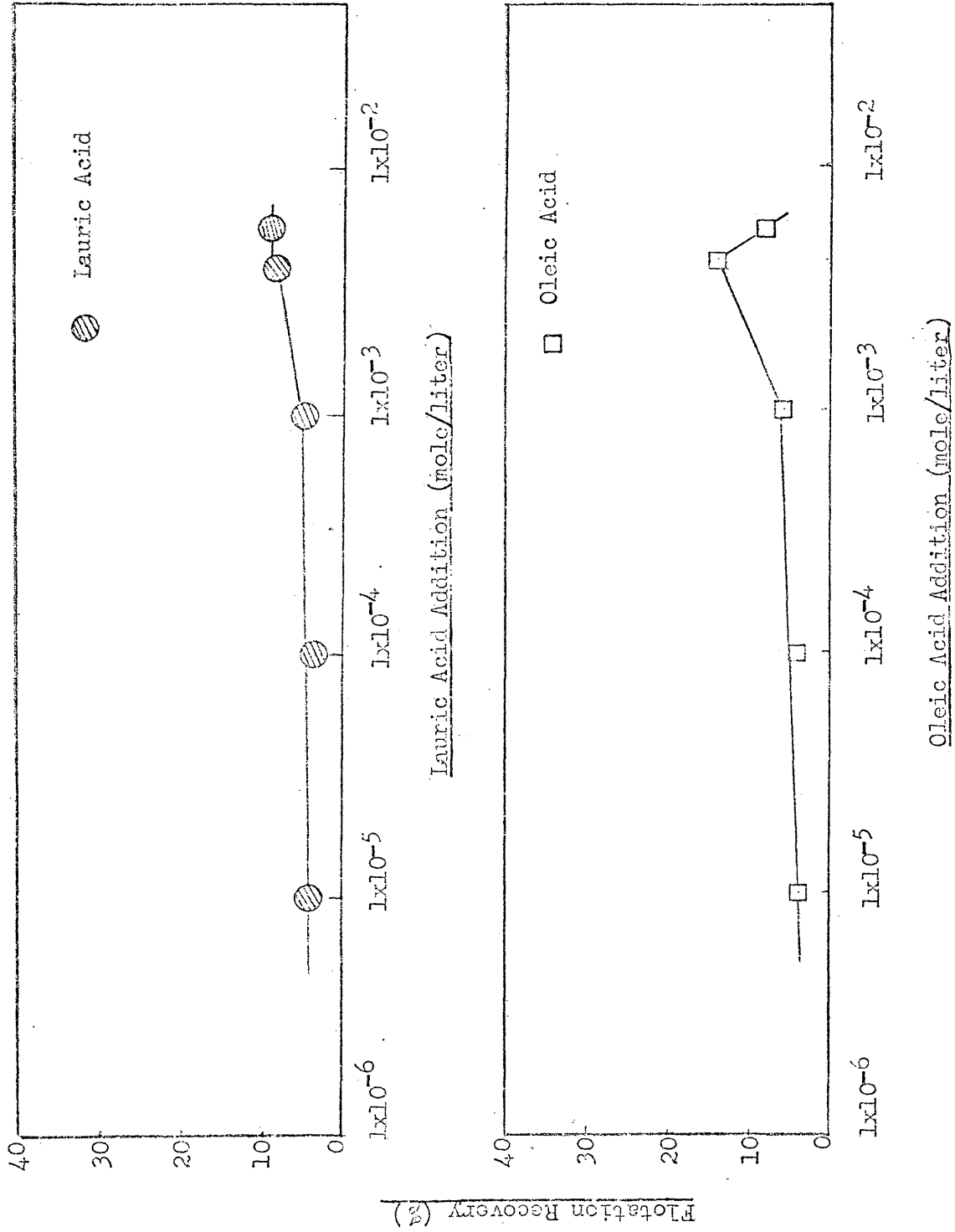


Figure 10. KNO_3 recovery as a function of lauric and oleic acid additions.

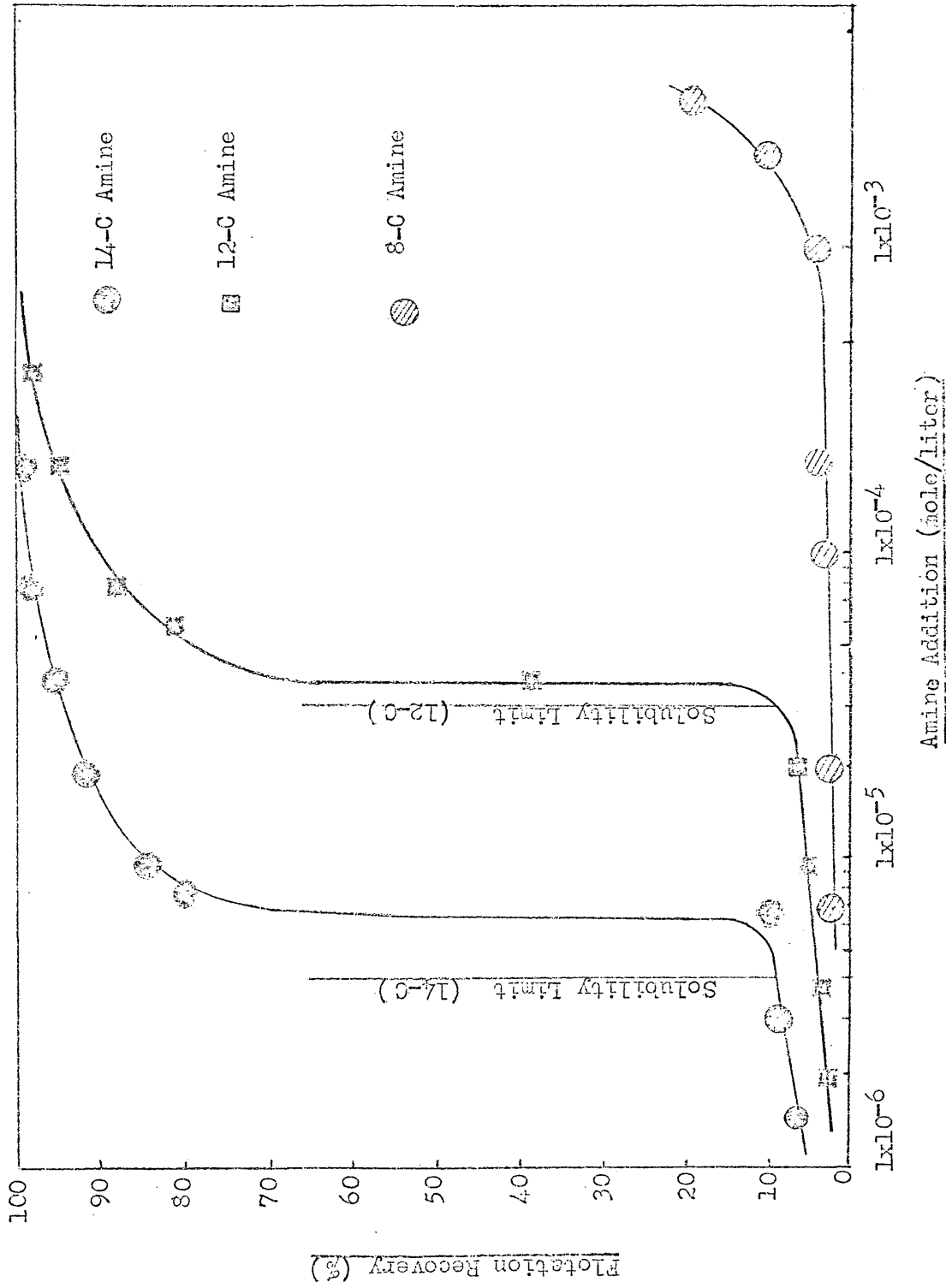


Figure 11. KNO₃ recovery as a function of amine additions.

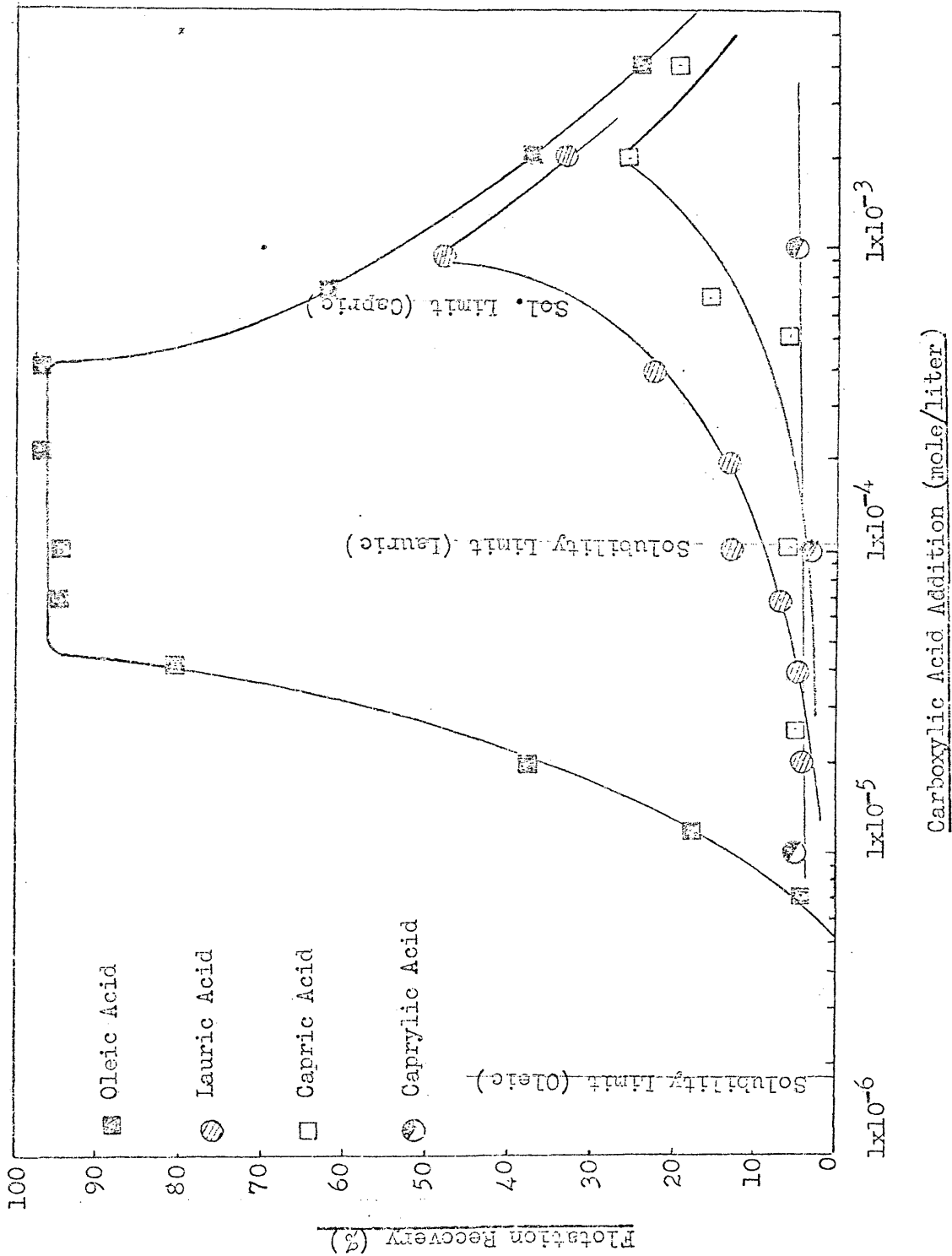


Figure 12. K_2SO_4 recovery as a function of carboxylic acid additions.

found at 1.6×10^{-4} mole per liter.

Figure 13 shows the effect of amine additions on K_2SO_4 . Excellent recoveries were obtained with relatively low collector additions. In the case of tetradecyl amine, a recovery of 96 percent was obtained with 2×10^{-5} mole per liter. With dodecyl amine a recovery of 98 percent was obtained with 4×10^{-5} mole per liter.

Solubility limits for dodecyl and tetradecyl amines were found at 8.0×10^{-4} and 1.5×10^{-6} mole per liter, respectively. The solubility limit of the octyl amine could not be determined because of its high solubility.

The two principal soluble salts contained in the natural saltpeter deposit are sodium nitrate and sodium chloride. Flotation experiments were conducted with these two salts with nonyl sulfonate in a sodium nitrate-sodium chloride brine. This brine was prepared by first saturating a solution with sodium nitrate and then saturating this solution with sodium chloride. A collector addition of 5×10^{-4} mole per liter was used, and a recovery of 78.5 percent of $NaNO_3$ was obtained, while a recovery of 7.5 percent of $NaCl$ was obtained in separate experiments.

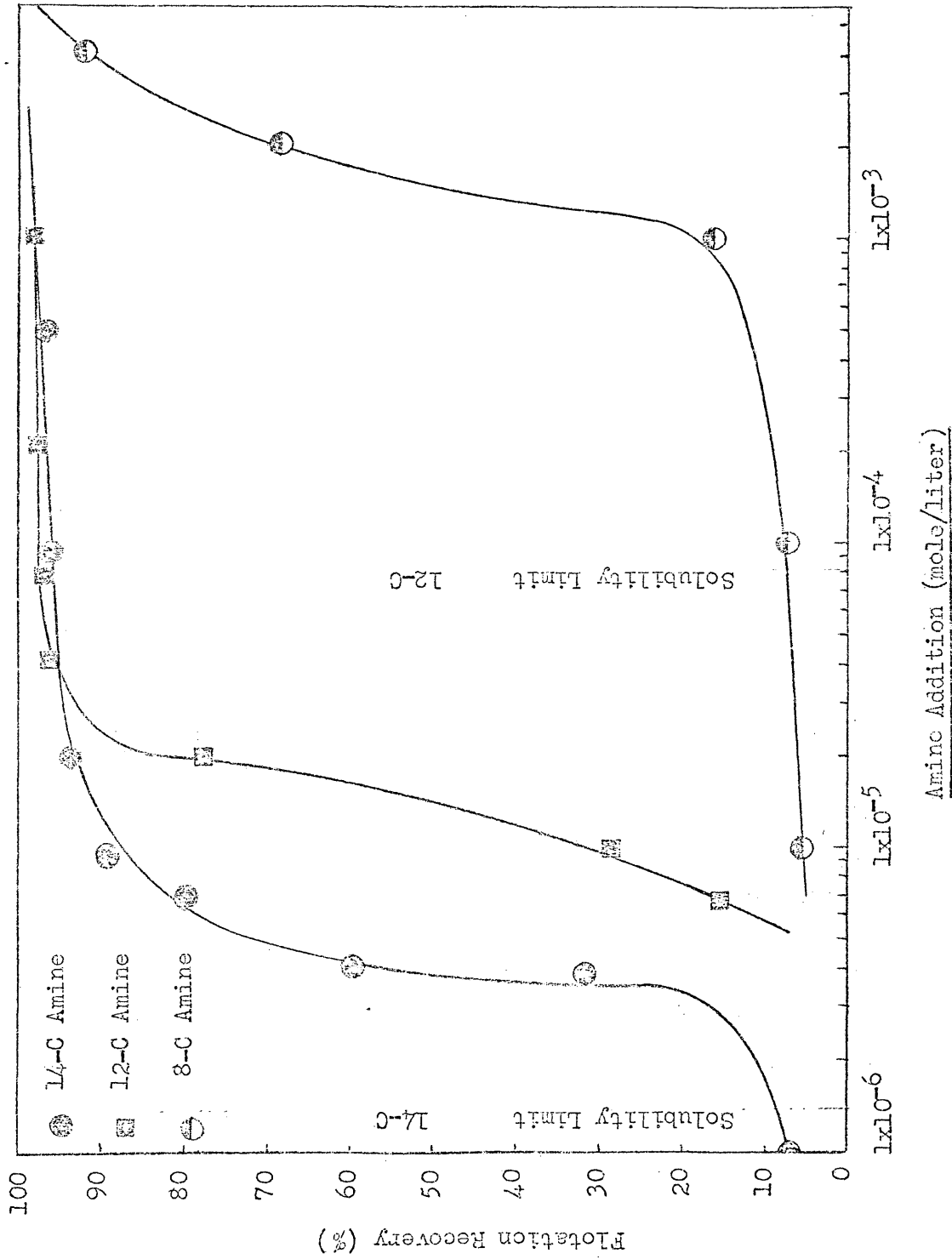


Figure 13. K₂SO₄ recovery as a function of amine additions.

Solubility Product Determinations

The solubility products of the collector salts formed were determined from the activity of the salt in its saturated brine and the molar concentration of the collector. Activities were calculated by utilizing equations defining activity coefficients for symmetrical and unsymmetrical electrolytes.⁽²⁾ For a symmetrical electrolyte such as KNO_3 , activity coefficients were calculated from:

$$f_{\pm} = \frac{a_{\pm}}{m}$$

and for an electrolyte such as K_2SO_4 ,

$$f_{\pm} = \frac{a_{\pm}}{1.5876 m}$$

where a_{\pm} = activity and m = molality

The activity coefficients of several 1-1 electrolytes at different molalities have been tabulated by Harned and Owen,⁽³⁾ and those values for NaNO_3 and KNO_3 are tabulated in Table II.

TABLE II - Mean activity coefficients of 1-1 electrolytes at 25°C

<u>m</u>	<u>NaNO₃</u>	<u>KNO₃</u>	<u>m</u>	<u>NaNO₃</u>	<u>KNO₃</u>
0.1	0.758	0.733	3.0	0.438	0.266
0.2	0.702	0.659	3.5	0.423	0.244
0.3	0.664	0.607	4.0	0.410	
0.5	0.615	0.742	4.5	0.398	
0.7	0.583	0.494	5.0	0.388	
1.0	0.548	0.441	5.5	0.380	
1.5	0.509	0.378	6.0	0.370	
2.0	0.481	0.327			
2.5	0.457	0.293			

Mean activity coefficients for K₂SO₄ at 25°C are tabulated in Table III.

TABLE III - Mean activity coefficients of potassium sulfate at 25°C

<u>m = Molality</u>	<u>± K₂SO₄</u>
0.1	0.441
0.2	0.361
0.3	0.317
0.5	0.264
0.7	0.233

By applying the above cited concepts and the experimental data of the solubility determinations, the solubility

products of some collector-salt compounds were calculated and are listed in Table IV.

TABLE IV - Solubility products of various collector salt compounds

<u>Compound</u>	<u>Formula</u>	<u>Brine</u>	<u>KSP</u>
Potassium laurate	$\text{CH}_3 - (\text{CH}_2)_{10} - \text{COOK}$	K_2SO_4	3.0×10^{-5}
Potassium oleate	$\text{CH}_3 - (\text{CH}_2)_7 - \text{CH} = \text{CH} - (\text{CH}_2)_7 - \text{COOK}$	K_2SO_4	4.5×10^{-7}
Dedecyl amine sulfate	$(\text{R} - \text{NH}_3)_2 - \text{SO}_4$	K_2SO_4	3.20×10^{-5}
Dodecyl amine nitrate	$\text{CH}_3 - (\text{CH}_2)_{11} - \text{NH}_3 - \text{NO}_3$	KNO_3	2.6×10^{-5}
Tetradecyl amine sulfate	$(\text{C}_{14}\text{H}_{29}\text{NH}_3)_2 - \text{SO}_4$	K_2SO_4	4.1×10^{-7}
Tetradecyl amine nitrate	$\text{C}_{14}\text{H}_{29}\text{NH}_3 - \text{NO}_3$	KNO_3	3.5×10^{-6}
Sodium octyl sulfonate	$\text{C}_8\text{H}_{17}\text{SO}_3\text{Na}$	NaNO_3	2.2×10^{-3}

DISCUSSION OF RESULTS

Summary of Current Theories

Bachmann⁽⁴⁾ has postulated that flotation of a soluble salt depends on its crystallographic properties rather than on its chemical properties. He explained the selective flotation of KCl from NaCl by a similarity between the dimensions of the KCl lattice and the quasi-crystalline structure of the amine collector. There is no similarity with the NaCl lattice. Bachmann's theory has been found to be correct on a number of salt minerals. The chains of the collector molecules can be compressed fairly strongly, but there is a limit which is controlled by spreading of the film on liquid surfaces or by crystalline modifications of the collector. However, the theory is not applicable to the flotation of silver salts, for example. AgCl is isomorphous with NaCl, but it floats very well with amines, while NaCl does not.

Fuerstenau and Fuerstenau⁽⁵⁾ interpreted the flotation of halide salts with aminium ions in such a way that ionic size controls the process. They stated that for flotation to occur the collector ion should fit into the crystal lattice at the surface. They extended this theory to the whole group of alkali metal halides and stated that only those minerals which have a cation similar in size to NH_3 will float. This theory does not explain why an anionic reagent such as an alkyl sulfate or sulfonate can separate two salts with the same anion such as KCl and NaCl , where the sulfate group cannot fit into the crystal surface.

Rogers⁽⁶⁾ postulated that if a soluble salt has a negative heat of solution, the adsorption of some type of collector is possible. Salts which have negative heats of solution will respond favorably to amines, sulfonates, and alkyl sulfates. Strongly hydrated salts with a positive heat of solution will float with fatty acids. The heat of solution rule could not be tested for the very soluble lithium, calcium, and magnesium halides. Collectors, even short-chain ones like sodium octyl sulfate, are not soluble in saturated solutions of these salts. Therefore, it is important to know the solubility

of a salt in a saturated solution when applying the heat of solution rule. If the solubility is very high it may not be possible to dissolve the collector in the saturated solution.

Rogers proposed two mechanisms for the adsorption of collectors on the soluble alkali chlorides:

1. Exchange adsorption of the collector ions; either with the ions in crystal lattice of the alkali chlorides, or with the gegen ions in the double layer at the crystal surface.
2. Hydrogen bonding between the collector ions and the molecules of water of hydration attached to the ions at a crystal surface.

The heat of hydration theory presents several drawbacks. The values for the heats of solution given by Rogers correspond to those in dilute solutions. The heats of solution are very different in saturated solutions not only numerically, but even their signs may change. Heats of solution in saturated brines are in many cases still unknown and have not yet been subjected to tests.

Halbich⁽⁷⁾ has presented a mechanism involving the formation of an insoluble compound at the surface by

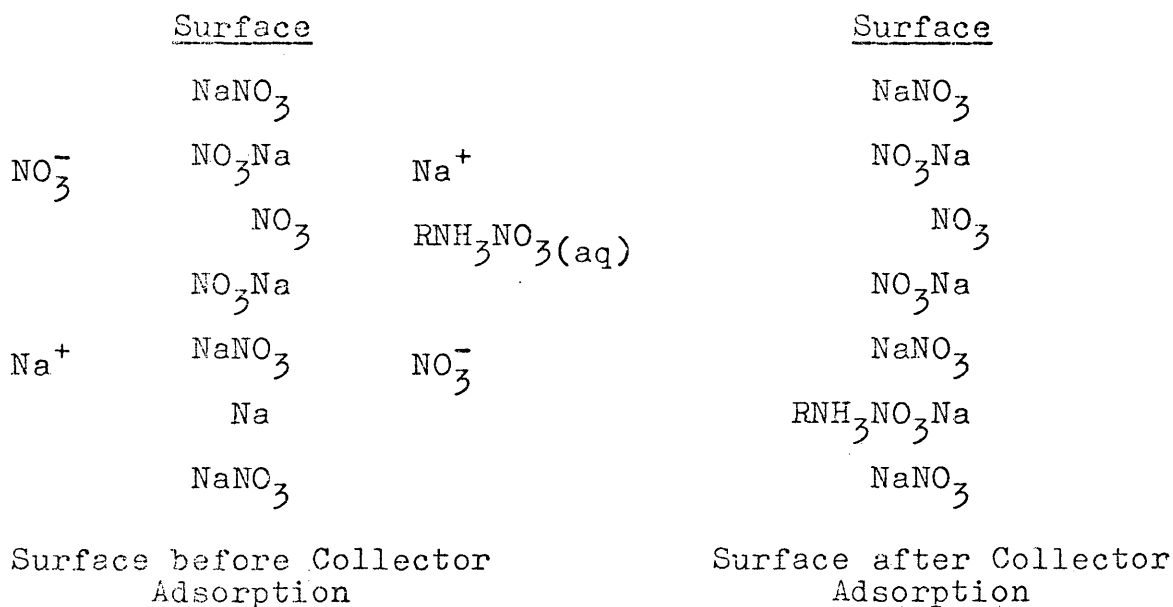
mutual neutralization of collector and salt ions. Several inadequacies have also been observed in salt flotation which cannot be explained by this mechanism.

Recently, R. J. Roman, M. C. Fuerstenau, and D. C. Seidel⁽⁸⁾ have suggested yet another mechanism that may be involved in soluble salt flotation. Their work involved the KCl and NaCl systems, and they showed rather clearly that an aqueous complex of amine chloride $\text{RNH}_3\text{Cl}_{(\text{aq})}$ was the species of amine that is probably responsible for flotation of KCl and that an aqueous complex of sodium carboxylate $\text{RCOONa}_{(\text{aq})}$ is probably the collector for NaCl. In addition, thermodynamic evidence was presented that indicated that solid particles of KCl and NaCl are oppositely charged in saturated brines. These phenomena were suggested to be responsible for the fact $\text{RNH}_3\text{Cl}_{(\text{aq})}$ would adsorb and probably fit into a chloride-vacant site on a positively charged KCl surface, while the negative end of the collector dipole would probably be repelled from the negatively-charged NaCl surface.

This present study is an extension of the KCl - NaCl work, and in view of the data that were obtained, the model presented by Roman, Fuerstenau, and Seidel⁽⁸⁾ appears to be overly simplified. This may be seen by examining first the KNO_3 and NaNO_3 systems. Just as with

KCl, potassium nitrate is floated with long-chain amines only after the collector is precipitated in solution (Figure 12). This fact suggests that $\text{RNH}_3\text{NO}_3(\text{aq})$ is probably the collector; that is, after precipitation of $\text{RNH}_3\text{NO}_3(\text{s})$ it seems logical that the following equilibrium will be present: $\text{RNH}_3\text{NO}_3(\text{s}) \rightleftharpoons \text{RNH}_3\text{NO}_3(\text{aq})$

Adsorption of this aqueous complex could then occur; actually it may fit into a vacant nitrate site as shown in the following schematic diagram:



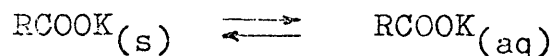
In the case of NaNO_3 , essentially no flotation could be obtained with any of the amines used. This fact was also observed in the case of NaCl .

When fatty acids were used to float NaNO_3 approximately 50 percent recovery was obtained with high

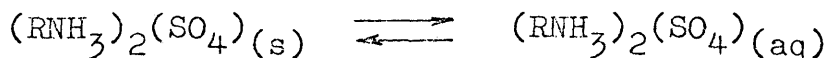
additions of caprylic acid in the absence of collector precipitation (Figure 6). With reference to Figure 8, it can be noted that this salt is also floated with octyl sulfonate before precipitation of sodium sulfonate and that after collector precipitation has occurred, recovery is reduced significantly. These facts suggest that the anionic collector ions, RCOO^- and RSO_3^- , are adsorbing on NaNO_3 .

Potassium nitrate is also floated with RSO_3^- , and it seems as if the adsorption of these collector ions may be due to electrostatic phenomena. It is not likely that adsorption could have occurred by hydrocarbon chain association, as suggested by Schubert,⁽⁹⁾ since it has been shown that the chain must contain at least 10 carbon atoms for this phenomenon to occur.⁽¹⁰⁾

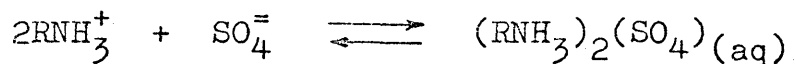
The collectors for K_2SO_4 appear to be RSO_3^- , $\text{RCOOK}_{(\text{aq})}$, and $(\text{RNH}_3)_2(\text{SO}_4)_{(\text{aq})}$. The aqueous complex, $\text{RCOOK}_{(\text{aq})}$ would be in equilibrium with $\text{RCOOK}_{(\text{s})}$ as described in the case of amine nitrate, that is



The equilibrium between solid and aqueous amine sulfate can also be described by



Another path for the formation may occur in these systems, especially in view of the divalency of sulfate, which is



Adsorption of $\text{RCOOK}_{(\text{aq})}$ could occur at a vacant K^+ site, while $(\text{RNH}_3)_2(\text{SO}_4)_{(\text{aq})}$ could occur at a vacant $\text{SO}_4^{=}$ site at the surface.

In view of the fact that the undissociated molecules $\text{RCOOK}_{(\text{aq})}$ and $(\text{RNH}_3)_2(\text{SO}_4)_{(\text{aq})}$ would probably be polarized as indicated, it would appear as if surface charge has little or no effect on the adsorption of such aqueous complexes, as was suggested previously with KCl and NaCl .⁽⁸⁾ The reasons for the adsorption of these species still remain to be learned.

In summary, it is apparent that the soluble salt flotation systems are exceedingly complex. By the very nature of these solutions, aqueous complexes of collector-salts are formed which are not normally encountered in flotation systems. In addition, the fact that these solutions contain from 5 to 10 times more water molecules than salt ions also presents phenomena not normally encountered, such as the fact that the electrical

double layer surrounding the solid particles is approximately only one ion thick. Obviously, much additional work is required before an understanding of the mechanisms of soluble salt flotation is achieved. This study is part of a long range program designed to gain this understanding.

CONCLUSIONS

1. Flotation experiments show that sodium nitrate floats well with octyl sulfonate. No substantial flotation was obtained with short-or long-chain amines. Of the carboxylates, only caprylic acid floated sodium nitrate and only to a relatively minor extent.
2. Potassium nitrate floats well with amines and octyl sulfonate. Carboxylic acids do not float potassium nitrate well even with relatively high collector additions.
3. Potassium sulfate floats well with amines and octyl sulfonate. With carboxylic acids, only oleic acid yields good flotation recoveries.
4. On the basis of results obtained in pure systems of sodium nitrate and sodium chloride in a nitrate-chloride brine, a flotation separation of these two salts should be possible with alkyl sulfonate.

5. In the flotation of soluble salts, collector adsorption occurs by more than one mechanism. In some cases collector anions are adsorbed, while in others aqueous complexes, such as $\text{RNH}_3^+\text{NO}_3^-(\text{aq})$ and $\text{RCOOK}(\text{aq})$, are probably the species responsible for flotation.
6. Although no satisfactory experimental technique is available for the determination of surface charge in soluble salt systems, this property should not be ignored. That is, it seems likely that in some cases the adsorption of collector anions is controlled by electrostatic phenomena.
7. A theoretical study of thermodynamic properties such as lattice energies and hydration of surfaces in brines appears to be required before an understanding of these complex systems will be achieved.

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