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Technical Progress Report for the Project

ELECTROCHEMISTRY OF *Thiobacillus ferrooxidans* REACTIONS WITH PYRITE

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EFFECT OF THIAMINE HYDROCHLORIDE ON THE REDOX REACTIONS OF IRON AT PYRITE SURFACE.

Introduction

The present investigation is a part of our studies on the electro chemical aspects of pyrite bioleaching involving <u>Thiobacillus ferrooxidans</u>. Previously (1,2) we have examined the effect of <u>T. ferrooxidans</u> and their metabolic products on the redox reactions of Fe^{2+}/Fe^{3+} couple at the pyrite surface. Results obtained suggest that beyond 1.5 days during their growth in a batch fermenter, the bacteria and their metabolic products completely cover the pyrite surface and shut down all electron transfer across the electrode-solution interface. In addition, it has been observed that the bacteria serve as the nucleation site for jarosite formation, which is found detrimental to bioleaching (2). In the present work we have focussed on the effect of the presence of vitamins on the redox chemistry of iron. To date, we have examined the effect of the presence of thiamine hydrochloride in the redox behavior of Fe^{2+}/Fe^{3+} at the pyrite surface. The results are described herein.

Experimental

Materials and methods

All chemicals were of reagent grade and used without further purification. Solutions (e.g. ferrous and ferric iron etc.) were prepared in de-ionized water and pH adjusted with sulfuric acid.

Cyclic voltammetry

An electrochemical cell equipped with a three-electrode system was employed. Pyrite was used as working electrode. Saturated calomel and platinum were used as reference and counter electrodes. Pyrite electrode was made of mineral pyrite by cutting a 2x2 cm^2 pyrite plate. Before use, pyrite electrode was polished with #600 metallographic paper, washed with plenty of water and finally rinsed with de-ionized water. A plastic o ring of approximately 1 cm in diameter was used to ascertain constant electrode surface area exposed to the solution. Potential and current measurements were performed using an EG&G Princeton Applied Research Model 273 Potentiostat/Galvanostat interfaced to an IBMPC.

Linear sweep voltammetry

Instrumentation and experimental conditions were the same as in the case of cyclic voltammetric studies. Only difference was that the cathode going scan was not followed by an anode going scan and vice versa.

Nuclear magnetic resonance spectroscopy

Proton magnetic resonance spectra were recorded on a Bauker AM-250 MHz NMR spectrometer using D_2O as solvent.

Results and Discussion

Cyclic voltammetry

Typical cyclic voltammograms of ferric sulfate at pH 1.7 in the absence and in the presence of thiamine hydrochloride are shown in Fig. 1 and 2 respectively. It is observed from Fig. 1 that the reduction of ferric ion to ferrous ion and the subsequent oxidation to ferric ion occur at around 0.407 and 0.481V (against sat. cal.) respectively. The reduction peak current is a little greater than the oxidation peak current. This observation suggests that the reduction reaction proceeds at a slightly faster rate at pyrite electrode surface at pH 1.7. Comparison of Fig. 1 and 2 reveals that in the presence of thiamine hydrochloride causes the cathodic peak to shift towards lower potential and the anodic peak to higher potential with an attendant reduction in both of the peak currents. This may be attributed to the polarization of the pyrite electrode resulting from adsorption of thiamine hydrochloride on to pyrite surface.

The above mentioned experiments, which were conducted at a scan rate of 50mV/sec, were repeated using a number of scan rates and the results are presented in Tables 1 and 2. It is observed in general that the separation of the cathodic and the anodic peaks increases with an increase in the scan rate. This is due to an increase in the irreversibility of the redox couple with an increase in the scan rate. In addition, a careful review of the data presented in Tables 1 and 2 would reveal that the peak current values do not increase linearly with increasing scan rates. This corresponds to the polarization of pyrite electrode at higher scan rates.

Experiments represented by Fig. 1 and 2 were repeated at different pH and the results are shown in Tables 3 and 4 respectively. It is observed, in general, that the peak potentials increase with an increase in pH. However, peak currents increase as pH is increased from 1.5, show a maximum value at pH 2 and then decrease again with an increase in pH beyond 2.

Linear sweep voltammetry

Typical linear sweep voltammograms of ferric sulfate at pH 1.7 in the absence and in the presence of thiamine hydrochloride are shown in Fig. 3 and 4 respectively. A comparison of these two figures would reveal that the cathodic peak shifts towards left (i.e. to lower voltage) due to the presence of thiamine hydrochloride in the system. As cited above, this may be due to polarization of the pyrite electrode caused by adsorption of thiamine hydrochloride.

Fig.5 and 6 represent linear sweep voltammograms of ferrous sulfate at pH 1.7 in the absence and in the presence of thiamine hydrochloride. These figures show that the anodic peak shifts to a higher potential when thiamine hydrochloride is present in the system (due to electrode polarization).

Nuclear magnetic resonance spectroscopy

A typical proton magnetic resonance (PMR) spectrum of thiamine hydrochloride is represented by Fig. 7. The PMR spectra of thiamine hydrochloride admixed with ferrous sulfate and ferric sulfate are shown in Fig. 8 and 9 respectively. A comparison of the these PMR spectra suggest that the resonance absorptions of various protons present in the thiamine hydrochloride molecule are shifted and brought closer to one another by the presence of paramagnetic ferrous ion. This effect is more pronounced if ferrous ion in the system is replaced by a stronger paramagnetic ion like ferric ion.

On the basis of the above information, one can not be sure whether ferrous and ferric ions have been complexed by thiamine hydrochloride or not. Consequently, the following qualitative experiments were performed:

0.0001M ferrous sulfate was added to an excess of thiamine hydrochloride at pH 1.7. Then potassium thiocyanate was added. A blood red color produced was taken as to reveal the presence of free or uncomplexed ferrous iron in the system.

The above test was repeated by replacing ferrous iron by ferric iron and using hydrogen peroxide in addition. The observed blood red color indicated that ferric ions were reduced to ferrous by hydrogen peroxide and the iron present in the system was free.

Conclusion

On the basis of the results discussed above, it may be concluded that thiamine hydrochloride does not undergo chemical interaction with ferrous or ferric iron. However, it may adsorb onto the pyrite surface causing polarization of the pyrite electrode.

References

1. Kim I. and B. Pesic
   Electrochemistry of interaction of *T. ferrooxidans* with pyrite, Mineral Bioprocessing, Engineering Foundation Conference, Santa Barbara, California, June 16-21, 1991. pp. 413-432.

2. Pesic B. and Inbeum Kim
   Electrochemistry of *T. ferrooxidans* interactions with pyrite, Hydrometallurgy and Aqueous Processing IV: Biotechnological Treatment of Minerals and Effluents, Metallurgical Society of AIME, Anaheim, CA, February 18-22, 1990, pp. 133-160.

Table 1

Results of cyclic voltammetry of ferric iron at pH 1.70 in the absence of thiamine hydrochloride.

Scan rate (mV/sec)	Reduction		Oxidation	
	E(V)	I(A)	E(V)	I(A)
25	0.407	1.09×10^{-4}	0.467	1.31×10^{-4}
50	0.407	1.48×10^{-4}	0.481	1.06×10^{-4}
100	0.394	2.17×10^{-4}	0.491	1.81×10^{-4}
200	0.390	3.91×10^{-4}	0.493	2.93×10^{-4}
400	0.380	4.98×10^{-4}	0.496	4.25×10^{-4}

Table 2

Results of cyclic voltammetry of ferric iron at pH 1.70 in the presence of thiamine hydrochloride.

Scan rate (mV/sec)	Reduction		Oxidation	
	E(V)	I(A)	E(V)	I(A)
25	0.385	6.31×10^{-5}	No peak	
50	0.383	1.00×10^{-4}	No peak	
100	0.365	1.40×10^{-4}	No peak	
200	0.356	3.30×10^{-4}	No peak	
400	0.340	4.30×10^{-4}	No peak	

Table 3

Results of cyclic voltammetry of ferric iron at different pH in the absence of thiamine hydrochloride.

pH	Reduction		Oxidation	
	E(V)	I(A)	E(V)	I(A)
2.8	0.365	2.10×10^{-5}	0.545	1.96×10^{-4}
2.5	0.372	2.30×10^{-5}	0.530	1.03×10^{-4}
2.0	0.415	2.39×10^{-4}	0.495	2.96×10^{-4}
1.7	0.407	1.48×10^{-4}	0.481	1.06×10^{-4}
1.5	0.395	1.63×10^{-4}	0.476	9.84×10^{-5}

Table 4

Results of cyclic voltammetry of ferric iron at different pH in the presence of thiamine hydrochloride.

pH	Reduction		Oxidation	
	E(V)	I(A)	E(V)	I(A)
2.8	Not clear		Not clear	
2.5	0.380	8.00×10^{-5}	No peak	
2.0	0.380	1.54×10^{-4}	No peak	
1.7	0.340	1.00×10^{-4}	No peak	
1.5	0.300	6.57×10^{-5}	No peak	

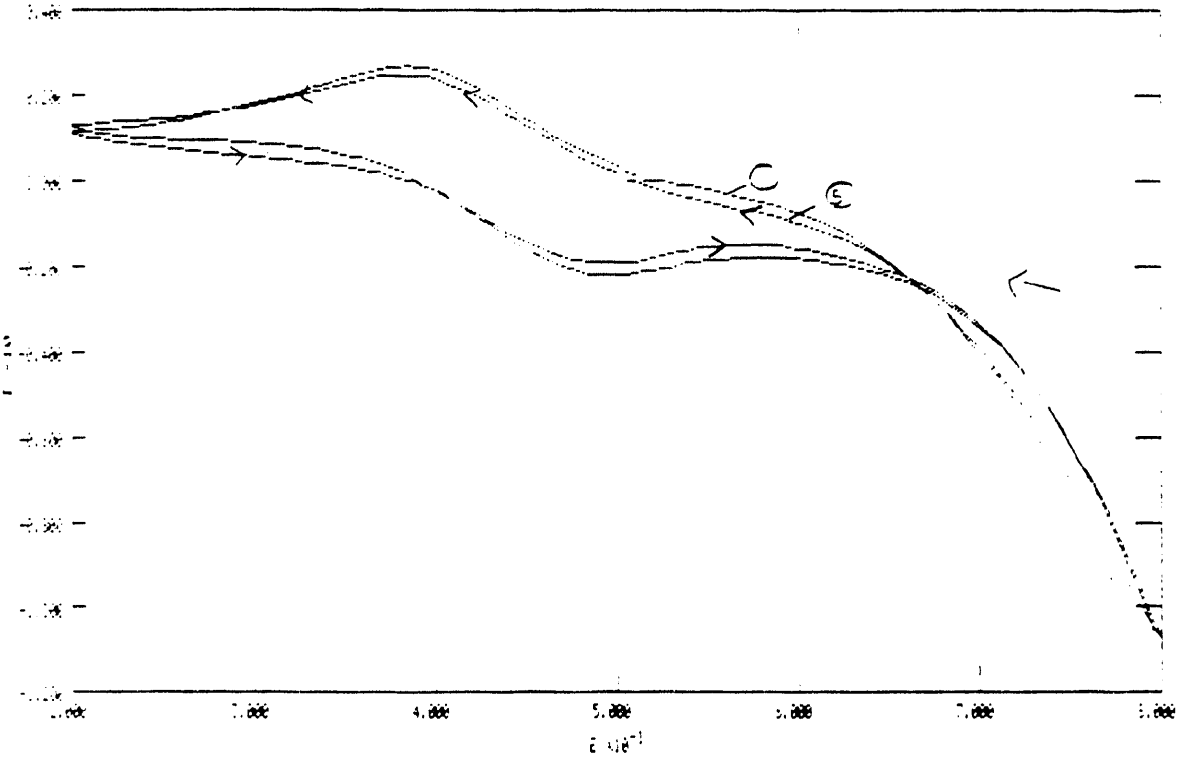

Fig. 1 Cyclic voltammogram of ferric sulfate in the absence of thiamine hydrochloride at pH 1.7.

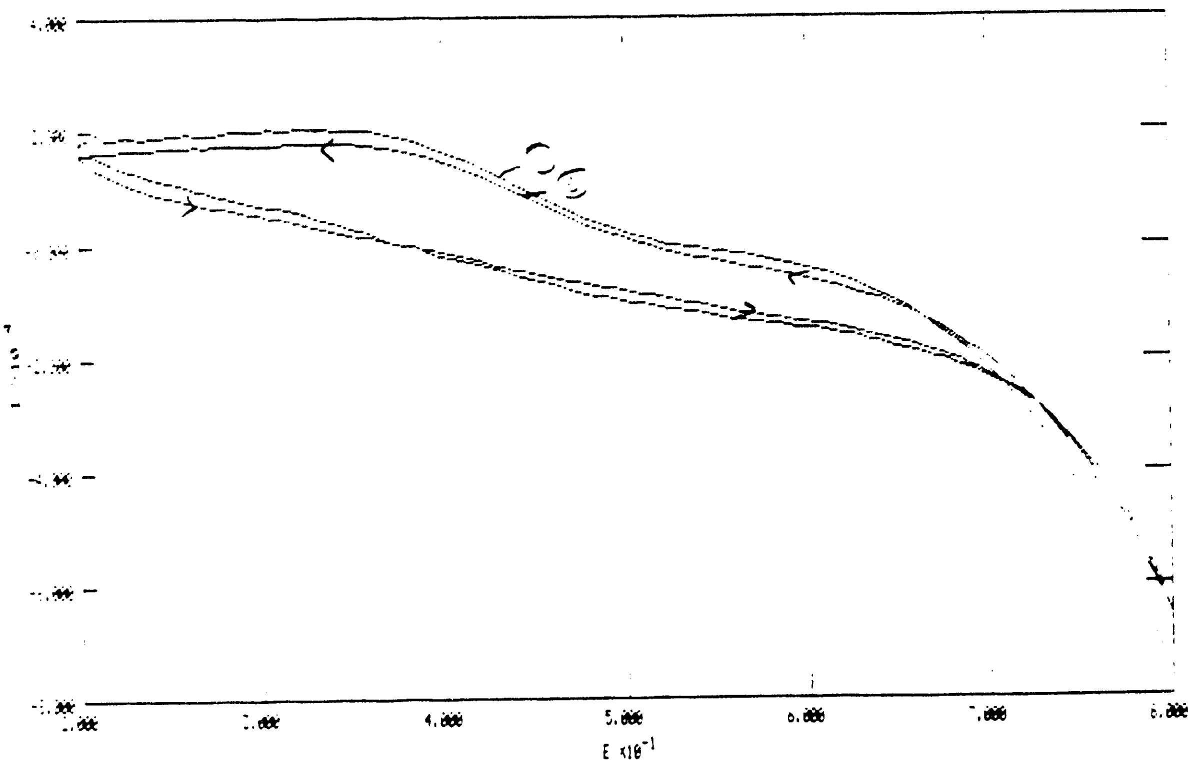

Fig. 2 Cyclic voltammogram of ferric sulfate in the presence of thiamine hydrochloride at pH 1.7.

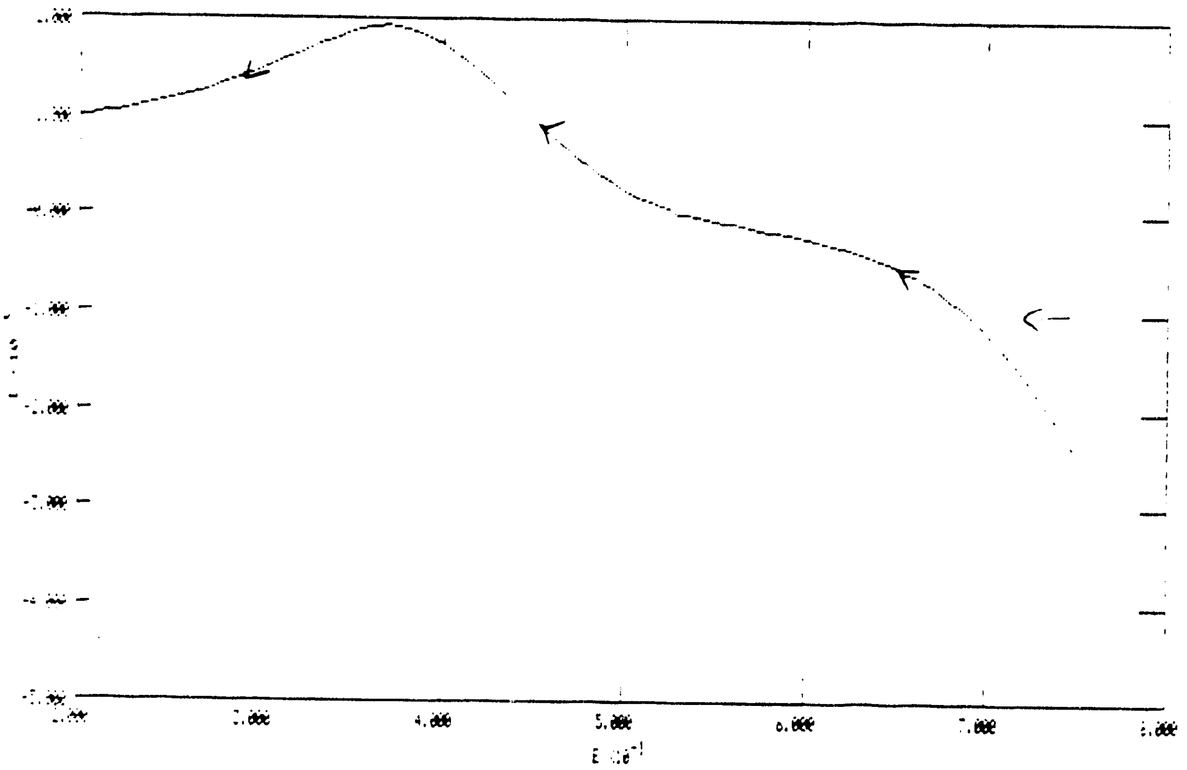

Fig. 3 Linear sweep voltammogram of ferric sulfate in the absence of thiamine hydrochloride at pH 1.7.

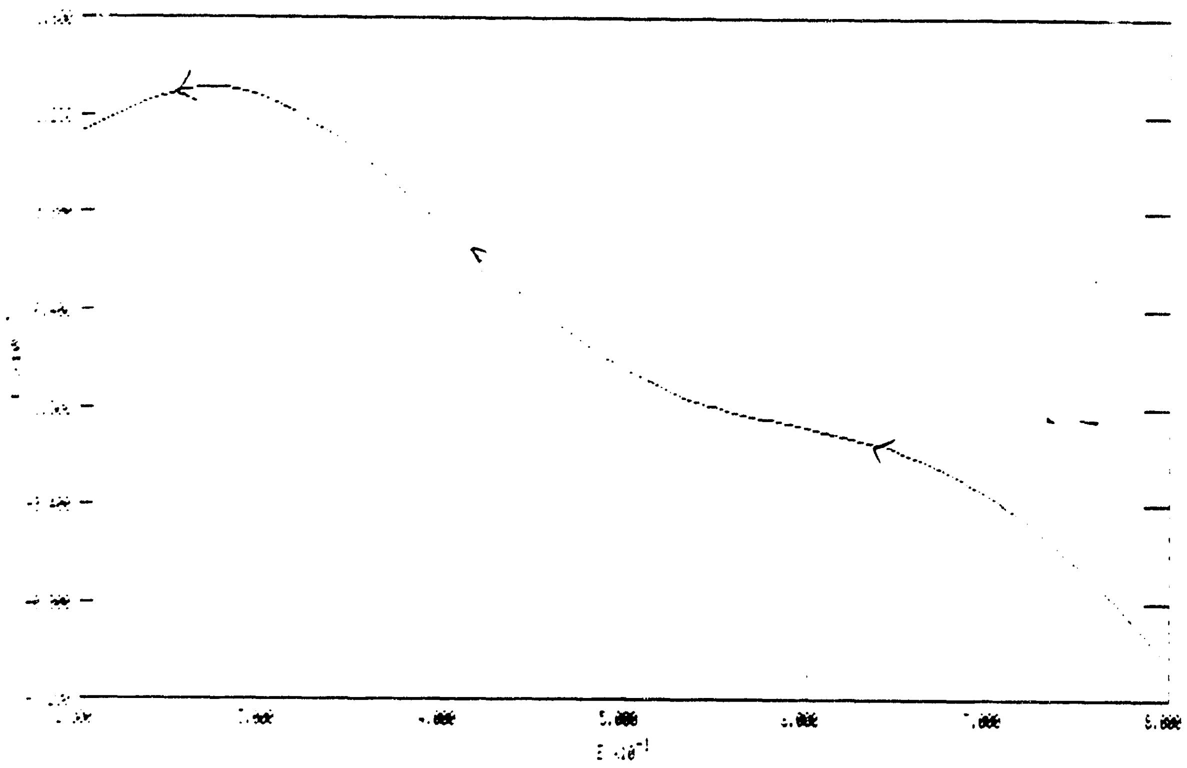

Fig. 4 Linear sweep voltammogram of ferric sulfate in the presence of thiamine hydrochloride at pH 1.7.

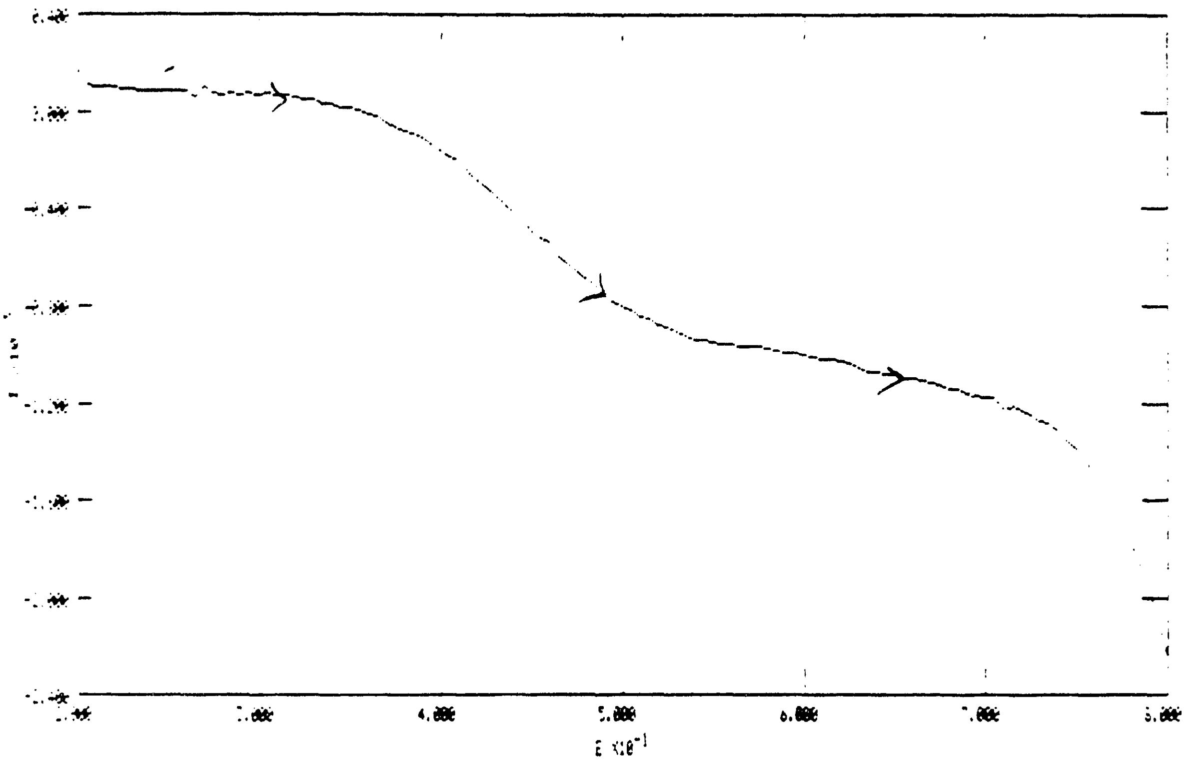

Fig. 5 Linear sweep voltammogram of ferrous sulfate in the absence of thiamine hydrochloride at pH 1.7.

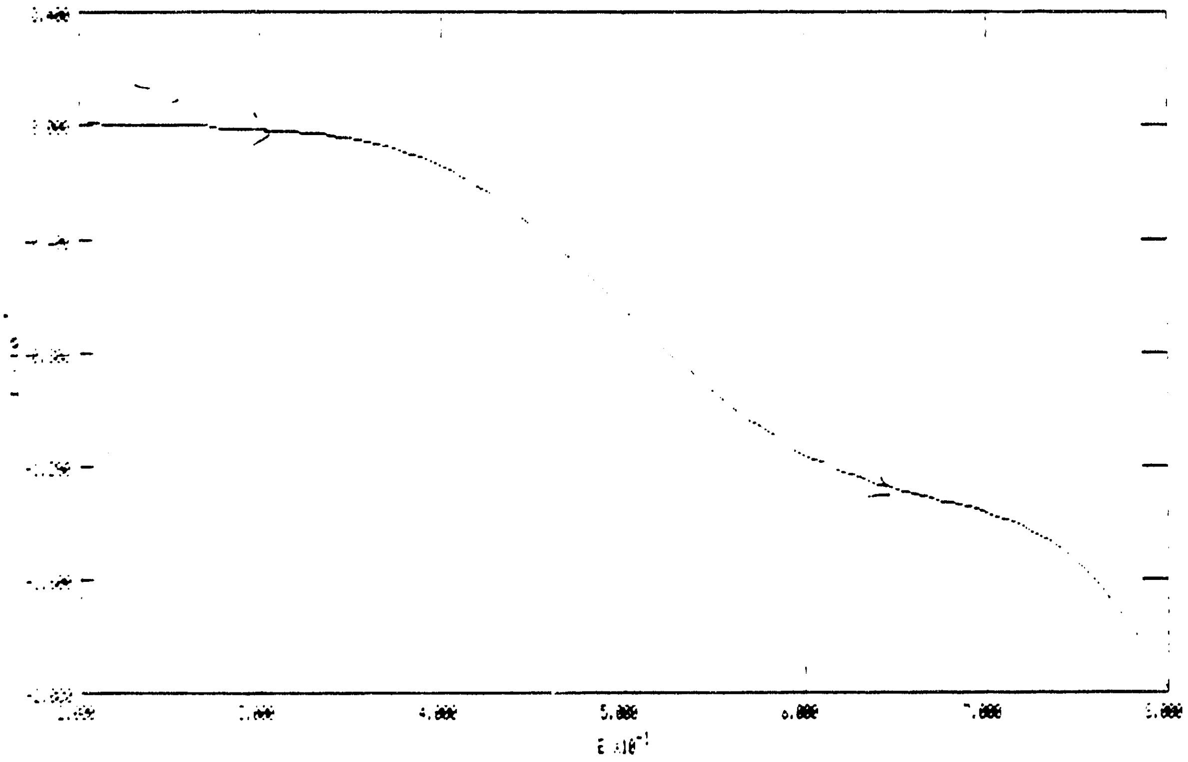

Fig. 6 Linear sweep voltammogram of ferrous sulfate in the presence of thiamine hydrochloride at pH 1.7.

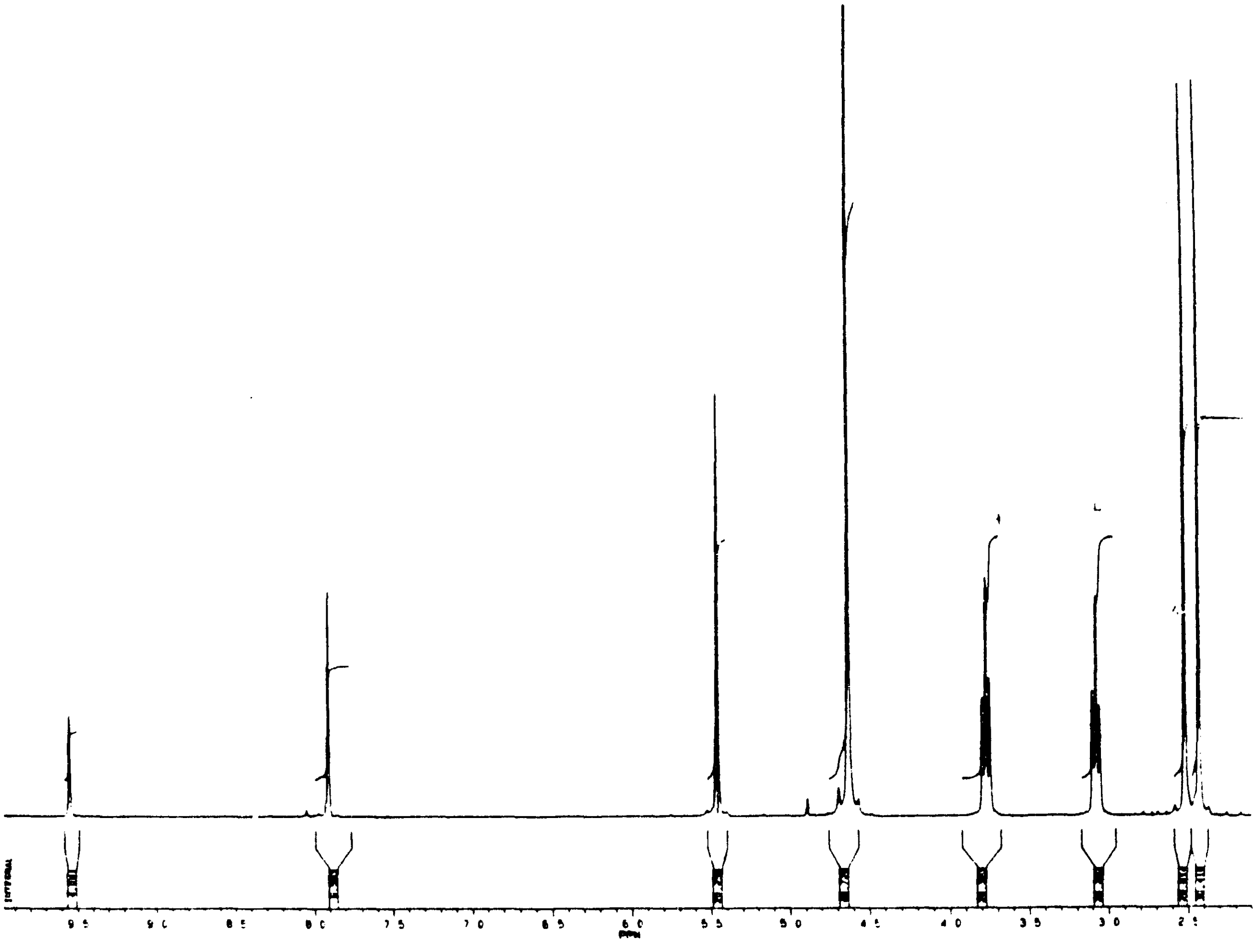

Fig. 7 PMR spectrum of thiamine hydrochloride in solution.

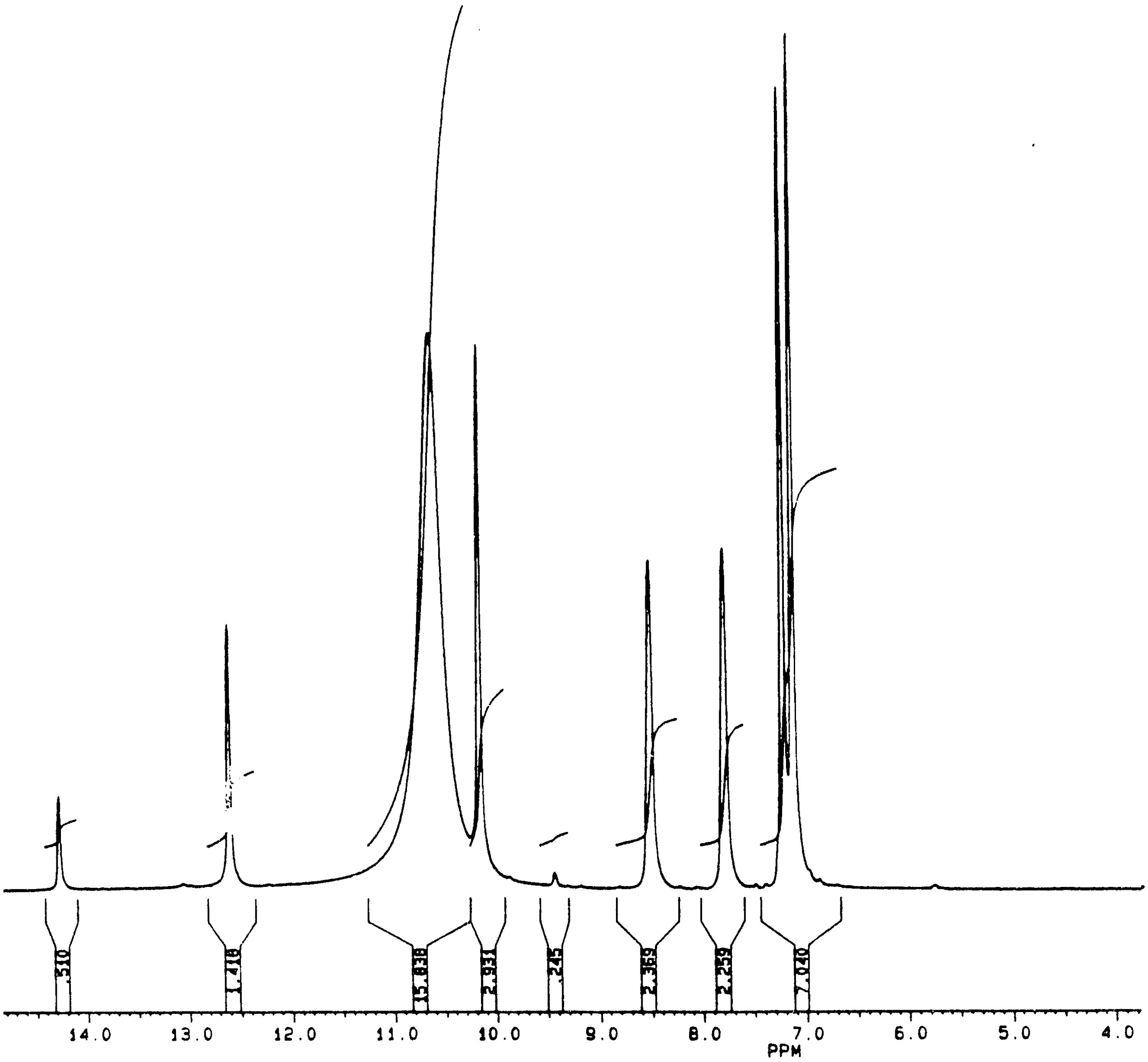

Fig. 8 PMR spectrum of thiamine hydrochloride ferrous sulfate mixture in solution.

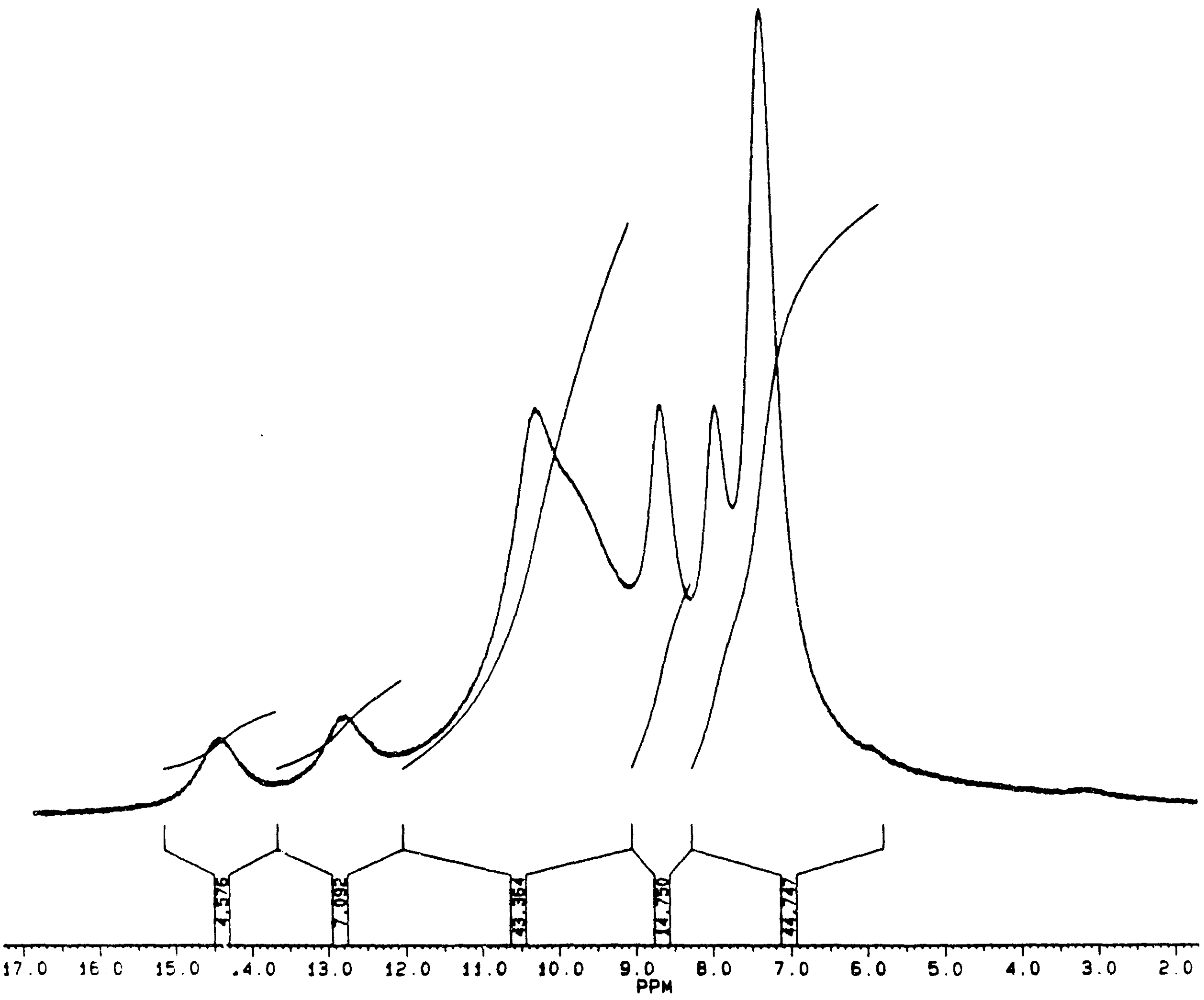

Fig. 9 PMR spectrum of thiamine hydrochloride ferric sulfate mixture in solution.

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