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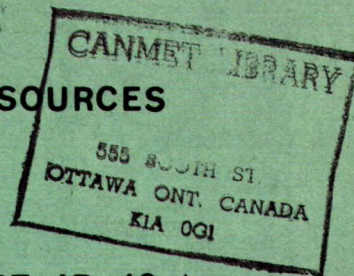
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STUDY OF THE ELECTROKINETIC PROPERTIES AND FLOATABILITY OF A SAMPLE OF NATURAL CORUNDUM

by

A. PAGE

MINERAL PROCESSING DIVISION

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ABSTRACT

The electrokinetic properties of natural corundum (Al_2O_3) in a supporting electrolyte of sodium chloride were studied using an automated potentiometric titration apparatus. The zero-point-of-charge was found to occur at a pH of 6.2.

Using a modified Hallimond tube, the floatability of corundum was determined as a function of pH for an anionic and cationic collector. The collector ions function as counter ions in the double layer, consequently an anionic collector must be used when corundum is positively charged and cationic when it is negatively charged.

The results obtained show that the electrokinetic data of corundum can be used to predict its floatability in an aqueous system.

*Senior Mineral Research Technician, Metallic Minerals Research Laboratory, Mineral Processing Division, Department of Energy, Mines and Resources, Ottawa, Canada.

INTRODUCTION

Theory

The lattice of corundum consists of oxygen atoms arranged approximately in hexagonal closest packing with the close-packed layers parallel to (0001). The cations lie between these layers. The aluminum atoms occupy two thirds of the available octahedral holes. Each oxygen atom is coordinated by four aluminum atoms and each aluminum atom is coordinated by six oxygens. The lattice structure of corundum is shown in Figure 1.
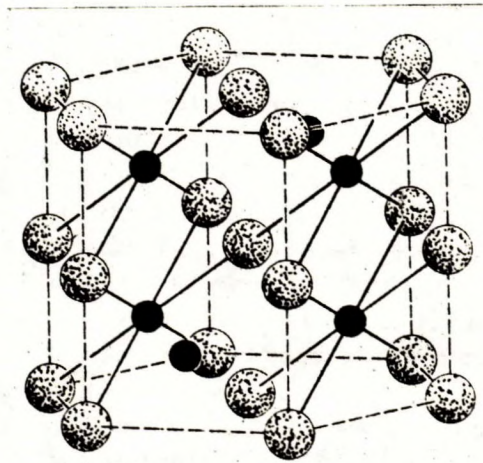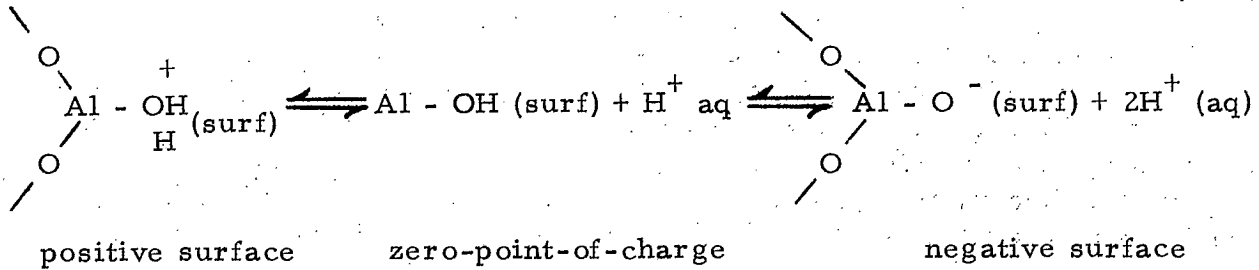

Figure 1. Lattice Structure of Corundum.

After the mineral is fractured, some aluminum atoms at the surface will not be surrounded by six oxygen atoms, and some oxygen atoms will not be surrounded by four aluminum atoms. If the mineral is placed in an acqueous solution, there will be a transfer of ionic species to the solid phase. As in the case of most insoluble mineral oxides, the potential-determining ions of corundum are H^+ and OH^-. Hydrogen ions will migrate to the oxygen atoms in the lattice structure that have an incomplete coordination of atoms. Similarly, hydroxyl ions will be transferred to the aluminum atoms. Consequently, surface hydroxides are produced which may ionize as an acid or a base.

A two-step process involving surface hydration followed by dissociation of the surface hydroxide has been advocated by O'Connor [1] et al as the mechanism by which the surface charge is established.

Schematically, this dissociation of the hydrated surface to produce a charged surface may look like this:

$$\begin{array}{c}\backslash\\ O\backslash\\ Al - OH^{+}_{\substack{\\H}}(surf)\\ /\\ O\\ /\end{array} \rightleftharpoons Al - OH\ (surf) + H^{+}\ aq \rightleftharpoons \begin{array}{c}\backslash\\ O\backslash\\ Al - O^{-}\ (surf) + 2H^{+}\ (aq)\\ /\\ O\\ /\end{array}$$

positive surface   zero-point-of-charge   negative surface

When predicting the effectiveness of an ionic collector in froth flotation, a most important parameter is the zero-point-of-charge of the mineral species. Because the collector ions function as counter ions in the double layer, a cationic collector must be used when the mineral species is negatively charged, and an anionic collector when positively charged. Adsorption of the collector ions will increase as the surface charge increases. Consequently, in order to produce hydrophobic surfaces, which should result in a high flotation recovery, the zeta potential must be sufficiently high to attract a large number of collector ions.

The purpose of this report is to show that there is a definite relationship between the floatability of corundum and its surface characteristics as obtained through electrokinetic studies.

EXPERIMENTAL PROCEDURES

(a) Sample Preparation

The natural corundum used in this study was obtained from the
Geological Survey of Canada, Ottawa, Ontario. Crystal fragments of
relatively pure corundum were hand-picked from the ore and reduced to
minus 14 mesh by means of a cone crusher. The corundum was cleaned
as follows:

a)   The iron impurities introduced during crushing were removed
     with low- and high-intensity magnetic separators.

b)   the non-magnetic fraction was treated by heavy liquid (methylene
     iodide - specific gravity 3.33) to remove orthoclase feldspar,
     muscovite and biotite.

c)   the sink fraction was then ground down and separated into eight
     size fractions between 48 and 400 mesh.

d)   the 48 to 65-mesh fraction was leached in concentrated HF (48%)
     at room temperatures for a period of 52 hours to remove any
     remaining silicates.

e)   this sample was washed thoroughly with double-distilled water and
     finally stored in boiled double-distilled water. The sample was
     purged with nitrogen gas periodically.

f)   just prior to the experimental work, this fraction was dried under
     vacuum at 140°F and stored in a nitrogen atmosphere.

All tests were done using the 48 to 65-mesh fraction (specific gravity
3.95).

Microscopic examination of a polished section of this fraction
showed impurities in only 1% of the particulates. As Figure 2
indicates, the apparent impurities are imbedded within the particles and
therefore would not affect the surface characteristics. An X-ray diffraction
analysis showed high crystallinity and no indication of a second phase.

All inorganic chemicals were of reagent grade and were used
without further purification.

Figure 2. Polished sections of -48+65 mesh fraction, magnification X140.

(b) Potentiometric Titrations

The zero-point-of-charge of corundum was determined using an automated potentiometric titration apparatus which was designed and built at the Mines Branch. The theory of operation of this apparatus is described in detail by Sirois et al (2) and will not be treated in depth here. There are many automatic titrators in use and their main function is to titrate to a predetermined end-point on a continuous basis. However, the apparatus used in this study is designed to permit the system to come to a relative equilibrium between the addition of each aliquot of titrant.

All adsorption tests were done in a 600-ml reaction vessel (beaker),containing glass and reference pH electrodes, thermo-compensator, teflon-covered impeller, and two glass delivery tubes (one for nitrogen and the other for titrant; see Figure 3. The complete apparatus, (a) reaction vessel, (b) pH meter, (c) strip-chart recorder, (d) programable power supply, (e) control box with meter relay, (f) titrant injector, is shown in Figure 4.

Sodium chloride (ionic strength 0.01) was used as a supporting electrolyte throughout the study. Three hundred and fifty milliliters of the supporting electrolyte were added to the reaction vessel, and a pH of 7 was attained by purging with nitrogen gas. The nitrogen tip was then retracted above the surface of the solution and 15.0 grams of 48 to 65-mesh corundum were introduced. After the system had approached equilibrium, the first aliquot of titrant was added manually; all subsequent additions were automatic.

The titrants were hydrochloric acid (2×10^{-2} N) and sodium hydroxide (10^{-2} N).

The nitrogen gas was passed through a purification train which consisted of:

a) 10% KOH,
b) 10% HCl,
c) 2 flasks containing distilled water,
d) 1 flask containing glass wool (to remove fine water droplets).

The gas was used to produce an inert atmosphere above the suspension to prevent the absorption of carbon dioxide. Absorption of carbon dioxide in an aqueous system will generate a dilute solution of carbonic acid thereby decreasing the pH.

By titrating with and without solids, and plotting the equivalents of titrant added against the resulting equilibrium pH in each case, the equivalents of titrant adsorbed is determined at any pH.
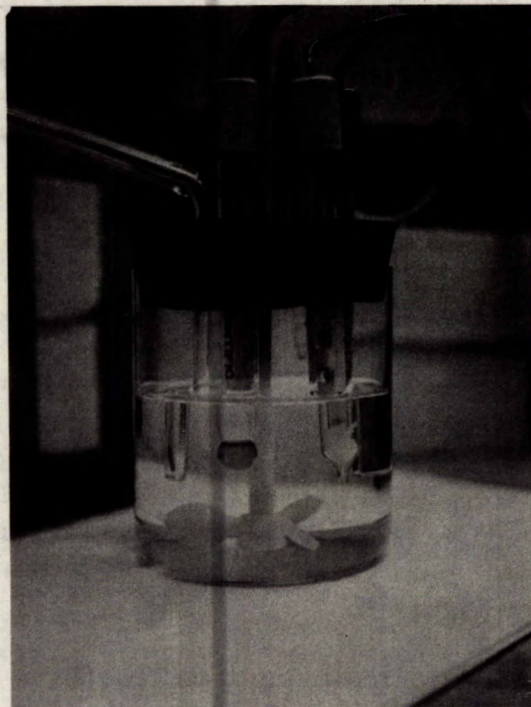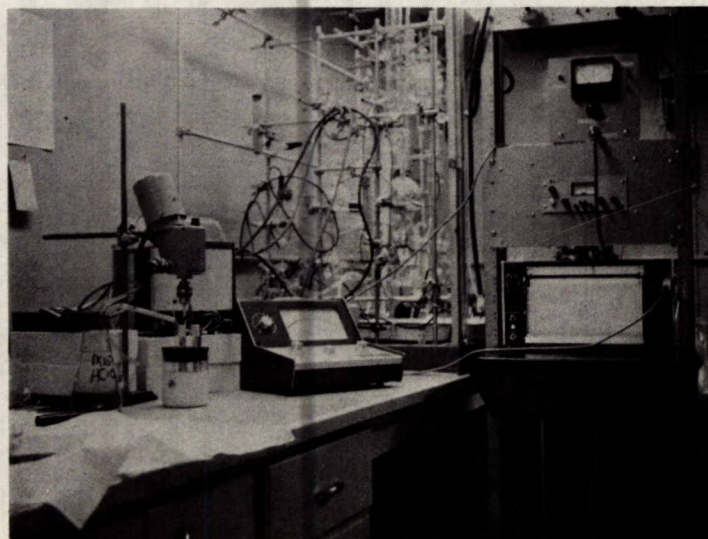
Figure 3. Reaction Vessel.

Figure 4. pH Meter with Electrodes in Reaction Vessel,
Coupled to Strip-Chart Recorder.

(c) Flotation Tests

All flotation tests were done in an inert nitrogen atmosphere with a modified Hallimond tube which permitted close control of all variables encountered in flotation. Experimental results were reproducible to within 3%.

The experimental procedures were as follows:

a) a one-gram sample of corundum was added to a 200-ml volumetric flask which was filled to the mark with distilled water.

b) a volume of water equal to the volume of reagents to be added was removed from the flask and the mineral was allowed to condition for three minutes on a wrist-action shaker.

c) the pH was adjusted using HCl or NaOH and the mineral conditioned again for two minutes.

d) the collector was then added with a further conditioning of two minutes. When using the cationic collector the addition of a frother was necessary (one ml of methylisobutylcarbinol, 1.5 mg/ml).

e) The mineral and solution were then placed in a dry box (in a nitrogen atmosphere) and 60 mls of solution was removed for pH measurement, the remainder was transferred to the Halimond tube.

f) Following a further two-minute conditioning period in the cell, nitrogen gas was passed through the porous glass plate for 16 sec at a flow rate of 43.5 cc/min and the corundum was floated.

g) After each test the float and non-float were collected, filtered, dried, and weighed to calculate the per cent recovery.

The nitrogen gas used for flotation was cleaned in the manner described previously.

Experimental Results and Discussion

The surface charge σs (coulombs/cm^2) may be calculated from the following equation:

$$\sigma s = F (\Gamma H^+ - \Gamma OH^-)$$

where F = Faraday's constant (96,501 coulombs) and

ΓH^+ and ΓH^- = adsorption densities (equivalents per cm^2).

Because accurate surface-area measurements are difficult to obtain when dealing with such large particles (48 to 65-mesh) the adsorption densities are plotted in arbitrary units as shown in Figure 5.

Potentiometric titration of a mineral suspension will permit the determination of the zero-point-of-charge and the surface charge as a function of pH. In order to calculate the zeta potential one must have complete information concerning the double-layer (thickness of Stern Layer, location of plane of shear). Such a calculation would result in a highly theoretical value and was not done here.

The experimental data which are presented in Figure 5, show that increasing the pH from 5.0 to 6.2 causes the adsorption density to decrease from a high positive value to zero and decreasing the pH from 10.0 to 6.2 causes the adsorption density to decrease from a high negative value to zero. Thus the zero-point-of-charge of the sample of corundum under investigation was found to occur at a pH of 6.2.

The flotation tests were done using an anionic and cationic organic electrolyte as collectors, sodium alkylarylsulfonate and trimethyldodecyl-ammonium chloride respectively. These collectors were selected because they are strong electrolytes and therefore do not hydrolyze over the pH range under study.

The effect of the concentration of sodium alkylarylsulfonate and trimethyldodcylammonium chloride on the flotation recovery of corundum was determined at two constant pH values, 4 and 10. As seen from Figure 6, the minimum concentration of the anionic collector that will effect a recovery over 95 per cent at pH 4 is 0.05 grams per liter. At a pH of 10, 1.32 grams per liter of the cationic collector effected a flotation recovery of 100 per cent, as shown in Figure 7. Using the above concentration of each collector, two series of flotation tests were done to determine the effect of hydrogen-ion concentration on flotation recovery. Figure 8 illustrates the results. The recovery of corundum decreased from 92% at a pH of 5.5 to 15% at a pH of 6.2 using sodium alkylarylsulphonate as collector. The recovery decreased from 100 per cent at pH 10 to less than one per cent at a pH of 6.2 for the cationic reagent. Superimposed on the recovery curves is the charge density curve shown in Figure 5. It is readily seen that there is a close relationship between the flotation recovery and the adsorption density, both expressed as a function of pH. The anionic collector, which is not as selective as the cationic collector, shows a recovery of 15 per cent at the zero-point-of-charge, and therefore does not follow the adsorption density curve as closely as was expected. However, there is the correct trend showing that as the charge density decreases the floatability also decreases. The exact composition of the anionic collector, as the name suggests, is not known.
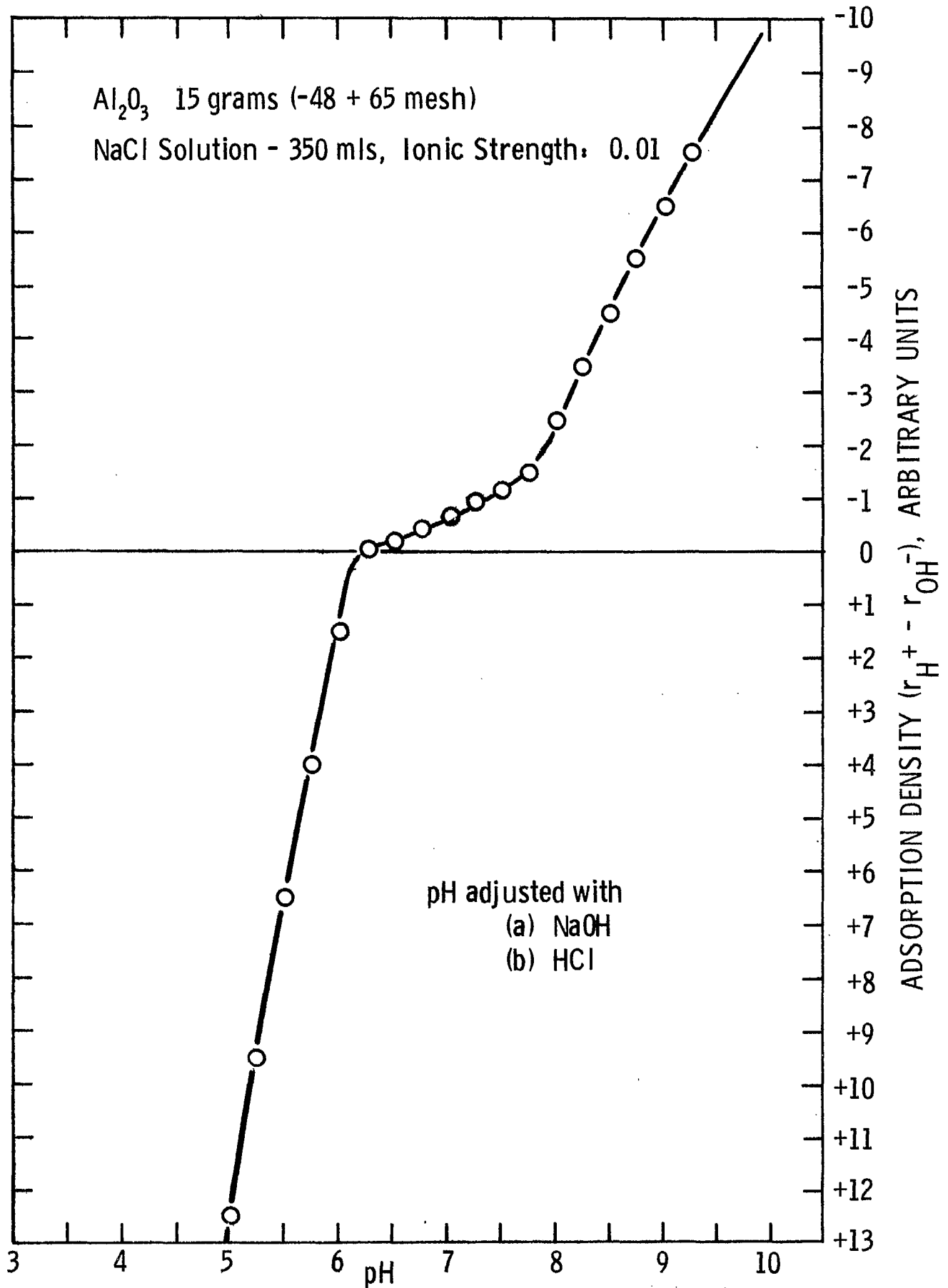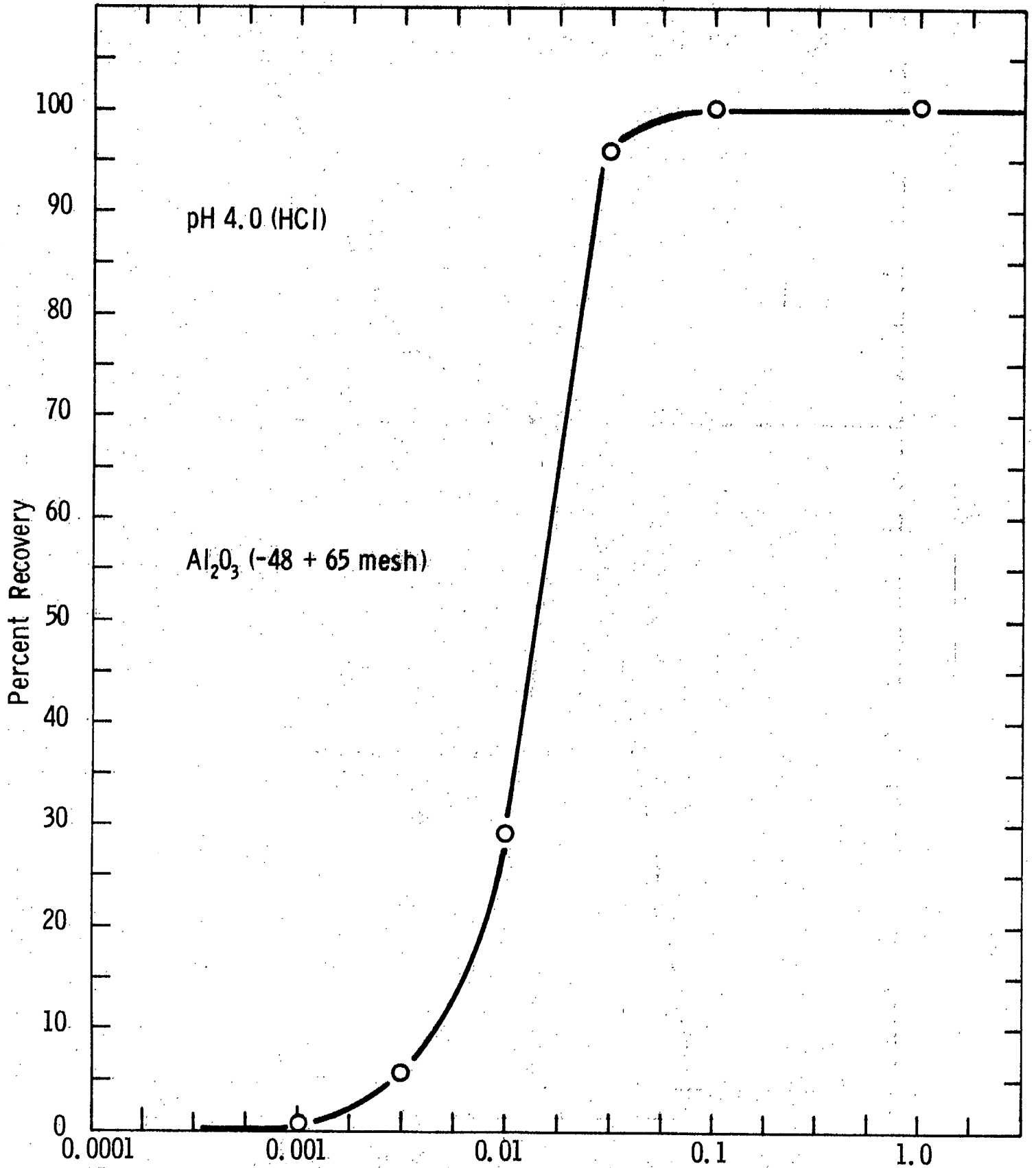
Figure 5. Adsorption Curve for Corundum Sample.

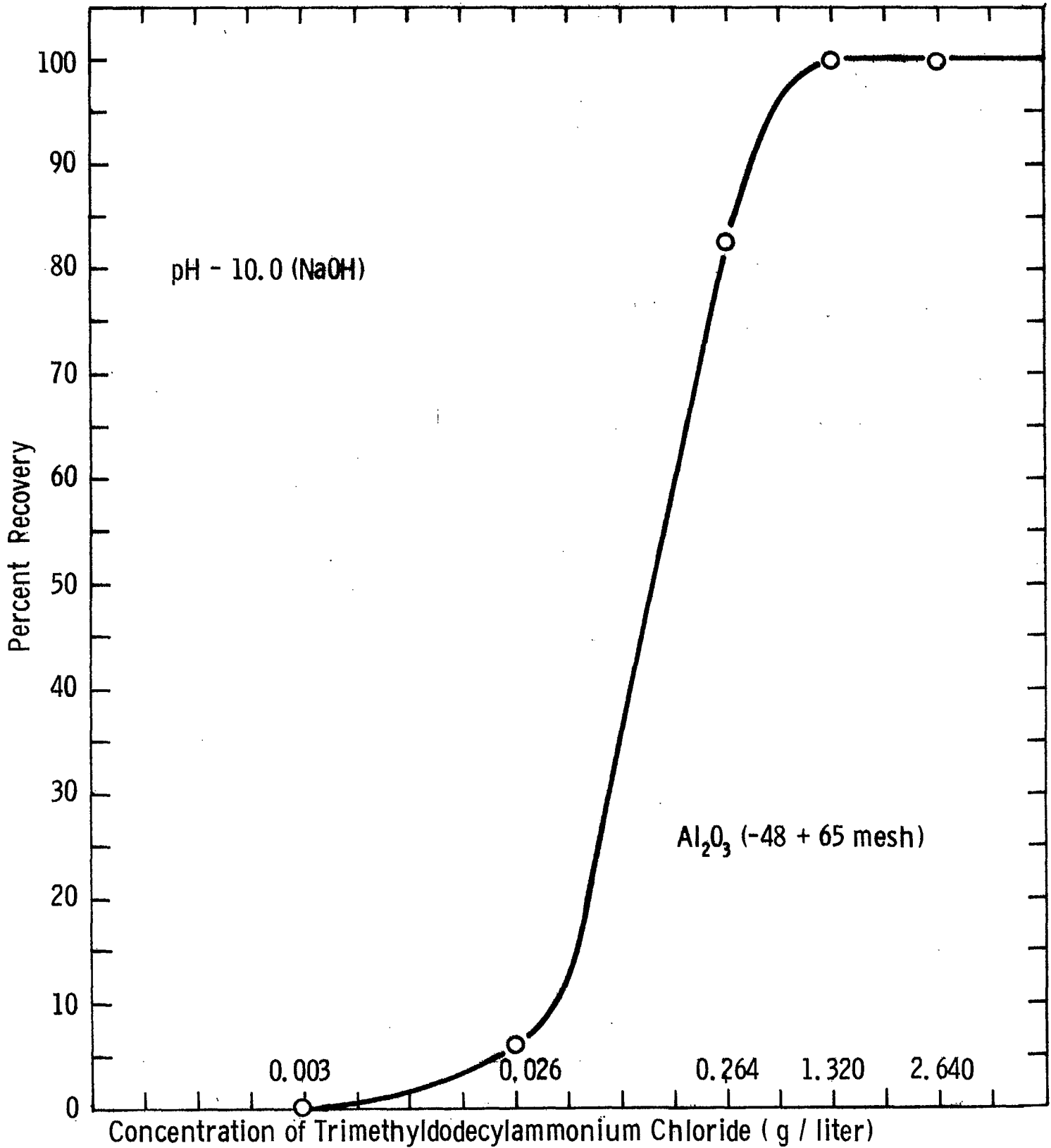Figure 6. Concentration of Collector vs Percent Recovery of Corundum.

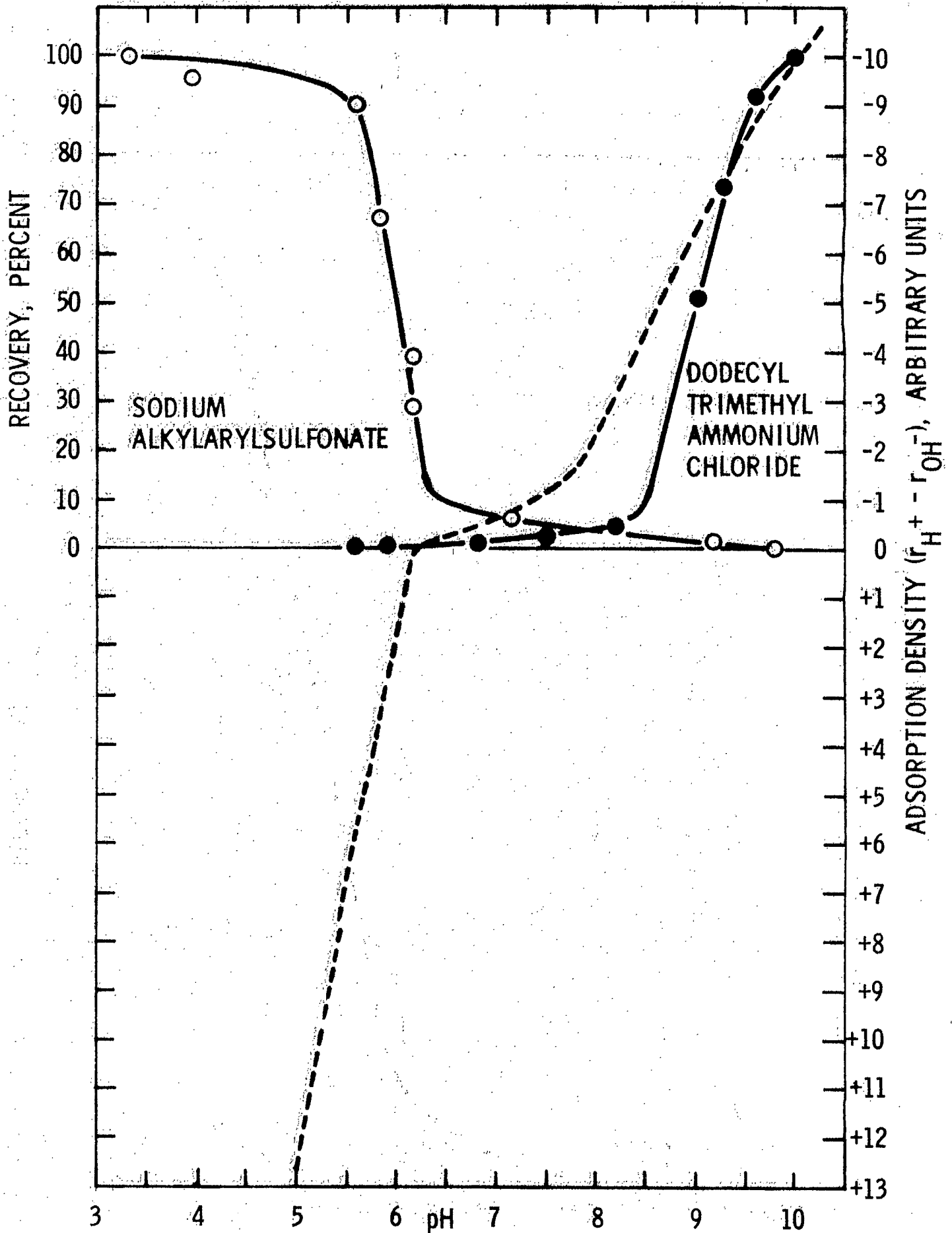Figure 7. Concentration of Collector vs Percent Recovery of Corundum.

Figure 8. Effect of pH on the Recovery of Corundum at Constant Collector Concentration.

CONCLUSIONS

By means of potentiometric titration, the charge density curve of corundum was obtained and its zero-point-of-charge was found to occur at a pH of 6.2. Flotation tests, using both an anionic and cationic collector produced results which were in agreement with the electrokinetic data. Consequently, the importance of electrokinetic data is demonstrated not only to predict the type of collector required but also to determine relative flotation efficiencies.

REFERENCES

1. D.J. O'Connor, P.G. Johanson, and A.S. Buchanan, Transaction Faraday Society, 52, 229 (1955).

2. L.L. Sirois, G.E. Alexander, A.P. Page and A.A. Winer, "Development of an Automated Potentiometric Titrator for the Study of Surface Electric Phenomena", MPI (P) 68-41.

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