

University of Nevada

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Adsorption Study of Amphoteric Surfactants On
Mineral Surfaces Using Infrared Spectroscopy

A thesis submitted in partial fulfillment of the
requirements for the degree of Master of Science
in Metallurgical Engineering

by

Satish Kumar Khanna

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The thesis of Satish Kumar Khanna is approved: *and very interesting to work with him. I am also pleased to see for his personal and professional progress in the investigation.*

P. K. Khanna

Thesis advisor

Ross W. Smith

Department chairman

Ed M. Brien

Dean, Graduate School

University of Nevada

Reno

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assignments are made by comparison with the spectra of acetic acid, oleic acid, metal acetates, glycine and glycine hydrochloride.

Deriphat 151 has $\nu_{as} \text{COO}^-$ at 1345 cm^{-1} and ν_s at 1410 cm^{-1} . Adsorption on the hematite surface shifts $\nu_{as} \text{COO}^-$ to 1335 cm^{-1} , indicating that the carboxyl group chemisorbs to the hematite surface. On the other hand the amino group of deriphat 151 seems to physically adsorb on the hematite.

The variation in the intensity of absorption of $\nu_s \text{COO}^-$ (1410 cm^{-1}) of chemisorbed deriphat 151 on hematite as a function of pH is similar to the intensity variation of $\nu_s \text{COO}^-$ (1410 cm^{-1}) of oleic acid adsorbed on hematite. Although the flotation behavior of hematite with oleic acid can be explained on the basis of $-\text{COO}^-$ group chemisorbed on the surface, the flotation of hematite with deriphat 151 requires the association of physical adsorption of amino group at low and intermediate pH.

ABSTRACT

Adsorption of deriphat 151 on hematite as a function of pH is studied using Attenuated Total Reflection Spectroscopy. The band assignments are made by comparison with the spectra of acetic acid, oleic acid, metal acetates, glycine and glycine hydrochloride.

Deriphat 151 has $\nu_{as} \text{COO}^-$ at 1645 cm^{-1} and ν_s at COO^- at 1410 cm^{-1} . Adsorption on the hematite surface shifts $\nu_{as} \text{COO}^-$ to 1535 cm^{-1} , indicating that the carboxyl group chemisorbs to the hematite surface. On the other hand the amino group of deriphat 151 seems to physically adsorb on the hematite.

The variation in the intensity of adsorption of $\nu_s \text{COO}^-$ (1410 cm^{-1}) of chemisorbed deriphat 151 on hematite as a function of pH is similar to the intensity variation of $\nu_s \text{COO}^-$ (1410 cm^{-1}) of oleic acid adsorbed on hematite. Although the flotation behavior of hematite with oleic acid can be explained on the basis of $-\text{COO}^-$ group chemisorbed on the surface, the flotation of hematite with deriphat 151 requires the assumption of physical adsorption of amino group at low and intermediate pH.

INTRODUCTION

The study of adsorption of ions and molecules at the mineral-water interface is important in mineral processing for many reasons. Flotation, flocculation and dispersion are few areas where the behavior of particulate solids depends upon the adsorbed molecules and ions at the solid-liquid interface. The studies on adsorption are often conducted by indirect methods such as electrophoresis and streaming-potential measurements. Infrared spectroscopic methods present the possibility of direct observation of adsorbed species, however, there are many difficulties which have to be overcome before the IR-spectroscopy can become a routine tool for the adsorption studies.

Transmission spectroscopic methods usually need some kind of medium for the samples, and often nujol or alkali-metal halides are used for this purpose. Partly because of the difficulties arising from the interaction of the samples with the media, and partly because of the small quantities of the samples which must be used for transmission spectroscopy (e.g., up to 0.5% in KBr), the adsorbed species are difficult to observe by this method. Attenuated Total Reflection (ATR) spectroscopy seems promising. The objectives of this investigation are twofold: to explore the usefulness of ATR methods for adsorption studies; and to investigate the adsorption of ions and molecules at mineral-water interface, in systems of interest.

The main system of interest in this study has been the adsorption of deriphats on hematite, because deriphats have been successfully used as collectors in the flotation of hematite⁽¹⁾. Deriphats are amino acids, and have both carboxyl and amino groups. To aid in the study of

adsorption of the carboxyl group of deriphats on hematite, the adsorption of carboxyl groups of acetic acid, oleic acid and glycine were also studied. The adsorption of octylamine and glycine were studied to help understand the adsorption of the amino group of deriphats.

Spectrophotometer. The results show that the adsorption of all the adsorbates, the adsorption of octylamine and glycine were also studied. The adsorption of octylamine and glycine were studied to help understand the adsorption of the amino group of deriphats.

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EXPERIMENTAL

IR PROCEDURE AND MATERIAL

IR PROCEDURE

The spectra were obtained mostly with ATR, using a Beckman IR-10 Spectrophotometer. The double beam mode of the IR-10 was used in all our work, the attenuation of reference beam was necessary to compensate for the low intensities which are common in ATR. Germanium reflectance plate having a 45° angle of incidence was used for obtaining all the ATR spectra.

Few transmission spectra were deemed necessary and were obtained using KBr pellets. The KBr pellets were all 1.2 ± 0.1 cm in diameter, 0.2 to 0.3 mm in thickness, with a 0.5% concentration of the sample in the KBr matrix. The pellets were formed by means of a Wilks MP-2 "Mini Press".

Spectrophotometer was calibrated by recording the spectrum of polystyrene film (Beckman Item #40) each day when the spectra of the samples were taken.

The spectrum of Germanium reflectance plate was recorded before taking any spectrum of the samples to make sure that the plate was clean and did not have any adsorbed species from the previous experiment. A representative ATR spectrum of Germanium reflectance plate is shown in Figure 1A.

MATERIALS

Glacial acetic acid used was reagent grade and manufactured by Du Pont.

Metal acetates and glycine were reagent grade; octylamine and oleic

acid were technical grade and all were manufactured by Eastman.

Hematite was obtained from Wards Natural Science Establishment, Inc., and is supposed to be the massive red variety from Negauree, Michigan. Hematite was crushed in a jaw crusher and ground to -200 mesh using a disc pulverizer, and stored in an airtight container for subsequent studies. The disc pulverizer was cleaned by grinding some silica sand before grinding the hematite. The ATR spectrum of hematite, without any treatment, is shown in Figure 1B.

Technical grade deriphath 151 was manufactured by General Mills Chemical, Inc. The deriphath 151 is an amino acid ⁽²⁾ and like all amino acids exists as positively charged species, negatively charged species, and as "zwitter ions."

The physical and chemical properties of deriphath 151 reported by the manufacturer are:

1. Chemical Structure: sodium N-coco β - aminopropionate.
2. Formula: $\text{RNH CH}_2\text{CH}_2\text{COO Na}$.
3. Physical Form: flake.
4. Isoelectric Range, pH: 2.1 to 4.2.
5. Typical Chain Lengths
and configuration of
the radical R: C_8 -3%; C_{10} -5%; C_{12} -50%; C_{14} -23%;
 C_{16} -11%; oleyl-5%; stearyl-3%.

SAMPLE PREPARATION AND RESULTS

SAMPLE PREPARATION

In an attempt to physically adsorb acetic acid and octylamine, hematite was heated at 750°C in air for 3 hours and then exposed to the adsorbent vapors in a closed vessel. The exposure time was two hours for octylamine and half hour for acetic acid. The spectra of hematite thus treated was recorded.

In an attempt to chemisorb acetic acid, hematite was heated in an aqueous solution of acetic acid pH 2.7 for one hour at 93°C, filtered, washed, and dried at 66°C for 12 hours. The dried hematite was screened through 200 mesh and the spectra were recorded.

To study the adsorption taking place during a flotation operation, flotation tests were conducted. Flotation was carried out in a modified Hallimond tube ⁽³⁾, using oleic acid, glycine and deriphat 151 as collectors. The pH was adjusted by the addition of NaOH or HCl solutions. The concentrates were filtered, washed, and dried at 66°C for 12 hours, and screened through 200 mesh and spectra were recorded.

RESULTS

The ATR spectra of glacial acetic acid, hematite exposed to acetic acid vapors and hematite treated with heated acetic acid solution are shown in Figures 2, 3, and 4 respectively.

The spectra of metal acetates was recorded in order to aid in the interpretation of the spectra of the adsorbed carboxyl group. The transmission spectra of metal acetates are shown in Figure 5.

The ATR spectra of oleic acid, and hematite floated with oleic

acid are shown in Figure 6.

The ATR spectra of octylamine, and hematite exposed to octylamine vapors are shown in Figure 8.

The ATR and transmission spectra of glycine and the ATR spectrum of deriphat 151 are shown in Figures 9 and 10 respectively.

The ATR spectra of hematite floated with glycine and deriphat 151 at pH 9.0 are shown in Figure 11.

The ATR spectrum of hematite exposed to octylamine vapor is shown in Figure 8. This spectrum is similar to that of glycine floated on hematite, and therefore it is concluded that the absorption by this peak is due to glycine. The absorption maxima of hematite exposed to octylamine vapor are listed in Table 1.

The ATR spectrum of hematite exposed to octylamine vapor is shown in Figure 8. This spectrum is similar to that of glycine floated on hematite, and therefore it is concluded that the absorption by this peak is due to glycine. The absorption maxima of hematite exposed to octylamine vapor are listed in Table 1.

The ATR spectrum of hematite floated with octylamine vapor is shown in Figure 8. The absorption maxima of hematite floated with octylamine vapor are listed in Table 1.

* The ATR spectrum of hematite exposed to octylamine vapor is shown in Figure 8. This spectrum is similar to that of glycine floated on hematite, and therefore it is concluded that the absorption by this peak is due to glycine. The absorption maxima of hematite exposed to octylamine vapor are listed in Table 1.

DISCUSSION

ADSORPTION OF CARBOXYL GROUPS

Glacial acetic acid like other carboxylic acids ⁽⁴⁾ exists as a mixture of monomers and dimers especially at room temperature. The dimers are formed through strong hydrogen bridges between the carboxyl and the hydroxyl groups of the two molecules ⁽⁵⁾. This hydrogen bridge in the case of acetic acid is so strong that the dimers exist even in the vapor phase up to 150°C ⁽⁶⁾.

The ATR spectrum of glacial acetic acid in the region 1800-900 cm^{-1} was recorded by smearing the acid on the germanium reflectance plate and is shown in Figure 2. The band assignments and references are listed in Table 1.

The ATR spectrum of hematite exposed to acetic acid vapor is shown in Figure 3. This spectrum is similar to that of glacial acetic acid, and therefore it is concluded that the adsorption in this case is physical*. The spectrum contains frequencies for both monomer and dimer species and it is difficult to ascertain from our data whether any appreciable dissociation of dimers into monomers takes place during physical adsorption.

The ATR spectrum of hematite heated with acetic acid, shown in Figure 4, has prominent frequencies at 1560 and 1410 cm^{-1} . The above frequencies were assigned to the $\nu_{\text{as}} \text{COO}^-$ and $\nu_{\text{s}} \text{COO}^-$ respectively.

* In this context physical adsorption implies that acetic acid shows characteristic frequencies of $-\text{COOH}$, i.e. $\nu \text{C=O}$ at 1725 cm^{-1} , $\nu \text{C-O}$ at 1280 cm^{-1} and $\rho_{\text{s}} \text{COH}$ at 1192 cm^{-1} , in contrast the adsorption of $-\text{COOH}$ as $-\text{COO}^-$ which shows characteristic frequencies of $\nu_{\text{as}} \text{COO}^-$ and $\nu_{\text{s}} \text{COO}^-$ is called chemisorption.

TABLE 1

INFRARED FREQUENCIES FOR GLACIAL ACETIC ACID

| Band Assignment | Band Frequency, cm^{-1} | | Reference |
|---|--|-------------------------------------|-----------|
| | Observed cm^{-1} (this work) | From Literature cm^{-1} | |
| ν C=O, Mono species | 1752 | 1740-1800 | (4) |
| ν C=O, Dimers | 1700 | 1680-1740 | (4) |
| ρ_{AS} CH ₃ , Mono species | 1445 | 1445 | (6) |
| δ OH, (in plane) | 1440 | 1440 | (4) |
| ρ_{AS} CH ₃ , Dimers | 1401 | 1401 | (6) |
| ρ_{S} CH ₃ , Mono species | 1350 | 1340 | (6) |
| ν C-O, Mono species | 1280 | 1279 | (6) |
| ρ_{S} COH, Mono species | 1192 | 1192 | (6) |
| ρ_{R} CH ₃ , Dimers | 1045 | 1068 | (5) |
| ρ_{R} CH ₃ , Mono species | 1000 | 990 | (6) |

This assignment presumes that the acetate ion is chemisorbed* to the surface of hematite. Because the above assigned frequencies are in the same range as the $\nu_{as} \text{COO}^-$ and $\nu_s \text{COO}^-$ frequencies observed in the metal acetates and the aqueous acetate ion (Table 2), it is difficult to ascertain from the present data whether the chemisorption of the carboxyl group is through a chemical bond with the surface Fe^{+++} or through hydrogen bonding with the surface OH groups.

The ATR spectra in the region $1800\text{--}900 \text{ cm}^{-1}$ of oleic acid and hematite floated with oleic acid are shown in Figure 6, and the bond assignments of oleic acid, sodium oleate, hematite heated with acetic acid and the references are listed in Table 3.

The ATR spectrum of hematite floated using oleic acid shows a broad band from 1300 to 1510 cm^{-1} with a maxima at 1410 cm^{-1} . This frequency at 1410 cm^{-1} is assigned to the symmetric stretch frequency of the carboxyl group. A very weak band at 1520 cm^{-1} is assigned to asymmetric stretch frequency of the carboxyl group. Because the above assigned frequencies are in the same range as the symmetric and asymmetric stretch frequencies of the carboxyl groups of sodium oleate and the aqueous acetate ion, it is difficult to ascertain from the present data whether the chemisorption of the carboxyl group of the oleate ion is through a chemical bond with the surface Fe^{+++} or through hydrogen bonding with the surface OH groups. Peck et al., (9) attribute the

* In this context physical adsorption implies that acetic acid shows characteristic frequencies of $-\text{COOH}$, i.e. $\nu \text{C=O}$ at 1725 cm^{-1} , $\nu \text{C-O}$ at 1280 cm^{-1} and $\rho_s \text{COH}$ at 1192 cm^{-1} , in contrast the adsorption of $-\text{COOH}$ as $-\text{COO}^-$ which shows characteristic frequencies of $\nu_{as} \text{COO}^-$ and $\nu_s \text{COO}^-$ is called chemisorption.

TABLE 2

INFRARED FREQUENCIES AND BAND ASSIGNMENTS FOR ACETATE ION AND SOME METAL ACETATES

| Compound | Formula | Band Frequencies, cm^{-1} | | | Reference |
|-----------------------|--|------------------------------------|--------------------------------|------------|-----------|
| | | $\nu_{\text{as}}(\text{COO}^-)$ | $\nu_{\text{s}}(\text{COO}^-)$ | Difference | |
| Acetate ion (Aqueous) | $\text{C}_2\text{H}_3\text{O}_2^-$ | 1556 | 1413 | 143 | (7) |
| Sodium acetate | $\text{Na}(\text{C}_2\text{H}_3\text{O}_2) \cdot 3 \text{H}_2\text{O}$ | 1578 | 1414 | 164 | (7), (8) |
| Potassium acetate | $\text{K}(\text{C}_2\text{H}_3\text{O}_2)$ | 1570 | 1395 | 175 | This work |
| Magnesium acetate | $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot x\text{H}_2\text{O}$ | 1545 | 1405 | 140 | " |
| Calcium acetate | $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$ | 1555 | 1410 | 145 | " |
| Strontium acetate | $\text{Sr}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 1/2 \text{H}_2\text{O}$ | 1555 | 1420 | 135 | " |
| Barium acetate | $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ | 1565 | 1415 | 150 | " |
| Nickelous acetate | $\text{Ni}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4 \text{H}_2\text{O}$ | 1550 | 1415 | 135 | " |
| Zinc acetate | $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2 \text{H}_2\text{O}$ | 1550 | 1440 | 110 | " |

chemisorption of the oleate ion on hematite through oleate formation on the surface which is different from the bulk precipitation of ferric oleate.

The intensity of IR absorbance at 1410 cm^{-1} which is the $\nu_s\text{ COO}^-$ vibration of the adsorbed oleate species, versus pH is shown in Figure (9). Peck et al., has reported similar curves using the intensity of absorbance of $\nu_s\text{ COO}^-$ vibration versus pH which correlate well with his flotation recovery curves.

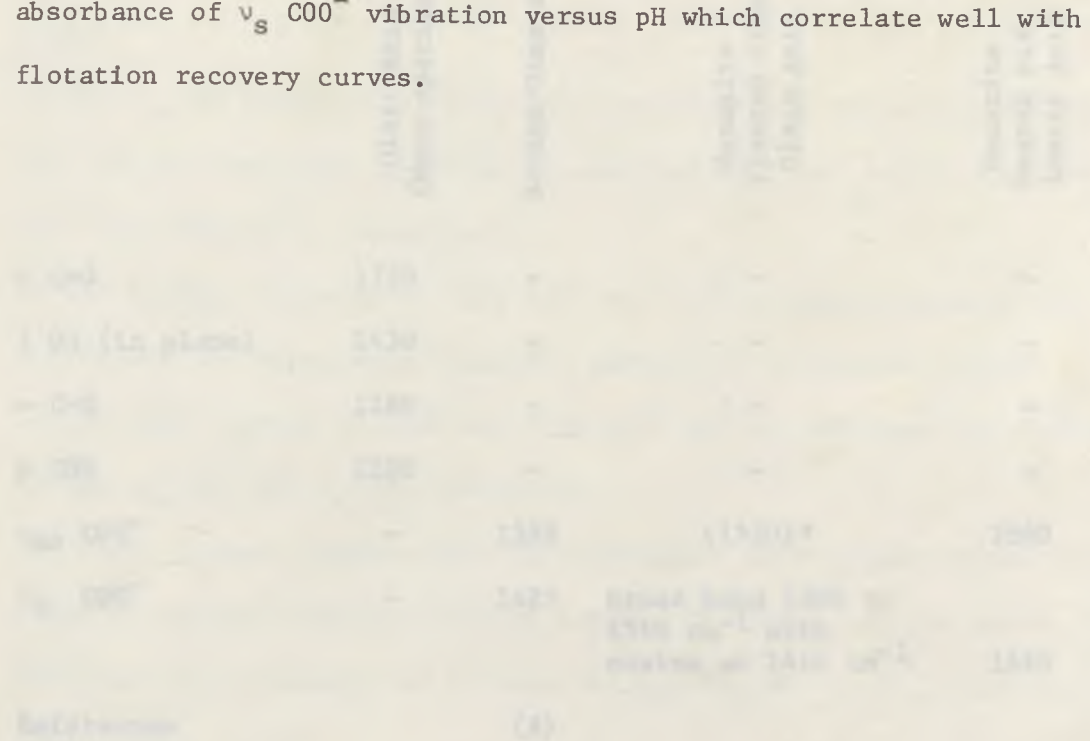


Figure 9. Intensity of IR absorbance at 1410 cm^{-1} versus pH. The background is subtracted.

TABLE 3

INFRARED FREQUENCIES AND BAND ASSIGNMENTS FOR OLEIC ACID,
SODIUM OLEATE, HEMATITE FLOATED USING OLEIC ACID AND HEMATITE
HEATED WITH ACETIC ACID

| Band Assignment | Observed Band Frequencies, cm^{-1} | | | |
|------------------------------------|---|---------------|---|--|
| | Oleic Acid (Mono species) | Sodium Oleate | Hematite Floated with Oleic Acid | Hematite Heated with Acetic Acid |
| ν C=O | 1720 | - | - | - |
| δ OH (in plane) | 1430 | - | - | - |
| ν C-O | 1280 | - | - | - |
| ρ COH | 1200 | - | - | - |
| ν_{as} COO ⁻ | - | 1555 | (1520)* | 1560 |
| ν_{s} COO ⁻ | - | 1425 | Broad band 1300 to 1510 cm^{-1} with maxima at 1410 cm^{-1} | 1410 |
| References | (9) | | | |

* intensity is very weak and barely distinguishable from the background.

ADSORPTION OF AMINO GROUPS

The ATR spectra of octylamine and hematite exposed to octylamine vapors are shown in Figure 8, the band assignments and references are listed in Table 4.

On comparing the ATR spectrum of octylamine with the ATR spectrum of hematite exposed to octylamine vapor the following observations are made:

- a) the ν_{as} NH vibration at 3330 cm^{-1} and the ν_g NH vibration at 3260 cm^{-1} in the octylamine spectrum are shifted to lower values of 3210 cm^{-1} and 2990 cm^{-1} , respectively,
- b) the δ_s NH₂ vibration at 1590 cm^{-1} in the octylamine spectrum disappears in the spectrum of hematite exposed to octylamine vapors,
- c) new bands appear at 1620 and 1540 cm^{-1} and are assigned respectively to the δ_{as} NH₃⁺ and δ_s NH₃⁺ vibrations.

The above changes suggest that the octylamine is hydrogen bonded to the hematite surface probably through surface OH groups because the δ_s NH₂ vibration in octylamine is replaced by δ_{as} NH₃⁺ and δ_s NH₃⁺ vibrations on adsorption.

The hematite with adsorbed octylamine was soaked in distilled water for an hour, filtered, washed and dried at 66°C for 12 hours. The ATR spectrum showed no adsorption. Thus showing that the adsorbed octylamine was removed during washing and drying.

Flotation experiments at different pH were conducted using dodecylamine. The flotation concentrate was filtered, washed, and dried at 66°C for 12 hours. The ATR spectrum failed to show any adsorption of

TABLE 4
 COMPARISON OF THE FREQUENCIES AND BAND ASSIGNMENTS
 OF OCTYLAMINE AND HEMATITE EXPOSED TO OCTYLAMINE

| Band Assignment | Observed Frequencies, cm^{-1} | | |
|---|--|-----------------------------------|------------|
| | Octylamine | Hematite exposed to Octylamine | Reference |
| ν_{as} NH | 3330 | (3210)* | (11) |
| ν_{s} NH | 3260 | 2990 | (11) |
| ν_{as} CH ₃ | 2930 | 2930 | (12) |
| ν_{as} CH ₂ | 2890 | 2890 | (13) |
| ν_{s} CH ₂ | 2820 | 2820 | (13) |
| δ_{as} NH ₃ ⁺ | -- | (1620)* | (11) |
| δ_{s} NH ₂ | 1590 | -- | (11), (14) |
| δ_{s} NH ₃ ⁺ | -- | 1540 | (11) |
| δ_{as} CH ₃ | 1450 | 1450 | (12) |
| δ CH ₂ | 1430 | (1430)* | (13) |
| δ_{s} CH ₃ | 1370 | (1370)* | (12) |

* intensity is very weak and barely distinguishable from the background.

dodecylamine on hematite. Because flotation took place therefore dodecylamine must have been, at least, weakly adsorbed on hematite and was subsequently removed during the washing and heating periods, as in the case of octylamine.

The IR and Raman spectra in the region $1000-700\text{ cm}^{-1}$ of glycine are shown in Figure 9. The IR spectrum is very weak and was interpreted by comparing it with the Raman spectrum. The band assignments and references are listed in Table 6. On comparing the IR spectrum of glycine with the literature spectrum it is seen that all the intensities of absorption are much weaker in IR, as the frequencies are shifted towards lower frequencies in IR.

The IR spectrum of hematite floated using glycine at pH 9.0 is shown in Figure 11, and the band assignments are given in Table 7. The spectrum shows weak bands at 1513 and 1391 cm^{-1} . These frequencies, by comparison with the carboxyl groups previously discussed and the frequencies of glycine hydrochloride listed in Table 8, are assigned to the ν_{2a} (120 cm^{-1}) and ν_2 (100 cm^{-1}) of the carboxyl group of glycine. Absorbed on the hematite surface, perhaps similar to fatty acids $\nu_{C=O}$ of $\sim 1700\text{ cm}^{-1}$ observed in glycine hydrochloride at 1710 cm^{-1} is replaced by ν_{2a} (120 cm^{-1}) and ν_2 (100 cm^{-1}) at 1513 and 1391 cm^{-1} . The absorption of glycine at pH 9.0 through carboxyl group is as is expected, because, at pH 9.0 glycine exists predominantly as $\text{O}_2\text{CCH}_2\text{COO}^-$ (19).

In acid solution one will expect the absorption of glycine to hematite surface through amino group which would result in a spectrum similar to that of glycine hydrochloride. However, the spectrum of

ADSORPTION OF DERIPHAT 151

Glycine is the lowest molecular weight representative of the amino acids. Amino acids exist as dipolar (zwitter) ions in the crystalline state regardless of the number of carbon atoms separating the amino group from the carboxyl group (17).

The ATR and transmission spectra in the region $1800-900 \text{ cm}^{-1}$ of glycine are shown in Figure 9. The ATR spectrum is very weak and was interpreted by comparing it with the transmission spectrum. The band assignments and references are listed in Table 5. On comparing the ATR spectrum of glycine with the transmission spectrum it is seen that:

- a) the intensities of absorption are much weaker in ATR,
- b) the frequencies are shifted towards lower wavenumbers in ATR.

The ATR spectrum of hematite floated using glycine at pH 9.0 is shown in Figure 11, and the band assignments and references listed in Table 7. The spectrum shows weak bands at 1520 and 1390 cm^{-1} . These frequencies, by comparison with the carboxyl groups previously discussed and the frequencies of glycine hydrochloride listed in Table 8, are assigned to the $\nu_{\text{as}} \text{COO}^-$ and $\nu_{\text{s}} \text{COO}^-$ of the carboxyl group of glycine adsorbed on the hematite surface, because similar to fatty acids $\nu \text{C=O}$ of $-\text{COOH}$ observed in glycine hydrochloride at 1710 cm^{-1} is replaced by $\nu_{\text{as}} \text{COO}^-$ and $\nu_{\text{s}} \text{COO}^-$ at 1520 and 1390 cm^{-1} . The adsorption of glycine at pH 9.0 through carboxyl group is to be expected, because, at pH 9.0 glycine exists predominantly as $\text{NH}_2 \text{CH}_2 \text{COO}^-$ (19).

In acid solution one would expect the adsorption of glycine on hematite surface through amino group which would result in a spectrum similar to that of glycine hydrochloride. However, the spectrum of

TABLE 5

INFRARED FREQUENCIES AND BAND ASSIGNMENTS OF GLYCINE

| Band Assignment | Observed Frequencies, cm^{-1} | | |
|------------------------------------|---|---|------------|
| | Transmission | ATR | Reference |
| $\nu_{\text{as}} \text{COO}^{-1}$ | 1610 | 1605 | (15), (16) |
| $\delta_{\text{as}} \text{NH}_3^+$ | 1590 | 1580 | (15), (16) |
| $\delta_{\text{s}} \text{NH}_3^+$ | 1515 | 1495 | (15), (16) |
| δCH_2 | 1440 | Indistinguishable from the Background | (15) |
| $\nu_{\text{s}} \text{COO}^-$ | 1410 | 1400 | (15), (16) |
| $\rho_{\omega} \text{CH}_2$ | 1330 | 1290 | (15) |
| $\delta_{\text{t}} \text{CH}_2$ | Indistinguishable from the Background | Indistinguishable from the Background | (15) |
| $\rho_{\text{r}} \text{NH}_3^+$ | 1130 1110 | 1120 1100 | (15) |
| $\nu_{\text{as}} \text{CCN}$ | 1030 | Indistinguishable from the Background | (15) |
| $\rho_{\text{r}} \text{CH}_2$ | 910 | Indistinguishable from the Background | (15) |

hematite concentrate floated with glycine at pH 2.7, washed and dried at 66°C for 12 hours failed to show any evidence of adsorbed glycine. Since flotation took place therefore it is concluded that adsorption of glycine at pH 2.7 must be weak and the glycine was removed in the subsequent washing and drying operation as in the case of octylamine.

The ATR spectrum of deriphath 151 in the region 4000-900 cm^{-1} is shown in Figure 10, the band assignments and references listed in Table 6.

The ATR spectrum of hematite floated using deriphath 151 at pH 9.0 is shown in Figure 11, the band assignments and references listed in Table 7.

The ATR spectrum of hematite floated using deriphath 151 at pH 9.0 is similar to the spectrum of hematite floated using oleic acid, thus indicating that the surface species are carboxylates. This conclusion is further strengthened by the pH dependence of the intensity of adsorption at 1410 cm^{-1} of both hematite floated using deriphath 151 (shown in Figure 12) and hematite floated using oleic acid (shown in Figure 7).

The spectrum of hematite concentrate floated with deriphath 151 at pH 2.7, washed and dried at 66°C for 12 hours, like in the case of glycine and dodecylamine failed to show any evidence of adsorption.

TABLE 7
 INFRARED FREQUENCIES AND BAND ASSIGNMENTS OF HEMATITE
 FLOATED USING GLYCINE AND DERIPHAT 151

| Band Assignment | Hematite Floated Using Glycine | Hematite Floated Using Deriphat 151 | Reference |
|--|---|---|-----------------|
| ν_{as} CH ₃ | Indistinguishable from the Background | (2930)* | (12) |
| ν_s CH ₃ | Indistinguishable from the Background | 2880 | (12) |
| ν_{as} CH ₂ | Indistinguishable from the Background | Indistinguishable from the Background | (13) |
| ν_s CH ₂ | Indistinguishable from the Background | (2820)* | (13) |
| ν_{as} COO ⁻ | 1520 | 1535 | (15), (16) |
| δ NH ₂ | 1590 | Indistinguishable from the Background | (15), (16) |
| δ_{as} NH ₃ ⁺ | -- | -- | (8), (15), (16) |
| δ_s NH ₃ ⁺ | -- | -- | (8), (15), (16) |
| ν_s COO ⁻ | 1390 | Broad band 1300 to 1510 cm ⁻¹ with maxima at 1410 cm ⁻¹ | (15), (16) |
| ρ_{as} NH | Indistinguishable from the Background | (1470)** | (15), (16) |
| ρ_r NH ₃ ⁺ | -- | -- | (15), (16) |

* intensity is very weak and barely
distinguishable from the background

**shoulder on the broad band 1300-1510 cm⁻¹

TABLE 8

COMPARISON OF THE INFRARED FREQUENCIES OF GLYCINE
AND ITS HYDROCHLORIDE,
(16)
DATA FROM SLIFKIN, SMITH, AND WALMSLEY

| GLYCINE | | GLYCINE HCl | |
|---------|---|-------------|---|
| 1595 | COO ⁻ antisym. stretch | 2896 | N-H and O-H stretch, broad peak |
| 1415 | COO ⁻ sym. stretch | 1710 | C=O stretch of unionized carboxyl group |
| 1609 | NH ₃ ⁺ antisym. deformation | 1575 | NH ₃ ⁺ antisym. deformation |
| 1525 | NH ₃ ⁺ sym. deformation | 1478 | NH ₃ ⁺ sym. deformation |
| 1134 | NH ₃ ⁺ rock frequency | 1412 | coupling of O-H bending |
| 2100 | NH ₃ ⁺ bend | 1200 | vibration and C-O stretch |
| 2940 | N-H stretch broad and | 853 | -OH out of plane deformation |
| 2550 | C-H stretch overlapping | | |

FLOTATION BEHAVIOR OF HEMATITE USING DERIPHAT 151

The ATR spectra of hematite floated using deriphath 151 at pH 5.0, 6.0, 7.0, 8.0, 9.0 and 10.0 were recorded. The intensity of absorbance of the $\nu_s \text{COO}^-$ at 1410 cm^{-1} and the flotation data of Smith, Haddenham and Schroeder⁽¹⁾ are plotted as a function of pH in Figure 12. Both the flotation recovery and IR absorbance drops rapidly above pH 9.0. The flotation recovery remains above 90 percent up to pH 2.0 whereas the IR absorbance gradually drops and becomes zero at pH 5.0. At pH below pH 2.0 the flotation recovery experiences a rapid decrease.

(18)

According to Lai⁽¹⁸⁾ at PZC the negative sites on the mineral oxide surface are numerically equal to the positive sites and are relatively few when compared to the neutral sites. Neutral sites are expected to be symmetrically distributed about the PZC of a mineral. Above the PZC as the negative sites increase and the positive sites rapidly decrease with increasing pH. The opposite is true for a pH decrease below the PZC.

The similarity between the plots of IR absorbance versus pH of hematite floated using deriphath 151, and that of hematite floated using oleic acid, seems to indicate that flotation at pH 9.0 is due to the negatively charged species of deriphath 151, which are adsorbing on the positive sites present on the hematite surface. Since the isoelectric range of deriphath 151 is 2.1 to 4.2, the negatively charged species of deriphath 151 increase with increasing pH. However, since PZC of hematite is 6.7, positive sites on the surface of hematite decrease with increasing pH, thus resulting in a net drop in adsorption and flotation recovery.

Since the flotation recovery remains above 90 percent till pH 2.0 whereas the IR absorbance gradually decreases to zero at pH 5.0, it leads one to believe that the adsorption of both, the positively charged amino groups and the negatively charged carboxyl groups on the negative and positive surface sites of hematite, is responsible for the flotation in the pH range 9.0 to 5.0, and the adsorption of positively charged amino group in the pH range below pH 5.0. The decrease in flotation below pH 2.0 is due to the decrease in negatively charged surface sites.

The reason we did not see the adsorption of the amino group is that washing and drying of the concentrate removes the weakly adsorbed species. This conclusion is supported by our experiments on octylamine. Flotation due to "zwitter ions" adsorbing on the neutral sites of the hematite surface is a distinct possibility around the PZC. This adsorption is also probably weak and could not be observed by our IR procedure because of the washing and drying of the concentrate prior to recording the spectrum.

Further work will be necessary to substantiate the above qualitative explanation of the flotation behavior of hematite using deriphat 151.

SUMMARY AND CONCLUSIONS

IR studies of adsorption of carboxyl and amino groups on hematite surface with ATR show:

1. When hematite is exposed to acetic acid vapors, acetic acid physically adsorbs on hematite.
2. When hematite is heated in aqueous acetic acid solution the adsorption of acetic acid is through the carboxyl group.
3. The adsorption of octylamine on hematite by exposing to octylamine vapors is through hydrogen bonding because the -NH_2 group in octylamine converts to -NH_3^+ group. This adsorption is weak and the adsorbed species are removed on washing and drying.
4. Adsorption of oleic acid is through the carboxyl group. The IR intensity of absorbance of $\nu_s \text{COO}^-$ at 1410 cm^{-1} correlates with the flotation recovery.
5. The adsorption of the carboxyl groups of glycine and deriphat 151 occurs in basic pH.

The ATR spectrum of flotation concentrate of hematite using dodecylamine does not show the presence of dodecylamine. Dodecylamine is probably hydrogen bonded to the surface and is removed during washing and drying, similar to the case of octylamine adsorption.

The flotation behavior of hematite using deriphat 151 can be explained on the basis of electrostatic model using PZC of hematite and the isoelectric range of the deriphat 151. The flotation takes place by the adsorption of both the carboxyl and the amino groups. The relative adsorption of the two groups is dependent on the pH.

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FIG. 1A ATR SPECTRUM OF GERMANIUM
PLATE.

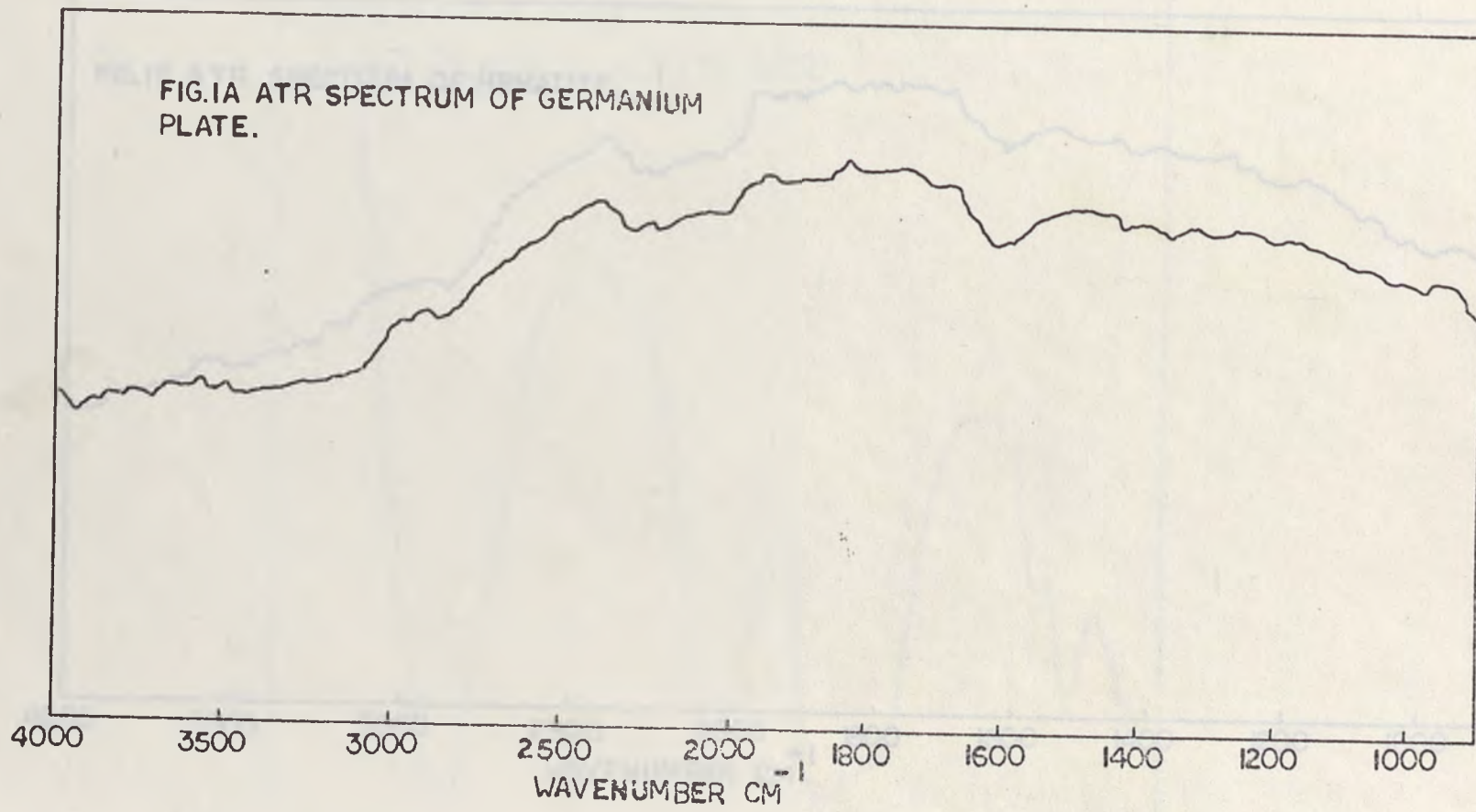
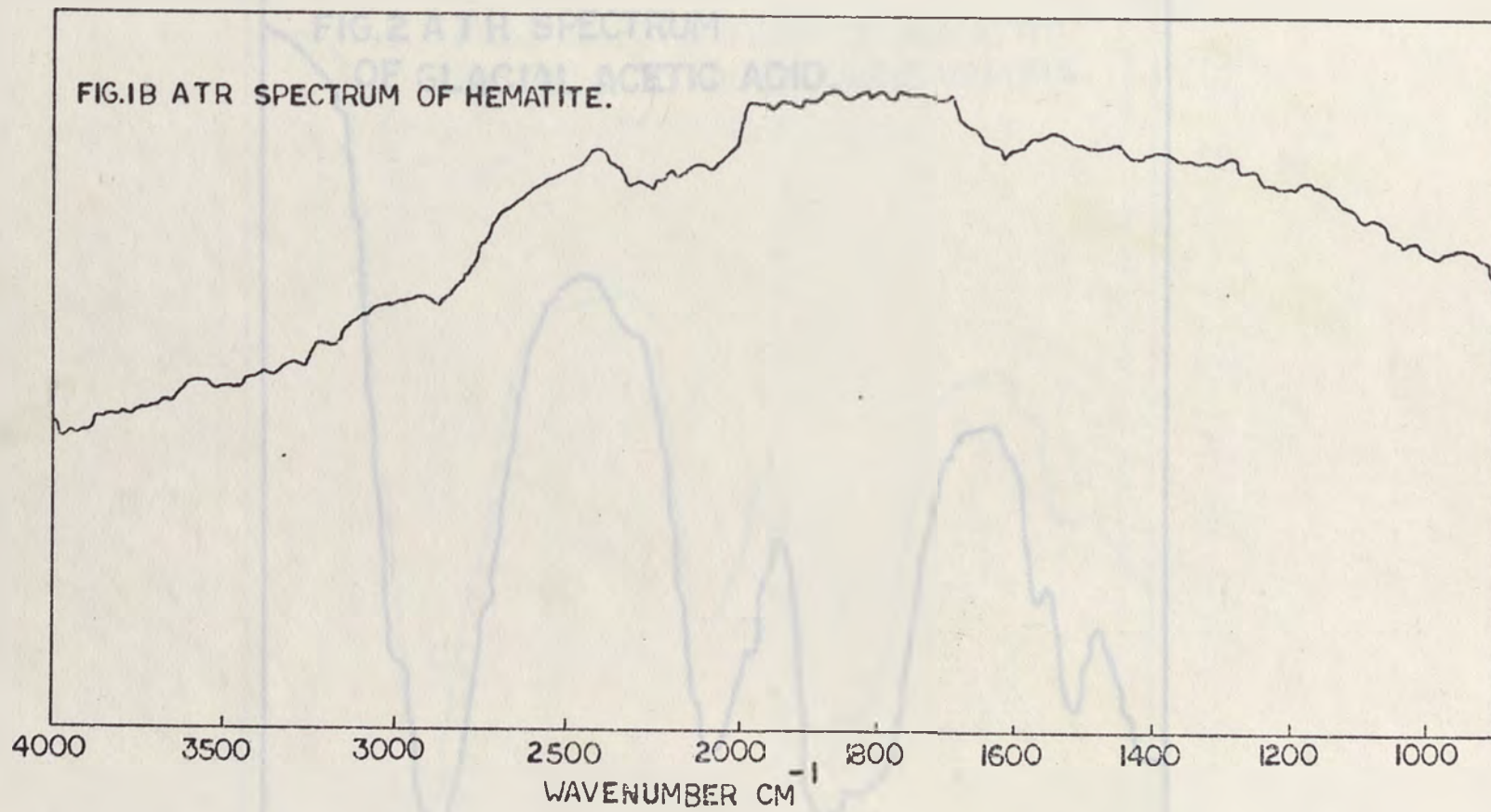
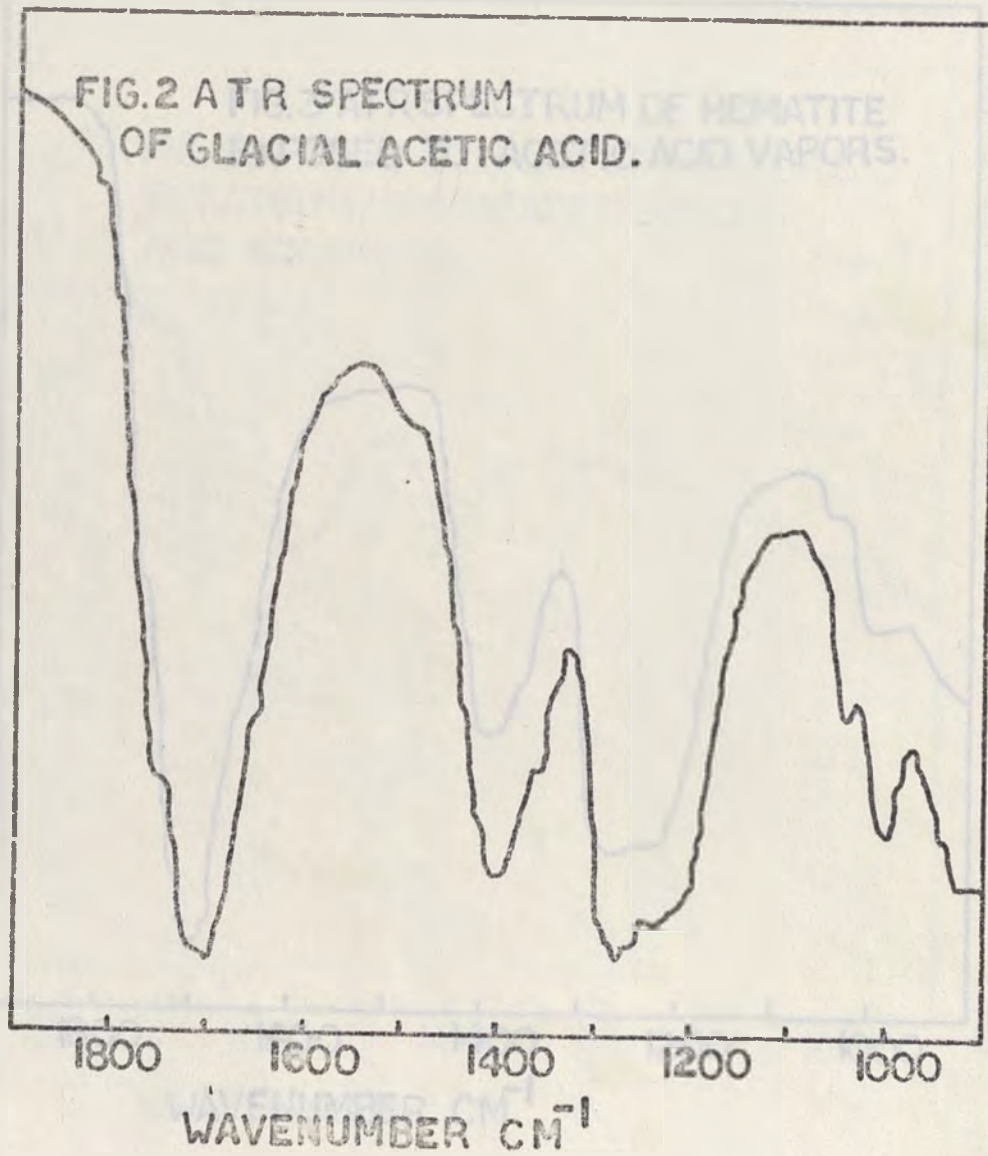
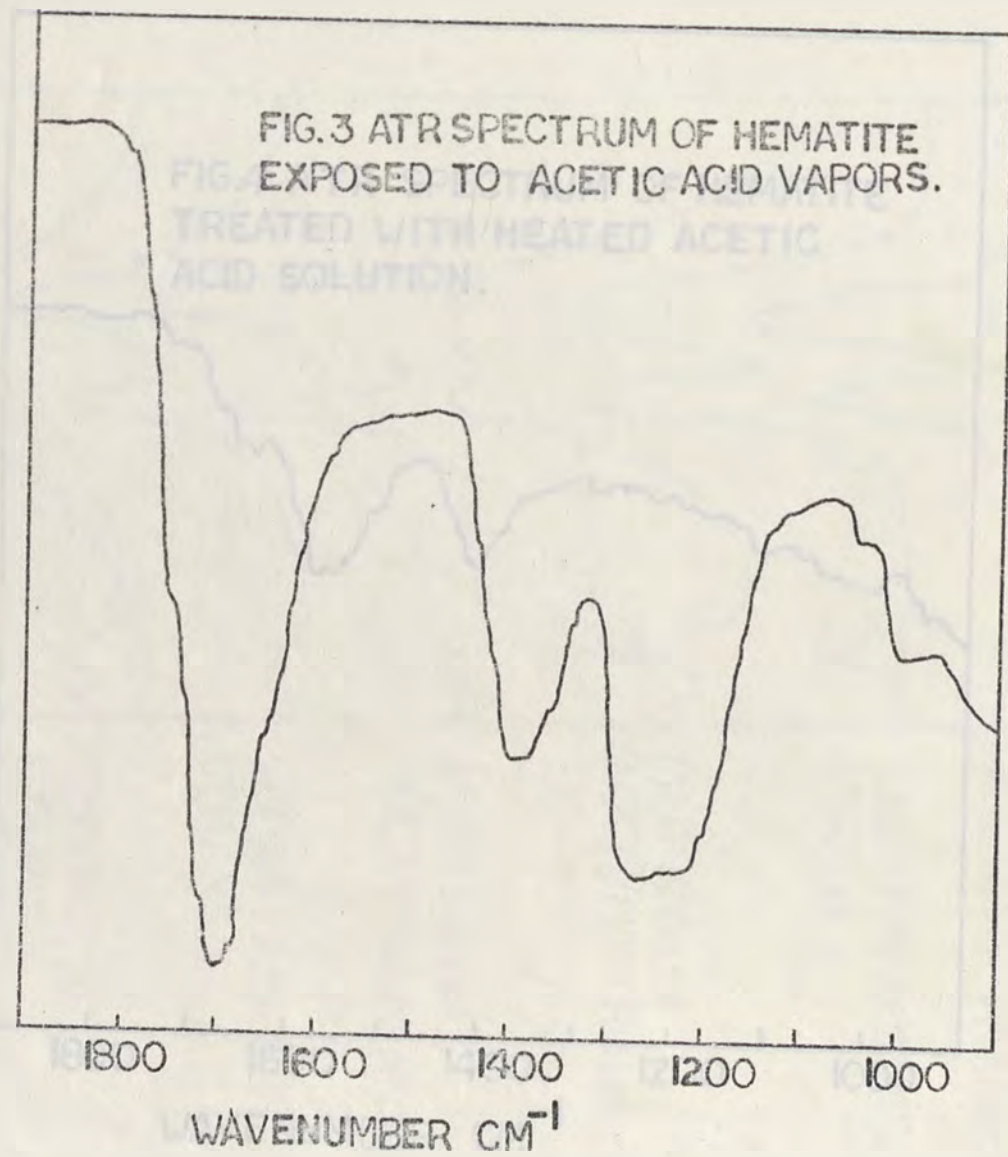


FIG.1B ATR SPECTRUM OF HEMATITE.







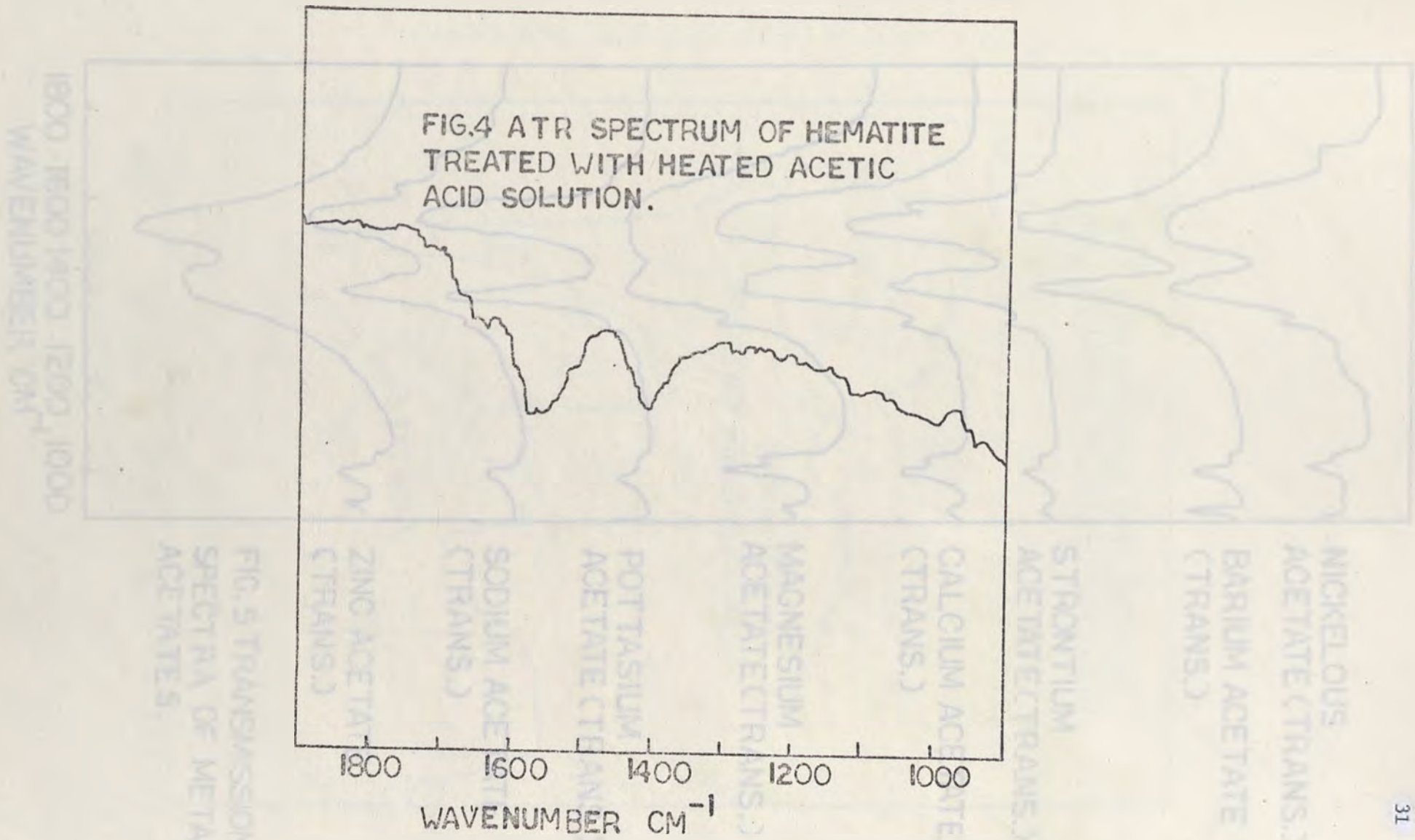
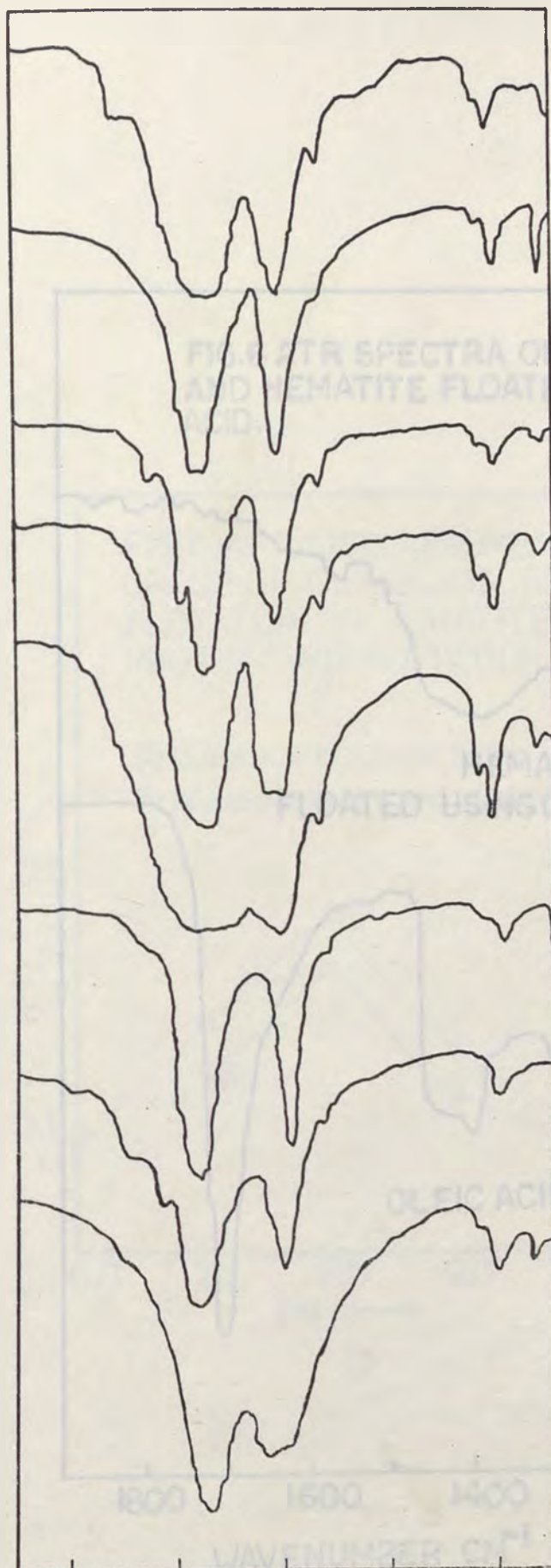


FIG.5 TRANSMISSION SPECTRA OF METAL ACETATES.



NICKELOUS
ACETATE (TRANS.)

BARIUM ACETATE
(TRANS.)

STRONTIUM
ACETATE (TRANS.)

CALCIUM ACETATE
(TRANS.)

MAGNESIUM
ACETATE (TRANS.)

POTTASIUM
ACETATE (TRANS.)

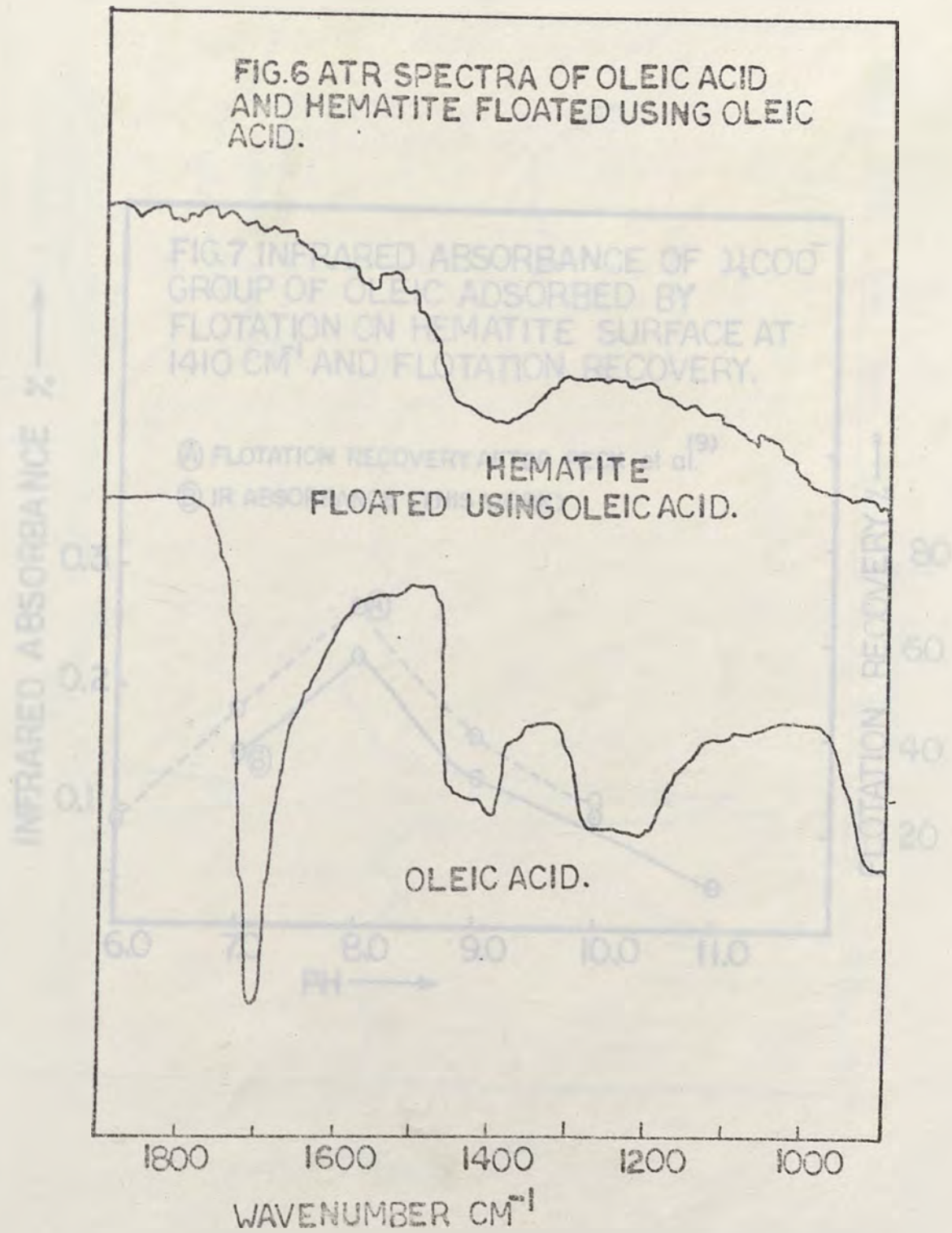
SODIUM ACETATE
(TRANS.)

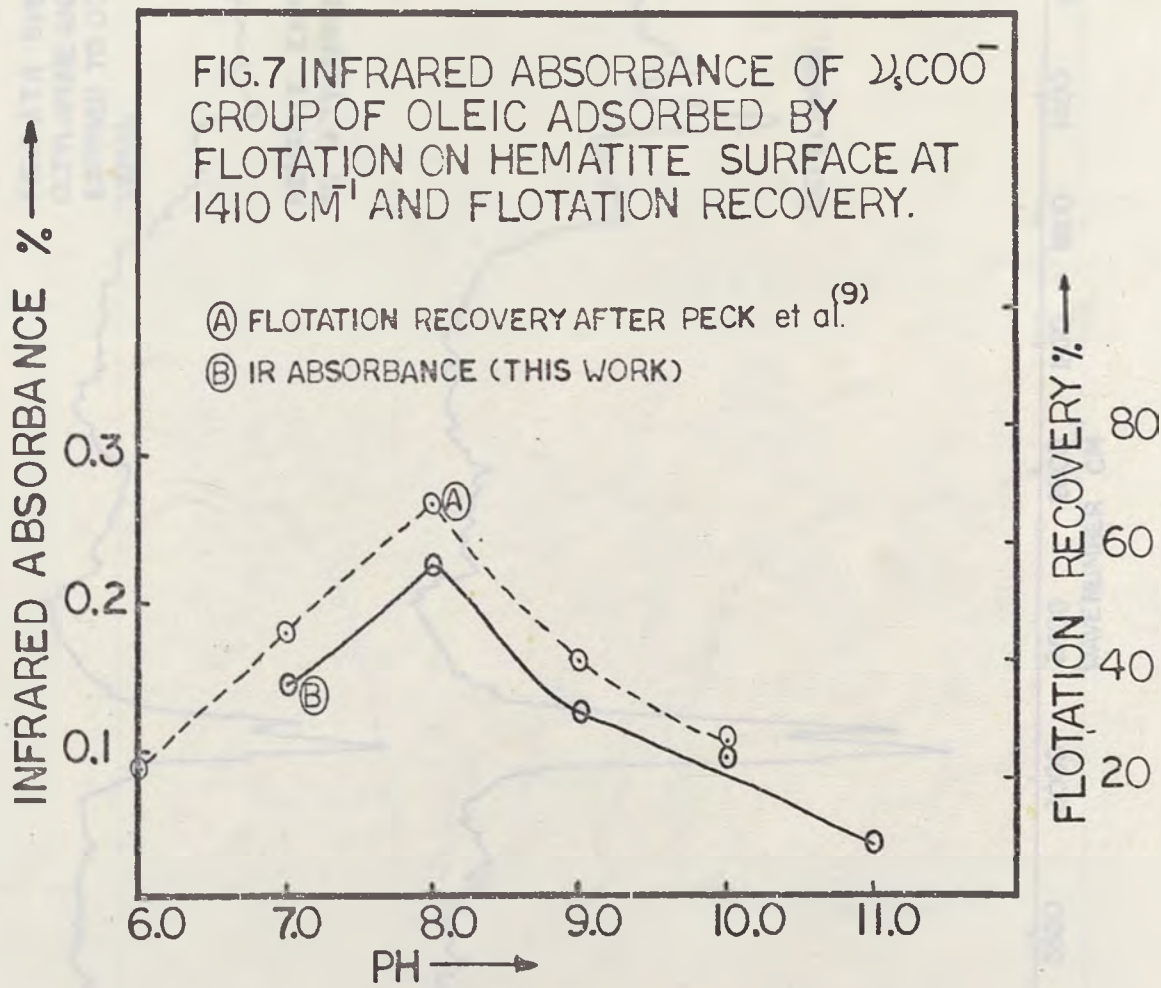
ZINC ACETATE
(TRANS.)

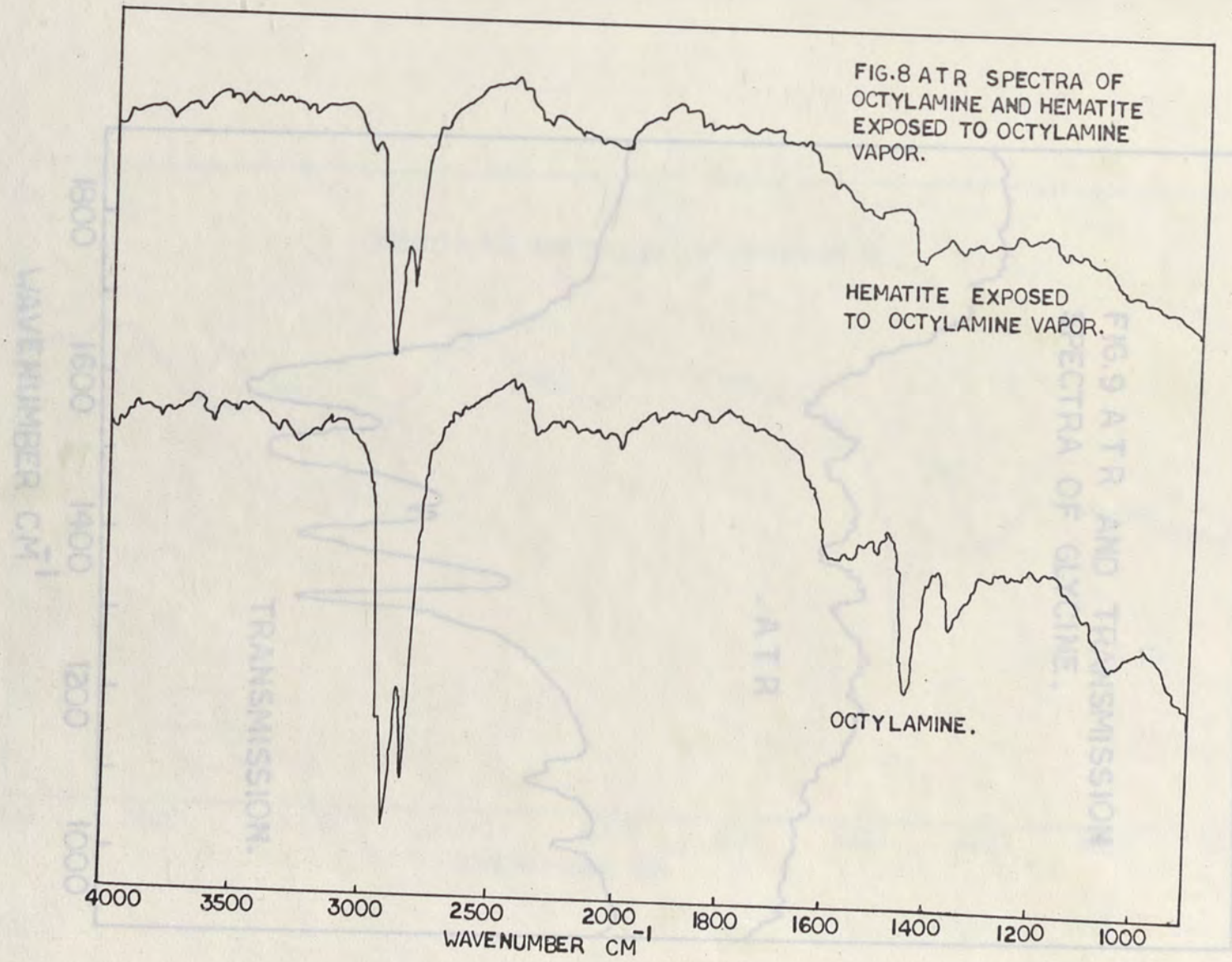
FIG. 5 TRANSMISSION
SPECTRA OF METAL
ACETATES.

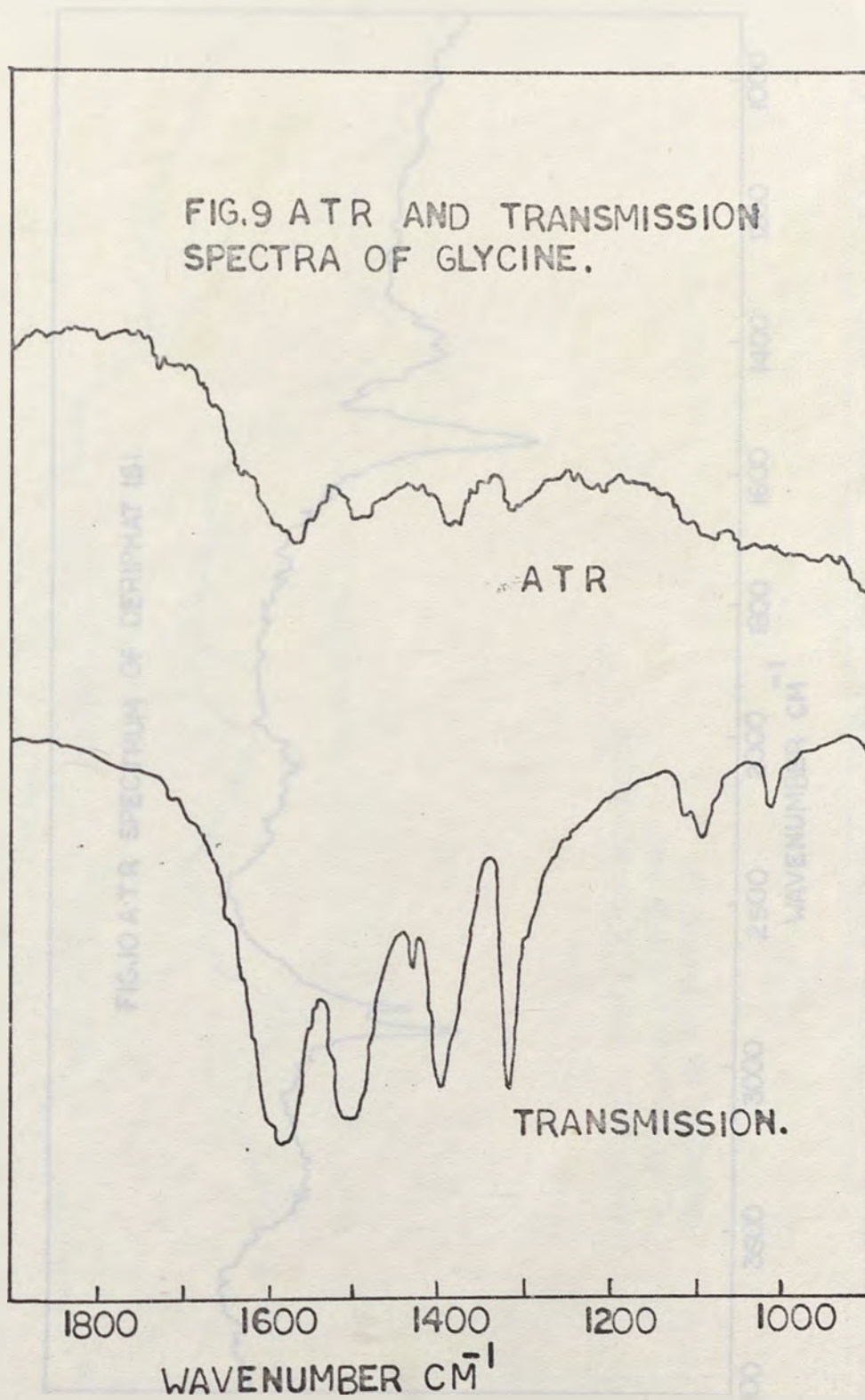
1800 1600 1400 1200 1000
WAVENUMBER CM^{-1}

FIG.6 ATR SPECTRA OF OLEIC ACID
AND HEMATITE FLOATED USING OLEIC
ACID.









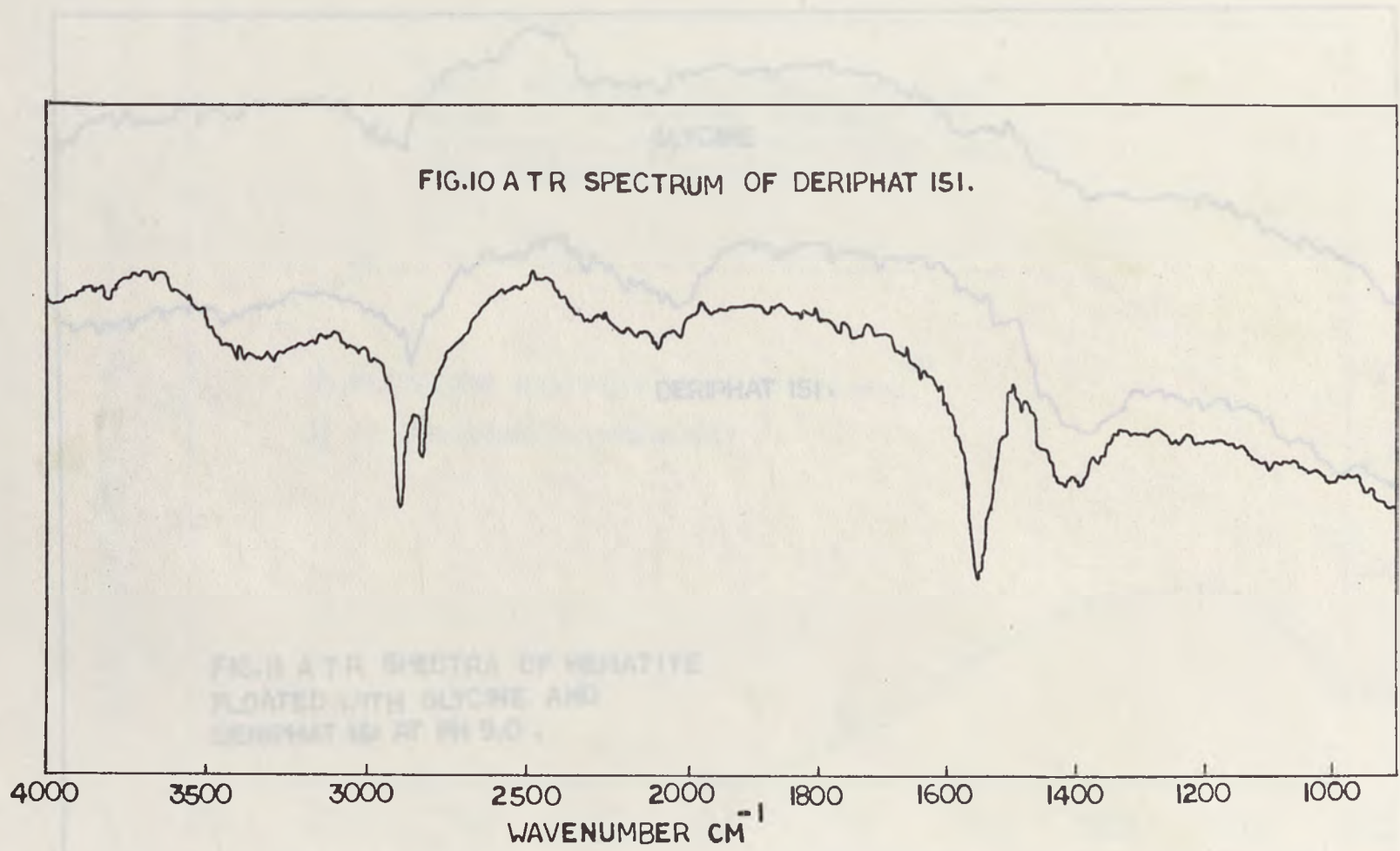


FIG.11 ATR SPECTRA OF RELATIVE
FLOATED WITH GLYCINE AND
DERIPHAT 151 AT PH 9.0.

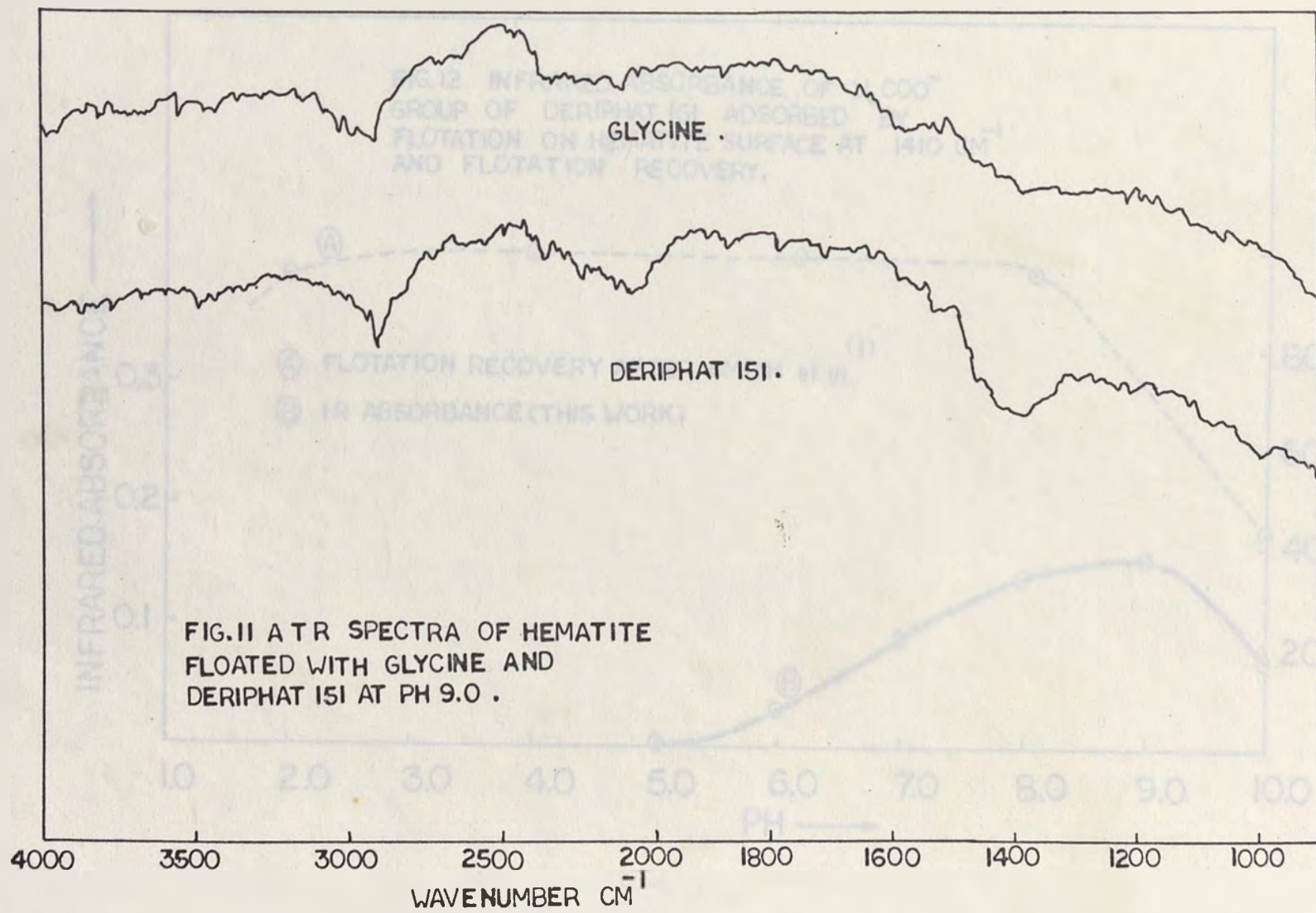


FIG.II ATR SPECTRA OF HEMATITE FLOATED WITH GLYCINE AND DERIPHAT 151 AT PH 9.0 .

FIG.12 INFRARED ABSORBANCE OF ν_6 COO⁻ GROUP OF DERIPHAT 151 ADSORBED BY FLOTATION ON HEMATITE SURFACE AT 1410 CM⁻¹ AND FLOTATION RECOVERY.

