

FLOTATION OF ANDALUSITE
WITH OLEIC ACID AND PETROLEUM SULFONATE

by

Eung Ha Cho
(Visiting Professor)

FOREWORD

This study was conducted by Dr. Eung Ha Cho, Professor, Mineral Processing Engineering Department, West Virginia University, Morgantown, WV 26506, during the period of June 1, 1989 - July 31, 1989 at the North Carolina State University, Minerals Research Laboratory, Asheville, NC 28801.

FLOTATION OF ANDALUSITE
WITH OLEIC ACID AND PETROLEUM SULFONATE

by

Eung Ha Cho
(Visiting Professor)

ABSTRACT

The flotation of andalusite with each petroleum sulfonate and oleic acid has been studied with a Hallimond cell. Also, the zeta potential of this mineral has been measured in the presence of each of these anionic collectors. In both systems, the concentration of petroleum sulfonate was 3.6×10^{-4} molar and those of oleic acid were 8.7×10^{-5} and 4.4×10^{-4} molar.

It has been found that andalusite can be floated almost completely below its pzc (pH=5.5). The adsorption of petroleum sulfonate on the positively charged surface below its pzc is considered to be by physisorption. It has also been found that the flotation of andalusite with oleic acid occurs with a maximum recovery around pH 7. It appears that two models can explain this flotation peak, one for the autoactivation and the other that advocates the adsorption of surface active acid-soap dimer which gives a concentration maximum around pH 8.

INTRODUCTION

Andalusite is a aluminosilicate mineral with the chemical composition of $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$. The mineral has the orthosilicate structure where chains of aluminum-oxygen octahedra are linked laterally by silicon and aluminum atoms.

Andalusite can be floated with anionic and cationic collectors. Choi and Oh (1,2) made a detailed investigation and comparison of the surface properties of andalusite and kyanite and correlated these with simple flotation tests. They found good flotation of andalusite with oleic acid between pH 4 and pH 9 with rapid decline outside this range. Manser (3) shows that andalusite can be floated with dodecylamine in pH between 3 and 10 and that sodium fluoride activates this cationic flotation.

This study is concerned with the flotation response of andalusite with each oleic acid and petroleum sulfonate and correlation of these with variation of surface charge of the mineral when contacted with the solution containing each of these anionic collectors.

EXPERIMENTAL

The andalusite sample obtained from China was used in this study. Lumps of the mineral was crushed with a hammer and ground in an automatic pestle and mortar. This ground material was screened to obtain a size fraction of 65 -200 mesh. This size fraction was treated with a magnetic separator to remove magnetic impurities, and then deslimed by decantation. This size fraction was used for all the flotation tests in this study. The result of chemical analysis on the sample shows that Al_2O_3 is 60.3 percent; SiO_2 , 38.3 percent; and Fe_2O_3 , 0.25 percent. The mineral composition of the sample was estimated by comparing these values

with the values in pure andalusite under the assumption that there were no other aluminum-containing minerals. The sample would contain 95.8 percent andalusite, 1.2 percent quartz, and 3 percent other minerals.

Oleic acid was diluted with methanol to control the small dosages of the reagent for the experiments. The petroleum sulfonate with the molecular weight of 490 and the purity of 85 percent was diluted with water and used in this study. The rest of the composition of the sulfonate was basically mineral oil.

Sample preparation for the zeta potential measurement included dry grinding of the size fraction of the mineral with a pestle and mortar. One hundred mg of this material was conditioned for 10 minutes in 100 ml of solution containing oleic acid or petroleum sulfonate. HCl or NaOH was used to adjust the solution pH. The sample was allowed to settle for 5 minutes, and then the pH was measured. The suspension was used for the zeta potential measurements.

Flotation was effected with the equipment and the technique described in the literature (4). A 2.5 g sample of andalusite was conditioned for 10 minutes in a 100 ml solution containing a desired amount of oleic acid or petroleum sulfonate. The pH of the solution was adjusted by adding HCl or NaOH. After the conditioning, the system was left unstirred for 3 minutes, then the pH was measured, and this was recorded as the flotation pH. Then the pulp was transferred to a Hallimond cell and the flotation was effected for one minute with a flow rate of 1 ml/sec.

RESULTS AND DISCUSSION

The variations of zeta potential of andalusite with pH in the absence and presence of petroleum sulfonate are compared in Figure 1. One can see from this figure that the zeta potential of the

mineral is reduced greatly and reversed in the presence of 3.6×10^{-4} molar petroleum sulfonate below its pzc (pH = 5.5). One can also see from Figure 1 that the zeta potential is still reduced above its pzc, the reduction decreases as the pH increases, and no reduction is observed above pH 8. The reduction and reversal of zeta potential below its pzc is a clear indication that the anion of sulfonate adsorbs on the positively charged surface by electrostatic attraction. However, the fact that the anion of sulfonate adsorbs on the negatively charged surface at pH between 5.5 and 8 is likely an indication that the adsorption is by the effect of the hydrocarbon chain in the sulfonate. It is reminded that the petroleum sulfonate used in this study is a collector with a long hydrocarbon chain with the molecular weight of 490.

The adsorption of petroleum sulfonate below its pzc and the small but significant adsorption at pH between 5.5 and 8 are reflected in the flotation recovery as shown in Figure 2. One can see from Figure 2 that the flotation is virtually complete below pH 5 and virtually nil above pH 7. The effect of hydrocarbon chain on the adsorption of the sulfonate and thus on the flotation recovery is clearly demonstrated by the significant flotation recovery values above its pzc. The recovery values are 93 percent at pH 5.5, 75 percent at pH 6, and 35 percent at pH 6.5.

Figure 3 shows the variations of zeta potential of andalusite with pH in the absence and presence of oleic acid. One can see from this figure that the reduction in the zeta potential results from contacting with oleic acid in solution over a wide range of pH (3 to 11). This reduction indicates that oleic acid adsorbs on andalusite over the wide range of pH. Now, the reduction in the zeta potential can be compared with the flotation recovery of andalusite as shown in Figure 4. One can see from Figure 3 that the reduction in the zeta potential is much greater at pH between 3 and 5.5 than at pH between 5.5 and 11. However, since the flotation occurs with a maximum around pH 7, it can be seen that the reduction is not consistent with the flotation recovery.

There are two models with which the flotation of andalusite with oleic acid as shown in Figure 4 can be explained. One model is by autoactivation by Fuerstenau and Palmer (5). This model involves the mechanism in which chemisorption occurs by: (1) slight mineral dissolution followed by hydrolysis of the contained metal ions to hydroxy complexes, (2) adsorption of hydroxy complexes by either hydrogen bonding or water formation, and (3) collector adsorption on these metal ion sites.

The other model (6) is that acid-soap dimer, $(RCOO)_2H^-$ with a concentration maximum around pH 8, is extremely surface active. Adsorption of acid-soap dimer around pH 8 leads to the maximum flotation at this pH. As a matter of fact, many minerals give a flotation peak around pH 8 with oleic acid. These include hematite, columbite, zircon, tantalite, ilmenite, rutile, and garnet. It is noteworthy here that the flotation peak of hematite at pH 8 cannot be explained by the autoactivation mechanism. The reason is that upon slight dissolution of hematite, ferric ion might be produced and that $FeOH^{2+}$, first hydroxy complex of ferric ion, forms predominantly around pH 3.

It may be worth mentioning here the flotation of quartz in the presence of aluminum ion with sulfonate (5). It has been observed from the flotation that the pH range in which at least 90 percent recovery is obtained falls between 3.8 and 8.4. This pH range is virtually coincided with the pH range to give favorable flotation as shown in Figure 4. It has been also observed that andalusite can release an appreciable amount of aluminum ions in an acid or a basic solution (7). These observations may induce one to believe that the flotation of andalusite with oleic acid is due to the autoactivation.

It is reminded that the reduction in the zeta potential as shown in Figure 3 is not consistent with the flotation recovery as shown in Figure 4. This inconsistency may be explained by the adsorption of acid-soap dimer around pH 7 which has lower negative charge than oleate ion per hydrocarbon chain, R, and by the

adsorption of oleate ion between pH 3 and 5.5. If this is the case, two models, one for the autoactivation (5) and the other that advocates the adsorption of acid-soap dimer (6) seem to be both responsible for the flotation of andalusite with oleic acid, which gives a maximum recovery around pH 7.

SUMMARY

Andalusite can be floated with sulfonate below its pzc (pH 5.5). The adsorption of anionic sulfonate on the positively charged andalusite surface below its pzc is considered to be by physisorption. The flotation peak of andalusite with oleic acid occurs around pH 7. This flotation peak may be due to the two adsorption models, one for the autoactivation and the other that advocates the adsorption of surface active acid-soap dimer, which gives a concentration maximum around pH 8.

REFERENCES

1. H. S. Choi and J. H. Oh, "Surface Properties and Floatability of Kyanite and Andalusite," J. Inst. Min. Metall. Japan, 1965, 81 (927), pp. 614-620.
2. H. S. Choi and J. H. Oh, "Effect of the Weighed Average Charge of Surface Metallic Atoms on the Isoelectric Point of Kyanite, Andalusite, and Sillimanite," J. Inst. Min. Metall. Japan, 1966, 82 (941), pp. 755-762.
3. R. M. Manser, Handbook of Silicate Flotation, 1975, pp. 38, Warren Spring Laboratory.
4. D. W. Fuerstenau, P. H. Metzger and G. D. Seele, "How to Use This Modified Hallimond Tube...", Engineering and Mining Journal, March 1957, pp. 93-95.
5. M. C. Fuerstenau and B. R. Palmer, "Anionic Flotation of Oxides and Silicates," Flotation Volume 1, M. C. Fuerstenau (editor), Chapter 7, 1976, AIME.
6. K. Ananthpadmanabhan, P. Somasundaran, and T. W. Healy, "Chemistry of Oleate and Amine Solutions in Relation to Flotation," AIME Trans., 1979, Vol. 266, pp. 2003-2009.
7. T. J. Smolik, Harman, and D. W. Fuerstenau, "Surface Characteristics and Flotation Behavior of Aluminosilicates," SME Trans., 1966, Vol. 235, pp. 367-374.

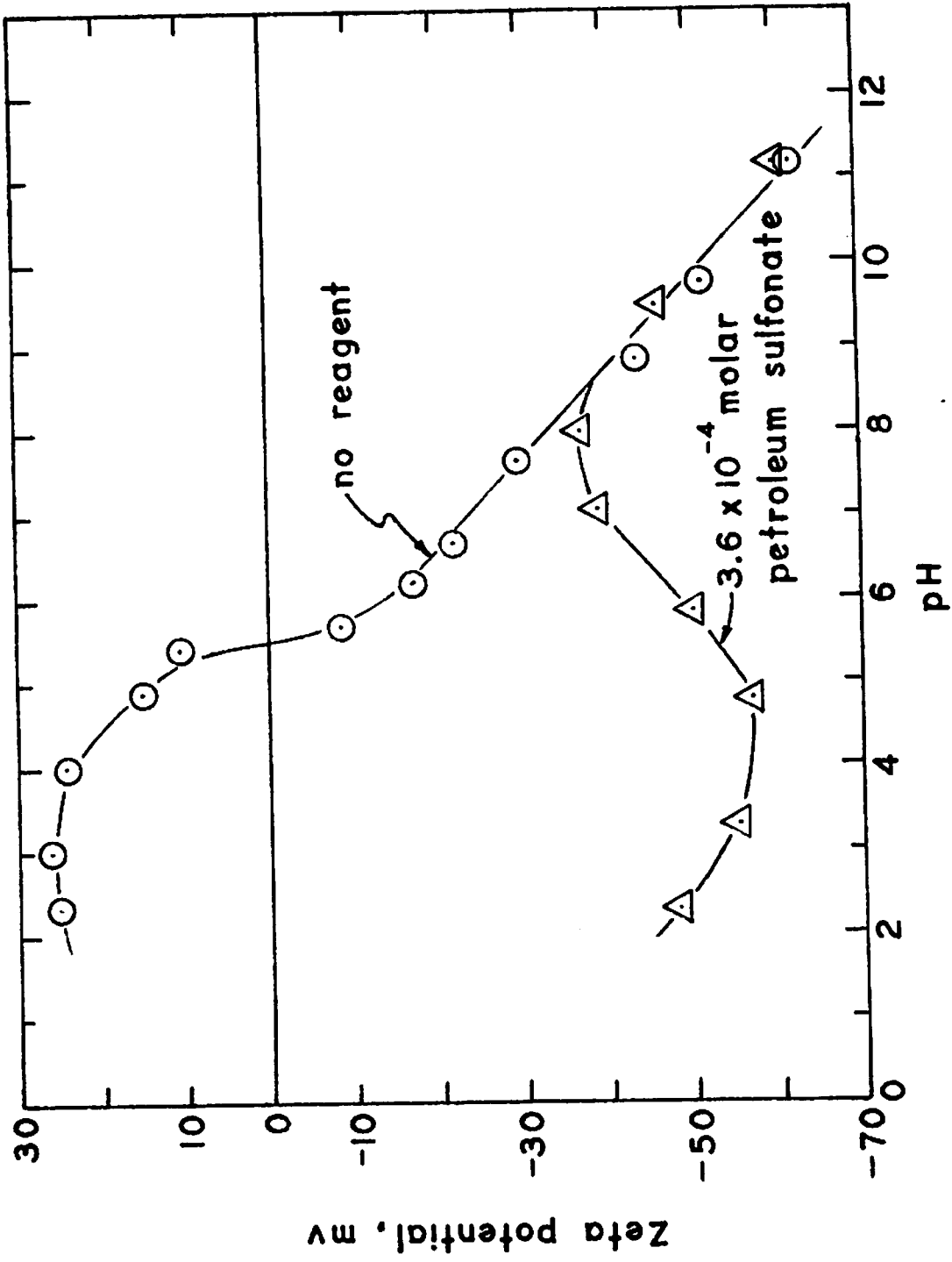


Figure 1. Zeta potential of andalusite as a function of pH in the absence and presence of petroleum sulfonate.

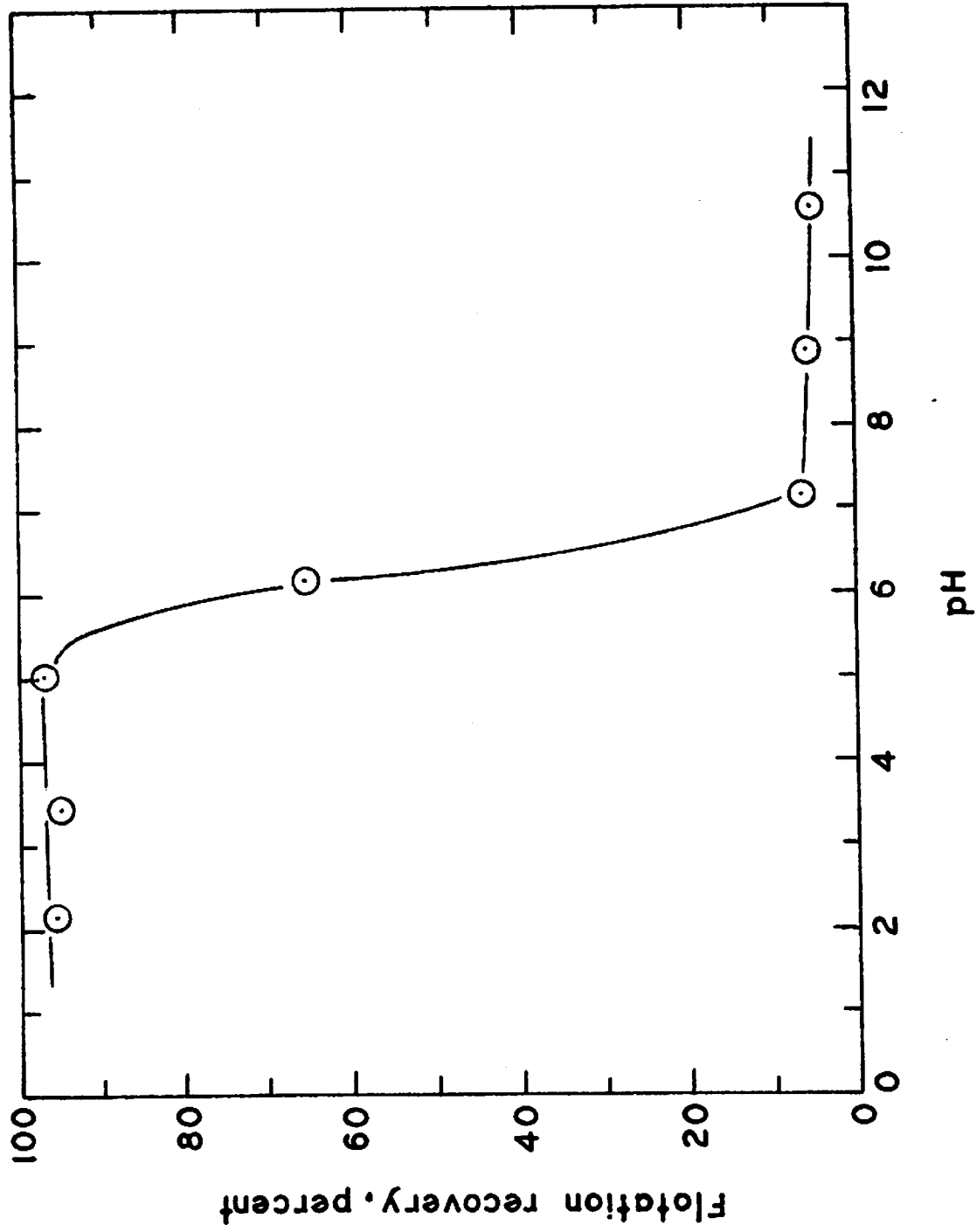


Figure 2. Flotation recovery of andalusite as a function of pH with 3.6×10^{-4} molar petroleum sulfonate.

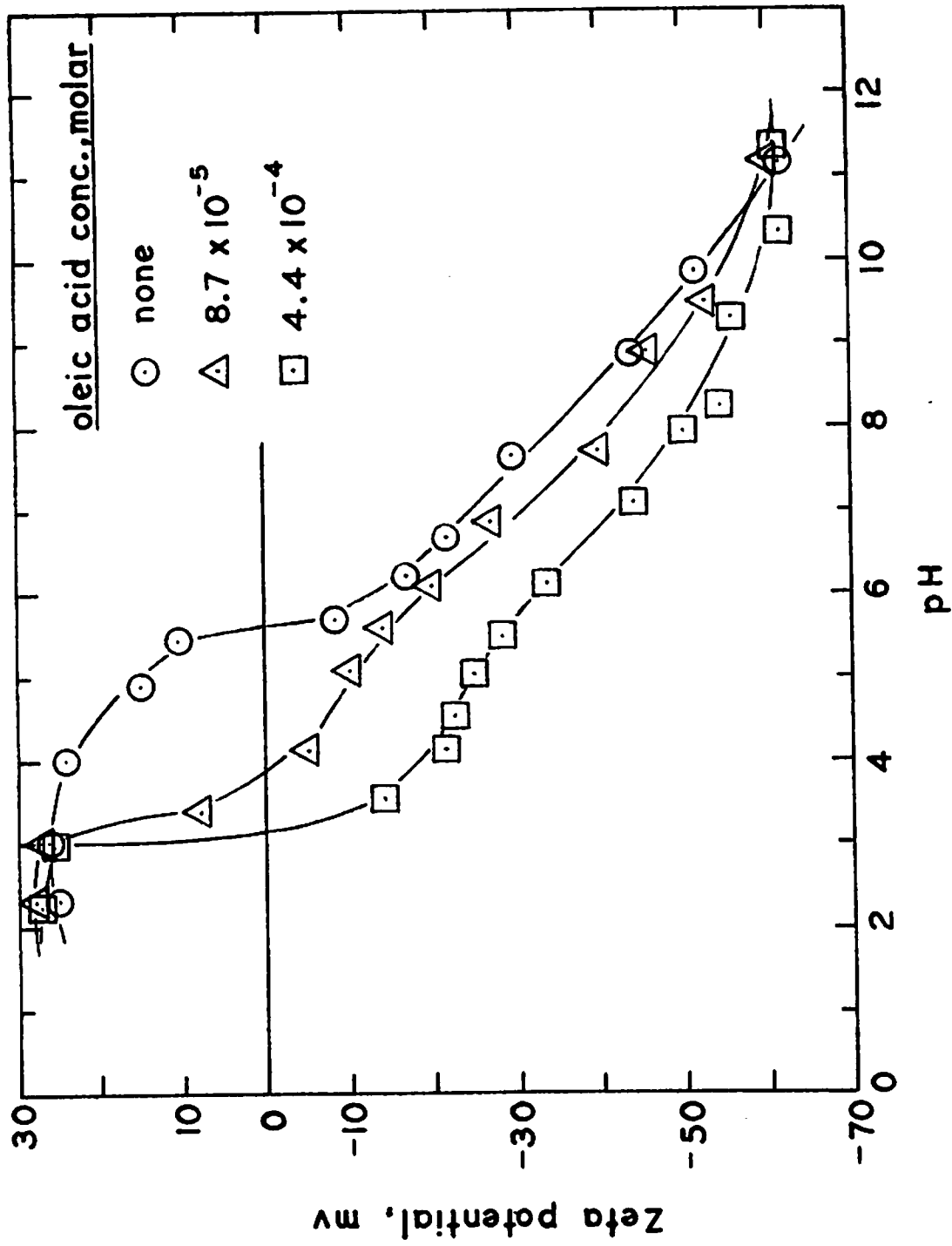


Figure 3. Zeta potential of andalusite as a function of pH in the absence and presence of oleic acid.

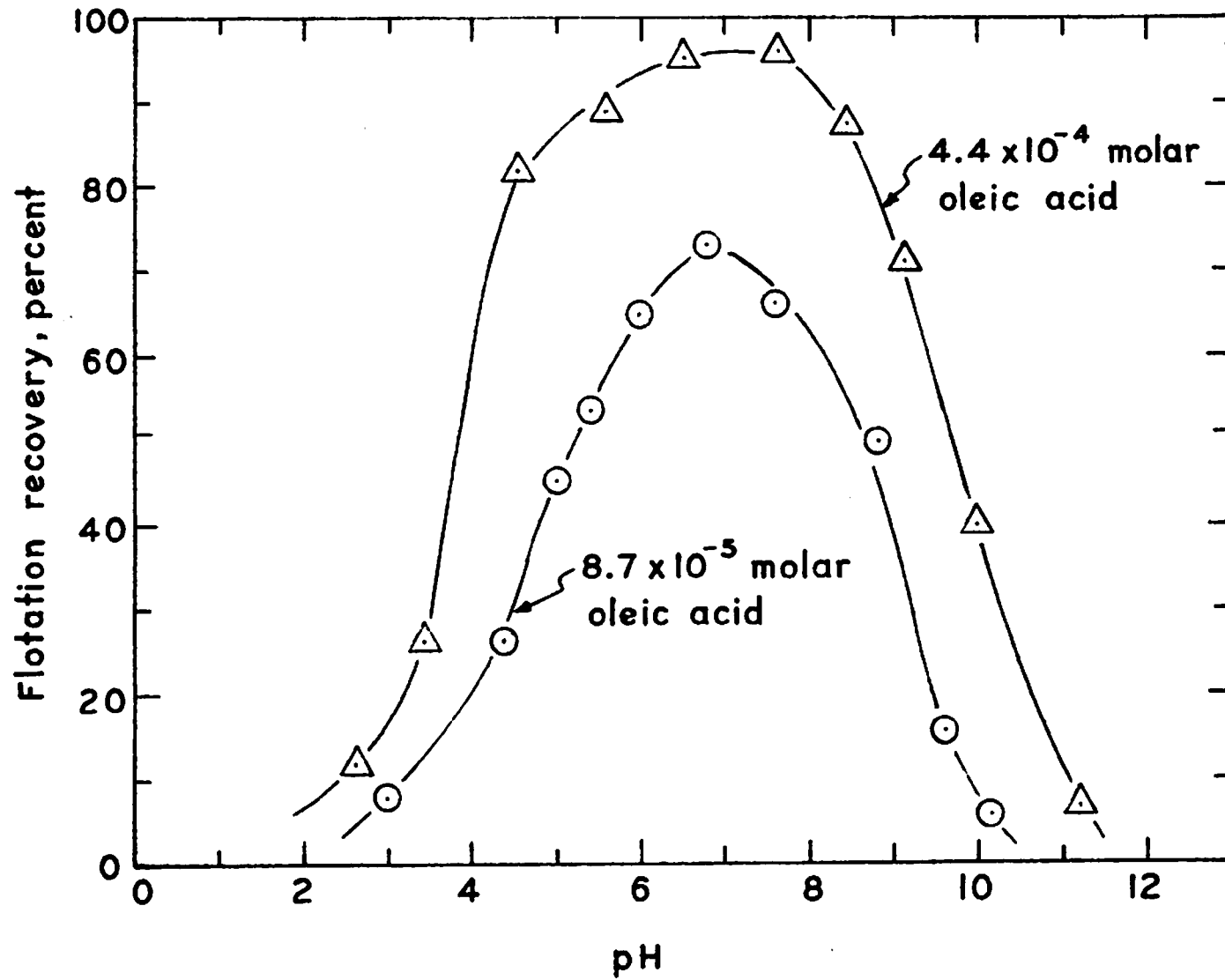


Figure 4. Flotation recovery of andalusite as a function of pH with oleic acid.