THE FLOTATION OF ZINC OXIDE MINERALS

WITH CHELATING AGENTS

by

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ABSTRACT

The flotation of the zinc oxide minerals smithsonite, hemimorphite and willemite with zinc chelating agents has been studied and the results compared to those obtained with conventional-type collectors. Measurements have been made of the solubility of the zinc oxide minerals, their electrokinetic characteristics and their interaction with dodecylamine and various zinc chelating agents. The nature of the collector layer on the zinc minerals has been investigated.

Zinc oxide minerals are readily floated with conventional type collectors such as oleic acid and long-chain alkylamines but the selectivity is poor. The most selective flotation method involves the use of long-chain alkylamines as collector preceded by an aqueous sulphidisation step, however, the concentrate grades are still poor.

Amines are adsorbed at the zinc oxide mineral/water interface by coulombic attraction and hydrophobic bonding. Sulphidisation reduces the solubility of the minerals and increases the coulombic adsorption of amine. Zinc chelating agents interact with the minerals by a heterogeneous chemical reaction which results in the formation of a layer of zinc chelate. This layer is unstable and detaches from the mineral surface giving rise to a colloidal dispersion in the supernatant solution.

Chelating agents which form insoluble, hydrophobic zinc chelates function as selective collectors for zinc oxide minerals in the Hallimond tube. However, under the shear

conditions which prevail in a laboratory flotation cell the collector layer becomes detached with a consequent loss of mineral flotability. Chelating agents which form insoluble, hydrophilic zinc chelates do not impart hydrophobicity to the zinc oxide minerals. Hydrophobic surfaces are obtained with 8-hydroxyquinoline, 2-methyl-8-hydroxyquinoline, dithizone and Lix 65N (an impure solution of 5-nonyl-2-hydroxy benzophenone oxime in kerosene).

It is concluded that chelating agents cannot be used to float zinc oxide minerals unless ways are found to increase the stability of the collector layer and to reduce the consumption of chelating agent.

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CHAPTER 1

1 INTRODUCTION

1.1 Occurrence of Zinc Oxide Minerals

The major source of zinc is the zinc sulphide mineral sphalerite. However, although over 80% of the world's primary production of zinc comes from this source, the existence of large deposits of zinc oxide minerals with high zinc grades means that the treatment of these ores cannot be ignored. In recent years new deposits of oxide material have been discovered and with the advent of improved processing techniques plants have been built. Examples of new deposits include Beltana (Australia) 1×10^6 tons at 37% Zn; Mae Sod (Thailand) 3×10^6 tons at 35% Zn; Inga (Brazil) 20×10^6 tons at 35% Zn. Other deposits presently being worked are in S.W. Africa, Sardinia, Iran, Morocco, etc. The zinc minerals of commercial interest are listed in Table 1.1.

TABLE 1.1 ZINC MINERALS OF COMMERCIAL INTEREST

Mineral	Formula	Composition % Zn
Sphalerite	ZnS	67.1
Wurtzite	ZnS	67.1
Smithsonite	$ZnCO_3$	52.1
Hemimorphite	$Zn_4Si_2O_7.(OH)_2.H_2O$	54.3
Hydrozincite	$3ZnCO_3.5Zn(OH)_2$	59.6
Zincite	ZnO	80.3
Willemite	Zn_2SiO_4	58.6
Franklinite	$(Fe, Mn, Zn)(Fe, Mn)_2O_4$	15-20

Smithsonite, hydrozincite, hemimorphite and willemite are usually called by the generic name of 'calamine ore'.

Zinc oxide minerals originated through the weathering and oxidation of the primary sulphide deposits resulting in the formation of a zinc sulphate solution. Zinc carbonate and silicate precipitated when this solution came into contact with carbonate rocks or available silicate. Many primary deposits are, therefore, capped by zinc oxide minerals containing smithsonite, hydrozincite, and willemite. In some cases zinc oxide mineral deposits occur alone either as the result of the complete oxidation of the sulphide minerals or the transport of the zinc sulphate solution some distance from the original primary ore body before precipitating. The most common gangue minerals associated with zinc deposits are calcite and dolomite with fluorite, quartz and limonite. A number of metals are commonly found substituted for zinc in the zinc oxide minerals including copper, cobalt, cadmium, manganese, lead, magnesium and iron, although usually only to a small extent (< 1%).

1.2 Recovery Methods

Zinc sulphide ores are fairly readily concentrated by conventional sulphide flotation to give concentrates containing as high as 60-65% Zn. Lower grades are obtained especially if the sphalerite is marmatitic or if the liberation of the zinc sulphide from other sulphides or the gangue is difficult. The zinc sulphide concentrate is treated by two main routes to produce zinc metal. These are a hydrometallurgical route which involves leaching with sulphuric acid and a pyrometallurgical route. Both process,

however, require that the zinc sulphide is oxidised to the oxide. Over 70% of zinc sulphide concentrates are treated hydrometallurgically.

The concentration of zinc oxide ores by conventional mineral processing techniques such as flotation is often difficult because of similarities in the surface chemistry of the gangue and zinc minerals and the presence of goethite slimes which coat all the minerals alike. In some cases, however, flotation with an amine after aqueous sulphidisation does produce an oxide zinc concentrate (1), (2), (3).

Two basic techniques have been developed to treat zinc oxide mineral ores and concentrates, namely fuming with a Waelz kiln and a sulphuric acid leach followed by electrolysis. The Waelz kiln is generally used to treat material rich in dolomitic material although it can also be used to treat silicate rich material (4). A purified zinc oxide concentrate is obtained from this process which can then be treated either by an acid leach or pyrometallurgically. The concentrate also contains lead and cadmium oxides.

Despite the fact that the zinc oxide minerals are readily soluble in sulphuric acid the hydrometallurgical process suffers from a number of disadvantages:-

i) If the ore contains carbonates as gangue material high acid consumptions are obtained which can render the process uneconomic.

ii) The process is unselective and extensive solution purification is required prior to electrolysis.

iii) If the ore contains zinc silicate minerals a highly stable colloidal silica dispersion is obtained which renders solid/liquid separation difficult. Furthermore under certain conditions a silica gel is formed which can occlude much of the zinc sulphate solution.

Various attempts have been made to avoid the problems encountered in an acid leach. These include leaching under alkaline conditions using complexing agents which form soluble zinc complexes. Sodium hydroxide (5), sodium cyanide (6) and aqueous ammonia (7) are some of the solvents which have been used. All these processes, however, suffer from the disadvantage that the dissolution kinetics are slow.

Both the fuming and hydrometallurgical processes are most efficient when the material to be treated is high grade. A preliminary concentration stage, such as flotation, therefore offers considerable advantages.

1.3 Aim of the Project

The objectives of this project were:

1 To examine the existing methods of floating zinc oxide minerals and to determine which method is the most selective.

2 To study the surface chemistry of the zinc oxide minerals to determine why a particular reagent combination gives more selective flotation of the zinc oxide minerals than others.

3 To determine the mechanism of interaction of zinc chelating agents with the surfaces of zinc oxide minerals and to assess whether or not such reagents can be used to render the minerals hydrophobic.

4 To compare the flotation of zinc oxide minerals with chelating agents to that obtained with conventional collectors.

CHAPTER 2

2 FLOTATION OF ZINC OXIDE MINERALS WITH CONVENTIONAL-TYPE COLLECTORS

2.1 Introduction

Gaudin (8) proposed four general flotation methods for the treatment of various base metal oxide minerals, such as cerussite, malachite and smithsonite as follows:-

1 Flotation of oxide minerals with long chain primary amines after sulphidisation of the minerals with alkali sulphide.

2 Flotation of the oxide minerals with carboxylic acids in the presence of gangue depressants. Sulphidisation with alkali sulphide can also be used as a pre-treatment step.

3 Flotation of the oxide minerals with thiol based collectors with and without a pre-sulphidisation stage with alkali sulphide.

4 Dissolution of the base metal minerals followed by precipitation of the metal as the free metal or as an insoluble compound and then flotation of the mixture to recover the metallic sponge or the insoluble compound.

In the particular case of zinc oxide minerals, the mineralogical composition of the ore and its structural features have a decisive effect on the choice of the method of recovering

these minerals. It is a characteristic that these minerals often occur in paragenesis with iron hydroxides. For this reason in certain cases even a high degree of grinding does not ensure a sufficient degree of the liberation of the zinc and iron minerals. In addition, the flotation properties of zinc oxide minerals are not only affected by the nature of waste rock, but also by the presence of multivalent cations dissolved in the pulp and by the amount of clay minerals in the treated ore (9).

The possibility of processing oxidised zinc ores has been examined by numerous authors (1), (2). In 1954. Rey et al (2) developed a moderately successful process which involves the addition of sodium sulphide followed by a collector of emulsified amine. Even with rigorous desliming and consequent loss of zinc before the flotation, however, this process gives low zinc recoveries and poor selectivity. The mechanism of flotation in this process is not well understood.

The carboxylic acid method is applicable with considerable success if the gangue is siliceous or clayey (10) and its applicability is limited if the gangue is highly ferruginous.

Thiol compounds collect zinc oxide minerals but as a general rule the hydrocarbon chain should contain four or more carbon atoms. Amyl and hexyl xanthate exhibit some collection of smithsonite but the selectivity is poor. Better results are obtained with mercaptans and at lower dosages than those used with xanthates, furthermore both smithsonite and hemimorphite are floated (11).

Thyssen et al (11) have studied the effect of previous sulphidisation on the flotation of calamine ores with xanthates

and dithiophosphates as collectors and they showed that sulphidisation did not have a beneficial effect. On similar lines, Stachursky (9) has attempted to float low grade zinc oxide minerals with ethyl xanthate after sulphidising by roasting at 450°C in the presence of elemental sulphur but no improvement was obtained.

In the AMMI group of mines (12), flotation of oxidised zinc ore with xanthates was carried out on an industrial scale in 1952. The procedure consisted of a warm sulphidisation process at 40-45°C followed by activation with copper sulphate and then flotation with xanthate. This process gave good results only on the ores which contained low clay content, and in the end the process was discarded because of heavy losses of zinc during the desliming stage and the low flotation recoveries obtained.

Despite the fact that several attempts have been made to float zinc oxide minerals, no general procedure has yet been developed. However, the method that has been most successful is the one involving a sulphidisation step of the ore followed by flotation with long-chain amines as collectors, (1), (2), (3).

To investigate the effect of the different conventional collectors on the flotation of an oxidised zinc ore, tests were done on a synthetic ore with collectors of hexadecylamine, oleic acid and amyl xanthate. In addition to determining the effect of collector dosage and pH, the effect of sulphidisation was also studied. The response of the individual zinc oxide minerals to the different collectors and the effect of sulphidisation was determined by Hallimond tube tests.

2.2 Experimental Materials and Techniques

Calamine Ore. --An ore sample was supplied by Consolidated Goldfields from Berg Aukas Mine (South West Africa). It consisted of drill cores taken from the oxide-rich part of the mine. Chemical and microscopic analysis showed that the ore assayed 48% zinc and that 87% of the zinc present was in the form of willemite, smithsonite and hemimorphite and the remainder as sphalerite. Liberation of the zinc minerals from the gangue (predominantly dolomite) occurred at very coarse sizes and was complete at below 300 um.

A semi-quantitative x-ray fluorescence scan was carried out on a representative sample of the ore and the results are shown in Table 2.1.

TABLE 2.1 COMPOSITION OF THE CALAMINE ORE

Element and Composition			
Major	Intermediate	Minor	Trace
Zn Si	Na Mg Fe Pb	Al S P Cl Ca	K Ti Mn Cu Mo Cd
> 5%	5-0.5	0.5-0.05%	< 0.005%

Pure Samples of Zinc Oxide Minerals Samples of smithsonite from Kelly (New Mexico) and hemimorphite from Newton County (Missouri) were hand-sorted and ground in a porcelain laboratory mill. The -30+150um fraction was used in Hallimond tube flotation tests. Both samples assayed 95% purity and their x-ray fluorescence analysis are shown in Table 2.2

TABLE 2.2 COMPOSITION OF THE ZINC OXIDE MINERALS USED

Mineral	Element and Composition			
	Major	Inter-mediate	Minor	Trace
Smithsonite $ZnCO_3$ Theoretical Zn content 52.1%	Zn	Mn Al Cu Cd	Si Fe Pb	Ca Mg
Hemimorphite $Zn_4Si_2O_7(OH)_2.H_2O$ Theoretical Zn content 54.3%	Zn Si	None	Ca Fe Cu	Mn Pb
Willemite Zn_2SiO_4 Theoretical Zn content 58.7%	Zn Si	S Ca Fe Pb	None	Cl K Mn Cd
	> 5%	5-0.5%	0.5-0.05%	<0.05%

The willemite sample was obtained from selected samples of the Berg Aukas ore by heavy liquid separation in Clerici solution. The heavy fraction was thoroughly washed with distilled water until no thallous ions were detected by a spot test with potassium iodide solution (see Table 2.2).

Reagents

Hexadecylamine (technical grade) and pure dodecylamine were obtained from Koch Light. 'Pure' oleic acid was supplied by BDH. Potassium n-amyl xanthate obtained from Dow Chemical was purified by dissolution in acetone followed by reprecipitation with ethyl ether. All the solutions were freshly prepared before use.

Cataflot P40 obtained from Prochinor, CECA S.A. and quebracho were used as carbonate gangue depressants. All other reagents were of 'Analar' grade.

Experimental Techniques

Batch Flotation Tests Flotation tests were conducted in a Denver cell on 500 g samples produced by mixing -2mm calamine ore with -2mm limestone in a laboratory rod mill at a pulp density of 60% solids by weight. The mixture was ground for 10 min. and the product was 95% finer than 75um The average grade of the synthetic ore was $23^{+}_{-}0.1\%$ Zn. In those tests where the ore was sulphidised prior to flotation, sodium sulphide was added before the collector solution. Conditioning times of 5 min. were used in both the sulphidisation and conditioning stages. The oleic acid was added as an ethanolic solution.

Microflotation Tests Microflotation tests were conducted on pure mineral samples in a 100 ml modified Hallimond tube. In these tests the mineral was conditioned with the collector for 5 min. and during this time the pH was adjusted to the required value by the addition of HCl or NaOH. In those cases where sulphidisation was required the mineral

was conditioned with 100 ml of 2.1×10^{-4}M '50 ppm) $Na_2S \times 9H_2O$ solution at pH 9 for 5 min. After removal of the excess sulphidising solution and repeated washing with distilled water, the collector solution was added and conditioning continued for a further 5 min. The sample was then transferred to the Hallimond tube and floated for 1 min. with a constant flow of nitrogen (40 ml/min.).

2.3 Results

Both hexadecylamine and oleic acid floated the zinc oxide minerals in the synthetic ore and this is demonstrated in the results summarised in Figs. 2.1 to 2.4 inclusive. Maximum zinc recovery with hexadecylamine was obtained at pH 8.5 and with oleic acid the recovery increased as the pH was made more alkaline 'Fig. 2.1).

In both cases there was no significant effect of pH on the concentrate grade but the concentrate obtained with hexadecylamine had a higher grade than that obtained with oleic acid. In the latter case the concentrate grade was not significantly different to the head grade.

Increasing the collector concentration at pH 8.5 increased the recovery and 100% recovery was obtained at amine and oleic dosages of 150 and 400 gt^{-1} respectively (Fig. 2.2).

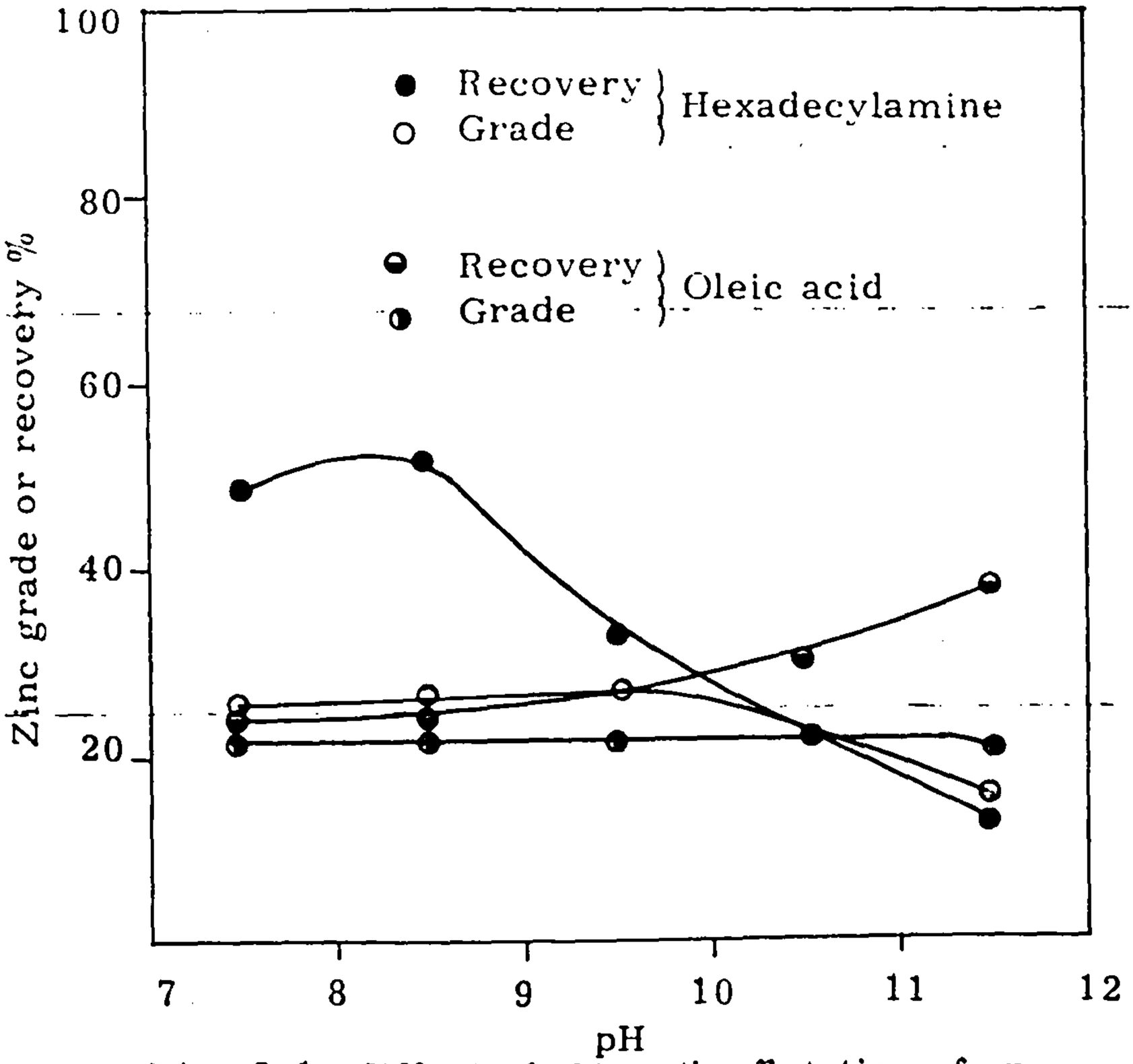


Fig. 2.1 Effect of pH on the flotation of an oxidised zinc ore (collector dosage: 100 gt^{-1})

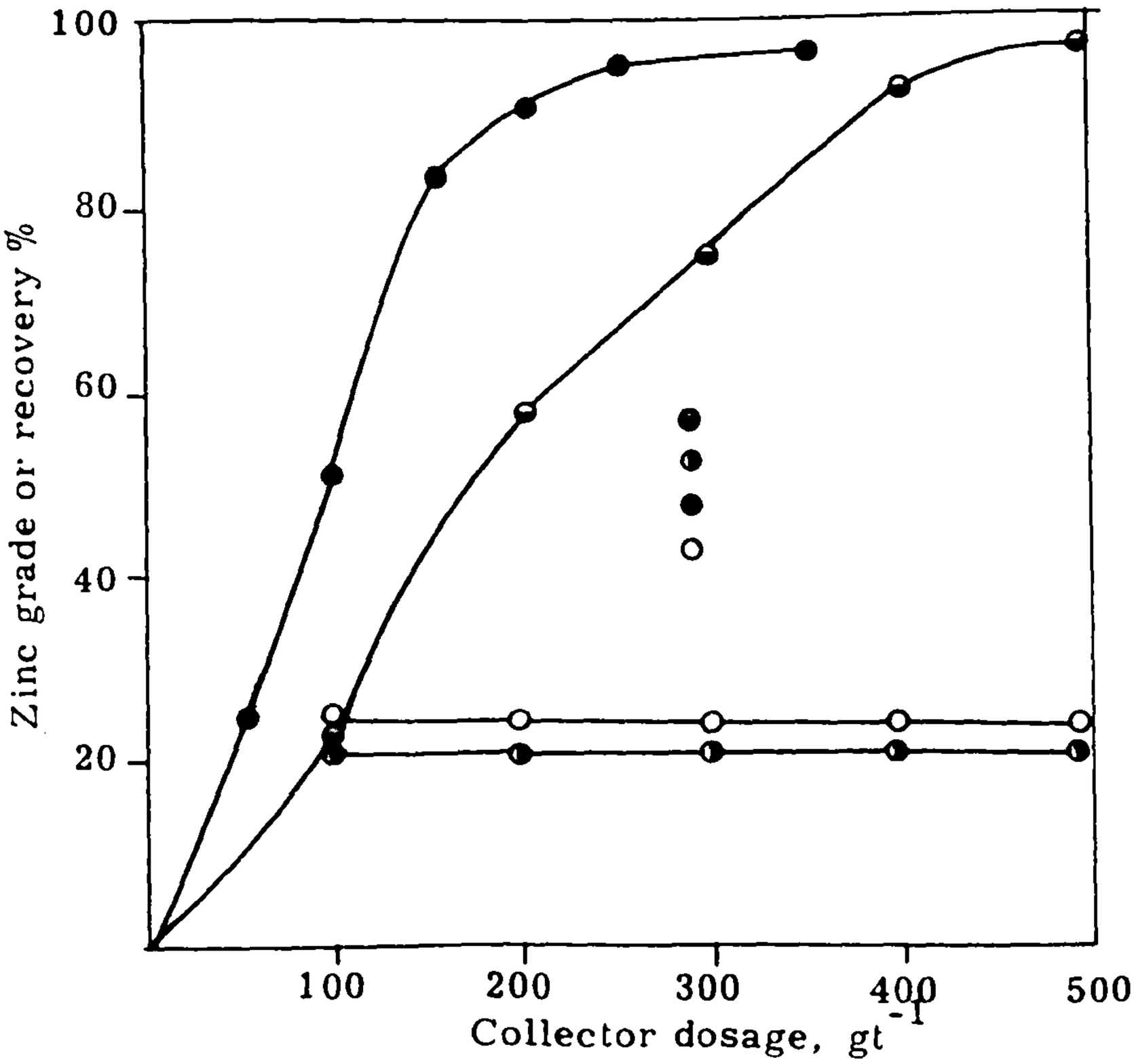


Fig. 2.2 Effect of collector dosage on the flotation of an oxidised zinc ore (pH 8.5)

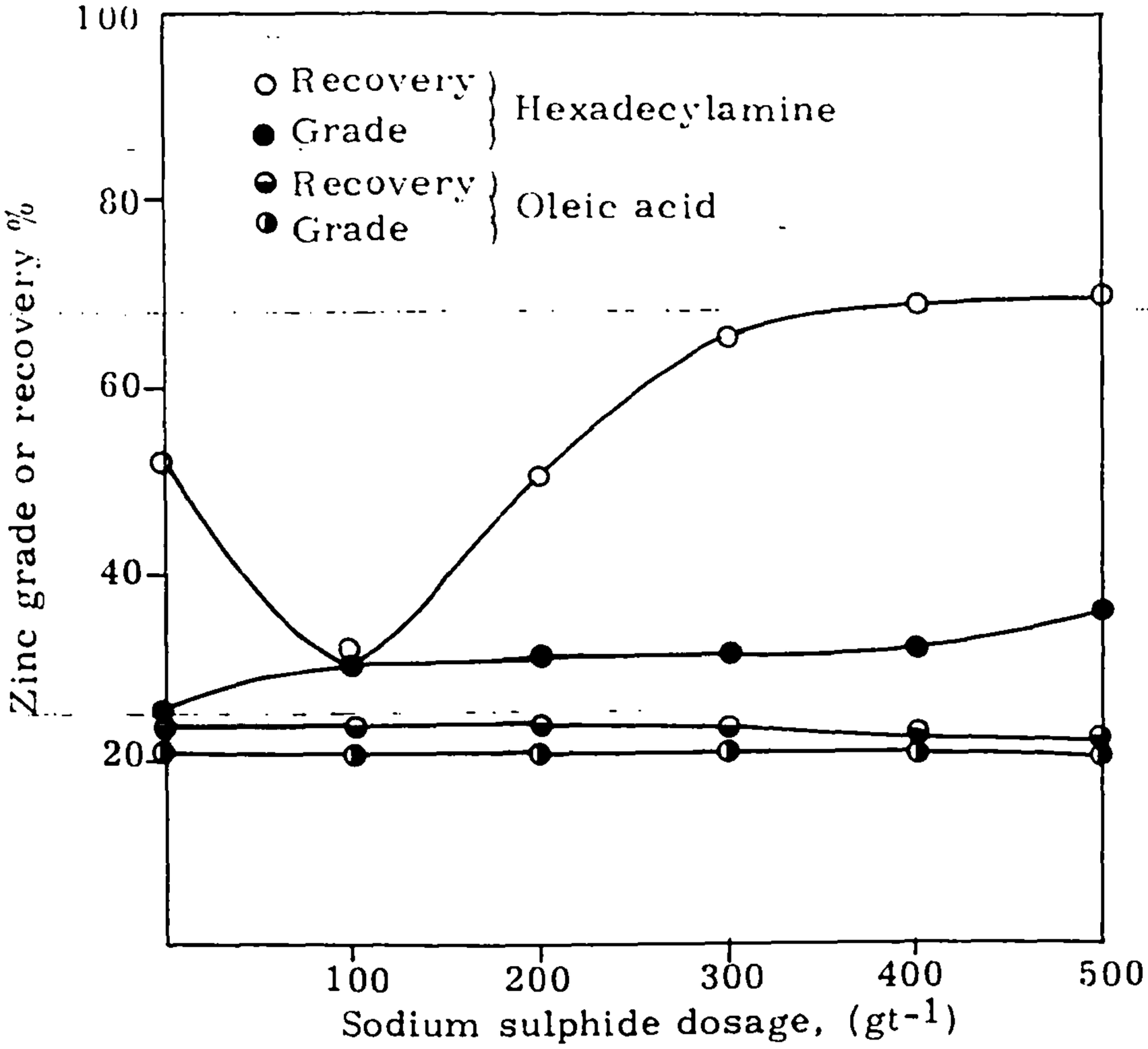


Fig. 2.3 Effect of sodium sulphide dosage on the flotation of an oxidised zinc ore. Collector dosage 100 gt^{-1} pH 8.5

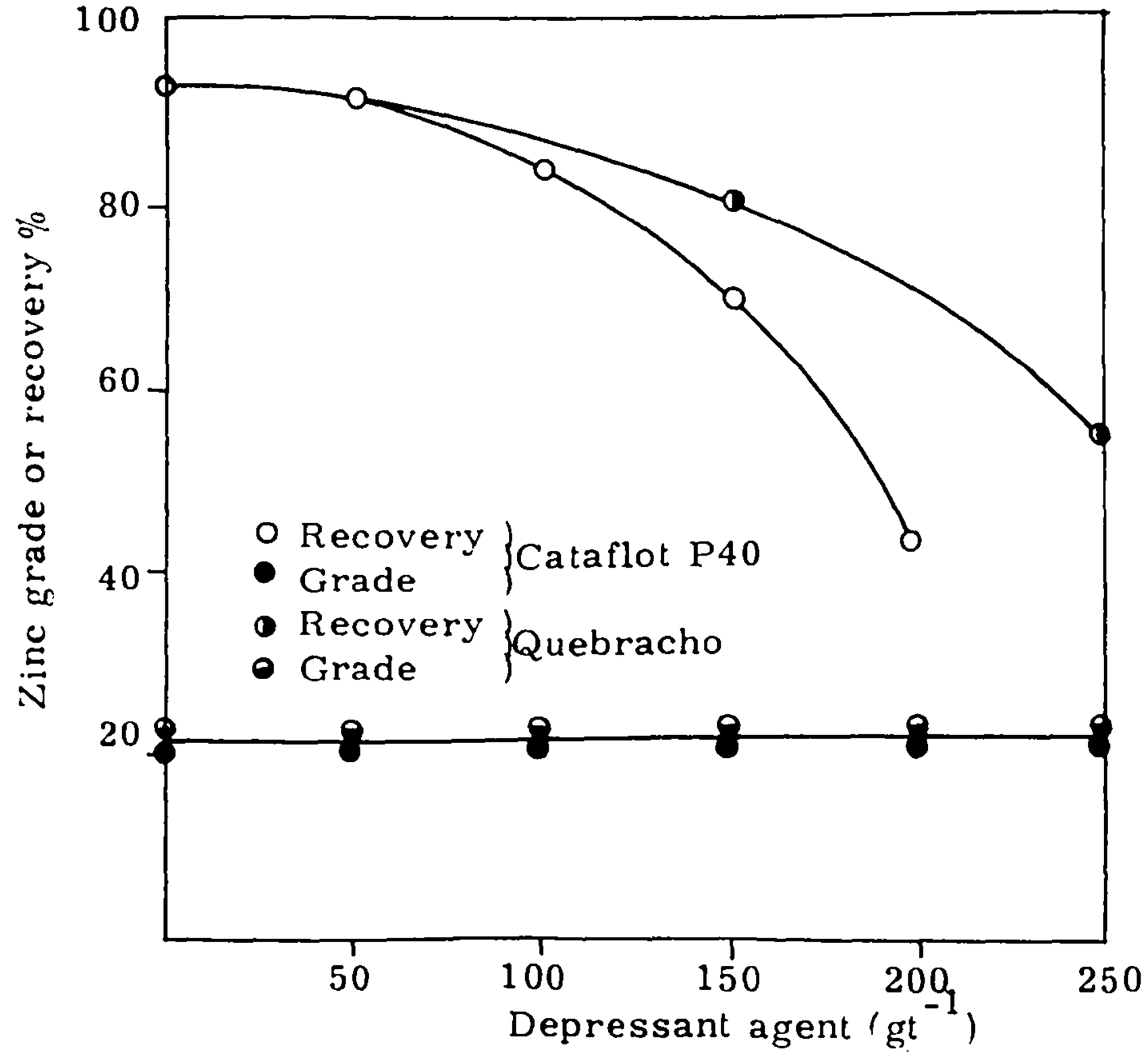


Fig. 2.4 Effect of depressant agents on the flotation of an oxidised zinc ore with oleic acid (400 gt^{-1}) at pH 9.5

The higher oleic acid dosage required does not however imply that oleic acid is a weaker collector than hexadecylamine because the tests with oleic acid were not done at the same pH corresponding to maximum recovery. The concentrate grade was independent of collector dosage.

Sulphidising the zinc minerals had no effect on flotation with oleic acid but the zinc recovery with hexadecylamine did increase with sodium sulphide dosage after an initial reduction in recovery at low sulphide dosages (Fig. 2.3).

The concentrate grade obtained with hexadecylamine after sulphidisation was slightly higher than that obtained without sulphidisation. The addition of quebracho and Cataflot P40 did not improve selectivity with either collector. Both Cataflot P40 and quebracho reduced the zinc recovery with oleic acid (Fig. 2.4) but flotation with hexadecylamine was unaffected.

Recovery of the zinc oxide minerals was low with potassium amyl xanthate as collector even at dosages as high as $1 Kg\, t^{-1}$ and the addition of sodium sulphide and copper sulphate prior to collector addition did not improve it.

To summarize, batch flotation tests on a synthetic ore with oleic acid, hexadecylamine and amyl xanthate have confirmed that although both oleic acid and hexadecylamine are collectors for oxidised zinc minerals only the amine exhibits any selectivity, that amyl xanthate is a poor collector even after sulphidisation and activation of the zinc minerals and that sulphidisation enhances flotation with hexadecylamine. These results clearly showed that a closer investigation of the flotation of the different zinc oxide minerals with amine collectors, with and without prior sulphidisation was warranted.

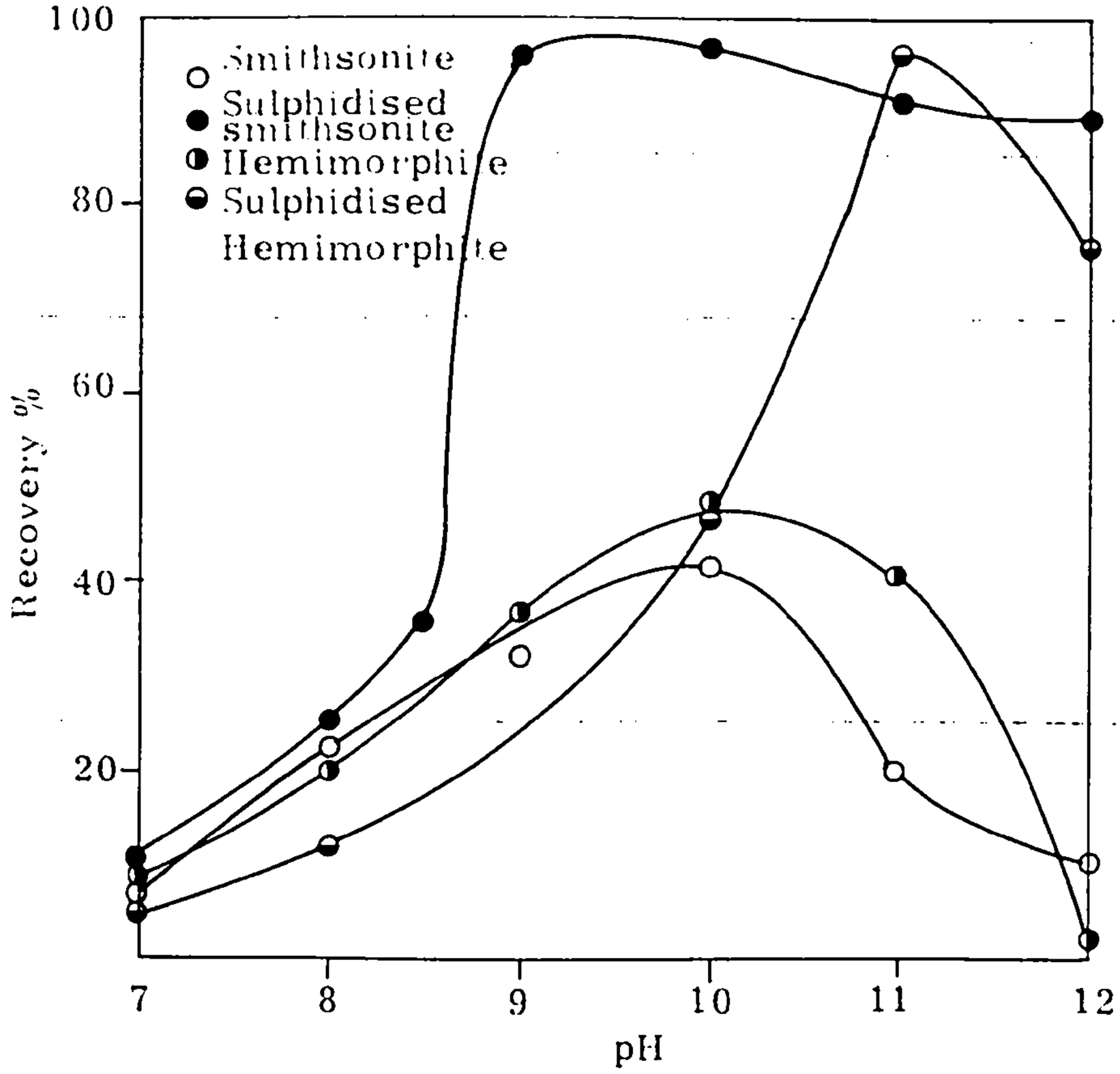


Fig. 2.5a Effect of pH on the flotation of zinc oxide minerals with dodecylamine (2×10^{-5}M)

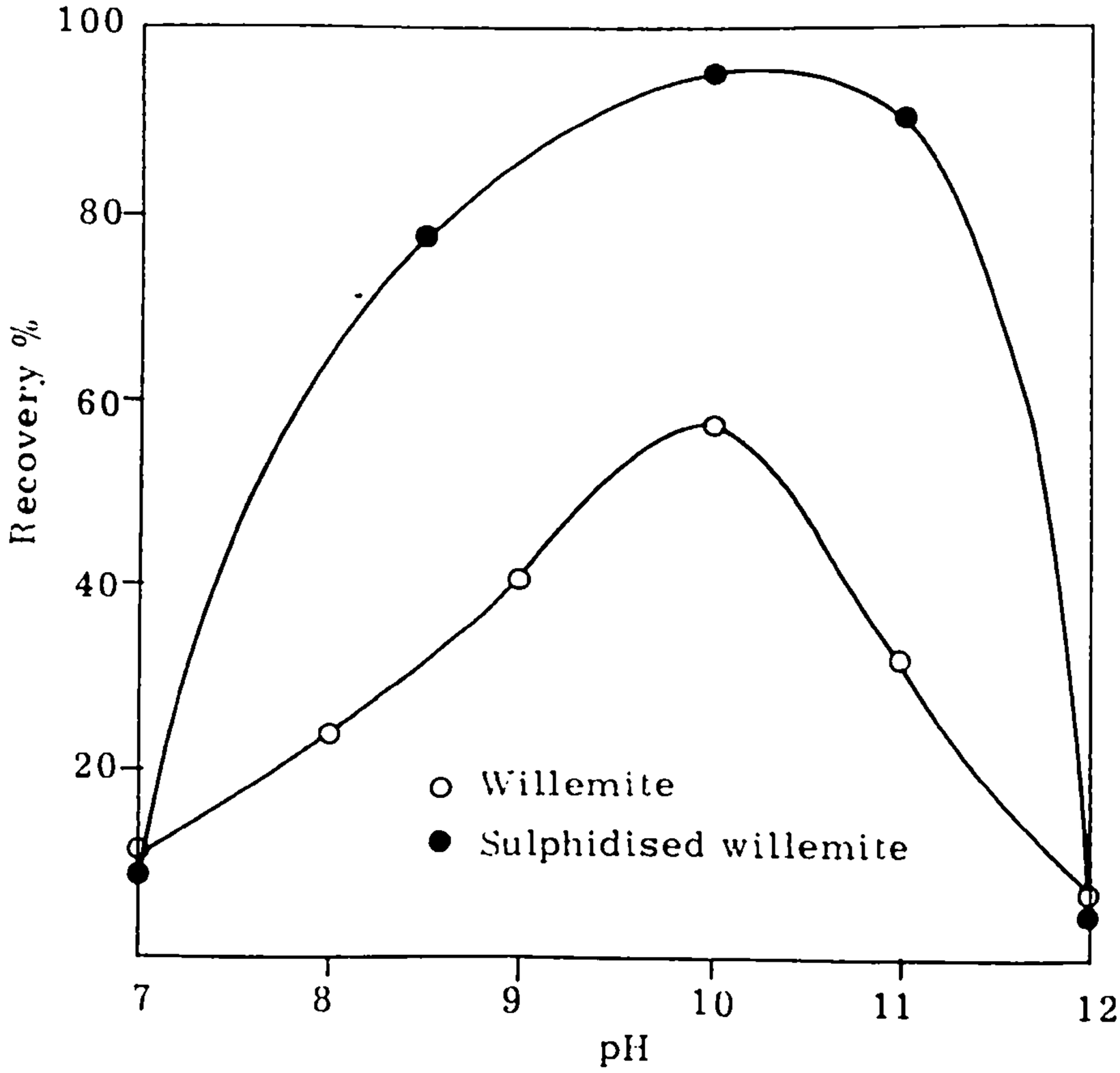


Fig. 2.5b Effect of pH on the flotation of willemite with dodecylamine (2×10^{-4}M)

The Hallimond tube flotation results obtained with smithsonite, hemimorphite and willemite and a collector of dodecylamine are summarised in Figs. 2.5a and 2.5b. The recovery of all three minerals increased as the pH was increased from pH 7.0 to a maximum at pH 10.0. Sulphidising the minerals prior to flotation increased the recoveries and in the case of hemimorphite the pH corresponding to maximum recovery increased from 10.0 to 11.0.

2.4 Discussion and Conclusion

Batch flotation tests on a synthetic ore containing zinc oxide minerals and dolomite have shown that zinc oxide minerals can be floated with long chain 'conventional' collectors like oleic acid and hexadecylamine. In both cases however the selectivity is poor but hexadecylamine is slightly more selective than oleic acid.

Hallimond tube flotation tests have confirmed that pure samples of willemite, hemimorphite and smithsonite have similar flotation responses with dodecylamine and that maximum recovery is obtained at pH 10.0. This pH is somewhat higher than the value of 8.5 found in the batch tests and the difference in amine chain length or the presence of calcium carbonate species could be possible reasons.

Sulphidisation improved the flotation recovery of smithsonite, hemimorphite and willemite with hexadecylamine and dodecylamine but had little effect on flotation with oleic acid and amyl xanthate. In addition to improving the zinc oxide minerals

recovery with hexadecylamine, sulphidisation also improved the concentrate grade from 23 to 30% Zn. These results suggest that sulphidisation is selective for the zinc oxide minerals and has little effect on the dolomite. Similar observations were obtained by Van Lierde (13) who showed that dolomite could be floated with amines in the presence of sodium sulphide but that the amine dosage required was much higher than that required to float zinc oxide minerals.

The addition of two specific carbonate gangue depressants, quebracho which is a high molecular weight natural product containing mainly phenolic groups and Cataflot P40 a low molecular weight polyacrylate, did not exhibit any effect in improving the concentrate grade.

The results obtained show that of the conventional collectors commonly used for the treatment of oxidised base metal minerals only amines exhibit any selectivity for zinc oxide minerals and even then sulphidisation is a necessary preliminary step. Little is known about the mechanism of interaction of amines with zinc oxide minerals or the role of sulphidisation. Before improved collectors for the treatment of oxidised zinc minerals can be developed it is necessary that knowledge of the surface chemistry of these minerals and the sulphidisation reaction be obtained.

CHAPTER 3

3 THE SURFACE CHEMISTRY OF ZINC OXIDE MINERALS IN AQUEOUS SOLUTION

3.1.0 Introduction

Hydrophilic solids such as most minerals, when immersed in water acquire a surface charge because of the ionization of surface sites, or the preferential adsorption of ions. Because the system as a whole must be electrically neutral, the surface charge must be balanced by an opposite excess charge in the liquid phase. Due to coulombic attraction counterions will tend to concentrate in the vicinity of the solid surface, giving rise to an electrical double layer, while ions of similar charge (co-ions) are repelled. Although the formation of an electrical double layer is well known, complete details regarding the origin of the potential at the solid surface are still lacking. The mechanisms suggested for the development of the potential at the solid/water interface can be classified into three main categories; specific chemical interaction, lattice substitution and hydration of lattice atoms (14).

Specific Chemical Interactions These include reactions between the solid and the aqueous phase which lead to the formation of different surface compounds or surface species. This is one of the most common mechanisms of charge generation and is operative in many systems including oxides, silicates, and semi-soluble salts. The formation and subsequent dissociation of

surface acid groups is involved. A typical example is presented by quartz where surface silanol groups dissociate to release hydrogen ions into the solution, leaving the surface negatively charged.

Lattice Substitution The second mechanism whereby the solid surface may acquire a potential is where a charge imbalance arises from lattice substitutions which results in the solid acquiring a fixed surface charge density. The classic example of this mechanism is shown by the clay-type minerals.

Hydration of Lattice Ions In this case, the potential developed by the mineral surface is determined by preferential hydration of surface atoms. This is exemplified in the case of sparingly soluble ionic solids, where an equilibrium exists between the ions making up the surface of the crystal and the same constituent ions in solution, the concentrations being determined by the solubility product of the solid. The surface potential of the solid will thus be fully determined by a thermo-dynamic 'adsorption) equilibrium.

According to the chemical nature of zinc oxide minerals, it is possible to postulate that smithsonite (natural zinc carbonate) owes its surface potential to the hydration of lattice ions, whereas hemimorphite and willemite (two natural zinc silicates) acquire a charge because of specific chemical interactions.

The properties of the electrical double layer are very dependent on the solubility characteristics of the minerals.

Minerals are either considered sensibly insoluble (e.g. quartz, alumina, rutile), their electrochemical properties being determined by the activity of hydrogen and hydroxyl ions, or they are considered to be partially soluble (e.g. zincite, calcite, etc.), yielding hydrolised species which are, in turn, adsorbed. In the latter case equilibrium is again determined by the activity of hydrogen and hydroxyl ions (15). The zinc oxide minerals can be classified in this latter group of minerals since they present rather high solubilities in aqueous solution.

Much of the research on the ionic double layer of 'soluble' zinc minerals has been carried out on zincite (ZnO) (15) (16) (17). Although, however, the interaction of zinc oxide with its aqueous environment might differ in detail from that of the more complex zinc oxide minerals, some common features exist because the zinc oxide compounds release zinc ions in solution. These in turn hydrolise, depending on the pH, according to the following reactions.

$$ZnO_{(s)} + H_2O \rightleftharpoons Zn^{+2} + 2OH^-$$

$$Zn^{+2} + OH^- \rightleftharpoons Zn(OH)^+$$

$$Zn^{+2} + 2OH^- \rightleftharpoons Zn(OH)_{2\ (aq)}$$

$$Zn^{+2} + 3OH^- \rightleftharpoons Zn(OH)_3^-$$

$$Zn^{+2} + 4OH^- \rightleftharpoons Zn(OH)_4^{-2}$$

These hydrolysis products can then be re-adsorbed onto the mineral surfaces.

3.1.1 Electrical Double Layer of the Zinc Oxide Minerals/Solution Interfaces

The adsorption of long chain electrolytes such as amines at the zinc oxide minerals/water interface will be influenced by the sign and magnitude of the mineral's surface charge. Furthermore, one of the effects of sulphidisation might be to change the surface charge thus making surfactant adsorption greater or smaller depending on the nature of the surfactant. A detailed study of the zinc oxide mineral/water interface is therefore required to elucidate the electrical double layer characteristics under different sulphidisation, pH and surfactant conditions. A schematic representation of the double layer according to the Stern-Grahame's model is shown in Figure 3.1. This figure also shows the drop of potential across the double layer.

The electrical double layer may be considered as consisting of a diffuse layer of point charges and an 'inner' layer of thickness δ, about equal to the radius of a hydrated ion, able to contain a certain maximum number of counterions per square centimeter. This is called the Stern layer and it is separated from the diffuse layer by the Stern plane. The closest distance of approach of counterions to the surface is the Stern plane. A Langmuir-type adsorption equilibrium is assumed between the ions in solution and those in the Stern layer, where the adsorption energy is divided into electrical and van der Waals contributions. The electrical potential at the Stern layer is indicated by Ψ_δ. Stern also considered the possibility of the specific adsorption of ions and assumed that these would be located close to the surface and within the Stern layer. These specifically adsorbed ions may lose their hydration shells in the direction of the surface.

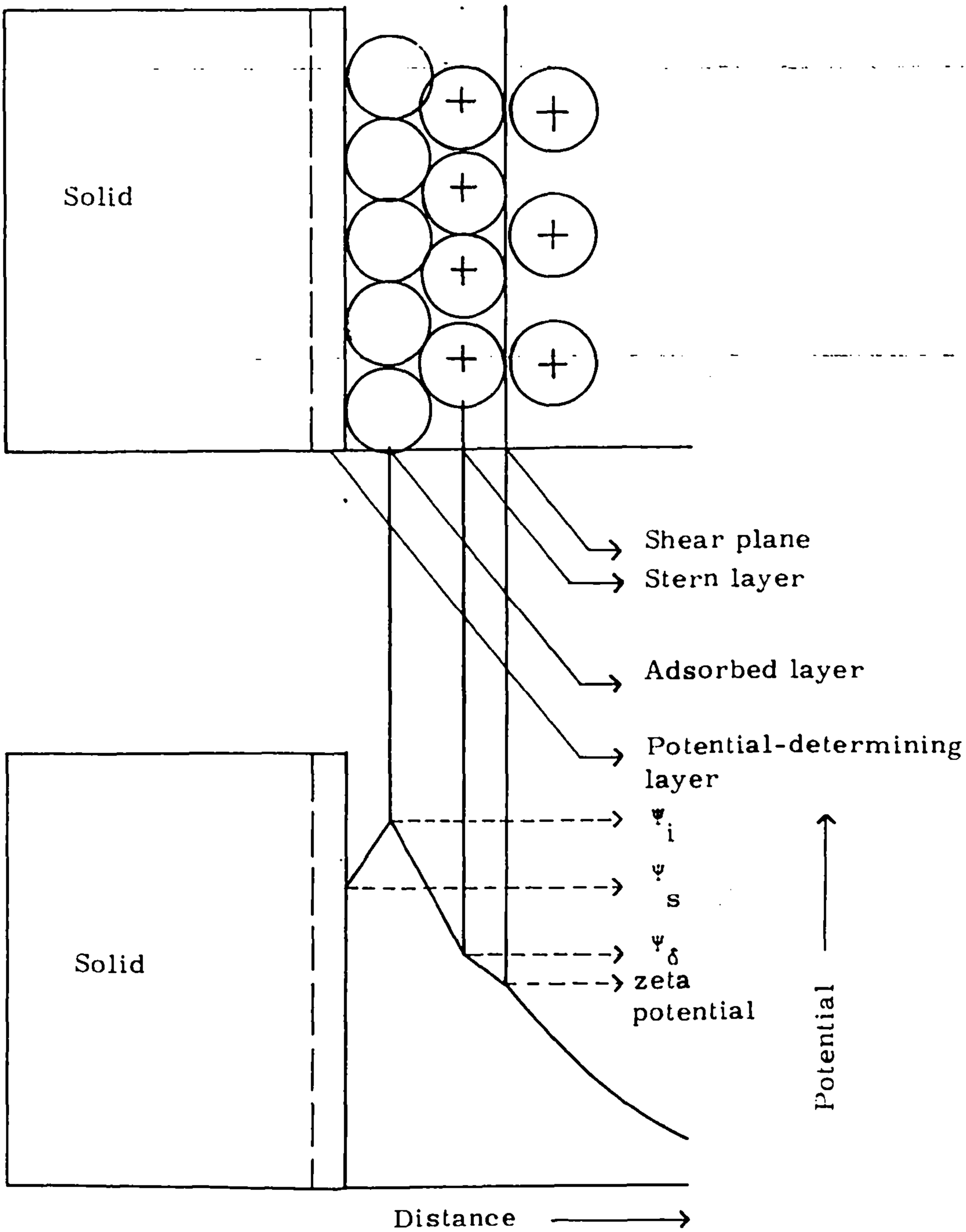


Fig. 3.1 Schematic representation of the electrical double layer

Grahame (18) supplies evidence that the Stern layer can be divided into two regions which he designates the 'inner' and 'outer' Helmholtz planes. The outer Helmholtz plane is considered to be the locus of nearest approach of the centres of the hydrated counterions and lies at a distance δ from the surface. The inner Helmholtz plane is the locus of nearest approach of the centres of specifically adsorbed ions and lies at a distance x_1 from the surface. In the absence of specific adsorption, no centres of ions occur between the outer Helmholtz plane and the surface charge.

In addition to the potential determining ions which change the surface potential of the solid ψ_s there are some ions known as specific adsorption ions which reverse the sign of ψ_δ without changing ψ_s. This reversal of sign shows that the ions are adsorbed by some forces other than that of coulombic attraction.

Experimentally the only potential that can be measured is the zeta potential which is the potential at a shear plane located just outside the Stern plane. When an electric field is applied to a suspension of mineral particles the particles migrate to the electrode bearing an opposite charge. In doing so they take with them that part of the electrical double layer which is enclosed between the solid surface and the shear plane. The exact location of the shear plane is not known, but the zeta potential is generally assumed to be a good approximation to the Stern potential. This approximation is however, only valid under certain conditions, and if the zeta potential or surface potential is high, large errors can be incurred by this assumption.

The difference between the zeta potential and surface potential in the absence of specific adsorption effects can be demonstrated by comparing the zeta potential with the surface potential estimated from the Nernstian expression:

$$\Psi_s = \frac{kT}{ze} \text{ Ln } \frac{a}{a_o} \qquad 3.1$$

where k = Boltzmann constant

T = absolute temperature

z = valence of potential-determining ion

e = electronic charge

a = activity of the potential-determining ion

a_o = activity of the potential-determining ion at the z.p.c.

which can be applied to a large number of solids. Generally the estimated surface potential is very much higher than the zeta potential which, since the potential in solution (Ψ) decreases exponentially according to

$$\Psi_x = \Psi_s e^{-\kappa x} \qquad 3.2$$

where Ψ_x = potential at a distance x from the surface

κ = Debye-Huckel function

x = distance from the surface.

shows that the shear plane is not close to the solid surface. The Debye-Huckel function is the reciprocal of the ionic radius, which is a measure of double layer thickness. It is described by the following expression

$$\left(\frac{8\pi n z^2 1^2}{\bar{e} kT}\right)^{\frac{1}{2}}$$

where, e = dielectric constant and n = total concentration of symmetrical indifferent electrolytes.

The most important parameter which may be used to describe the electrical double layer characteristics of a mineral is the zero point of charge (z.p.c.). This is the concentration of potential-determining ions at which there is no net surface charge and where there is no net adsorption of potential-determining ions. Experimentally the z.p.c. is determined by measuring the adsorption of potential-determining ions, and for oxides and silicates this is done by potentiometric titrations because in this case the potential-determining ions are H^+ and OH^-. An estimate of the z.p.c. can also be obtained from electrokinetic measurements but here zero zeta potential or the iso-electric point (i.e.p.) only corresponds to the z.p.c. when there are no specific adsorption effects.

Considerable uncertainties exist concerning the zero point of charge of oxides. The z.p.c. values of oxides in general depend on the crystal structure, the co-ordination number and chemical nature of the metal ion, the stoichiometry and presence of impurities, the degree of bulk and surface hydration, etc. Moreover, the z.p.c. of the same oxide may differ from sample to sample due to differences in one or more of the above properties. For instance, Blok and de Bruyn (16) presented experimental evidence that the zero point of charge of the ionic double layer on ZnO depends on the method of preparation of the oxide, and they attributed this to changes in surface composition resulting from the inclusion of foreign anions, specifically Cl^- and NO_3^-, in the solid lattice during the precipitation process. Thus, the z.p.c. of the hydrated ZnO precipitate has been reported to vary from pH 8 to 10.

3.1.2 Adsorption of Collectors

Collectors for oxides and silicate minerals are usually amphipatic molecules which contain a polar group and a long, non polar alkyl chain. The nature of the polar group on the molecule or ion, determines whether there is a chemical interaction or merely an electrostatic attraction with the mineral surface, whereas the structure of the hydrocarbon chain determines the extent of its interaction with the aqueous environment (19). A number of forces are presumed to contribute to the adsorption of a collector onto the mineral surface. Hence, the total interaction energy is written as consisisting of two main contributions,

$$\Delta G^{o}_{ads} = \Delta G^{o}_{elec} + \Delta G^{o}_{spec} \qquad 3.3$$

where ΔG^{o}_{elec} is the electrostatic contribution that arises when dealing with an ionic collector interacting with a charged site on the mineral surface. This interaction is given by:

$$\Delta G^{o}_{elec} = zF\psi_{\delta} \qquad 3.4$$

which is zero at the z.p.c. Any adsorption which occurs under these conditions will be given by the term ΔG^{o}_{spec} which represents the free energy associated with specific interaction terms. This general term can be subdivided as follows:-

$$\Delta G^{o}_{spec} = \Delta G^{o}_{chem} + \Delta G^{o}_{HB} + \Delta G^{o}_{h} + \Delta G^{o}_{CH_2} + \Delta G^{o}_{solv} + ... \qquad 3.5$$

Introducing this relation into 3.3 gives the following:-

$$\Delta G^{o}_{ads} = \Delta G^{o}_{elec} + \Delta G^{o}_{chem} + \Delta G^{o}_{HB} + \Delta G^{o}_{h} + \Delta G^{o}_{CH_2} + \Delta G^{o}_{solv.} + \ldots . \quad 3.6$$

where

ΔG^{o}_{chem} represents the free energy due to the formation of covalent bonds with surface sites. In this case the adsorption process should be termed chemisorption, and G^{o}_{chem} may be the largest contribution to the adsorption energy.

ΔG^{o}_{h} and ΔG^{o}_{solv} are the hydriogen bonding energy and adsorption energy respectively, produced by hydration effects. The magnitude of these terms is usually low.

$\Delta G^{o}_{CH_2}$ refers to the direct interaction of the hydrophobic chain with the surface. For oxide minerals, which are hydrophilic, the contribution to the total free energy of adsorption is very small, and may even be positive.

ΔG^{o}_{HB} represents the interaction between the hydrocarbon chains of adsorbed ions at the mineral/solution interface through hydrophobic bonding. It can be expressed as:

$$\Delta G^{o}_{HB} = n\phi \quad 3.7$$

where n is the number of CH_2 groups in the chains and ϕ is the standard free energy for removing one mole of CH_2 groups from water through association. The value of ϕ is approximately 2.5 kJ $mole^{-1}$.

At this point, it is important to discuss terminology concerned with the mechanism of adsorption of organic ions at solid/liquid interface. If the collector is adsorbed only by such forces as electrostatic attraction and hydrophobic bonding - i.e. van der Waals interaction between the hydrocarbon chains - the process is termed physical adsorption- If the adsorption is via formation of a covalent bond between the collector molecule and metal ions in the surface, the process is called chemisorption Examples of physical adsorption in flotation systems include alkylammomium ions on quartz '20), '21) and the alumina-alkyl sulphonate systems '22), '23). Examples of collector chemisorption are hexanethiol-zincite and willemite system (24), and the oleate-fluorite system '25).

Much of the detailed work on mechanisms of long-chain electrolyte adsorption has been carried out with oxide minerals. A generally accepted mechanism has been postulated as follows (26).

At low concentrations, collector ions are adsorbed electrostatically as counter-ions in the diffuse part of the double layer 'physical adsorption) by ionic exchange; during this exchange, the zeta potential and Ψ_δ remain constant. Under these conditions, only the electrostatic adsorption potential is active, i.e. the only contribution to ΔG^o_{ads} in equation 3.6 is given by the term ΔG^o_{elec}. As the bulk concentration is increased the

adsorbed ions begin to associate through hydrophobic bonding and the adsorption increases markedly because of the enhanced adsorption potential produced by ΔG^{o}_{HB}. At the same time, the zeta potential and Ψ_{δ} decreases to zero and two-dimensional aggregates (hemimicelles) form at the solid/water interface. At higher concentrations, the zeta potential reverses and hydrophobic bonding between hydrocarbon chains becomes the main adsorption mechanism.

3.1.3 Interaction of Amine-type Collectors with Zinc Oxide Minerals

Alkyl amine-type collectors are widely used in the flotation of oxide minerals, particularly silicates. Many papers reviewing the mechanisms of action of this type of reagent have been published (20), (21), (27), (28).

The alkylamines are weak bases and in aqueous solution they hydrolise to give the very soluble amine cations according to the following equilibria,

$$RNH_{2\,(s)} \overset{K}{\rightleftharpoons} RNH_{2\,aq} \qquad 3.8$$

$$RNH_{2\,aq} + H_2O \overset{K_b}{\rightleftharpoons} RNH_3^{+} + OH^{-} \qquad 3.9$$

where $K_b = \dfrac{(RNH_3^{+})(OH^{-})}{(RNH_2)}$, where ( ) is the concentration in mole l^{-1}.

For dodecylamine $K_b = 4.3.10^{-4}$ moles l^{-1}, but this value is not significantly altered by a change in chain length. This contrasts with the value of $K = 2.0 \times 10^{-5}$ M which decreases with an increase in chain length.

From this equilibria it is clear that in acid media the cationic amine predominates and the over-all solubility of the amine is high. As the pH increases, however, the concentration of $RNH_{2_{aq}}$ increases at the expense of a decrease in RNH_3^+, until it reaches the value of K whereupon precipitation occurs. At pH values above 10.5 the unionized amine predominates, i-e, $(RNH_{2_{aq}}) > (RNH_3^+)$.

Some general statements can be made relative to the mechanisms of adsorption of cationic surfactants on oxides and silicates.

1 For significant adsorption and, therefore, flotation to occur, the surface potential of the mineral should be negative. This means that in general maximum adsorption occurs at pH values above the z.p.c. of oxides and silicates.

2 The effect of hydrocarbon chain length on adsorption is related to the free energy decrease (1.1 k T per CH_2 group) on expulsion of each CH_2 group from the aqueous phase by association of the hydrocarbon chains. Thus, the longer the hydrocarbon chain, the lower the critical hemimicelle concentration and the lower the molar quantity of collector required to give a certain adsorption density or flotation recovery.

3 The critical hemimicelle concentration depends on the ratio of charged to neutral amine species in the double layer, which in turn depends upon the surface electrical potential and the concentrations of charged and neutral species in the bulk solution.

4 The effect of pH on adsorption is two-fold:
a) H^+ and OH^- are potential-determining ions and therefore determine the sign and magnitude of the surface potential,
b) the OH^- concentration establishes the extent of hydrolysis of alkyl amine collectors.

5 Inorganic cations present in solution compete with the amine cations within the double layer thereby reducing amine adsorption (29), (30).

6 Multivalent anions, such as SO_4^{-2} and SiF^{-6} can adsorb on positive sites on minerals and, thus promote adsorption of cationic collectors on otherwise positively-charged oxides and silicates (31).

Unfortunately, few basic studies on the surface chemistry of zinc oxide minerals, whether in the absence or in the presence of long-chain alkyl amines have been published, and those which have only refer to smithsonite (32), (33), (34), (35).

Thus Araskhevich and Belov (32) have studied the flotation and electrokinetic behaviour of smithsonite in the presence of ANP (a commercial product containing a mixture of long-chain primary amines). At the same time, they studied the influence of different pH regulators and found that the optimum conditions for the flotation of smithsonite were obtained between pH 7. 5 to 9. 5 using Na_2S as a pH regulator. Belov and Molochnikova (34) studied the surface properties of smithsonite in the presence of various electrolytes and ANP as collector.

They concluded that the adsorption of the collector was maximum between pH 8.0-10.0 and decreased in the presence of very low concentrations of metallic cations in the following order:

$$Zn^{+2} > Cu^{+2} > Fe^{+2} > Fe^{+3}$$

Cases and his associates (35) have studied the smithsonite/alkylamine system more systematically and have established that the flotation is strongly dependent on the collector chain length. In addition, they have presented experimental evidence indicating that sulphide ions act as flotation activators through a sulphidisation process of the smithsonite surface.

3.1.4 Sulphidisation of Zinc Oxide Minerals

Alkali sulphides are commonly used as modifying agents in a number of mineral flotation systems. The action of these modifiers, however, can be two-fold since they can act either as activating or depressing agents.

It is well known that sulphide ions can enhance the flotation of oxide copper and lead minerals such as malachite and cerussite respectively with xanthate-type collectors (36)(37)(38). The accepted mechanism involves the formation of a chemisorbed layer of metallic sulphide by reaction of the aqueous soluble sulphide ions with metallic atoms forming the crystal lattice of the mineral.

The formation of the sulphidised layer at the mineral/water interface induces favourable surface modifications which

improve the subsequent sorption of collector and, therefore, better flotation results are obtained. Abramov (39) postulated that sulphidisation of oxide minerals produces an increase in hydrophobicity, but that this hydrophobization is only partial and insufficient to induce floatability without the addition of a collector. This was explained by an increase in the covalent bond/ionic bond ratio of the surface crystal lattice. The hydrophobic effect of sulphidisation was experimentally demonstrated with sulphidised malachite (40) and chrysocolla (41) by flotation using non-polar oil emulsions as collectors.

In addition, sulphidisation plays an important role in the stabilization of the oxide mineral surface. Firstly, it diminishes the usually high solubilities of these minerals, so preventing the release of cations into solution which can precipitate part of the collector in the bulk solution. Secondly the formation of the sulphidised layer contributes to the stabilization of the collector coating at the mineral/water interface. This means that the collector is more strongly attached to the surface making it more resistant to inter-particle attrition with the overall result that lower collector dosages are required (41)

Attempts to study the chemical factors involved in the sulphidisation reaction of oxide minerals were initiated by Mitrofanov et al (42) on both lead and copper oxide minerals. They determined the velocity of growth of the sulphidised layer on these minerals by using sulphidising solutions containing radioactive isotopes of sulphur. More recently Castro et al (43) (44) working on copper oxide minerals have found that in

addition to the formation of a sulphidised layer at the mineral surface, oxidation of excess sulphide ions occurs through a heterogeneous catalytic mechanism.

In section 2.3 it was shown that zinc oxide minerals can be more efficiently concentrated by flotation with dodecylamine as collector after a sulphidisation step. Unfortunately, no work has been found on the chemical factors involved in the sulphidisation of zinc oxide minerals. A systematic study of the sulphidisation of zinc oxide minerals was therefore made to determine why sulphidisation affects their flotation with dodecylamine.

3.2. Experimental Materials and Techniques

3.2.1 Solubility Determinations

The variation of the solubilities of smithsonite, hemimorphite and willemite in the pH range 5-11 at $20 \pm 1^{o}C$ was determined by shaking 1 g of each finely ground mineral, obtained by grinding the minus 150 um fraction in a vibratory Tema mill, for 5 min. in 100 ml aqueous solution in closed containers. The initial pH was adjusted by additions of sulphuric acid and sodium hydroxide solutions. Deoxygenated and CO_2-free water was used throughout. The samples taken at intervals from the stirred suspension were centrifuged to separate the solids and total soluble zinc was determined by atomic absorption spectrophotometry with a Hilger-Watts 'Atomspek' which has a sensitivity of 0.02 ug ml^{-1} Zn for 1% absorption. The pH was measured by a combined glass-calomel electrode calibrated with buffer solutions of pH 4.0, 7.0, and 9.2.

The effect of sulphidisation on the solubility of zinc oxide minerals was studied as follows: the smithsonite and hemimorphite were sulphidised with 100 ml of 1.10^{-3}M (240 ppm) $Na_2S.9H_2O$ solution at pH 10.5 for 4 hours. After this treatment the pH of the dispersions were adjusted to different initial pH values by the addition of either sulphuric acid or sodium hydroxide solutions and shaking continued.

3.2.2 Determination of the Electrophoretic Mobility of Zinc Oxide Minerals

Electrophoresis studies have been carried out on smithsonite, hemimorphite and willemite at different pH values and

in the presence of dodecylamine and sodium sulphide. These measurements were made using a Rank Bros. Particle Electrophoresis Apparatus (Mark II) with a flat cell. The mineral samples were the same as those described in Section 3.2.1. Small amounts of these samples were dispersed using ultrasonics in 25 ml of aqueous solution and the pH adjusted with either NaOH or H_2SO_4 after which the samples were conditioned for 5 min. These suspensions were considered to be freshly-prepared. Some of the suspension was used to wash the electrophoresis cell before making the measurements. In those cases where the effect of ageing was studied, the mineral samples were dispersed using ultrasonics in 1 litre of the appropriate solutions and then left until required. In the cases where the effect of sulphidisation was studied, sulphidisation was carried out by dispersing the minerals with ultrasonics in freshly prepared sodium sulphide solutions of different concentrations. The effect of dodecylamine on the electrophoretic mobility of zinc oxide minerals was studied by dispersing the minerals in dodecylamine solutions of different concentrations, and the effect of sodium sulphide in this series of tests was determined by using sodium sulphide solutions as pH modifiers.

The zeta potential (ζ) is related to the electrophoretic mobility of the particles, that is the velocity of migration of the particles under unit potential gradient, by the Helmholtz-Smoluchowski equation (45) modified where necessary by Henry's correction factor for retardation. Thus

$$u = \frac{E\zeta}{6\pi\eta} \cdot f(\kappa a) \qquad 3.10$$

where u = electrophoretic mobility

e = permittivity

η = viscosity of the dispersion medium

a = the average radius of the particles

κ = Debye -Huckel function, i.e. the reciprocal of the double layer thickness.

The function of $f(\kappa a)$ depends on the size, shape and orientation of the particles and its values, which vary between 1.0 and 1.5, are tabulated elsewhere (46).

Under the conditions used in the present work equation 3.10 simplifies to

$$\zeta = 12.83u\ f(\kappa a) \qquad 3.11$$

where ζ is measured in mV and the electrophoretic mobility in um sec^{-1}/volt cm^{-1}. However, because of uncertainties in the value of $f(\kappa a)$, the results are quoted as electrophoretic mobilities and where required estimates of ζ can be made by applying equation 3.11.

3.2.3 Dodecylamine Adsorption Studies

a) Determination of dodecylamine The concentration of dodecylamine in solution was determined by complexing the amine with an acidified alcoholic solution containing a sulphnapthelein indicator (47), e.g. bromo-cresol green, as complexing agent and then extracting the complex into chloroform. The indicator solution was prepared by dissolving 0.1 g bromo-cresol green in 60 ml of ethyl alcohol, acidifying with 0.5 ml concentrated sulphuric acid, and diluting with water to 100 ml.

In each determination, 1 ml of indicator solution was added to 5 ml of the sample solution and diluted to 10 ml; 5 ml of chloroform were then added and the mixture inverted rapidly about 50 times. The chloroform phase was then separated and the absorbance at 416 nm determined in a Perkin -Elmer Model 124 double-beam spectrophotometer (with 1 cm glass cells).

b) Determination of adsorption isotherms Adsorption isotherms of dodecylamine on smithsonite and hemimorphite were determined. These tests were carried out by shaking 1 g samples of the zinc oxide minerals in 100 ml dodecylamine solutions in closed containers for periods up to 1 week. The residual amine concentration was then determined. The pH of the solution in tests with hemimorphite was found to decrease during the conditioning time, and the final pH was often 0.5-1 unit less than the initial pH. With smithsonite no appreciable change was observed.

Sulphidisation tests The hemimorphite was sulphidised with 100 ml of $6.0 \cdot 10^{-4}$ M $Na_2S.9H_2O$ (147 ppm) at pH 10.0 for 15 min. After removal of the excess sulphidising solution and repeated washing with distilled water, different dodecylamine concentrations were added and conditioning continued for 1 week. For smithsonite the sulphidisation process was carried out under similar conditions, but only 50 ml of sulphidising solution was used after 15 min. (when no sulphide ions remained) 50 ml of dodecylamine solution was added to make the volume up to 100 ml. Conditioning was then continued. In the cases of unsulphidised and sulphidised minerals equilibrium was attained after 2 days.

Surface areas were determined by the dynamic one-point BET method, using a 'Monosorb' surface area analyser 'Quantachrome Corp.'). Values were reproducible to about 1% being 0.44 $m^1 g^{-1}$ for smithsonite, 0.65 $m^2 g^{-1}$ for hemimorphite and 0.59 $m^2 g^{-1}$ for willemite.

3.2.4 Sulphidisation of Zinc Oxide Minerals

a) Sulphide Ion uptake measurements These tests were conducted contacting 1 g samples of either smithsonite or hemimorphite with 100 ml $Na_2S.9H_2O$ solution at different pH values and concentrations. In the case of hemimorphite a finer sample 2.8 $m^2 g^{-1}$) was used due to the slow abstraction of sulphide ions with this mineral. After different periods of time the solid was separated by centrifugation and analysis of residual sulphide ions in solution was made. All experiments were carried out with freshly prepared $Na_2S.9H_2O$ solutions. Before dissolution sodium sulphide crystals were thoroughly rinsed with a dilute sodium hydroxide solution to eliminate soluble oxidation products 'thiosulphate, sulphate, etc). After drying the crystals on a filter paper the solution was prepared. A nitrogen atmosphere and deoxygenated and CO_2-free water were used throughout.

b) Sulphide ion analysis Sulphide ion concentration was determined spectrophotometrically by the method described by Fogo and Popowsky (48). This method involves the conversion of p-dimethylamino-aniline into methylene blue by coupling with HS^- or H_2S) in the presence of ferric ions. The absorbance of the resulting methylene blue solution was measured at 670 nm wavelength. A calibration curve was determined with known amounts of sulphide.

c) Reagents p-Dimethylamino-aniline was obtained from BDH. A solution containing 0.1 g in 100 ml of 5.5 M HCl was used.

Ferric chloride (BDH): 100 ml of 0.023 M $FeCl_3 . 6H_2O$ solution was mixed with 100 ml of 1.2 M HCl.

d) Procedure After the smithsonite and hemimorphite dispersions were centrifuged, a 10 ml aliquot of the clear supermatant solution was transferred to a 100 ml volumetric flask. 1 ml of p-dimethylamino-aniline solution was added and the flask closed very quickly to avoid loss of H_2S. After swirling the contents thoroughly, 1 ml of ferric chloride solution was quickly pipetted into the flask. The closed flask was allowed to stand for 30 min. and then the resulting methylene blue solution was diluted to the mark with distilled water before the absorbance was determined.

3.3.0 Results

3.3.1 Solubility Determinations

Smithsonite, hemimorphite and willemite dissolved slowly and equilibrium was established only after 7 days (Figs. 3.2, 3.3 and 3.4). Equilibrium pH values for smithsonite, hemimorphite and willemite were 7.6, 8.7 and 7.0 respectively and these values were independent of the initial pH. At initial pH values near the final values equilibrium was more rapidly established than under other conditions. At initial pH values below the equilibrium pH obtained with smithsonite (pH 7.6) the equilibrium zinc concentration was 9 ppm but at initial pH values above the equilibrium pH the zinc concentration was lower and the value decreased with an increase in initial pH. This contrasts with the behaviour obtained with hemimorphite where the equilibrium zinc concentration at high initial pH values was much higher than that obtained at initial pH values below the equilibrium pH. Willemite exhibited similar behaviour to smithsonite and the highest zinc concentrations were obtained at initial pH values near the equilibrium pH. In this case, however, the dissolution curves were parabolic and constant zinc concentrations were not obtained even after 6 days.

The effect of sulphidisation on the solubility of smithsonite and hemimorphite was studied. The results clearly show that sulphidisation decreased the solubility of smithsonite and that the equilibrium pH was not independent of the initial pH. Both these effects are demonstrated in Fig. 3.5. In contrast to the behaviour obtained with smithsonite, sulphidisation had no marked effect on the solubility of hemimorphite.

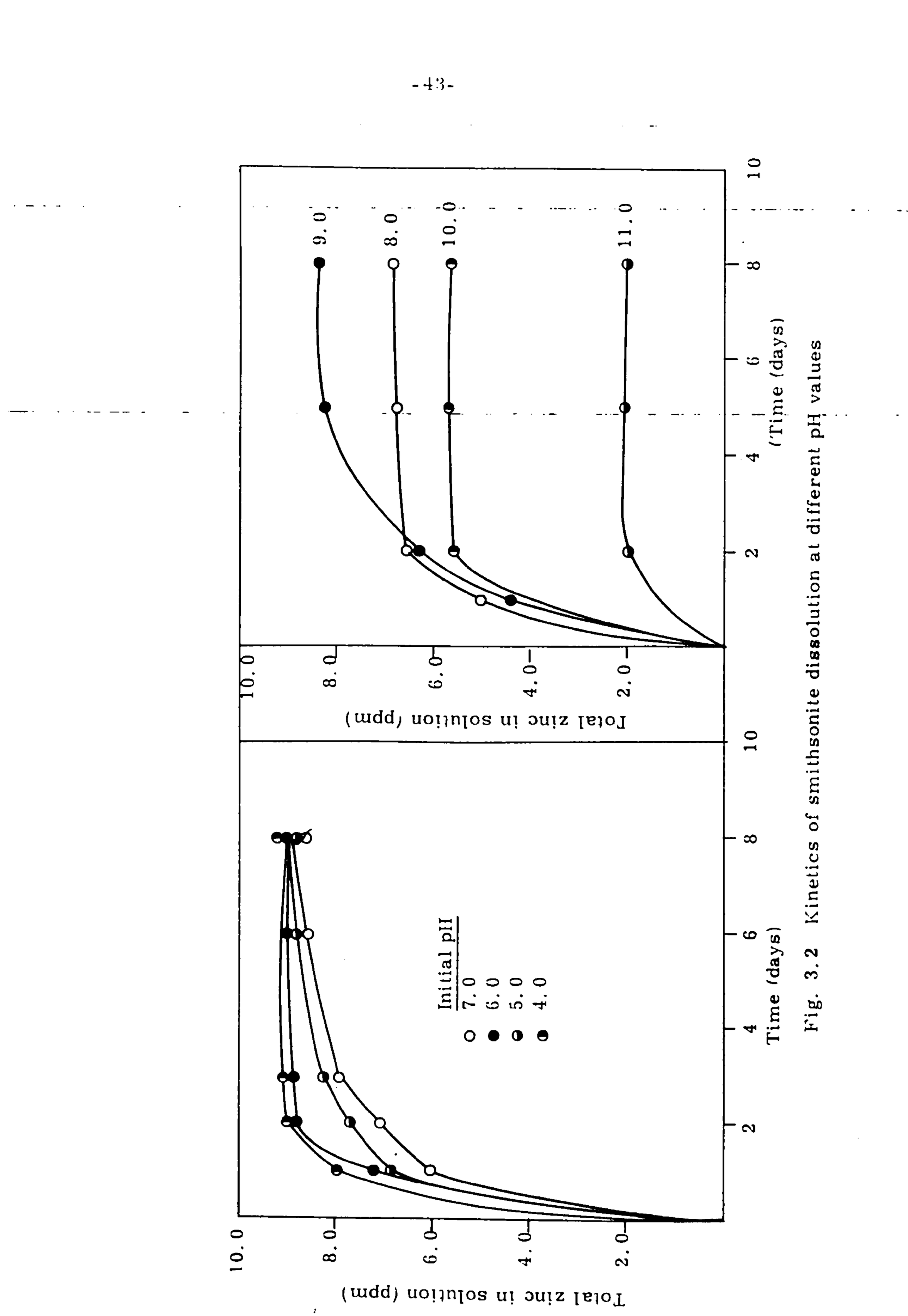


Fig. 3.2 Kinetics of smithsonite dissolution at different pH values

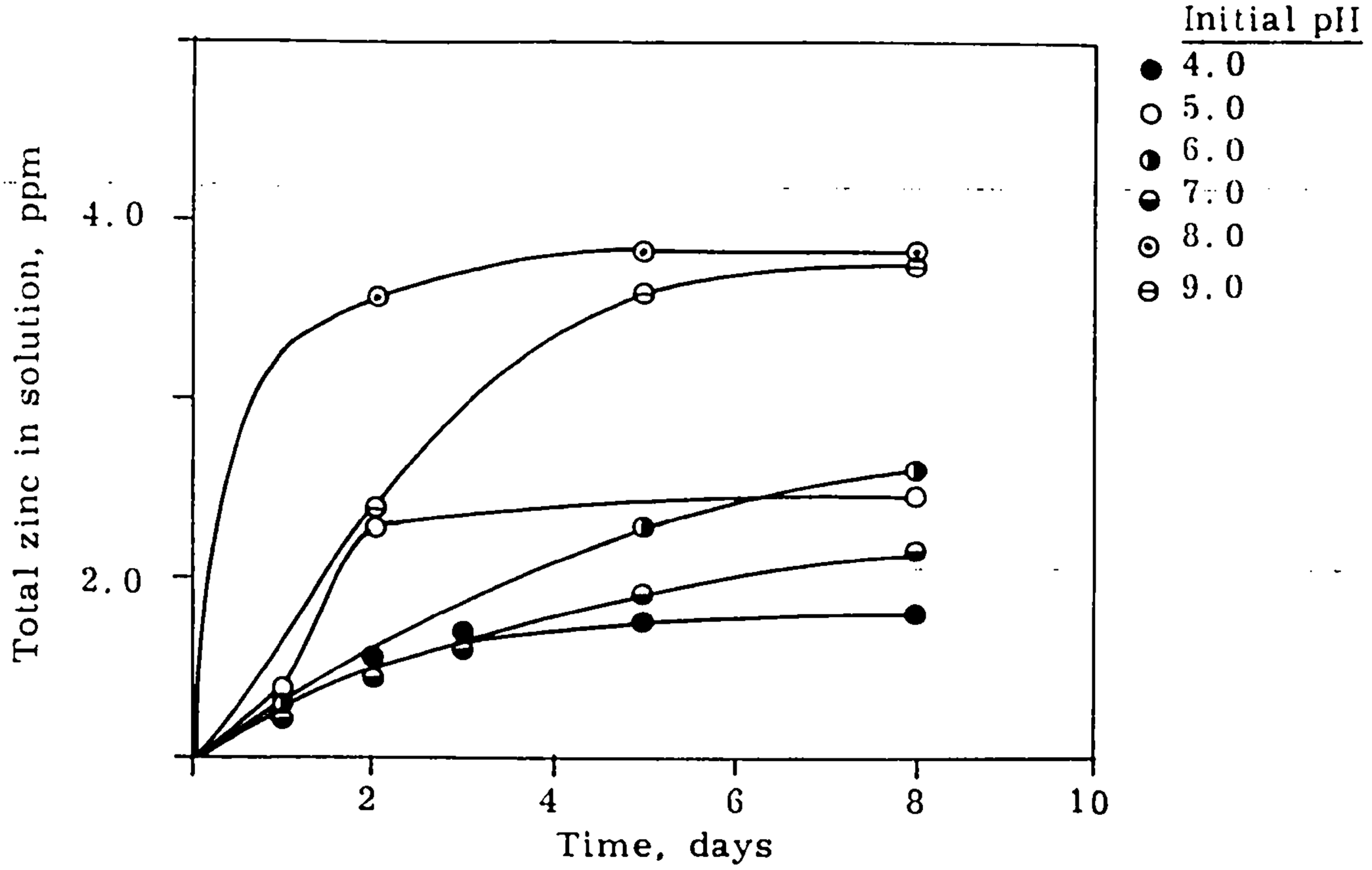


Fig. 3.3 Kinetics of hemimorphite dissolution at different initial pH values

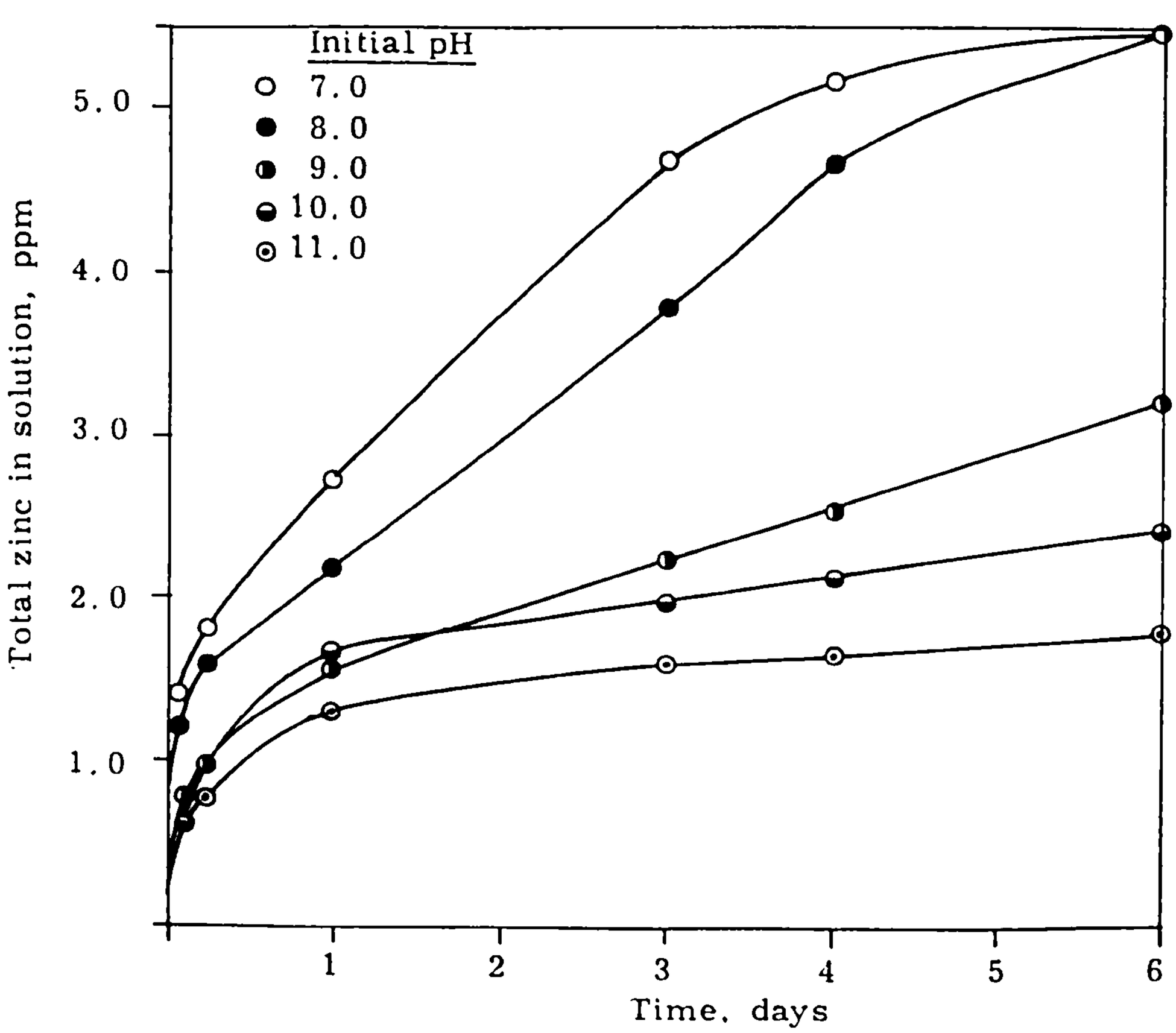


Fig. 3.4 Kinetics of willemite dissolution at different pH values

3.3.2 Electrophoretic Mobility Results

Suspensions of smithsonite and hemimorphite were aged for various lengths of time in solutions of $NaNO_3$ at different ionic strengths. The influence of pH on the electrokinetic properties are shown in Fig. 3.6. Between pH values of 5.8 and 9.0 the electrophoretic mobility of smithsonite was negative and almost constant, and at higher pH values the electrophoretic mobility became more negative. Ageing the smithsonite decreased the negative electrophoretic mobility throughout the pH range studied, but after 1 day the effect was not marked.

The electrophoretic mobility of hemimorphite (Fig. 3.7.) was also negative over the pH range studied; increasing the pH between 5.0 and 10.5 increased the negative electrophoretic mobility less than two-fold. Ageing did not have a marked effect. Increasing the ionic strength with $NaNO_3$ decreased the negative electrophoretic mobility of both minerals but not by as much as that normally associated with insoluble oxides (19) and this is demonstrated in Fig 3.8.

a) Effect of sodium sulphide on the electrophoretic mobility of zinc oxide minerals The dispersion of smithsonite in a sodium sulphide solution (1.10^{-3}M) had a marked effect on the electrophoretic mobility. High negative values were obtained and above pH 7.0, the electrophoretic mobility was essentially independent of pH (Fig. 3.9). Increasing the concentration of $NaNO_3$ from 0 to 1×10^{-2}M decreased the negative electrophoretic mobility by a small amount.

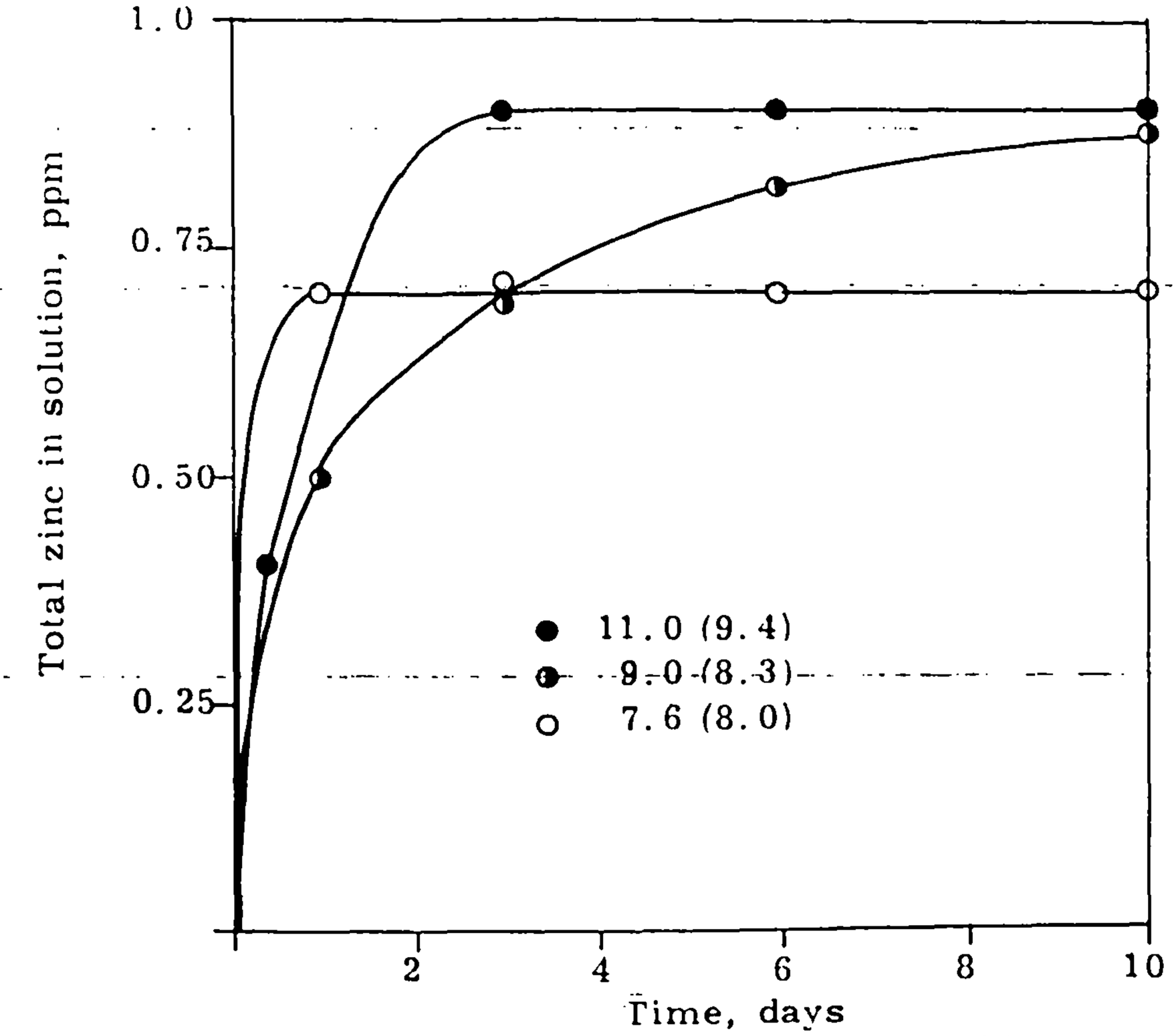


Fig. 3.5 Kinetics of dissolution of sulphidised smithsonite at different initial pH values (The final pH values after 10 days appear in brackets)

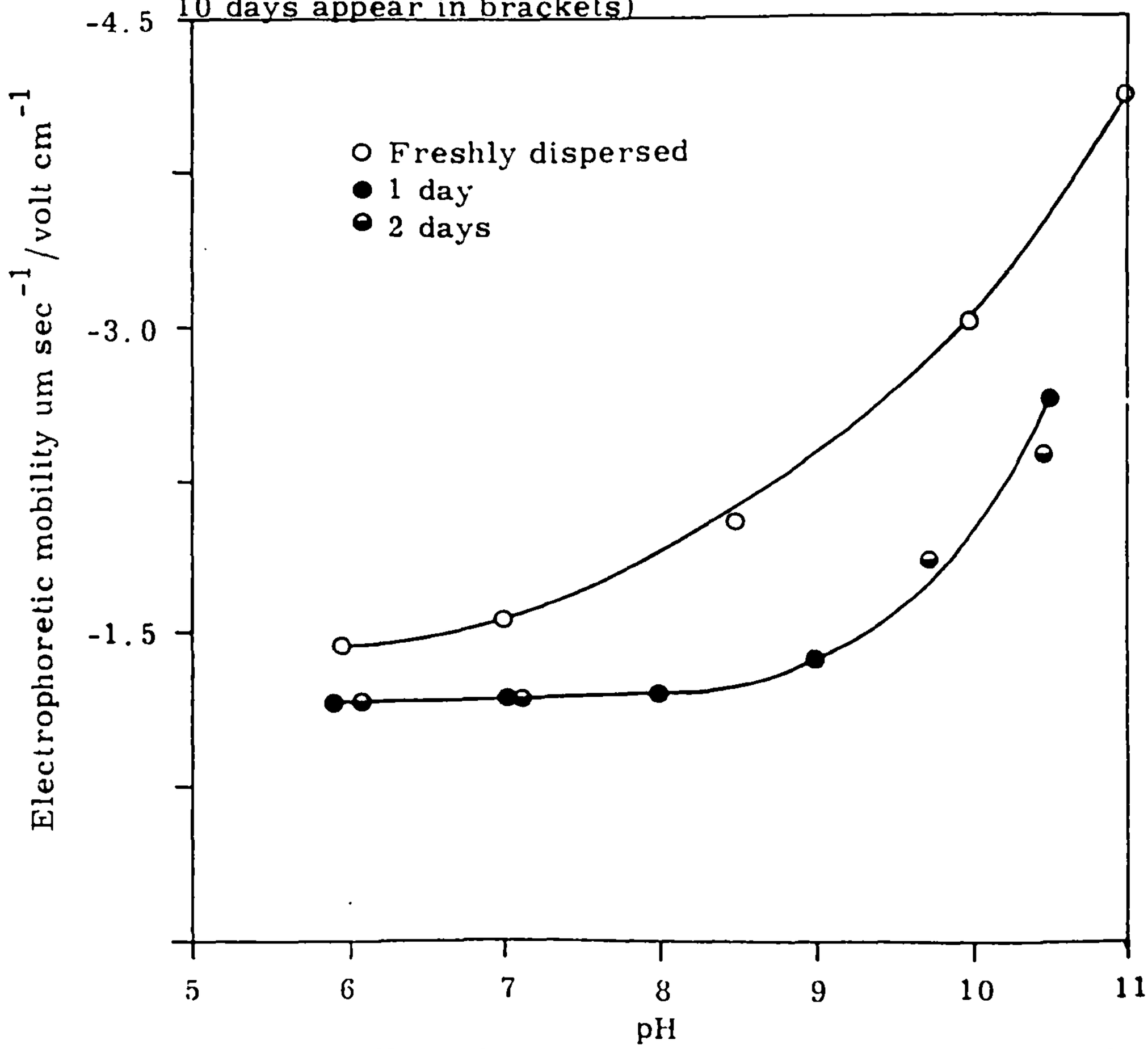


Fig. 3.6 Effect of pH on the electrophoretic mobility of smithsonite in distilled water

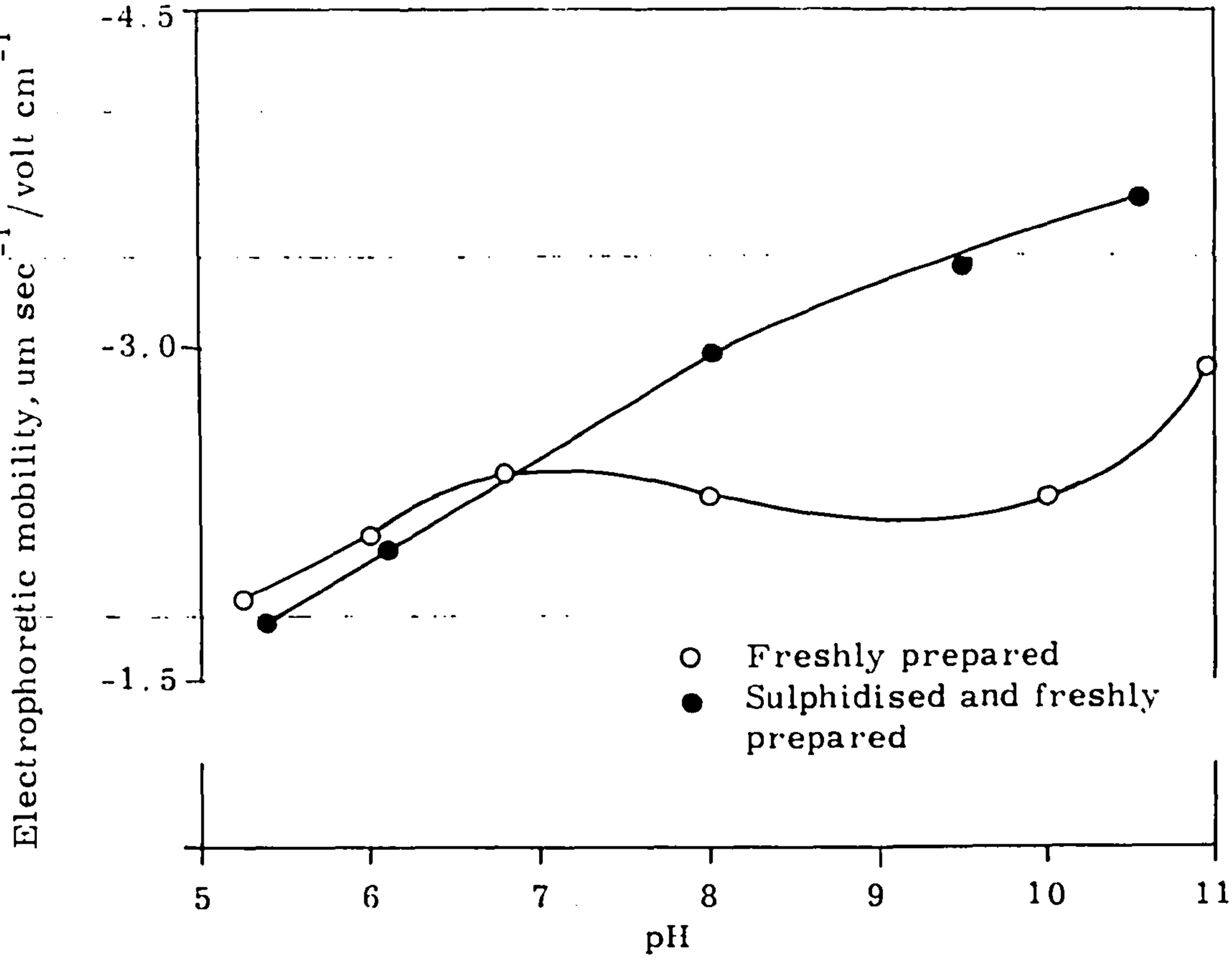


Fig. 3.7 Effect of pH on the electrophoretic mobility of hemimorphite in distilled water

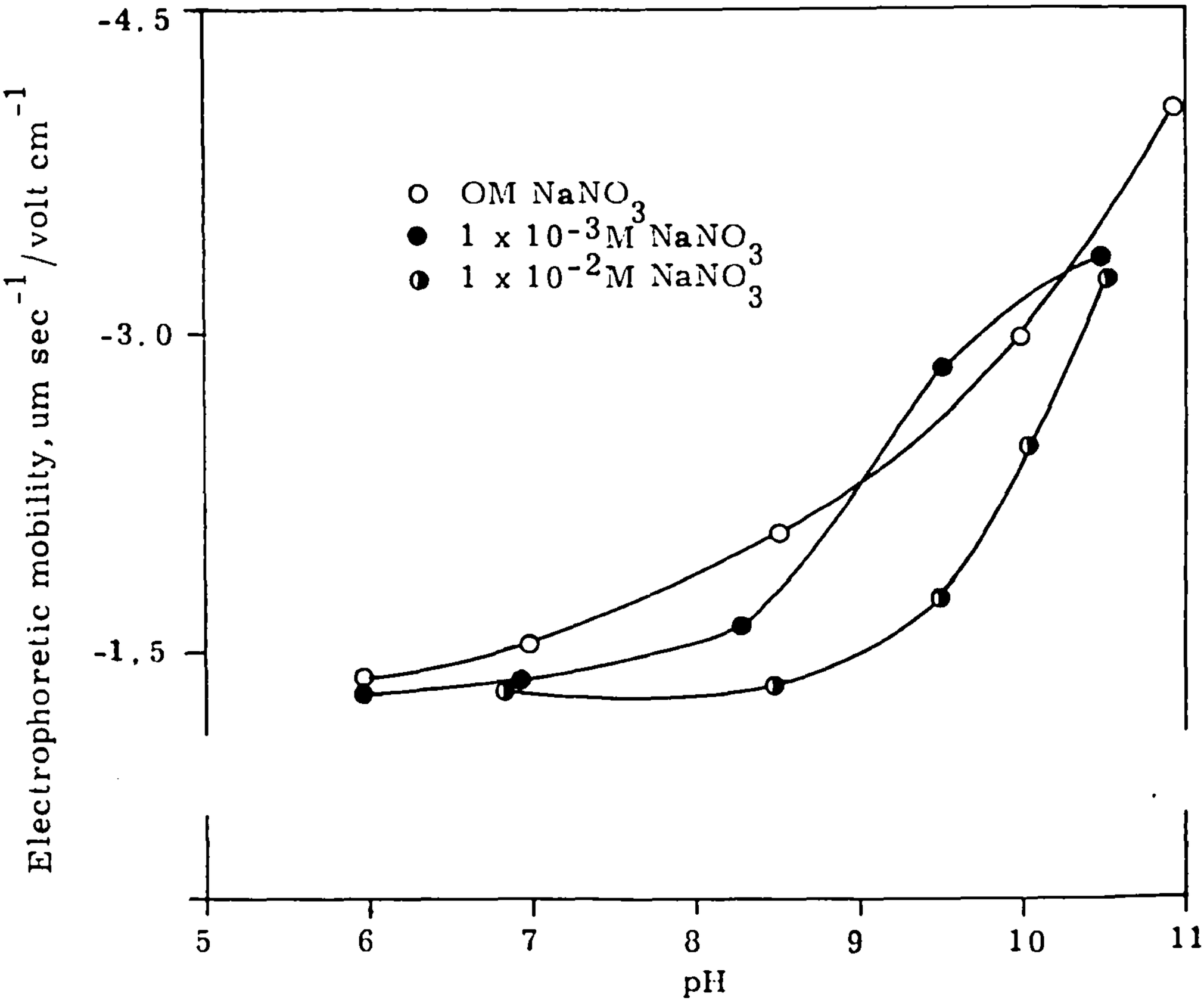


Fig. 3.8 Effect of pH on the electrophoretic mobility of freshly-dispersed smithsonite in solutions of different ionic strength

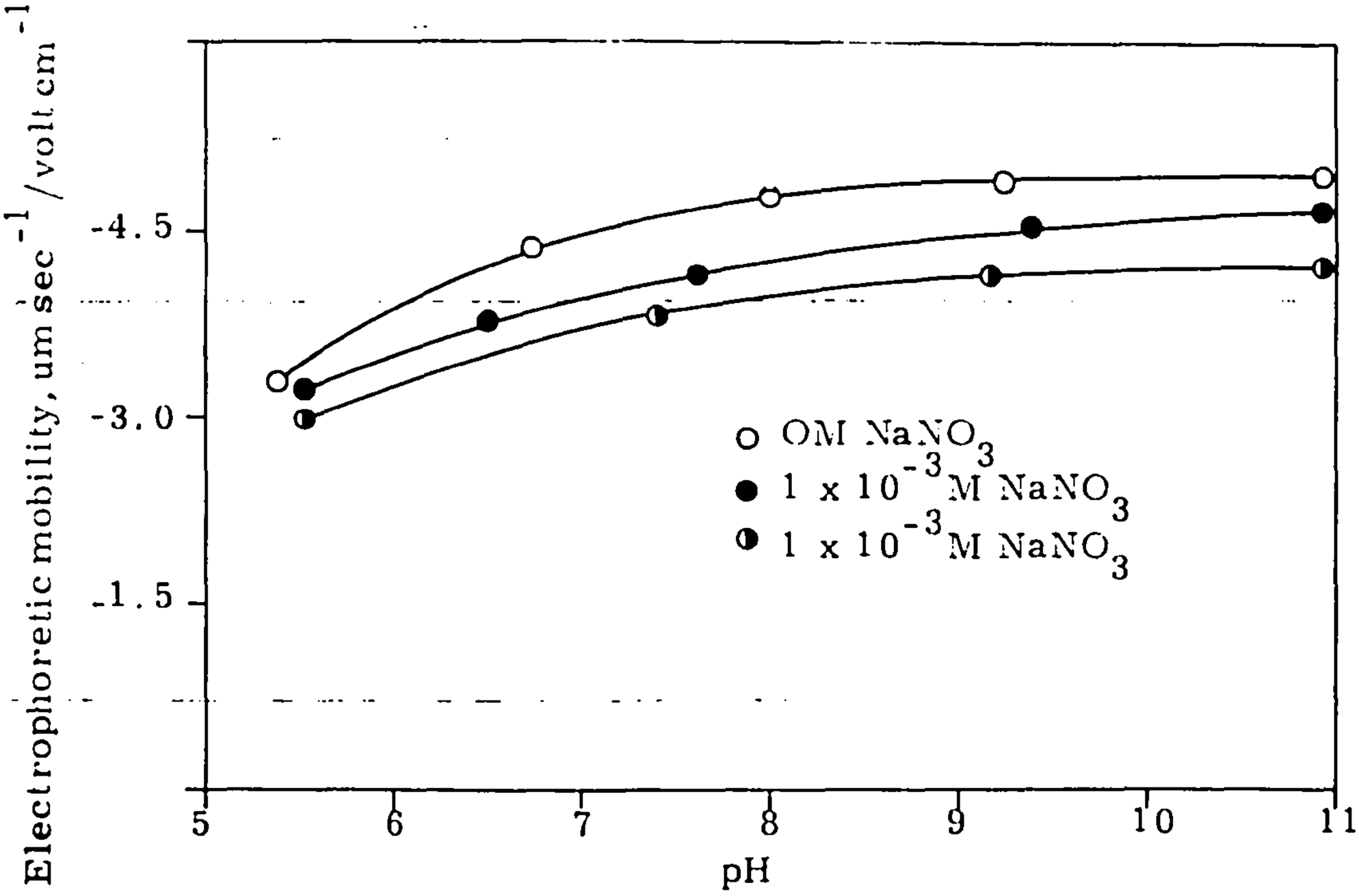


Fig. 3.9 Effect of pH on the electrophoretic mobility of freshly-prepared dispersion of sulphidised smithsonite

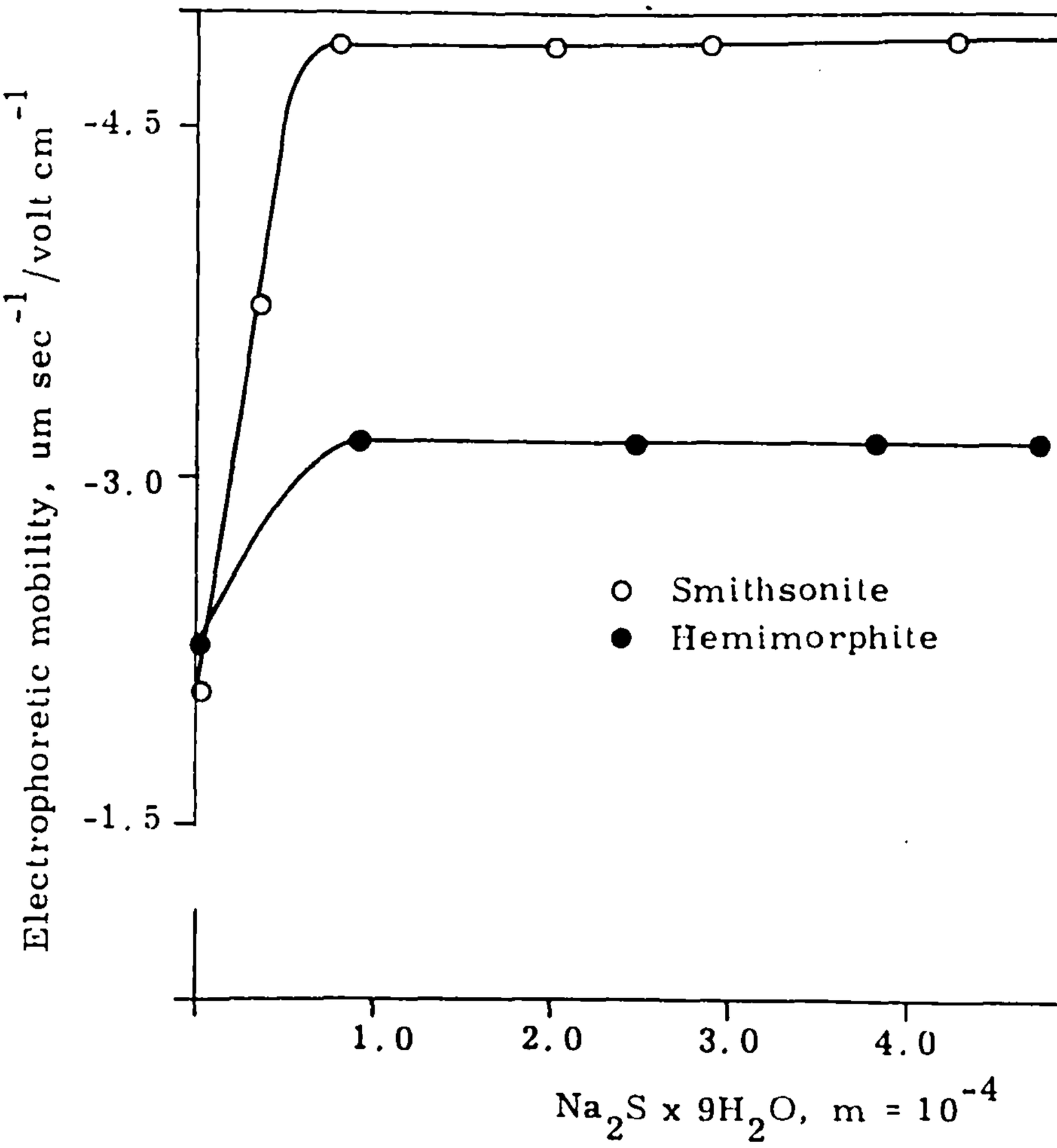


Fig. 3.10 Effect of sodium sulphide concentration on the electrophoretic of zinc oxide minerals

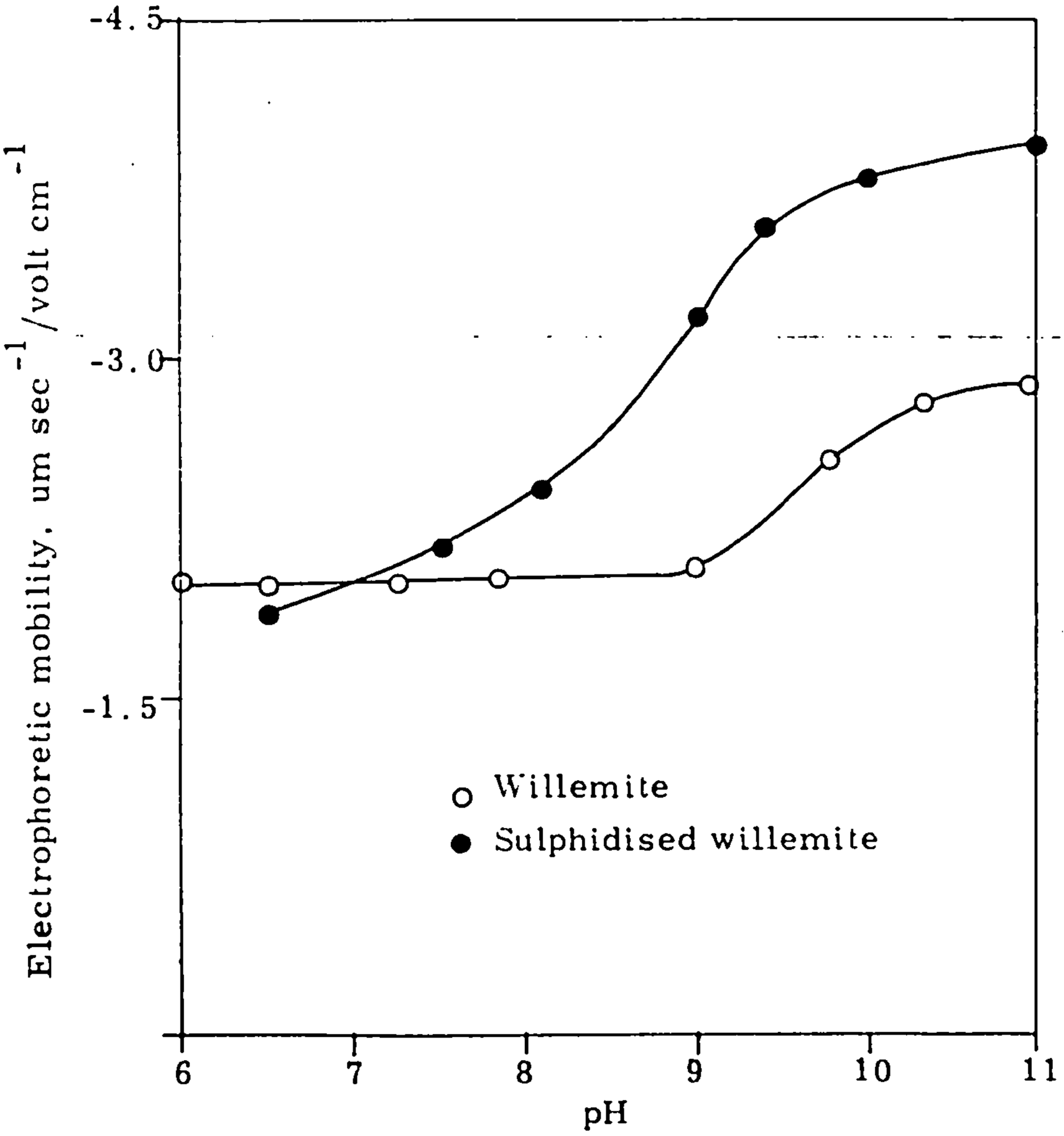


Fig. 3.11 Effect of pH on the electrophoretic mobility of freshly-dispersed willemite in distilled water

Sulphidisation of hemimorphite did not have a marked effect on the electrophoretic mobility between pH 5.5 and 7.5, but at higher pH values the electrophoretic mobility became more negative. However, the increase in electrophoretic mobility was not so dramatic as in the case of smithsonite. This is indicative of the lower reactivity of hemimorphite with sulphide ions. This is more clearly shown in Fig. 3.10, where the effect of sodium sulphide concentration on the electrophoretic mobilities of both smithsonite and hemimorphite at pH 8.5 are compared. In the case of smithsonite, $8.3.10^{-5}$M $Na_2S.9H_2O$ solution increased the negative electrophoretic mobility from -1.95 to -5.10 um sec^{-1}/volt cm^{-1}, whereas that of hemimorphite increased from -2.50 to -3.10 um sec^{-1}/volt cm^{-1} under the same conditions.

Willemite showed a similar electrokinetic behaviour to that of hemimorphite. Its electrophoretic mobility in water was independent of pH between pH 6 and 9, and at more alkaline pH values became more negative. Sulphidising the willemite increased the negative electrophoretic mobility in a similar way to that obtained with hemimorphite (Fig. 3.11).

b) Effect of dodecylamine on the electrophoretic mobility of zinc oxide minerals The electrophoretic mobility of sulphidised and unsulphidised smithsonite, hemimorphite and willemite was determined at different concentrations of dodecylamine and at different pH values. In the presence of dodecylamine at pH 8.5 the negative electrophoretic mobility of the three minerals decreased and then became positive, (Figs. 3.12

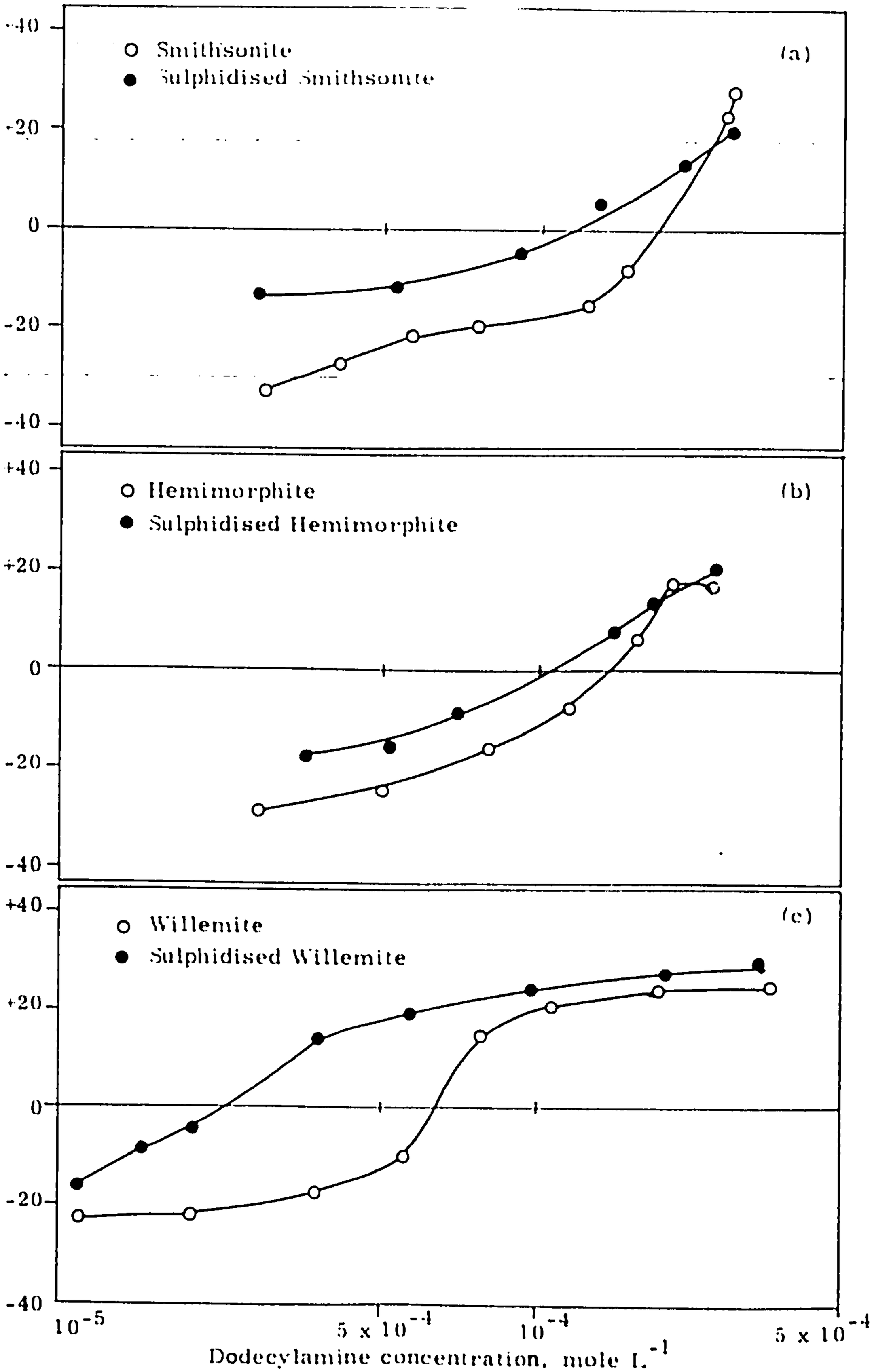


Fig. 3.12 Effect of dodecylamine in the electrophoretic mobility of zinc oxide minerals

a, b and c). Results after sulphidisation indicated that dodecylamine apparently adsorbed more strongly on the sulphidised smithsonite and willemite than on the unsulphidised samples as evidenced by the lower concentrations required to reduce the electrophoretic mobility to zero. Sulphidisation did not exhibit a marked effect on the electrophoretic mobility of hemimorphite in the presence of dodecylamine.

3.3.3 Dodecylamine adsorption studies

A series of tests was conducted to determine the variation of dodecylamine adsorption density at the smithsonite-hemimorphite/solution interface at various pH values. The results are presented in Fig. 3.13 and they show that the adsorption of dodecylamine on smithsonite was very dependent on pH. At pH values close to neutrality the adsorption was low and constant. At more alkaline pH values the adsorption increased steeply reaching a maximum value at pH 11.0. In contrast the adsorption of dodecylamine on hemimorphite was high compared to that on smithsonite and nearly independent of pH between 5.0 and 7.5. Above pH 7.5 the adsorption increased slowly, the maximum adsorption being at pH 10.0 and beyond this pH value the adsorption decreased again.

Dodecylamine was strongly adsorbed by smithsonite but the shape of the isotherm was not similar to that usually obtained with oxide minerals (20). The adsorption density was almost directly proportional to the eq ıilibrium amine concentration and there was no tendency for the adsorption density to level off at a coverage corresponding to a closely packed vertically orientated monolayer (i.e. 8.3 u moles m^{-2}). Sulphidisation of

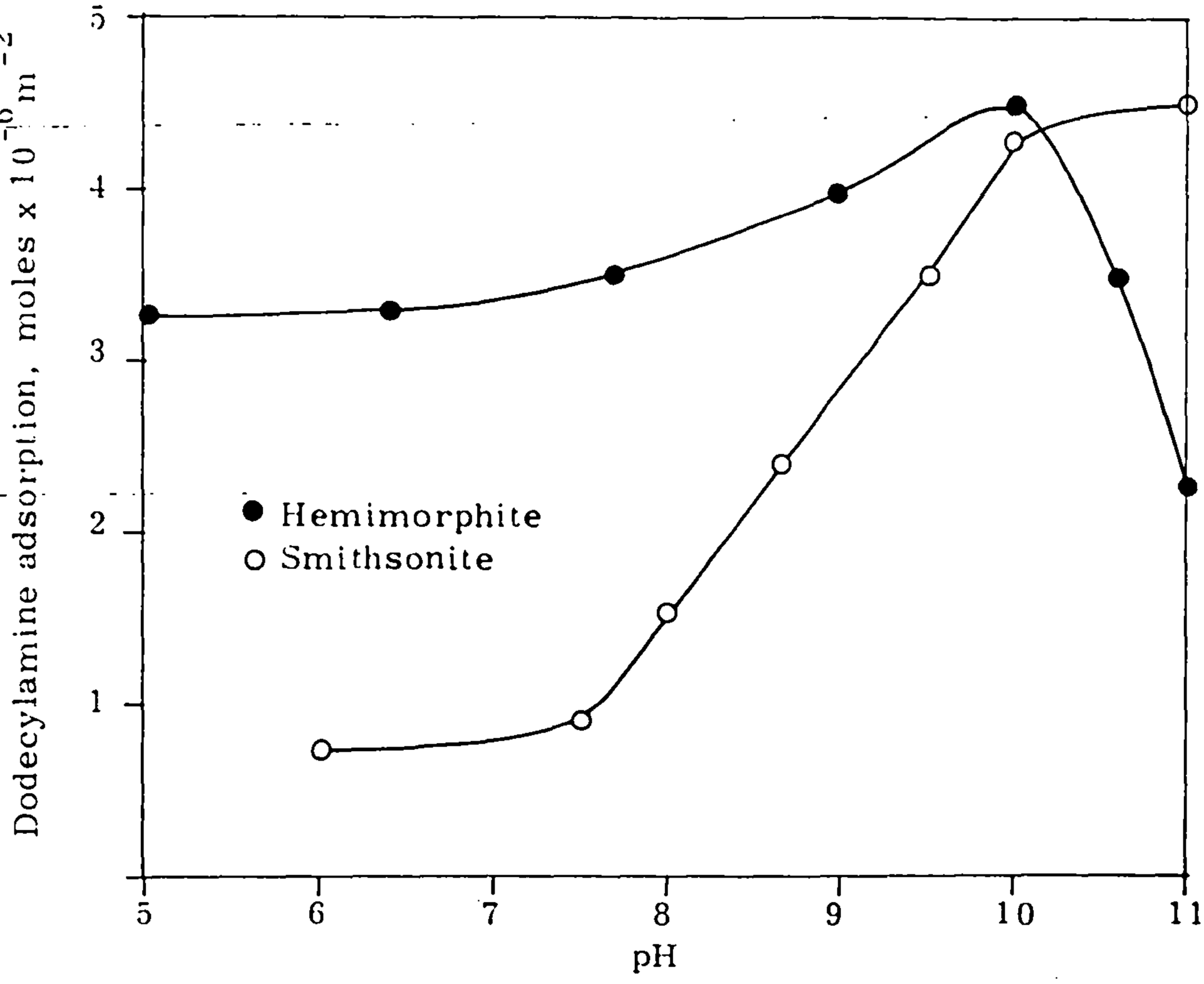


Fig. 3.13 Effect of pH on the adsorption of dodecylamine (5×10^{-5} M) on zinc oxide minerals after 1 day

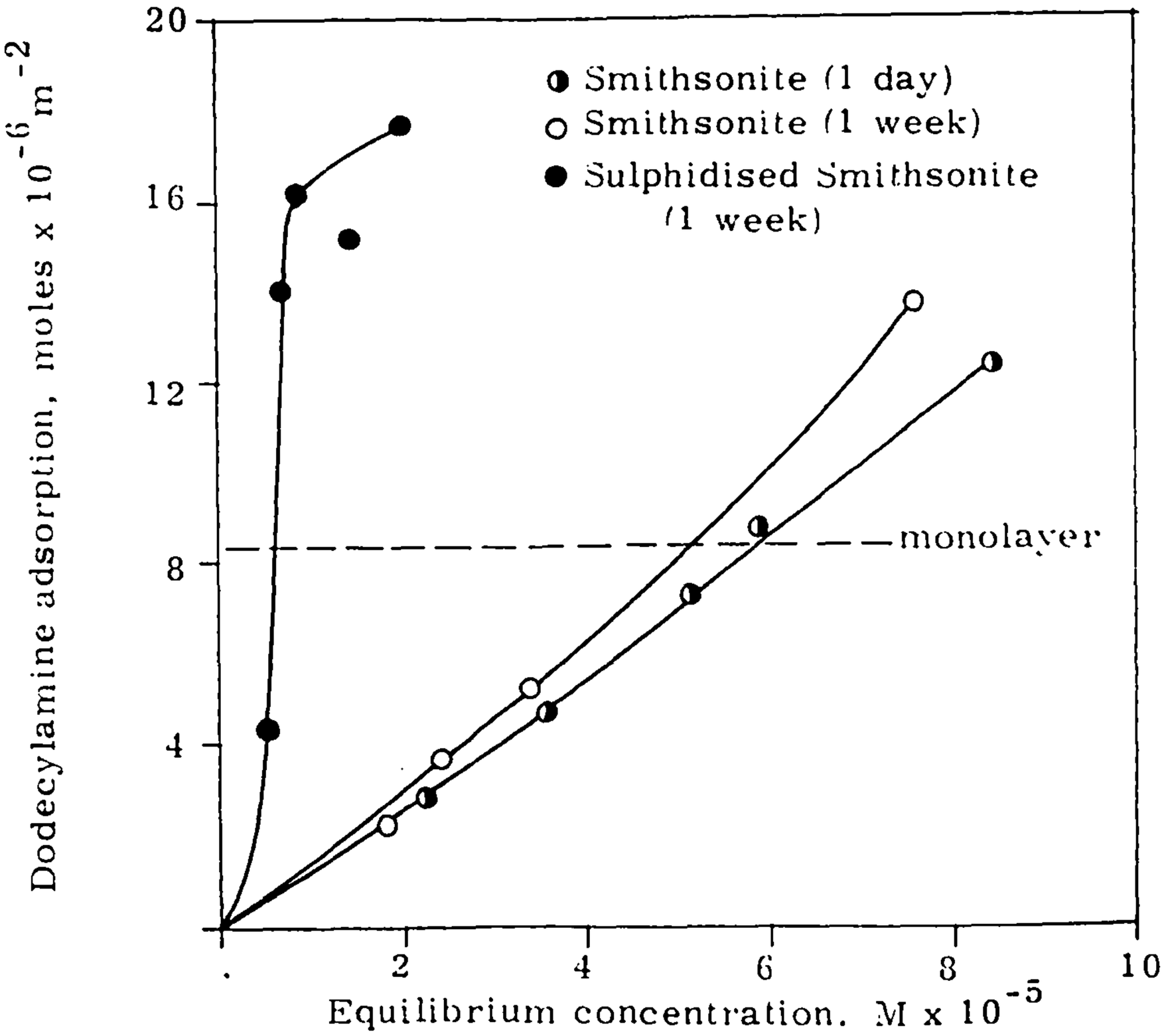


Fig. 3.14 Dodecylamine adsorption isotherm on Smithsonite at pH 7.6

the smithsonite increased the amine adsorption and in this case the adsorption density tended to level off at a value equivalent to two vertically oriented layers (Fig. 3.14).

The adsorption of dodecylamine by hemimorphite was of a similar magnitude to that with smithsonite, but the shape of the isotherm was Langmuirian with constant adsorption being obtained at 14 u moles m^{-2} (Fig. 3.15). Prior sulphidisation of the hemimorphite had little effect on the amine adsorption density. It must be pointed out that equilibrium was attained in 2 days for both smithsonite and hemimorphite.

3.3.4 Sulphidisation of Zinc Oxide Minerals

Both smithsonite and hemimorphite abstracted considerable amounts of sulphide from aqueous solutions, but the abstraction rate exhibited by smithsonite was greater than that of hemimorphite. This was demonstrated by the fact that even though both minerals abstracted all the sulphide from a 2.10^{-4}M $Na_2S.9H_2O$ solution after prolonged agitation, a hemimorphite specific surface area 6.4 times that of smithsonite was required to give comparable rates. The results shown in Fig. 3.16 clearly illustrate that when 1 g of hemimorphite with a specific surface area of 2.8 m^2g^{-1} was used, the sulphide abstraction rate was similar to that obtained with 1g of smithsonite with a specific surface area of 0.44 m^2g^{-1}. Sulphide abstraction by both minerals was independent of pH in the range 8.0 to 11.0, and in all cases total abstraction of the sulphide was obtained provided that agitation was continued for a long time.

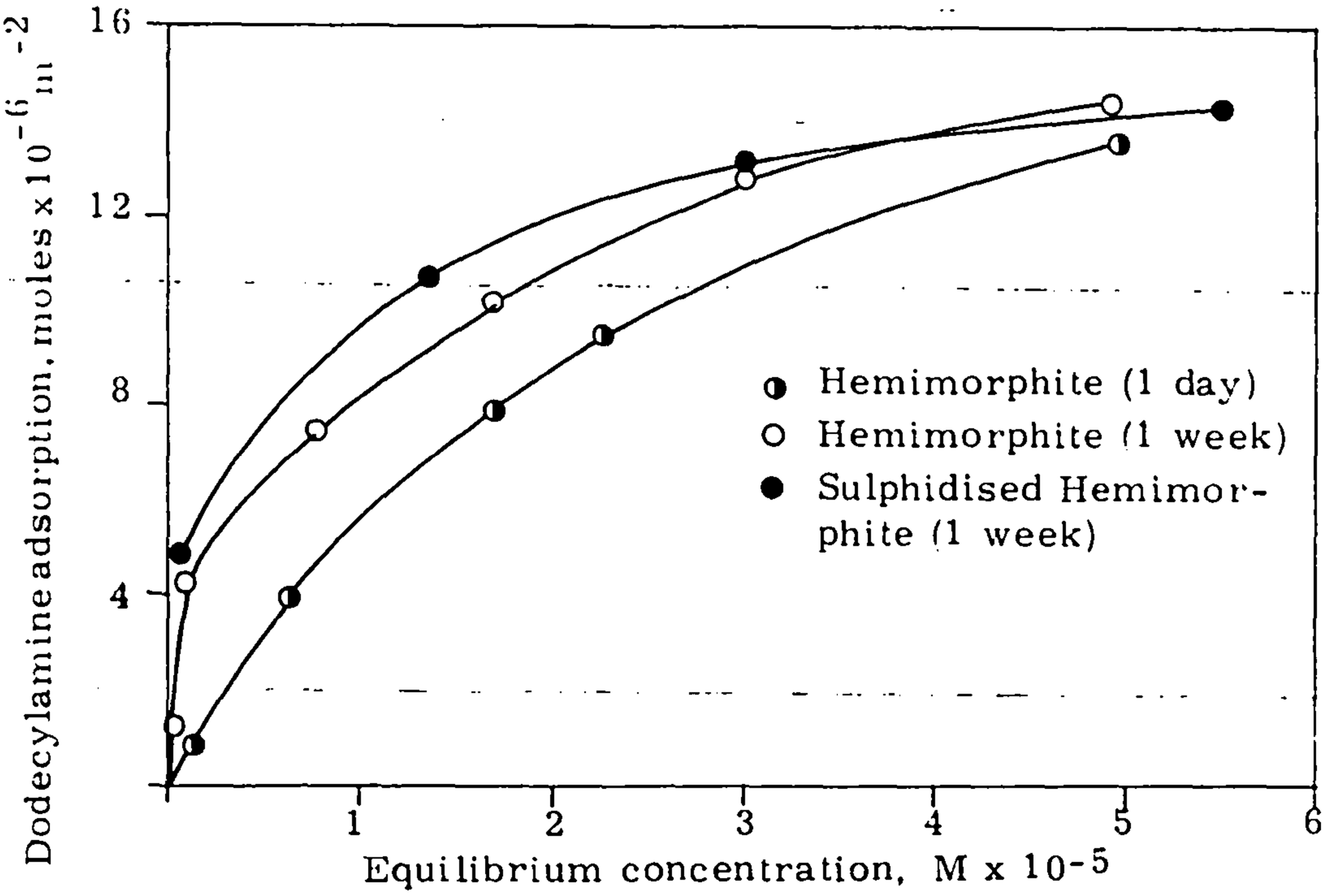


Fig. 3.15 Dodecylamine adsorption isotherm on hemimorphite at pH 8.7

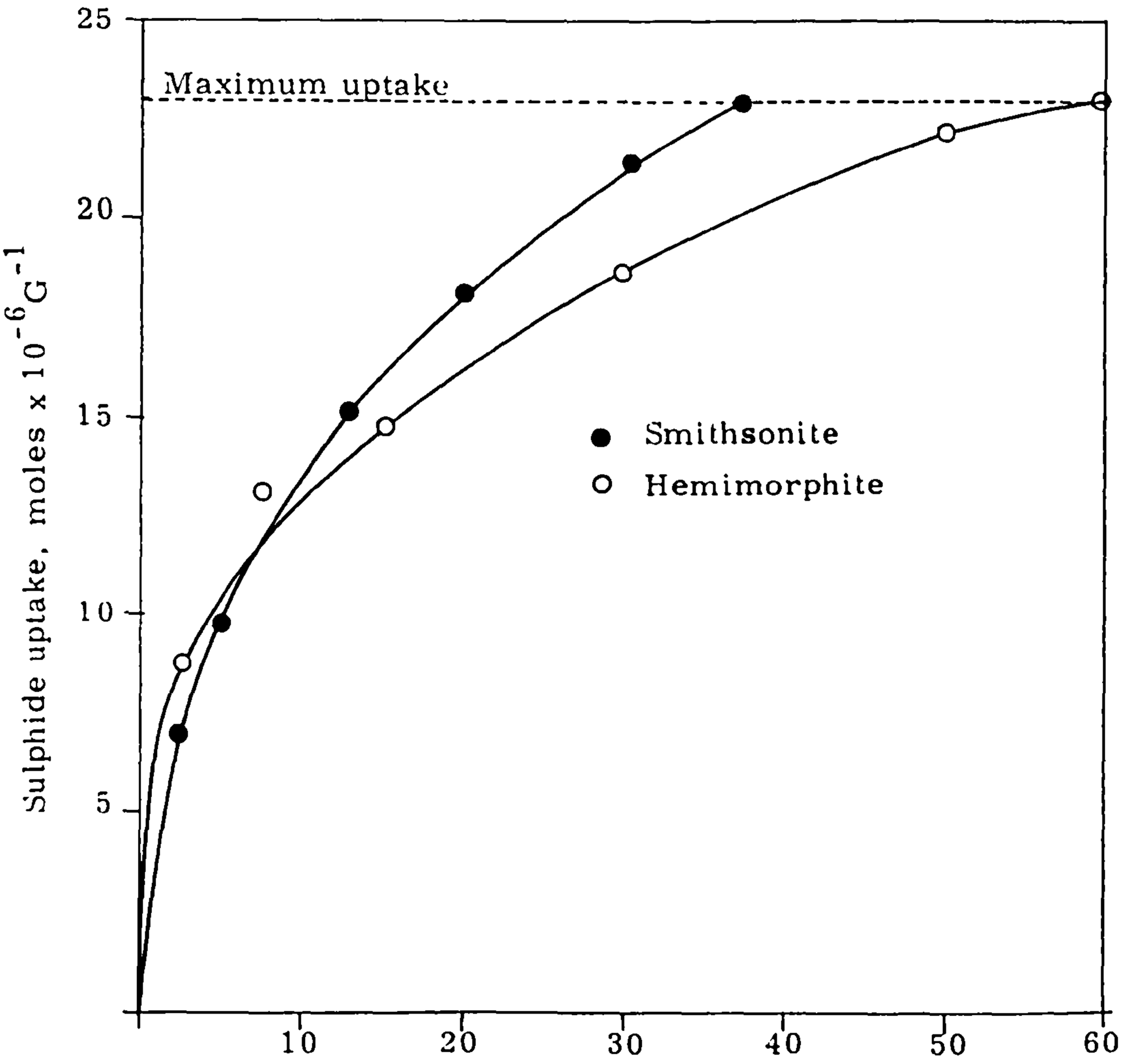


Fig. 3.16 Abstraction of sodium sulphide in the presence of zinc oxide minerals at pH 10.0 $Na_2S.9H_2O = 2.3 \times 10^{-4}$ M

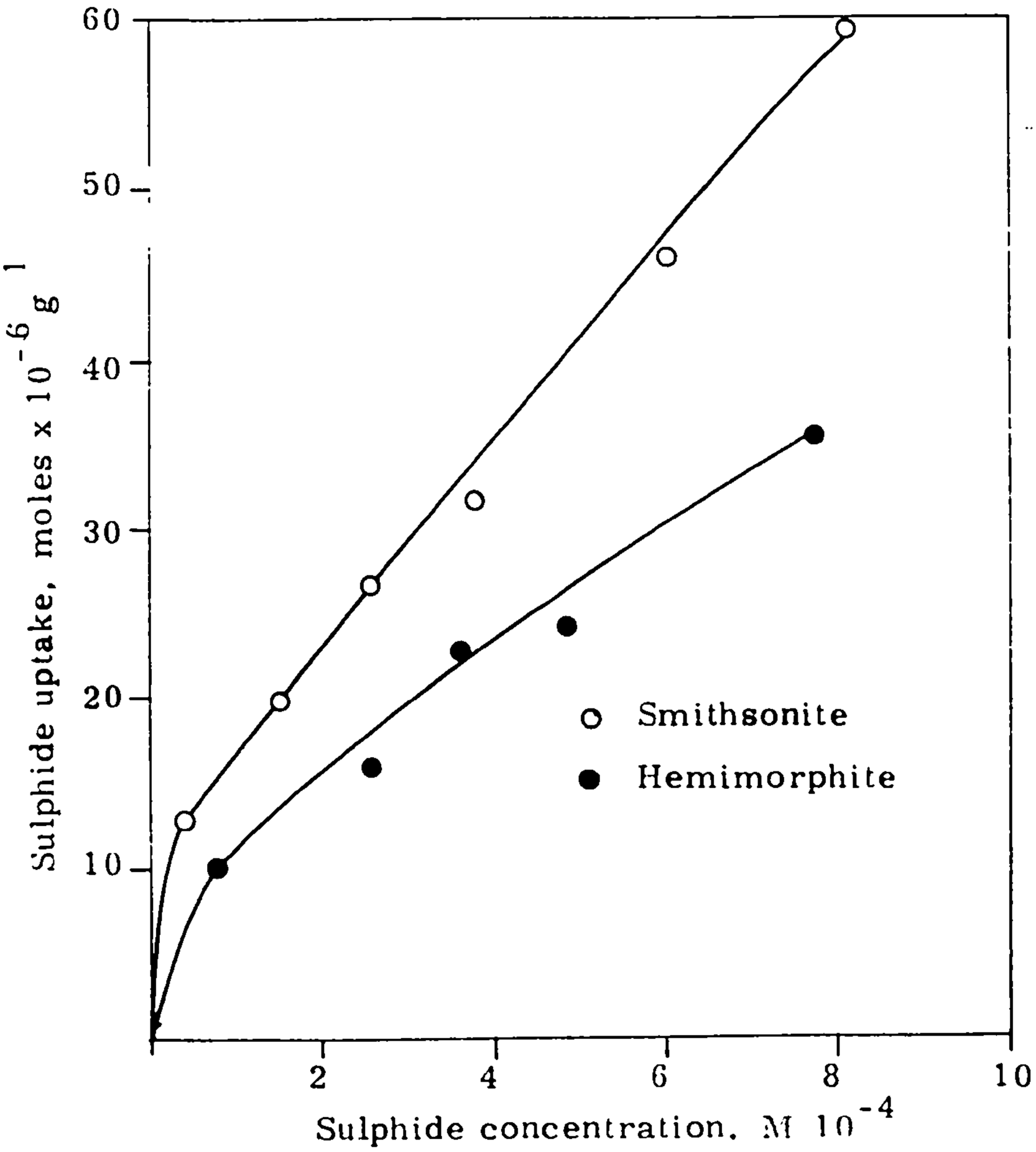


Fig. 3.17 Sulphide abstraction by zinc oxide minerals at pH 10.0

Further evidence that smithsonite abstracts sulphide at a greater rate than hemimorphite is shown in Fig. 3.17 where the abstraction is plotted as a function of residual concentration after agitation for 5 min. In both cases the amount of abstraction increased linearly with the residual concentration, but the abstraction by smithsonite was much higher than that by hemimorphite, especially when the difference in surface areas is taken into consideration.

3.4.0 Discussion

3.4.1 Solubility Determinations

The dispersion of zinc oxide minerals in aqueous solutions results in the release of a considerable amount of zinc ions and the attainment of an equilibrium pH, which is independent of the initial pH but dependent on the mineral. The equilibrium pH values are obtained within 1 day but the dissolution equilibrium is only completed after about 8 days.

These results show that zinc oxide minerals are amphoteric and consume hydroxyl ions at high pH values and hydrogen ions at low pH values. The abstraction of H^+ and OH^- ions can be attributed to the different dissolution mechanisms at high and low pH values and also to the adsorption of these ions at the oxide/water interface. Attempts were made to determine hydroxyl ion adsorption by fast potentiometric titration (49) but these were unsuccessful because zinc analysis of the solutions showed that it was not possible to measure adsorption without dissolution also occurring.

The dissolution of zinc oxide minerals in aqueous solutions can be described by the following equilibria.

Smithsonite

$$ZnCO_{3(s)} \overset{H_2O}{\rightleftharpoons} Zn^{+2} + CO_3^{-2} \qquad 3.12$$

$$K_s = a_{Zn^{+2}} \cdot a_{CO_3^{=}} = 10^{-9.7} \qquad 3.13$$

Hemimorphite

$$Zn_4Si_2O_7.(OH)_2.H_2O \xrightleftharpoons{H_2O} 4Zn^{+2} + Si_2O_7^{-6} + 2OH^- + H_2O \qquad 3.14$$

Willemite

$$Zn_2SiO_4 \xrightleftharpoons{H_2O} 2Zn^{+2} + SiO_4^{-4} \qquad 3.15$$

Depending on the pH the zinc ions will further react with hydroxyl ions to give various zincate species.

$$Zn^{+2} + OH^- \rightleftharpoons Zn(OH)^+ \qquad \log \beta_1 = 6.31 \qquad 3.16$$

$$Zn^{+2} + 2OH^- \rightleftharpoons Zn(OH)_2 \qquad \log \beta_2 = 11.19 \qquad 3.17$$

$$Zn^{+2} + 3OH^- \rightleftharpoons Zn(OH)_3^- \qquad \log \beta_3 = 14.31 \qquad 3.18$$

$$Zn^{+2} + 4OH^- \rightleftharpoons Zn(OH)_4^{-2} \qquad \log \beta_4 = 17.70 \qquad 3.19$$

Thus, at high pH values the concentration of Zn^{+2} in solution will be very low and the solubility of the mineral will be dependent on the formation of zincate species.

Of the three minerals studied in the present work detailed thermodynamic data is only available for smithsonite. When smithsonite dissolves in aqueous solution the total zinc concentration obtained is a function of the concentration of zinc ion, undissociated zinc carbonate and various zinc-hydroxyl species. However in the pH range 5.0 to 10.0 the concentration of most of these species is negligible compared to that of Zn^{+2} and $ZnOH^+$.

The dissolution of smithsonite in a closed container in the absence of added carbon dioxide is controlled by equation 3.13. The solubility of smithsonite (S) can thus be described by the following equation.

$$S = (Zn^{+2}) + (ZnOH^{+}) + (Zn(OH)_3^{-}) + (Zn(OH)_4^{-2}) \quad 3.20$$

and substituting from equations 3.16 to 3.19

$$S = (Zn^{+2}) + \beta_1(Zn^{+2})(OH^{-}) + \beta_3(Zn^{+2})(OH^{-})^3 + \beta_4(Zn^{+2})(OH^{-})^4 \quad 3.21$$

$$S = (Zn^{+2})\left\{1 + \beta_1(OH^{-}) + \beta_3(OH^{-})^3 + \beta_4(OH^{-})^4\right\} \quad 3.22$$

Simultaneously, the dissolution of smithsonite releases carbonate ions into solution which also undergo hydrolysis as follows,

$$H_2O + CO_2 \rightleftharpoons HCO_3^{-} + H^{+} \qquad K_{a_1} = 4.4 \cdot 10^{-7} \quad 3.23$$

$$HCO_3^{-} \rightleftharpoons H^{+} + CO_3^{-2} \qquad K_{a_2} = 5.6 \cdot 10^{-11} \quad 3.24$$

In a closed vessel in the absence of added CO_2 the solubility of smithsonite can also be described by the sum of the different carbonate species in solution, i.e.

$$S = (CO_2) + (HCO_3^{-}) + (CO_3^{-2}) \quad 3.25$$

From equations 3.23 and 3.24 leaves

$$S = (CO_3^{-2})\left(\frac{(H^{+})^2}{K_{a_1}.K_{a_2}} + \frac{(H^{+})}{K_{a_2}} + 1\right) \quad 3.26$$

and

$$(CO_3^{-2}) = \frac{S}{1 + \frac{(H^+)^2}{K_{a_1} . K_{a_2}} + \frac{(H^+)}{K_{a_2}}} \qquad 3.27$$

Substituting in equation 3.13 leaves

$$(Zn^{+2}) = \frac{K_s}{S} \left(1 + \frac{(H^+)^2}{K_{a_1} . K_{a_2}} + \frac{(H^+)}{K_{a_2}}\right) \qquad 3.28$$

Introducing equation 3.28 in equation 3.22 gives an expression for the solubility as a function of the OH^- concentration.

$$S^2 = K_s\left(1 + \frac{(H^+)^2}{K_{a_1} . K_{a_2}} + \frac{(H^+)}{K_{a_2}}\right)\left(1 + \beta_1(OH^-) + \beta_3(OH^-)^3 + \beta_4(OH^-)^4\right) \qquad 3.29$$

The solubilities calculated with this equation are shown in Fig. 3.18 as a function of pH. Minimum solubility of smithsonite is obtained between pH 8.0 and 9.0 and under these conditions the soluble zinc content is $2.8.10^{-4}$ (18 ppm). However, comparison of these theoretical results with the solubility measurements is not possible because equilibrium solubility -pH curves could not be obtained in the present work.

Although the final pH in the dissolution tests was independent of the initial pH the zinc content was not. At initial pH values below 7.6 the zinc content was constant at $1.4 . 10^{-4}$M (9ppm) but above this pH the zinc content decreased with increase in pH. The zinc content was therefore much lower than that theoretically predicted at pH 7.6 ($4.1 . 10^{-4}$M) and furthermore different zinc contents were obtained at the same final pH value.

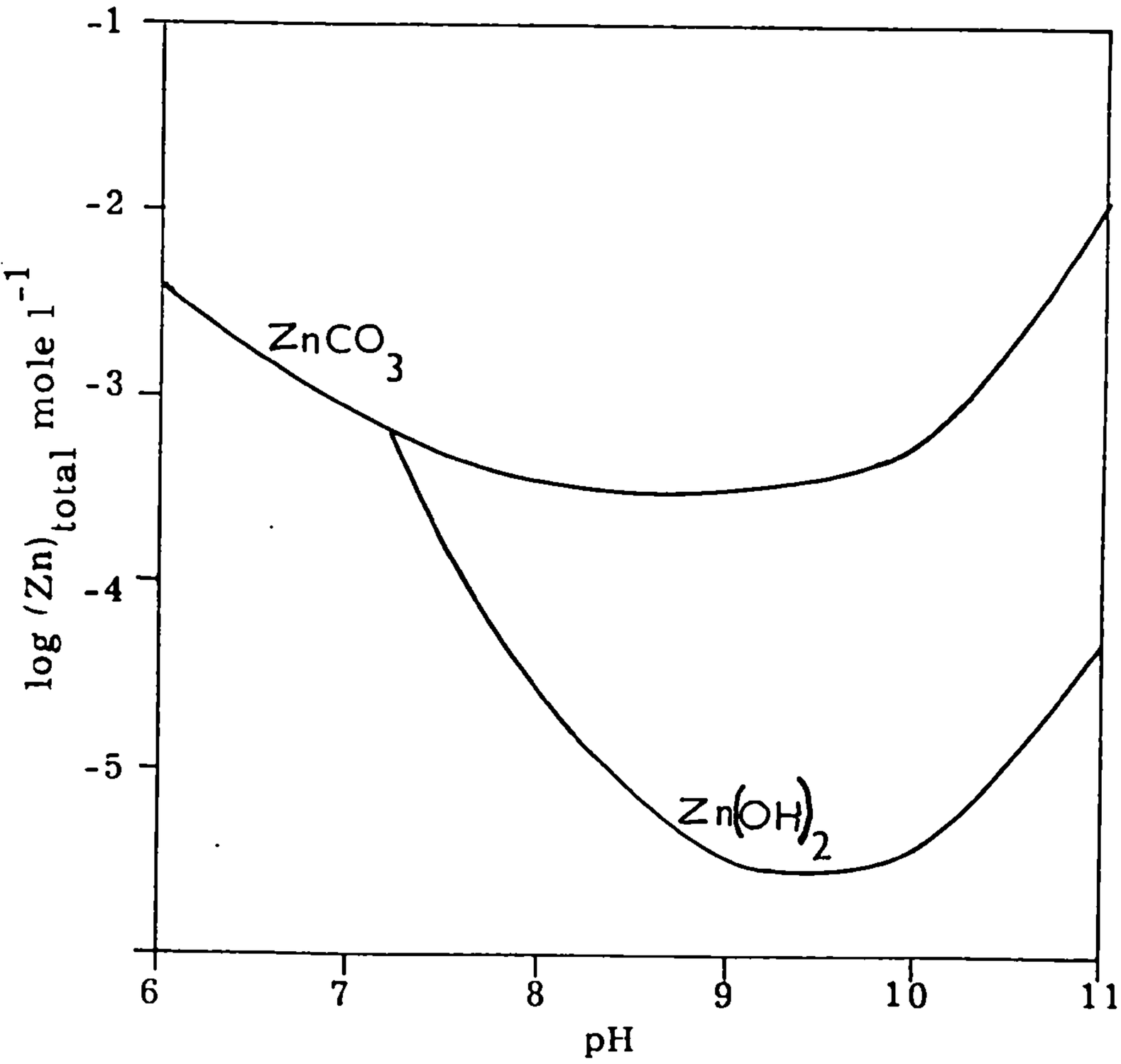


Fig. 3.18 Solubility diagram of smithsonite and zinc hydroxide ($K_s = 10^{-16.76}$) under CO_2-free conditions

There are a number of possible reasons for the difference between the theoretical and experimental results especially at pH values above 7.6. According to Werner and Stumm (50) zinc carbonate is thermodynamically unstable above pH 9.0 because it hydroxylates. Partial surface hydroxylation begins at pH 7.5 giving rise to the formation of a surface similar to that of hydrozincite ($3ZnCO_3 . 5Zn(OH)_2$). This compound is far more insoluble ($K_s = 10^{-14.7}$) than smithsonite and is very stable even in the presence of CO_2 partial pressure as low as 10^{-5} atm (51). Kesler and Shergold (6) have identified the presence of hydrozincite by x-ray diffraction during the dissolution of smithsonite in sodium hydroxide solution. They suggested the following reaction.

$$6ZnCO_{3(s)} + 6OH^- \rightleftharpoons 3ZnCO_3 . 3Zn(OH)_{2(s)} + 3CO_3^{-2} \qquad 3.30$$

Omission of this equilibrium could account for the discrepancy between the theoretical and experimental solubilities.

Hydroxylation of the smithsonite surface removes OH^- ions which would otherwise be available for complexation with the zinc. It is therefore possible that at high initial pH values the surface was hydroxylated so that the soluble zinc content was low. Different degrees of hydroxylation would then be obtained depending on the initial pH. Although such a mechanism explains why different zinc contents are obtained it does not show why the pH always returned to 7.6. It is however, probable that the equilibrium pH of 7.6 was obtained because of surface adsorption of hydroxyl ions rather

than dissolution of the smithsonite. If this were the case then the zinc content would be dependent on the initial degree of hydroxylation rather than the equilibrium pH.

In the dissolution tests care was taken to exclude CO_2, however while taking samples it is quite probable that some CO_2 dissolution occurred from the air. The presence of dissolved CO_2 would exert a common ion effect and thereby reduce the soluble zinc content.

Another possible explanation for the discrepancy between the theoretical and experimental behaviour of smithsonite can be attributed to surface changes brought about during the dry-grinding of the sample. It has been well established that grinding in some cases cause changes in the crystal properties of materials and these in turn can alter important properties such as surface charge, solubility, solid acidic properties, adsorption properties and solid state reactions of different types. These reactions are especially important in the grinding of carbonate minerals (52). Smithsonite which has a relatively low decomposition temperature yields carbon dioxide by grinding at room temperature. The most probable reaction is:-

$$ZnCO_{3(s)} \rightleftharpoons ZnO_{(s)} + CO_{2(g)} \qquad 3.31$$

where the oxygen is supplied by the carbonate itself, and hence the reaction is essentially independent of the oxygen partial pressure and dependent only on the partial pressure of carbon dioxide in the mill.

The smithsonite sample used in the solubility tests was prepared under conditions where the above reaction could have occurred. This means that the surface would have some of the properties of zincite (ZnO). In fact, the total soluble zinc obtained by dispersion of smithsonite in acid equeous solutions is comparable with the theoretical solubility of ZnO at pH 7.6 (see Fig. 3.18). This is additional evidence for the presence of zinc oxide on the smithsonite surface.

The existence of a ZnO-like surface does not, however, invalidate the mechanism proposed for the dissolution process when dispersion is carried out at alkaline pH values. The hydration of the surface zinc oxide results in the formation of a coating of zinc hydroxide which in turn can be rapidly transformed into hydrozincite by the fixation of CO_2 present in solution. This transformation can take place even at very low CO_2-partial pressures(51).

Sulphidisation showed a remarkable effect on the solubility of smithsonite and the soluble zinc concentration was reduced below 1 ppm. The solubility of sulphidised smithsonite was independent of the initial pH whereas the equilibrium pH was not. These results indicate that a sulphidised layer on the smithsonite surface was formed through a chemisorption reaction with soluble sulphide species. The sulphidised layer was not easily re-hydroxylated since after 10 days the total zinc in solution was still below 1 ppm. A more detailed study on the physico-chemical factors influencing the sulphidisation reaction will be presented in section 3.4.3.

The dispersion of hemimorphite at different initial pH values, similar to smithsonite, produced a constant equilibrium pH except when a high initial pH was used. Furthermore even though a constant final pH was obtained the soluble zinc content depended on the initial pH value. In this case, however, unlike smithsonite the zinc content decreased with a decrease in pH and over the pH range 5.0 to 9.0 the value varied between O and $4.6 \cdot 10^{-5}$M (3 ppm). Unfortunately it is not possible to comment on the theoretical solubility of hemimorphite because of insufficient thermodynamic data. It is, however, known that hemimorphite is more insoluble than smithsonite and so it is reasonable to expect a lower zinc concentration.

Willemite showed similar dissolution behaviour to smithsonite rather than to hemimorphite. This is surprising, but consideration of the crystal structures of both willemite and hemimorphite suggests that the availability of surface zinc atoms might be the reason for the differences in reactivity. In hemimorphite the zinc atoms are tetrahedrally co-ordinated with three oxygens of the silica tetrahedra and one hydroxyl. Each tetrahedra shares one oxygen with another tetrahedra to give the pyrosilicate group ($Si_2O_7^{-6}$). Water molecules exist in channels parallel to the (110) plane, held by two bonds to hydroxyl groups (53).

Willemite is a typical orthosilicate mineral formed by independent or isolated SiO_4^{-4} tetrahedra linked together only by Zn^{+2} cations. In this case the zinc atoms as well as the silicate ions are tetrahedrally co-ordinated with regard to oxygen and each

oxygen linked to a silicon atom can be simultaneously bound to two zinc atoms. The relatively complex tri-rhombohedral lattice structure of willemite is due to the fact that the tetrahedra of oxygen atoms round the zinc and silicon ions are so linked that every oxygen atom is common to three such tetrahedra. Thus, when willemite is ground a surface with a considerable number of exposed Zn^{+2} sites, with minimal formation of Si-O broken bonds through breakage of SiO_4^{-4} tetrahedra, can be expected (54). In addition, it is known that the general tendency in silicate composition towards combination of cations with the most polymerized silicon-oxygen groups is dependent on the polarizing power of the silicon ion. This is relatively low in the orthosilicate groups and high in the groups with shared oxygen (53). This means that zinc ions are more weakly attached to the orthosilicate structure of willemite than to the pyrosilicate structure of hemimorphite. Hence, when willemite is dispersed a dissolution behaviour similar to hemimorphite is not to be expected.

3.4.2 Zinc Oxide Mineral/Water Interface

a) Mechanism of charge generation The origin of the surface charge on the zinc oxide minerals will be dependent on the type of mineral and the ions formed in solution when the mineral dissolves. Thus smithsonite can be considered a salt-type mineral where the potential-determining ions include those which make up the crystal lattice, and hemimorphite and willemite are typical silicates or oxides with H^+ and OH^- ions as the potential-determining ions.

When smithsonite is dispersed in water dissolution occurs but some of the ions have a greater affinity for the surface than

the others so that a net surface charge is obtained. Zinc and carbonate ions are the major potential-determining ions but the concentration of both these species will be dependent on the pH so that H^+ and OH^- can also be considered potential-determining ions. Furthermore it is probable that the various zincate species and bicarbonate ion formed by hydrolysis of the Zn^{+2} and CO_3^{-2} will also exert a potential-determining effect.

It is not possible to predict the exact nature of the surface reactions because it is not known whether the zincate species are formed in solution and then adsorbed or alternatively the zincate species are formed on the surface. However, the following simplified equations show a possible reason why the electrophoretic mobility became more negative with an increase pH.

Hydrolysis of a surface carbonate site

$$-CO_3^- + H_2O \rightleftharpoons CO_3H + OH^- \qquad 3.32$$

Increasing the pH will favour the formation of negative carbonate sites.

Hydrolysis of zinc sites

$$-Zn^+ + H_2O \rightleftharpoons -ZnOH + H^+ \qquad 3.33$$

This reaction suggests that by decreasing the pH positive sites should be formed so that at low pH values a positive smithsonite would be expected.

In the solubility tests it was suggested that hydrozincite was formed on the surface of smithsonite at high pH values. The potential-determining ions for hydrozincite will be the same as those for smithsonite and so although the dependency of the electrophoretic mobility on the concentration of potential-determining ions might change the over-all effect will not markedly alter.

It has been shown by a number of authors (55)(56) that the i.e.p. of the solutions, i.e. where the concentration of the anionic and cationic metal complexes are equal,in equilibrium with salt-type minerals such as malachite and azurite and the oxides corresponds to the minimum solubility of the mineral. and also to its isoelectric point.

The theoretical minimum solubility of smithsonite in a closed system in the absence of atmospheric CO_2 occurred at approximately pH 9.0. It can therefore be argued that under these conditions the i.e.p. of the solution and also that of smithsonite should occur in the same pH region.

The electrophoretic mobility measurements in the present work were made on solutions which had contacted atmospheric CO_2. It is therefore important to construct logarithmic concentration - pH curves for smithsonite in the presence of CO_2 to determine whether or not the presence of CO_2 alters the pH at minimum solubility and also the i.e.p. For this purpose the following additional equilibria are required.

The dissolution of smithsonite in acidic solutions can be represented by the equilibria.

$$ZnCO_{3(s)} + 2H^{+} \rightleftharpoons Zn^{+2} + CO_{2_{aq}} + H_2O \qquad pK = -6.91 \qquad 3.34$$

for which it can be readily shown that

$$\log (Zn^{+2}) = 6.91 - 2pH - \log (CO_2) \qquad 3.35$$

In an open vessel the concentration of CO_2 in solution will be dependent on the partial pressure of CO_2 in the air above the vessel. At equilibrium

$$(CO_2)_{aq} = 3.39 \times 10^{-2} P_{CO_2} \qquad 3.36$$

which at a partial pressure of $10^{-3.52}$ gives an aqueous CO_2 concentration of 1.02×10^{-5} moles l^{-1}. Substituting this value in equation 3.35 gives an expression for the zinc concentration as a function of pH, i.e.

$$\log (Zn^{+2}) = 11.9 - 2pH \qquad 3.37$$

The zinc ions released during smithsonite dissolution may undergo hydrolysis according to equations 3.16 - 3.19 and also form a soluble bicarbonate complex as follows (57).

$$Zn^{+2} + HCO_3^{-} \rightleftharpoons ZnHCO_3^{+} \qquad \log K = 2.1 \qquad 3.38$$

where

$$\log (ZnHCO_3^{+}) = \log (Zn^{+2}) + \log (CO_2)_{aq} + pH - 4.26 \qquad 3.39$$

In contact with air this becomes

$$\log (ZnHCO_3^{+}) = \log (Zn^{+2}) + pH - 9.25 \qquad 3.40$$

It is also possible for the formation of a soluble zinc carbonate complex ($ZnCO_3^{o}$) to occur according to the following equation (57)

$$Zn^{+2} + CO_3^{-2} \rightleftharpoons ZnCO_{3\,aq}^{o} \qquad \log K = 5.3 \qquad 3.41$$

$$\log (ZnCO_3^o) = \log (Zn^{+2}) + \log (CO_{2\,aq}) + 2pH - 11.31 \qquad 3.42$$

In the presence of air, therefore

$$\log (ZnCO_3^o) = \log (Zn^{+2}) + 2pH - 16.3 \qquad 3.43$$

The results obtained from these calculations are summarized in Table 3.1 and Fig. 3.19. The sum of all the soluble zinc species gives the line that surrounds the shaded area, i.e. the solubility of smithsonite in the presence of atmospheric CO_2 at any pH.

TABLE 3.1 LOGARITHMIC CONCENTRATION OF SOLUBLE ZINC SPECIES IN EQUILIBRIUM WITH $ZnCO_3$ SOLID AND ATMOSPHERIC CO_2

pH	Zn^{+2}	$ZnHCO_3^+$	$ZnCO_3^o$	$ZnOH^+$	$Zn(OH)_3^-$	$Zn(OH)_4^{-2}$	Approx. total
5	1.90	-2.35	-4.40	-0.79	-10.79	-16.40	1.90
6	- 0.10	-3.35	-4.40	-1.79	- 9.79	-14.40	-0.09
7	- 2.10	-4.35	-4.40	-2.79	- 8.79	-12.40	-2.00
8	- 4.10	-5.35	-4.40	-3.79	- 7.79	-10.40	-3.50
9	- 6.10	-6.35	-4.40	-4.79	- 6.79	- 8.40	-4.24
10	- 8.10	-7.35	-4.40	-5.79	- 5.79	- 6.40	-4.40
11	-10.10	-8.35	-4.40	-6.79	- 4.79	- 4.40	-4.02
12	-12.10	-9.35	-4.40	-7.79	- 3.79	- 2.40	-2.37

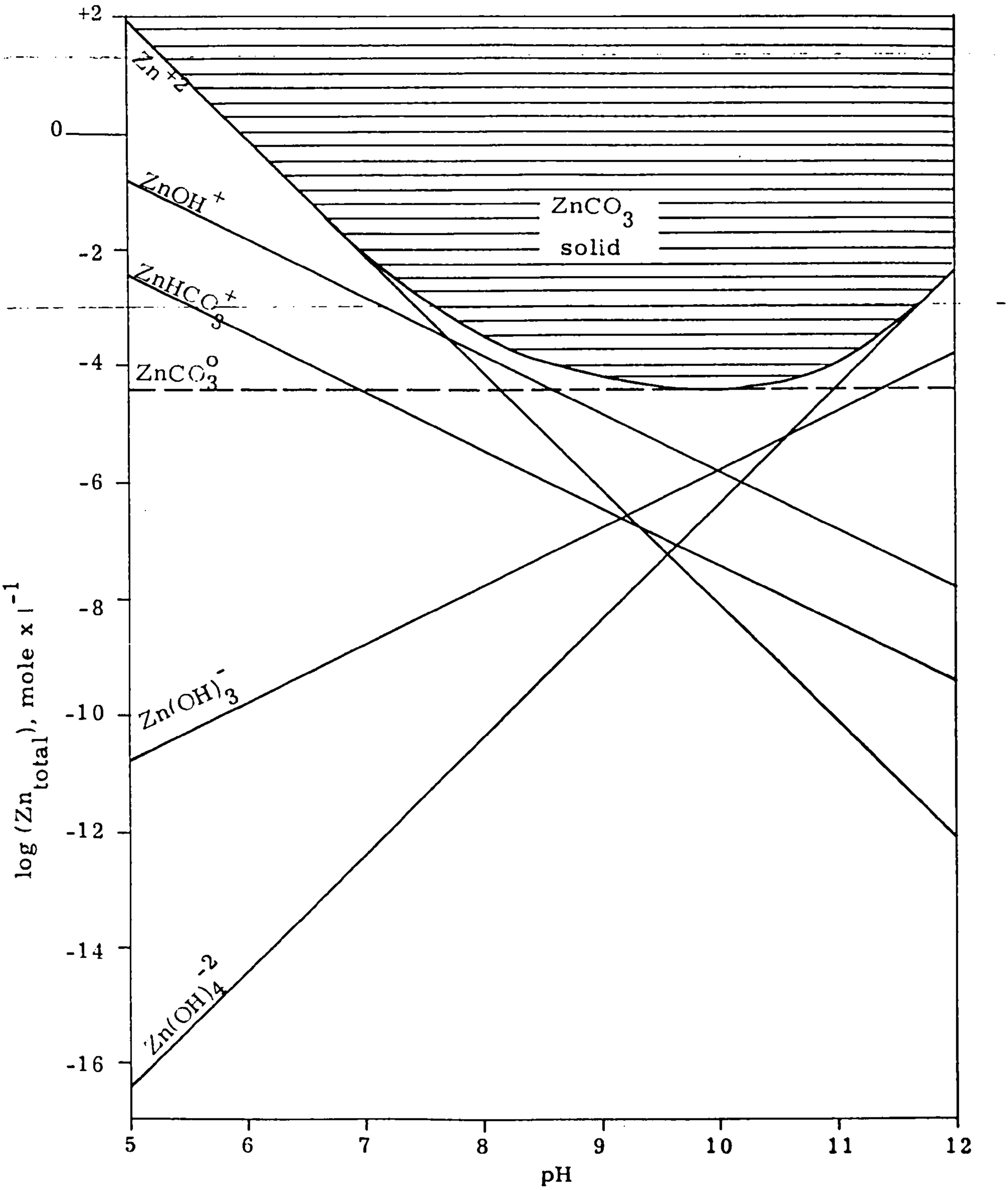


Fig. 3.19 Solubility diagram of smithsonite in equilibrium with atmospheric CO_2

The minimum solubility occurs at a pH of approximately 10.0 and this corresponds also to the isoelectric point of the solution In the absence of specific adsorption effects and any polymeric zinc species it follows therefore that the i.e.p. of the solid and also its z.p.c. should occur at this pH value. These values are somewhat higher than those calculated for smithsonite in a closed vessel. It can, therefore, be concluded that the addition of CO_2 increases the theoretical i.e.p. of the solution and of smithsonite. Figure 3.19 also shows that if it is assumed that the reactions on the smithsonite surface are analogous to those in solution then the concentration of $Zn(OH)_3^-$ and $Zn(OH)_4^{-2}$ should have a considerable effect on the surface potential at pH values above the z.p.c. and $Zn(OH)^+$ and Zn^{+2} below. Through coagulation studies of silver bromide sols, Matijevic et al (58) have postulated the existence of a cationic polynuclear zinc complex with the general formula $(Zn_{n+2}(OH)_{2n+1})^{+3}$ which would be stable at pH values above 8.0. However, the results obtained indicate that if this cationic species is present it does not seem to play an important role in the present system.

Comparison of the electrokinetic results obtained with smithsonite with the theoretical thermodynamic results shows that whereas the latter predicts a positive surface below a pH of approximately 9.0 to 10.0, a positive electrophoretic mobility was not obtained. Similar results were obtained by Healy and Jellet (15) with ZnO. They concluded that even if an i.e.p. existed at neutral to acid pH values the dissolution of the ZnO would prevent determination of the electrokinetic potential.

The fact that the equilibrium pH value of smithsonite suspensions was pH 7.6 suggests that this could correspond to the z.p.c. where the adsorption of H^+ and OH^- ions is equal. If this is the case then the experimental z.p.c. is some 2pH units below that predicted by thermodynamic considerations. The latter, however, assumes that the anions and cations in solution have similar affinities for the solid surface. A number of authors (18), (59), (60) have agreed that this is not the case and that anions are more strongly adsorbed than cations.

According to Grahame's treatment of the double layer it is possible to define the adsorption density, Γ_i, of an ion i of concentration C_i as follows

$$\Gamma_i = k_i C_i \exp(-W_\delta / kT) \qquad 3.44$$

where, W_δ is the work of adsorption of the species i at the plane δ where the potential is Ψ_δ ; and kT is the Boltzmann constant multiplied by the absolute temperature, (4.17×10^{-21} V coulomb at 25^oC)

For the adsorption of cations the work of adsorption becomes,

$$W_\delta^+ = z_+ e (\Psi_\delta + \phi_+) \qquad 3.45$$

and for anion adsorption

$$W_\delta^- = z_- e (\Psi_\delta - \phi_-) \qquad 3.46$$

where, z_+, z_- are the valence of cation and anion respectively

ϕ_+, ϕ_- correspond to the cation and anion specific chemical adsorption potentials

e = electronic charge, 1.6×10^{-19} coulomb.

If it is assumed that ψ_δ is directly proportional to the zeta potential obtained from electrophoretic mobilities (see Fig. 3.2) and that for each of the zinc ionic species the specific adsorption potential is zero, a diagram showing the adsorption density (Γ_i/k_i) of the different zinc species in solution by substitution in equation 3.44 can be constructed (Fig. 3.20). The concentrations of the different zinc species were obtained from Table 3.1. The absisa is the adsorption scale in arbitrary (molar) units of (Γ_i/k_i).

Consideration of this model of the smithsonite surface and the electrophoretic mobility data shows that the model is an over-simplification. Even if allowance is made for the fact that a negative zeta potential is obtained at pH 6.0, for example, the model predicts that the adsorption of cationic zinc species is greater than that of the anionic species. Clearly to correct the model the chemical adsorption potential of the anions must be greater than that of the cations.

In the case of hemimorphite and willemite the surface charge will be controlled by either broken Si-O bonds or by the charge in the structural silicate. When Si-O bonds are broken during the comminution process a very reactive surface results

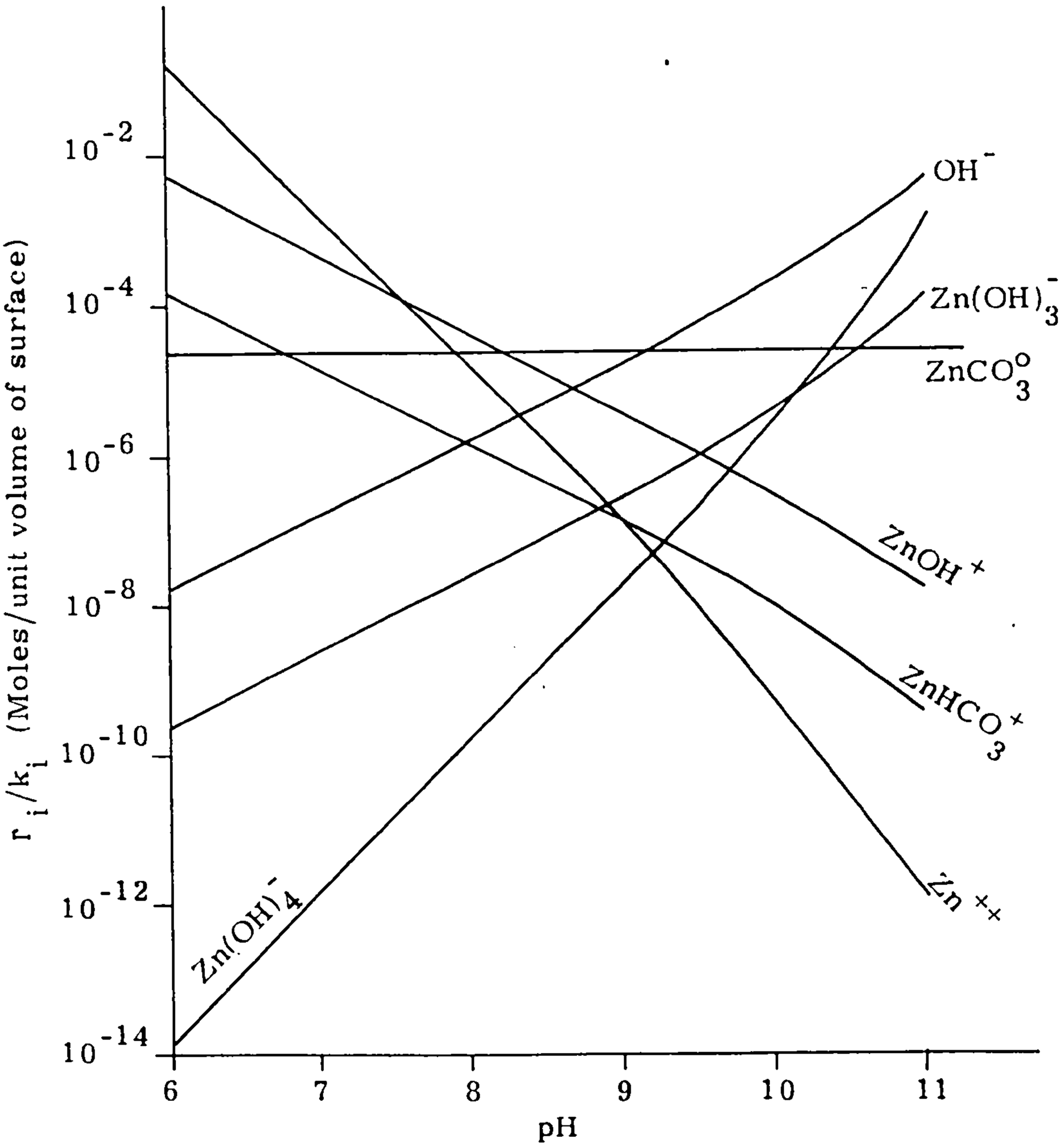
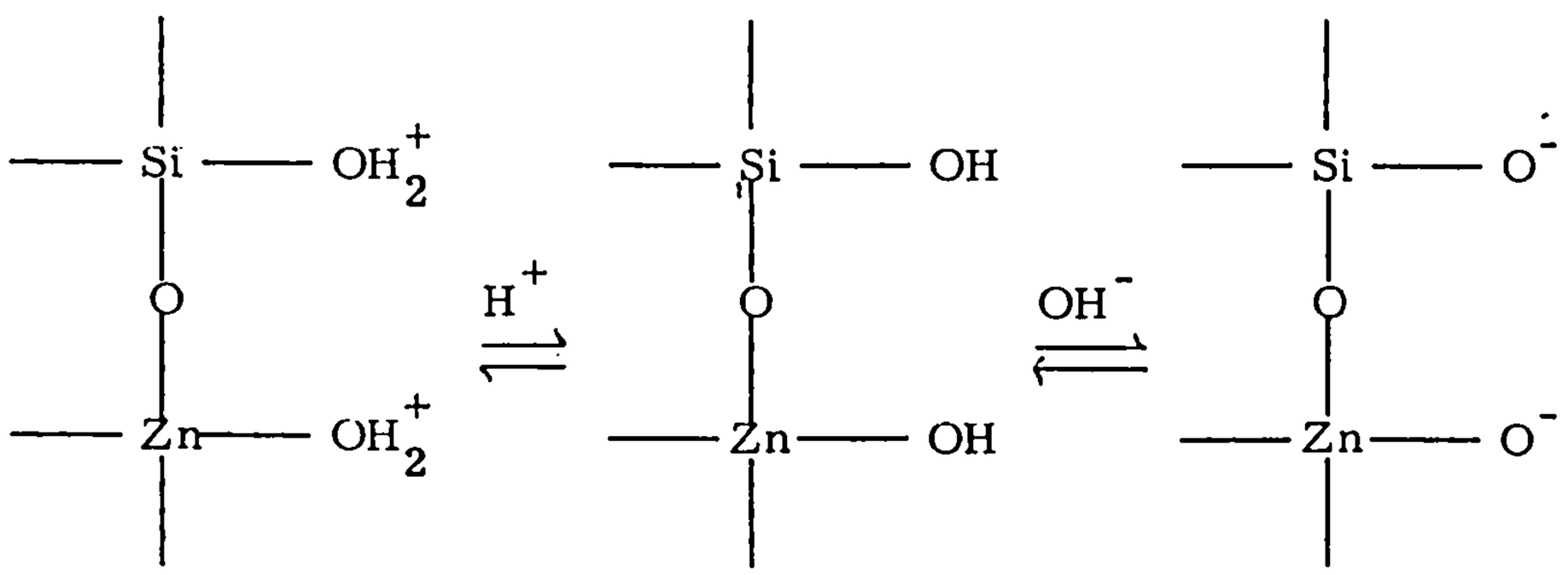


Fig. 3.20 The effect of pH on the surface composition (in moles/unit volume of interface) of smithsonite in water

and when exposed to water vapour Si^+- and O- sites chemisorb water to cover the surface with hydroxyl groups. In aqueous solution these surface hydroxyl groups can ionize or adsorb H^+ to give a negative or positive charge at the surface depending on the pH. At the same time, zinc ions can undergo hydrolysis either on the surface or in solution and then be re-adsorbed. This can be illustrated schematically as:



3.47

This means that the surface of these two zinc silicate minerals when immersed in water tend to behave as if it were the surface of a composite oxide made up of SiO_2 and ZnO, H^+ and OH^- and the different zinc species being potential-determining ions. However, despite the fact that hemimorphite and willemite consumed considerable amounts of H^+ ions when dispersed in aqueous solution at pH values below 8.7 and 7.0 respectively, no positive electrophoretic mobilities were obtained (Figs. 3.7 and 3.11). It is probable that similar to the smithsonite the adsorption of anionic zinc species is greater than that of the cationic species.

During the ageing of smithsonite, hemimorphite and willemite the electrophoretic mobilities decreased slightly over

the first day and thereafter remained constant. These changes in mobility were probably caused by the dissolution of the minerals because within this period a major proportion of the solubility values was reached. The possibility of other surface hydration, diffusion of surface species etc. cannot, however, be completely excluded.

b) Effect of sodium sulphide The effect of sodium sulphide on the zinc oxide minerals would appear to be two-fold. First the sulphide ions are specifically adsorbed into the electrical double layer and this is demonstrated by the increase in negative electrophoretic mobility obtained when Na_2S was added to suspensions of the minerals in water. Secondly the sulphide or hydrogen sulphide ions chemically react with the mineral surface to give a layer of zinc sulphide. This is discussed in more detail in section 3.4.3.

c) Effect.of dodecylamine adsorption on the electrokinetic properties of zinc oxide minerals The adsorption and electrokinetic data obtained with zinc oxide minerals in the presence of dodecylamine indicates that the adsorption of amine follows the generally accepted theory of long chain electrolyte adsorption by oxides and silicates. In general as the amine adsorption increased the negative electrophoretic mobility of the minerals decreased to zero and then became positive. This is consistent with the model that at low concentrations the amine cations are adsorbed coulombically and then at high concentrations, adsorption beyond that required to neutralize the surface sites occurs by hydrophobic bonding between the hydrocarbon chains of the amine cations (or possibly the neutral amine molecules if the pH is high enough) and amine already absorbed.

Chemical interaction between the amine and zinc surface sites is unlikely because an analogous reaction does not occur in aqueous solution.

In the presence of sodium sulphide the electrophoretic mobility of the zinc oxide minerals became more negative, the effect being greatest with smithsonite. This can be explained by the specific adsorption of anionic sulphide species into the Stern layer or alternatively the formation of a ZnS layer for which soluble sulphide species would be potential-determining ions. An increase in negative surface potential could explain the increase in amine adsorption obtained after sulphidisation of the zinc oxide mineral because of increased coulombic attraction. However it should be noted that the residual soluble sulphide level in the amine adsorption tests was lower than in the electrokinetic tests. A lower surface potential would therefore be expected under the conditions used in the adsorption tests. It is unlikely, however, that the surface potential would be lower than that of an unsulphidised sample.

Both in the amine adsorption tests on sulphidised and unsulphidised zinc oxide minerals adsorption densities in excess of a closed packed vertically oriented monolayer were obtained. Cases et al (35) has obtained similar results and explained them by proposing that the amine condenses two-dimensionally at the smithsonite/water interface. The upper limit of adsorption, according to this theory, should correspond to the formation of a bi-molecular layer with the outermost ions oriented with their polar groups pointing towards the aqueous phase. However, Cases

and his co-worker's results on smithsonite either do not extend as far as a bi-molecular layer or alternatively they display no tendency to level off under such conditions. Similarly the results obtained in this work do not support or disprove the theory. The results obtained with hemimorphite do show that the adsorption density levels off but at values somewhat more than two vertically oriented layers even if allowance is made for the available surface area being larger than that obtained by N_2 adsorption.

3.4.3 The Sulphidisation Reaction of Zinc Oxide Minerals

The abstraction of soluble sulphide species by smithsonite and hemimorphite corresponds to many layers. Similar observations have been made with the copper oxide minerals (43)(44) and here the abstraction was attributed to the formation of multilayers of copper sulphide and the oxidation of the sulphide ions to thiosulphate. No thiosulphate was detected in the present work by the method of Sorbo (61) and therefore oxidation is not a source of sulphide abstraction in this case. The exact stoichiometry of the sulphidisation reaction is not known but the driving force must be that zinc sulphide is much more stable than the zinc oxide minerals. At alkaline pH values it is probable that the surface of smithsonite will be either converted to hydrozincite or zinc hydroxide (6) and that the sulphidisation reaction takes place with this layer. Under these pH conditions (pH 10.0) the predominant sulphide species will be HS^- (pK_{a_1} = 7.0; pK_{a_2} = 12.9) and this ion is probably involved in the reaction especially since the sulphide abstraction was independent of the pH in the range 7.0 to 11.0.

$$xZnCO_3 + 2OH^- \rightleftharpoons (x-1)ZnCO_3 \cdot Zn(OH)_2 + CO_3^{-2} \quad 3.48$$

$$(x-1)ZnCO_3 \cdot Zn(OH)_2 + HS^- \rightleftharpoons (x-1)ZnCO_3 \cdot ZnS + OH^- + H_2O \quad 3.49$$

Direct identification of a sulphide layer is difficult. Attempts were made with x-ray diffraction and with an electron probe microanalyser to detect zinc sulphide on smithsonite but they were unsuccessful because the levels were below the detection limits of the instruments. Recently, Cases et al (35) has shown by ESCA studies that the sulphide is chemically fixed to zinc atoms in the smithsonite surface. However, some criticism can be levelled against this technique because it involves drying the sample and observing it under high vacuum.

Both smithsonite and hemimorphite exhibited parabolic hydrosulphide ions abstraction curves (Fig. 3.16) which indicates that the first layers of ZnS formed inhibited the diffusion of HS^- ions to the reaction interface. However, smithsonite abstracted HS^- ions more rapidly than hemimorphite. This is not surprising considering the structure and chemical nature of hemimorphite. The penetration of HS^- ions into the hemimorphite structure, mainly through the existing channels parallel to the (110) planes (53) or pores, to react with zinc atoms will involve the breaking of -Zn-O-Si- bonds. Therefore, a collapse of the bonded zinc-oxygen and silicon-oxygen tetrahedra will be produced, leaving an insoluble silica-rich structure as result. This silica-rich structure and the ZnS layer will slow down and eventually stop the diffusion of HS^- ions towards the 'fresh' surface of hemimorphite much more than in the case of smithsonite, where HS^- has to diffuse through only a ZnS layer.

3.4.4 General Comments

The results obtained in this study show that sulphidisation of the zinc oxide minerals increases selectivity in amine flotation because it improves the stability of the mineral surface, especially that of smithsonite, increases the negative surface potential of the minerals and therefore increases the adsorption of cationic amine. Most of the gangue minerals such as silicates and carbonates will also exhibit negative surface potentials under the conditions used to float the zinc oxide minerals. However whereas sulphidisation enhances the amine adsorption on zinc oxide minerals it will not have an effect on that of the gangue minerals.

The adsorption of amine by the zinc oxide minerals is basically coulombic followed by hydrophobic bonding. This is not a very selective collector adsorption mechanism and it is therefore unlikely that high grade concentrates would be obtained without the use of highly selective gangue depressants. An alternative approach would be to develop collectors with a polar group which have a high selectivity for zinc in the mineral surface. Such reagents might be based on those chelating agents which form insoluble zinc complexes in aqueous solution.

CHAPTER 4

4 THE COMPLEXATION REACTION

4.1 Theoretical Generalities

It is well established that metallic ions are always solvated when dissolved in aqueous solution, and that the formation of a solvation shell reduces the energy of the system through the interaction of water dipoles with the ion. In fact, the hydration energy of many metal ions is of the order of several hundred kJ $mole^{-1}$.

A complexation reaction involves the replacement of one or several solvent molecules in the first hydration sphere by other specific reagents. All reagents bound to a central ion are called ligands. The complexation of a metal ion in aqueous solution can be expressed by the following simplified equation:

$$M(H_2O)_n + L \rightleftharpoons M(H_2O)_{n-1}L + H_2O \qquad 4.1$$

L can be either a molecule or an ion. The remaining aquo groups in the complex may be successively replaced by other L groups until the complex ML_n is formed. Reactions of this type include not only complex formation in homogeneous solution but also the formation of precipitates. Precipitation occurs if the ligand links two or several metallic ions together, so that the network of a coagulate or an ordered crystal lattice results.

If a metal forms a complex entity, ML_n, the maximum number of bound ligands is the co-ordination number of the metal ion. It may be noted, however, that a metal ion can have more

than one characteristic co-ordination number depending on the oxidation state of the central atom and on the nature of the co-ordinated ligand.

4.2 Stability of Complex Compounds

It has been experimentally observed that some complexes, like cobaltammines, are evidently very stable because they can be kept indefinitely with no decomposition and in solution they do not give the usual analytical reactions of their constituent groups. On the contrary, other complexes such as the metal carbonyls are unstable, being destroyed by the action of heat or water. Hence, increasing attention has been paid more recently to the way in which complexes are formed and to the quantitative study of their stabilities.

The most important attempt to study the stability of metal complexes was the work by Bjerrum (62) on the formation of metal ammines in aqueous solution. According to Bjerrum, the formation of a complex in solution proceeds by the 'stepwise' addition of ligands to the metal. Thus, in a solution containing metal ions, M, and monodentate ligands, L, only soluble mononuclear complexes are formed. The system at equilibrium may be described by the following equations and equilibrium constants:

$$M + L \rightleftharpoons ML \qquad K_1 = \frac{(ML)}{(M)(L)} \qquad 4.2$$

$$ML + L \rightleftharpoons ML_2 \qquad K_2 = \frac{(ML_2)}{(ML)(L)} \qquad 4.3$$

$$ML_2 + L \rightleftharpoons ML_3 \qquad K_3 = \frac{(ML_3)}{(ML_2)(L)} \qquad 4.4$$

$$ML_{n-1} + L \rightleftharpoons ML_n \qquad K_n = \frac{(ML_n)}{(ML_{n-1})(L)} \qquad 4.5$$

There will be n such equilibria, where n represents the maximum co-ordination number of the metal ion M for the ligand L. Another way of expressing the equilibrium relations is the following,

$$M + L \rightleftharpoons ML \qquad \beta_1 = \frac{(ML)}{(M)(L)} \qquad 4.6$$

$$M + 2L \rightleftharpoons ML_2 \qquad \beta_2 = \frac{(ML_2)}{(M)(L)^2} \qquad 4.7$$

$$M + 3L \rightleftharpoons ML_3 \qquad \beta_3 = \frac{(ML_3)}{(M)(L)^3} \qquad 4.8$$

$$M + nL \rightleftharpoons ML_n \qquad \beta_n = \frac{(ML_n)}{(M)(L)^n} \qquad 4.9$$

The K_i's are called as the intermediate, or stepwise stability constants, and the β_i's are called the total or overall formation constants. The intermediate constants are related to the overall formation constants by the simple relationship:-

$$\beta_n = K_1 . K_2 ..... K_n \qquad 4.10$$

The term overall stability constant' can be applied not only to the complexes with the maximum number, but also to all the other species formed in solution as a result of stepwise

dissociation. It should be noted that for the sake of simplicity, charges and degree of solvation have been omitted.

With only a few exceptions, there is generally a slowly decreasing progression in the values of the stepwise stability constants in any particular system (63). Thus, as a ligand is added to the metal ion solution, ML is first formed. As addition of ligand is continued, the ML_2 concentration rises rapidly while the ML concentration decreases, then ML_3 becomes predominant, ML and ML_2 becoming unimportant, and so forth until the highest complex, ML_n is formed to the nearly complete exclusion of all others at very high ligand concentrations.

There exist several reasons for the progressive decrease in K_i values as the number of ligands increase:-

a) statistical factors;
b) increased hindrance if the ligands are more voluminous than the water molecules they replace;
c) electrostatic repulsion occurring mainly in complexes with charged ligands.

The change of enthalpy, ΔH, during a complexation reaction can be taken as a measure of the strength of the chemical bonds which are broken and reformed. Information on ΔH in complexation reactions is however, sparse and it is therefore more usual to consider the change in free energy during the reaction and the stability constants as measures of the tendency of a metal complex with a given ligand and the stability of the resulting complex.

There exist many complexes which are formed by simple electrostatic attraction between the metallic ion and an anion or a polar ligand. In this case no formation of a chemical bond is involved and only an ionic association exists. The change in enthalpy, ΔH, in such reactions is small and may even be positive (endothermic process). However, the formation constant is still large indicating that the entropy change associated with the reaction is much larger and positive. This is because of the liberation of many water molecules from the hydration shell accompanying the partial neutralization of charges.

4.3 Classification of Metal Cations

Schwarzenbach '64) classifies cations according to their electronic structures into the following three groups:-

Group A: Cations with a noble gas configuration.

Group B: Cations with a completely filled d subshell (18 electrons).

Group C: Transition metal ions with incomplete subshells.

Group A: Cations with a noble gas configuration (d^o cations). They are of low polarizability, i.e. their electron sheath are not readily deformed under the influence of an electric field. The alkali metals, the alkaline earth metals, and aluminium belong to this group. Purely electrostatic phenomena predominate, and the forces between small ions of high charge are particularly strong and give stable complexes. These cations

have a tendency to form complexes only with fluorine and oxygen as donor atoms in aqueous solution. Water is more strongly attached than ammonia, which has a smaller dipole moment. No sulphides are formed, either as precipitates or as complexes, since hydroxyl ions are always bound before hydrosulphide or sulphide ions. In addition, no reaction occurs with sulphur donors such as dithiocarbamates and xanthates and there is no color reaction with dithizone.

The large univalent alkali metal ions (K^+, Rb^+ Cs^+) exist in solution as hydrated ions and probably do not form other complexes. The smaller ions (Li^+, Na^+) form a few weak complexes with some highly charged chelating agents (EDTA). Alkaline earth metals present a much stronger tendency to form complexes but the tendency usually decreases with increasing ion size (from Be^{+2} to Ra^{+2}).

Group B: Cations with a completely filled d subshell. These cations have an outer shell of eighteen electrons, (d^{10}-d^{12}) and present high polarizabilities. The bonds in their complexes are predominantly covalent, the electrons of the co-ordinate bonds being provided by the ligands. Thus, the complexation tendency of these ions is completely different from that of the Group A ions. In this case, charge and radius of the metal ion are not the most important factors, but the difference in electronegativities of the metal ion and the donor atom plays a decisive role. This means that the bond strength increases with the ease with which the metal ion accepts electrons and the ease with which the ligand atom donates them. The

complexes are more stable the more noble the metal and the less electronegative the donor atom of the ligand.

Phosphorus and sulphur, which form covalent bonds, combine more easily than nitrogen and oxygen with metals in this group. However, it is often difficult to compare corresponding stabilities by means of equilibrium constants because side reactions and low solubilities in aqueous solutions prevent exact measurements.

Zinc atoms have the electron configuration $(n-1)d^{10}ns^2$ and the removal of two electrons gives rise to the formation of a dipositive oxidation state. Compared to the Group A metals, compounds of zinc are considerably more covalent in character. The stability of the inner d^{10} core is such that oxidation states higher than two are not formed.

Zinc ions form a wide variety of tetrahedral complexes particularly where nitrogen is present to act as donor atom. Thus stable complexes are formed with ammonia, amines such as ethylenediamine and also molecules where both nitrogen and oxygen are present to act as donor atoms, e.g. 8-hydroxy-quinoline and ethylenediaminetetracetic acid (65). Zinc complexes of dithiocarbamates and of other sulphur compounds have also been described (63).

Group C: Transition metal ions with incomplete subshells. These are ions with between zero and ten d-electrons (d^0-d^{10}). In this group the two tendencies characteristic of the metals of groups A and B can be distinguished. The predominating characteristic depends essentially on three factors:

the charge, the size and the ionization potential of the ion. On the basis of these factors, it is often possible to predict qualitatively the complexation ability of various metal ions. The most extensively studied is the series of divalent metals Mn, Fe, Co, Ni, Cu and Zn. In this series, the ionic radius decreases and the ionization potential increases up to copper. Accordingly, the stability increases progressively to reach a maximum with copper. This series of cations is said to follow the well-known Irving-Williams order (66).

The complexation tendency of metals belonging to the Irving-Williams series is particularly pronounced when nitrogen, carbon, or sulphur is the co-ordinating atom, but less pronounced with oxygen. This means that the last members of the series, e.g. Cu^{+2}, are more like the group B metals, whereas the first members are more like the group A metals. This rule is known to apply to complexes in which the ligands occupy not more than four co-ordination positions lying in the same plane. When all six co-ordination positions are filled, or when five ligands are present, the stabilities of the complex compounds may vary in a different order (64).

For the other transition metals, a general behaviour similar to that of the discussed series can be expected. The stabilities usually increase within a group with passing from the first to the second and from the second to the third transition series. In fact, many complexes of Pd(II) are more stable than the corresponding Ni(II) complexes but less stable than the Pt(II) complexes.

After reviewing the above classification of metal ions it is very important to point out that not all experimental facts fit satisfactorily into this scheme. The application of the ligand field theory, including modern concepts of π bonding, to stability problems in co-ordination chemistry has however explained many previously less well understood phenomena.

4.4 Classification of Ligands

For a complexation reaction to take place it is necessary that the participation of a ligand which can be a neutral molecule. or an ion is involved. Each ligand molecule or ion has one pair of unshared electrons which is donated to the metal to form a co-ordination bond. The metal, in turn, must have vacant orbitals of appropriate energy which can accept these electrons.

The nature of the atom which binds the ligand to the metal largely determines the ligand behaviour. Only a few ligand atoms will be considered here: the halogens, oxygen, sulphur, nitrogen, and carbon.

a) The halogens are able to co-ordinate only as the simplest anions fluoride, chloride. bromide, and iodide.

b) The most important ligand containing oxygen is water, the aquo complexes being the simplest ones since water is the solvent normally used. Mononuclear hydroxo complexes are first produced by deprotonation. but the formation of

polynuclear species and precipitation almost always follows (64) despite this fact, K_1 for OH^- as a ligand is known for most cations. Examples of other inorganic oxygen donors are: NO_2^-, NO_3^-, CO_3^{-2}, PO_4^{-3}, and polyphosphates; $S_2O_3^{-2}$, SO_3^{-2}, SO_4^{-2} and ClO_4^-. Organic complexing agents are able to provide oxygen as donor atom in the form of ether (R-O-R), and alcohol or phenol, and ketonic or carboxylic oxygen.

c) Sulphur donors are: HS^- and S^{-2}, $S_2O_3^{-2}$, SCN^-, thioethers (R-S-R), mercaptans and their anions (R-SH and $R-S^-$), thioketones and the mono- and dithio-carboxylate groups.

d) Nitrogen acts as a donor atom in a great variety of ligands, and particularly in ammonia. Deprotonated ammonia is a ligand for mercury, copper and zinc and many other metals. The NO_2^- ion is usually co-ordinated to metal ions through nitrogen as is also in the case with SCN^- ions. Organic nitrogen present in primary (RNH_2), secondary (R_2NH), and tertiary (R_3N) amines; carboxylic amides ($R-CO-NH_2$), nitroso compounds (R-N = O), oxime groups (C = N-OH), and azo groups (R-N = N-R) co-ordinates in complex formation.

Ligands with one atom which can be an electron donor are called <u>unidentate</u>. Water, ammonia, and the halide ions are all unidentate ligands. Organic molecules or ions containing two or several electron donor atoms are termed bi-, tri-, or generally <u>multidentate</u>. Examples of multidentate ligands are: xanthate (bidentate), diethylenetriamine (tridentate), triethylenetetramine (quadridentate), etc.

4.4.1 The Chelation Reaction

When the multidentate ligand contains donor atoms so arranged that two or more of the donor atoms can bind to the same central atom one or more ring structures can be formed. Such ring compounds are called chelates, and the multidentate reagents, chelating agents. Thus, the chelate effect is referred to as the enhanced stability of a complex system containing chelate rings compared to the stability of a system which is as similar as possible but contains none or fewer rings (63). The reason for the additional stability due to chelation frequently depends more on the spatial arrangement than on electronic factors.

The chelate effect is usually expressed as the difference between the logarithms of the stability constant of the chelate complex and the overall stability constant of the complex formed by the same metal ion with the corresponding monofunctional ligands. This is clearly exemplified by the following reactions:-

$$Zn^{+2} + 4NH_3 \rightleftharpoons Zn(NH_3)_4^{+2} \qquad \log \beta = 9.06 \qquad 4.11$$

$$Zn^{+2} + \text{penten} \rightleftharpoons (Zn\ \text{penten})^{+2} \qquad \log \beta = 16.2 \qquad 4.12$$

where penten corresponds to tetra-amino-tetraethyl-ethylenediamine. The system $(Zn\ penten)^{+2}$ in which 5 rings are formed is 10^7 times more stable than where no rings are formed. This effect depends on many factors. In the case of non-transition elements it is mainly an entropy effect while with transition metals it is partly an enthalpy effect.

The entropy contribution to the chelate effect is nearly equal in analogous systems and can be partly explained by the higher statistical probability of complex formation because the effective collision of fewer particles is required than in the formation of non-chelation complexes. Moreover, in the formation of chelate complexes a given ligand replaces two or more water molecules in the co-ordination sphere. Thus, the number of independent particles increases during chelate formation. This is better explained with the following example.

$$(Ni(H_2O)_6)^{+2} + 6NH_3 \rightleftharpoons (Ni(NH_3)_6)^{+2} + 6H_2O \qquad \log \beta\, 8.61 \qquad 4.13$$

$$(Ni(H_2O)_6)^{+2} + 3en \rightleftharpoons (Ni\ en_3)^{+2} + 6H_2O \qquad \log \beta = 18.28 \qquad 4.14$$

where en is ethylenediamine.

In equation 4.13 six ammonia molecules displace six water molecules, making no net change in the number of independent molecules. However, it is necessary for only three ethylenediamine molecules to displace the same six molecules (equation 4.14). This increases the disorder and therefore the entropy of the system. The entropy increase causes a considerable decrease in free energy (ΔG^o) so inducing a higher stability of the complex.

Another more graphic way to look at the chelation reaction is to visualize a chelate ligand with one end attached to the metal ion. The other end cannot then get very far away, and the probability of also becoming attached to the same metal ion is greater than if this other end were another independent molecule which would then have access to a much larger volume of the solution.

The chelate effect varies with the size of ring formed on co-ordination. It is usually a maximum for five- membered rings and only slightly smaller for six- membered rings. Although complexes with rings of larger sizes have been synthesized they show little sign of the chelate effect. This is partly because when the ring becomes sufficiently large (seven-membered or more), it is more probable that the 'other end' of the ligand molecule will interact with another metal ion rather than with the first one. In addition, another destabilizing influence for larger-membered rings is the relative difficulty of finding a sterically possible ring configuration. The relationship between the spatial configuration of free and co-ordinated multidentate ligands is currently the subject of research but it is already clear that ligand configuration is an important factor in determining the relative stabilities of complexes.

4.4.2 Mechanisms of the Chelation Reaction

Many compounds and ions, most of them organic in nature, form chelate rings with metal ions. Ring closure may take place with the formation of covalent or co-ordinate bonds or both. The ability to form a covalent bond requires the presence of an acidic group in the ligand, such as carboxyl, sulphonyl, enol, thioenol, or oxime. The most common functional groups containing donor atoms, and therefore able to co-ordinate with a metal, are:-

- $\ddot{N}H_2$, $-\ddot{N}H$ and $\rangle\ddot{N}$ (amines)

N-OH (oxime); -OH (alcohol)

C = O (carbonyl); -O- (ether)

-S- (thioether)

Chelation is favoured when any two of these groups occur in the 1.4 or 1. 5 positions of an organic molecule, with the formation of 5- and 6- membered rings respectively.

Multidentate ligands can thus be attached to a metal atom by two types of functional groups and chelate compounds are classified according to the number and type of attachments involved. The bidentate chelating agents have been divided into three classes:

1 Two acidic groups This type includes inorganic acids like carbonic and sulphuric, organic dicarboxylic acids like malonic, oxalic and phtalic; α-hydroxy-carboxylic acids like glycollic and salicylic; and dihydroxy-compounds like the glycols and pyro-catechol. Examples of metal complexes formed by this type appear in Figs. 4.1 and 4.2.

2. One Acidic and One co-ordinating group This is an especially useful class of organic reagents which can, through chelation, often satisfy simultaneously the oxidation number and the co-ordination number of the metal ion, i. e. the metal atom is bound both by salt-like and complex bonds to different parts of the molecule. When this occurs an uncharged species or inner complex is formed. Examples of this type are given by β-diketones, dimethylglyoxime, salicylaldehyde, 8-hydroxyquinoline, dithizone. quinaldic acid, etc. (Figs. 4.3 and 4.4)

3. Two co-ordinating groups These include those reagents containing two donor atoms which are bound to the metal ion through the formation of two co-ordinate bonds. Examples of these reagents are the diamines, like ethylenediamine, α - α'-dipyridyl, o-phenanthroline, dihydroxy-compounds like 1.2-glycols and glycerol and α-hydroxy-oximes like α -benzoin oxime. (Figs. 4.5 and 4.6).

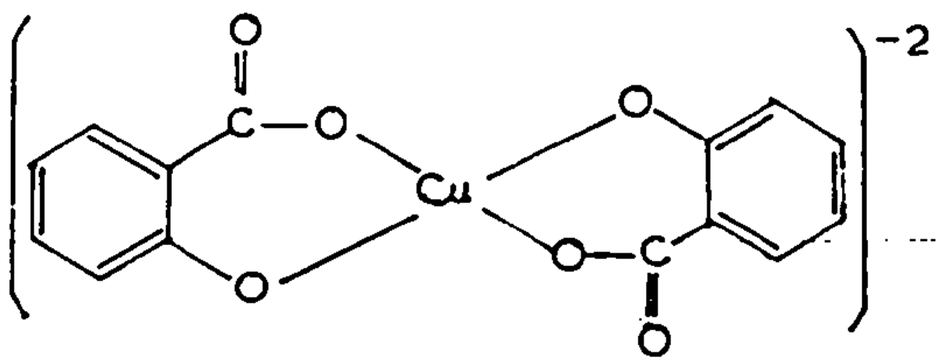


Fig. 4.1 Bis salicylato) cuprato (II) ion

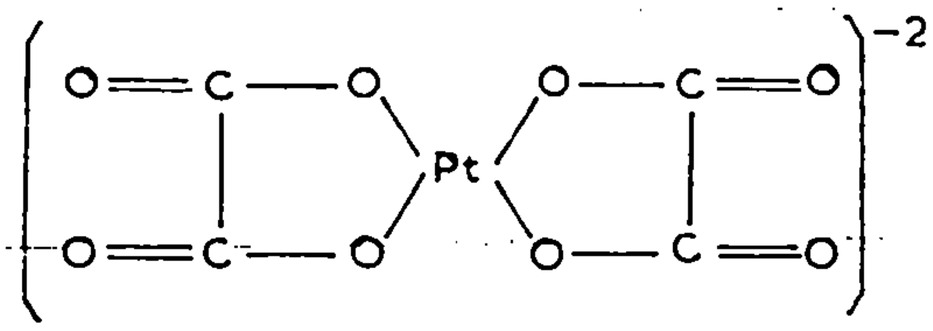


Fig. 4.2 Bis (oxalato)platinato (II) ion

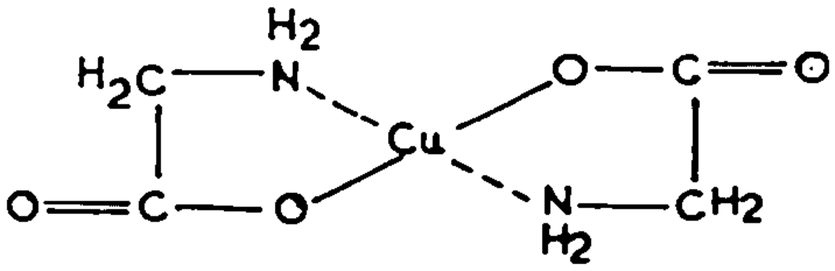


Fig. 4.3 Copper (II) glycinate

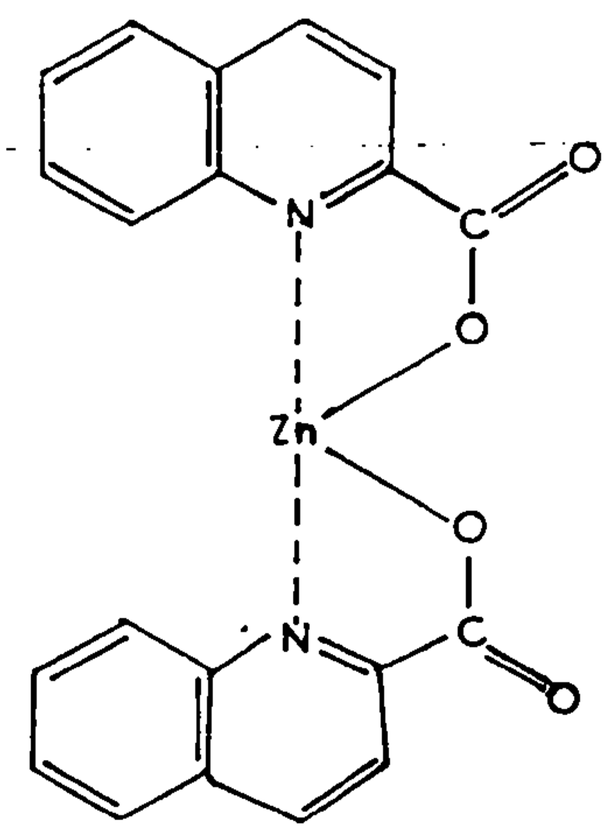


Fig. 4.4 Zinc (II) quinaldinate

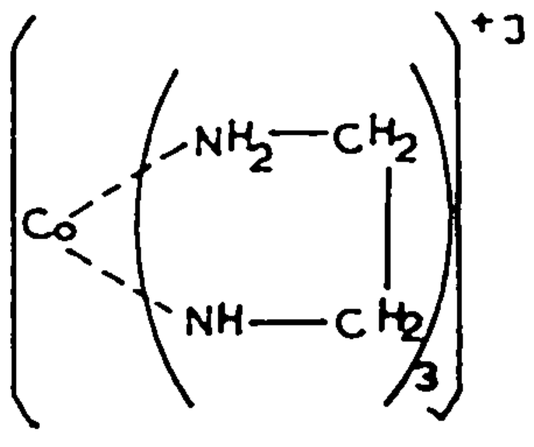


Fig. 4.5 Cobalt (II) ethylenediamine

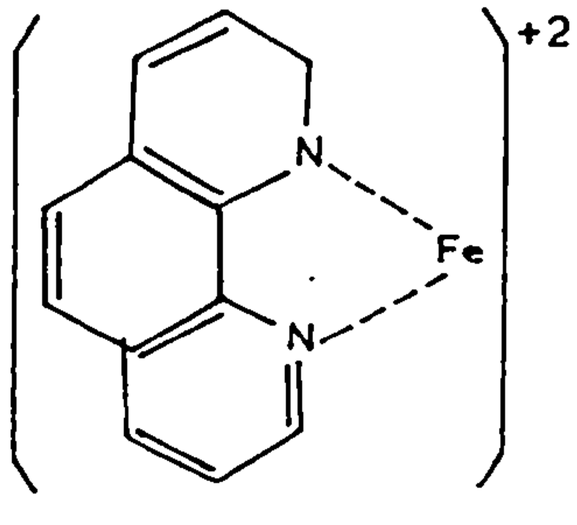


Fig. 4.6 Iron (II) - phenanthroline

4.5 Factors Influencing the Formation and Stability of Complexes

Several factors determine the stability of a complex formed between a particular metal ion and ligand. The values of stability constants vary over an extremely wide range and it is not always easy to estimate the relative importance of the various factors which contribute towards stability. However, experimental data quoted by several authors (65) (67) shows that the stability of complexes in solution is mainly determined by the physico-chemical characteristics of the central metal ions and the ligands.

4.5.1 Properties of the metal

The most important characteristics of the central atom, determining the stability of complex compounds, are the oxidation state (charge on the central ion in the case of ionic complexes), ionic radius and the electronic structure (polarizability).

1. Effect of charge and size of metal ions

The formation of many complexes can be explained in terms of simple electrostatic models. When the ligands are negatively charged, it is easily supposed from Coulomb's law that the interaction between the metal ion and the ligand is stronger when the charges are larger and/or the distance between their centres at equilibrium is smaller. This causes that the complexes are generally more stable. For example, various complexes of the following ions are more stable in the following order

$$Mg^{+2} > Ca^{+2} > Sn^{+2} > Ba^{+2}$$

increasing complex stability ←

decreasing ionic radius ←

When the ionic radii are almost the same, the complexes are more stable in the increasing order of the charge. For example, various complexes of the following ions are more stable in the order.

$$Th^{+4} > Y^{+3} > Ca^{+2} > Na^{+}$$

increasing complex stability ←

increasing charge ←

The interaction of metals with uncharged ligands can also be considered as electrostatic because the metal ion interacts with the ligand dipole. Hydration of metal ions falls in this category and it is found that the strength of hydration follows the Irving-Williams series. General acceptance of such a series as a guide to complex stability can, however, lead to erroneous conclusions especially if inner complexes are formed. The formation of inner complexes is accompanied by dehydration and it follows therefore that the factors which favour hydration, i. e. small ionic radius and/or high charge, will not favour complex formation.

2. Effect of polarizability. In general with less easily distorted central ions, e. g. the alkaline earth metals, the complex stability decreases with increasing radius of the cation. In the case of central ions with equal or nearly equal ionic radii and charges, the more distortable (polarizable) the central ion, the higher the stability of its complexes. Thus, for example, the

size of thallous ion is between that of potassium and rubidium ions, but due to its closed d-shell it is more polarizable and, therefore gives much more stable complexes with organic ligands.

4.5.2 Properties of the ligand

1. The electronegativity of the ligand donor atom; i.e. the tendency of the ligand atom to donate electrons into a covalent bond. The stability of the complex is found to increase with the ionization potential of the metal and with decreasing electronegativity of the ligand atom. In the electronegativity series F > O > N > Cl > Br > I C S, the complex stability increases from left to right.

2. Basicity When the ligand shows basic properties with respect to water as a solvent, a correlation is often noted between the base strength (i.e. the proton affinity) of a ligand and the stability of its metal complexes (i.e. its cation affinity). However, no broad generalization is possible. It is true that the perchlorate ion, which is an exceptionally weak base, has very little tendency to form metal complexes, but it is also common to find bases showing little correlation between the stabilities of their hydrogen and metal complexes. For instance, the cyanide ion is a rather strong base and the fluoride ion is a weak base, nevertheless aluminium forms much more stable complexes with the fluoride ion than with the cyanide ion. Only if the ligands are sufficiently similar in structure is a clear correlation noted between the strength of the proton complexes and the corresponding metal complexes.

3. Steric factors These are associated with the presence of a large group either attached to or near enough to a donor atom to cause steric hindrance between the ligands and hence a reduction in the stability of the complex. For instance, in the case of a mono-dentate ligand the donor atom of which has a large radius, steric hindrance may prevent the formation of complexes containing as many ligands as correspond to the maximum co-ordination number of the central atom. Steric hindrance is particularly significant with complexes of chelate-forming ligands since relatively minor changes in ligand structure may cause considerable changes in complex stability. This, for instance, accounts for the observation that the metal chelates of 2-methyl-8-hydroxyquinoline are less stable than those of either 8-hydroxyquinoline itself or its 4-methyl derivative. 4-Methyl-8-hydroxyquinoline behaves like the unsubstituted reagent because the methyl group is too far away from the nitrogen to affect sterically the process of complex formation.

4.6 Factors Determining the Solubilities of Complexes

In analytical practice the solubilities of metal complexes are very important. For instance, the analytical selectivity of dimethylglyoxime arises from the low solubilities of its nickel and palladium complexes, whereas the corresponding complexes of all the other transition metals are soluble in water.

In water the molecules are bound together by hydrogen bonding and therefore when hydration of water soluble compounds occurs the 'structure' of the water is modified. Simple organic molecules containing hydrophobic groups, e.g. alcohols, aldehydes, ketones, carboxylic acids and amines undergo hydration by

formation of hydrogen bonds with water. Sulphur atoms are less capable than oxygen of forming hydrogen bonds. Thus, the replacement of an oxygen atom in an organic molecule by sulphur is accompanied by a solubility decrease. The ability of nitrogen to form hydrogen bonds is about the same as that of oxygen in analogous compounds.

The introduction of aliphatic hydrocarbon chains and aromatic rings increases the hydrophobic character of a molecule. This involves a decrease in the solubility in water because of the inability of these groups to hydrate.

The electric charge of a molecule is also important in determining the solubility. Charged species, either cations or anions, have a sufficiently large electrostatic field to orientate water molecules around themselves. Those reagents which form electrically neutral complexes with metal ions generally give precipitates. However, those ligands which are strongly polar give soluble complexes in water even if they are electrically neutral. This explains, for instance, the solubility of the Cu(II) glycine complex. The copper complexes of anthranilic and quinaldinic acids, containing the same donor atoms, are however insoluble in water. The formation of polynuclear complexes can also decrease the solubility. For example, carbonates, phosphates, and sulphates usually give complexes in which their two donor atoms bind to different metal atoms and, therefore, the salts have a quasi-polymeric structure.

In order to increase the solubility in water of non-charged metal complexes, some ionizing groups (sulphonic or carboxylic groups) can be introduced into the ligand molecule. The hydration ability of this substituent favourably affects the solubility of the complex. For instance, the 8-hydroxyquinoline complex of iron (III) is uncharged and, therefore, it is practically insoluble in water; the analogous 8-hydroxyquinoline -5- sulphonic acid complex is readily soluble in water.

4.7 Selectivity and Specificity of Complex Formation

Whether or not complex formation is selective depends very much on what the complex is required for. A ligand may be selective for instance if it gives complexes with many metal ions but only one or two of these are insoluble. In another case the ligand may form complexes of similar stabilities with metal ions but only one of them absorbs radiation within a certain spectral range. Similarly other physical or chemical properties of the complexes may ensure selectivity between complexes of different metals.

Numerous examples exist where a ligand complexes with many metals but under different pH conditions. Varying the pII can control the ionization of the ligand and the extent of hydroxylation of the metal ion. Obviously to obtain complexation of the metal both the metal and the ligand must be in the appropriate form. A good example of this is 8-hydroxyquinoline which forms water insoluble precipitates with more than 30 cations. The number of metals precipitated under a given set of conditions can, however, be considerably reduced by selecting a suitable pH. A still greater degree of selectivity may be obtained by the addition of 'masking'

or other complexing (sequestering) reagents. Thus 8-hydroxyquinoline e.g. will precipitate very few metals from a buffer solution (ammonium acetate and acetic acid) in the presence of EDTA.

4.8 The Reaction of Zinc with Different Organic Chelating Agents

In this section a review of the precipitation reactions of zinc ions with different chelating reagents is presented.

1 Anthranilic Acid Zinc is quantitatively precipitated by this reagent in the pH range 4.7 to 7.0. However, it is subject to interferences by metals such as, Fe, Cd, Ni, Co, Mn, Pb, Hg, and Cu, which all form precipitates. The composition of the zinc-anthranilate precipitate is quite dependent on the solution conditions at the time of precipitation and it usually contains water of crystallization. The structural formula of the chelate is shown in Fig. 4.7.

2 Quinaldic Acid The precipitation of zinc-quinaldinate is complete in the pH range 2.3 to 6.5 (68). The precipitation is also subject to a number of interferences particularly from Cu, Ag, Hg(i), Hg(II), W and Mo. The zinc-quinaldinate chelate contains water of crystallization (Fig. 4.8).

3 Salicylaldoxime Zinc is quantitatively precipitated by salicylaldoxime in the pH range 7.0 to 8.0. This reagent is probably the least suitable because of the narrow precipitation pH, and the precipitation is stoichiometric only under closely specified conditions. The composition of the precipitate varies from that of the disalicylaldoximate, $Zn(C_7H_6O_2N)_2$ (at ordinary temperatures and

pH less than 8.5) to the monosalt, Zn $(C_7H_5O_2N)$ which is formed at any pH by digestion at 90 to 100°C for 10 min. the structural formula appears in Fig. 4.9.

4 8-Hydroxyquinoline (Oxine) This reagent appears to be one of the best precipitants of zinc. Zinc-oxinate has a solubility in water of less than 10^{-6}M. Although oxine is not a selective reagent, proper use of pH and masking agents allows the separation from nearly all common interferences except large amounts of cobalt, nickel and cadmium.

Zinc is quantitatively precipitated in the pH range 4.6 to 13.4, but the usual conditions given for the precipitation specify acetic acid-acetate or basic tartrate solutions. Precipitation from acetate solutions at pH 5.0 gives a pure precipitate in the presence of Cu, Pb, Mn, the alkali and alkaline earth metals. The structure of the zinc-oxinate chelate is shown in Fig. 4.10.

5 2-Methyl-8-hydroxyquinoline;8-hydroxyquinaldine This reagent is similar to oxine in its analytical properties but seems to be more selective. In general, the pH range of quantitative precipitation of zinc-8-hydroxyquinaldinate does not differ greatly from that of zinc-oxinate. The structure of the chelate is shown in Fig. 4.11.

6 Dithizone (diphenylthiocarbazone). It is particularly notable among organic reagents for its wide applicability to the solvent extraction of cations. Zinc reacts with dithizone over a wide pH range from 5.0 to 10.5. The structural formula of the zinc-dithizonate chelate is shown in Fig. 4.12.

7 Other organic precipitants. Zinc can also be precipitated by cystine, 4-hydroxybenzothiazol, 2.7-aminofluorene, and a dye produced by coupline 8-oxine with p-amino-benzoic acid.

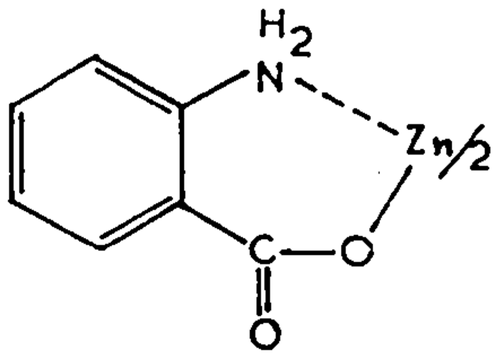


Fig. 4.7 Zinc (II) anthranilate

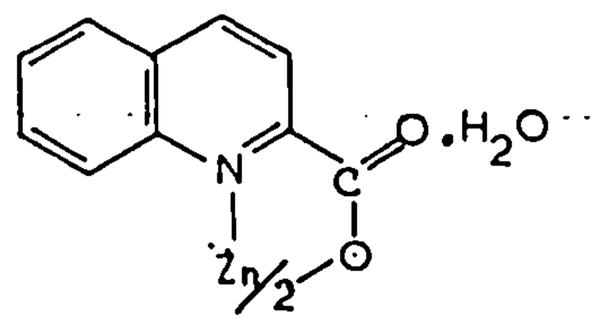


Fig. 4.8 Zinc (II) quinaldinate

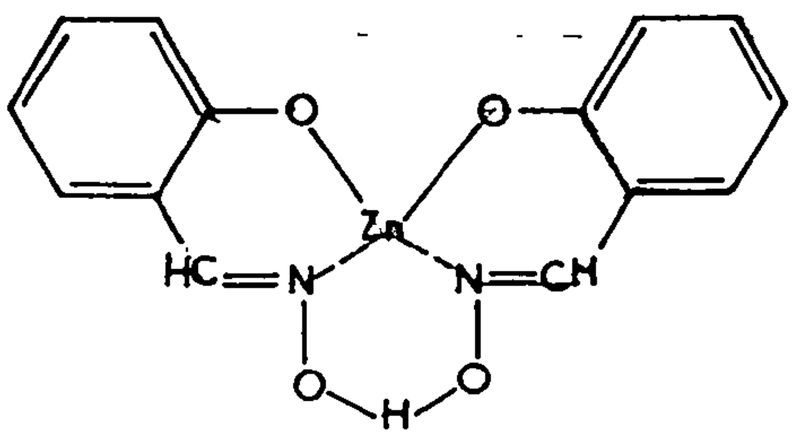


Fig. 4.9 Zinc (II) disalicylaldoximate

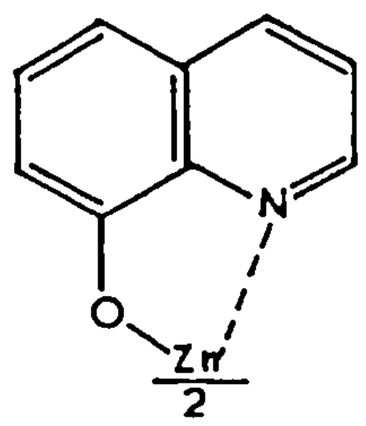


Fig. 4.10 Zinc (II) oxinate

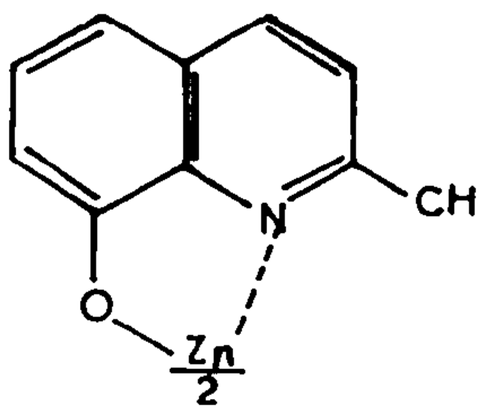


Fig. 4.11 Zinc (II) methyloxinate

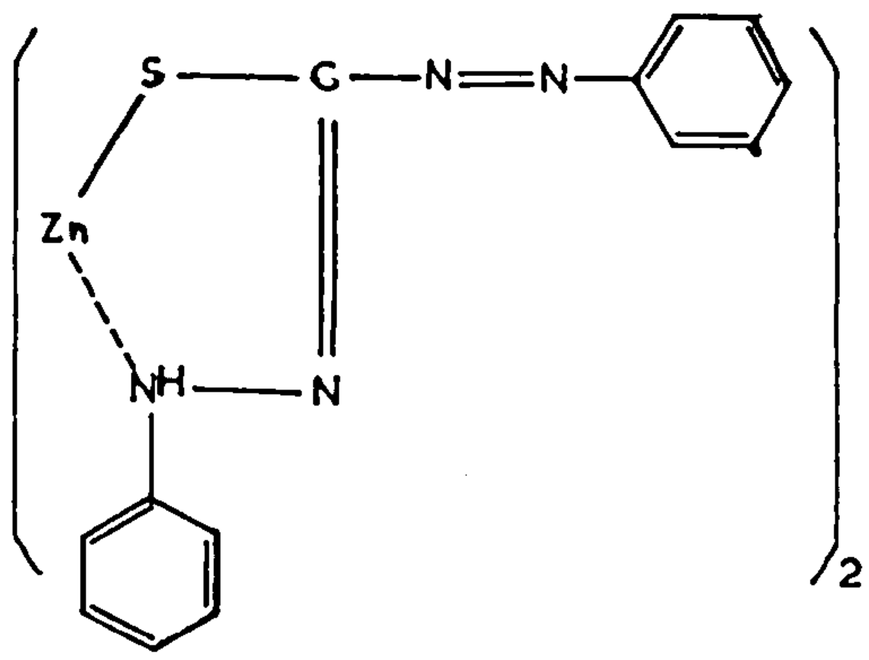


Fig. 4.12 Zinc (II) dithizonate

CHAPTER 5

5 THE FLOTATION OF ZINC OXIDE MINERALS WITH ZINC CHELATING REAGENTS

5.1 Introduction

The use of chelating agents in flotation is not new. In 1927 Vivian (69) concentrated cassiterite using a collector of cupferron. Holman (70) studied the flotation of nickel oxide ores with dimethylglyoxime and also suggested that taurine might be used in the treatment of oxidised lead ores. More recently Peterson et al (71) has shown that potassium octyl-hydroxamate reacts with structural copper atoms of chryocolla to form a hydrophobic chelation compound which renders the mineral hydrophobic. Alkyl hydroxamates have also been shown to be good collectors for iron ores (72) and in the Soviet Union analogous compounds are used in the commercial flotation of tin ores (73) and other complex ores (74) (75). Other chelating agents which have been suggested for the flotation of oxidised copper minerals include diphenylguanidine (76) and benzotriazole (77). In the latter case an oleophilic insoluble copper chelate is formed on the copper mineral which then makes the mineral susceptible to emulsion flotation.

Among the few attempts to float zinc oxide minerals is that of Erlenmeyer et al (78) who showed that 8-hydroxyquinoline had collecting properties. They also argued that many of the reagents used in analytical chemistry to produce selective precipitation of metallic species might also be selective collectors.

Rinelli and Marabini (79) have studied a collector combination of 8-hydroxyquinoline and fuel oil for the flotation of both oxidised lead and zinc ores. Unfortunately their results were not very encouraging.

From the work which has been done on the collection of minerals with chelating agents it is apparent that a hydrophobic mineral surface is only obtained if the metal chelation compound is insoluble and hydrophobic. Little is known, however, about the extent of the surface reaction required to give a hydrophobic surface or the stability of the surface compound.

5.1.1 Selection of the Zinc Chelating Agents

The wetting characterisitcs of the various zinc chelate compounds were determined with a two-liquid flotation technique (80). It was assumed that if the precipitated complex concentrated at the oil/water interface or was extracted into oil then it was both hydrophobic and oleophilic. The zinc complex was precipitated by adding 25 ml of 3.0×10^{-2} M chelating agent solution to 25 ml of 1.5×10^{-2} M $ZnCl_2$ whilst keeping the pH constant at 7.0 by addition of HCl and NaOH.

A 10 ml aliquot of the fine dispersion was transferred to a separating funnel containing 10 ml of n-hexane. The mixture was then shaken vigorously for 1 min and then allowed to stand so that the position of the precipitate could be observed. A summary of the results is given in Table 5.1.

TABLE 5.1 WETTING PROPERTIES OF DIFFERENT ZINC CHELATES AS DETERMINED BY TWO-LIQUID FLOTATION TESTS

Zinc Chelate	Precipitation Region	Two-Liquid Flotation Tests
Zn-Anthranilate	4.7- 7.0	Negligible concentration at interface (Hydrophilic)
Zn-Quinaldinate	2.3- 6.5	" " " "
Zn-Salicylaldoximate	7.0- 8.0	" " " "
Zn-8-Hydroxy-quinolinate	4.4-11.0	complete concentration at interface (hydrophobic)
Zn-2-Methyl-8-hydroxyquinolinate	4.4-11.0	Total extraction into organic phase (very hydrophobic)
Zn-Dithizonate	5.0-10.5	Total extraction into organic phase (very hydrophobic)
Zn-Lix 65N	3.0-10.0	" " " "

The results clearly show that although a number of chelating agents give insoluble zinc compounds not all the precipitates are hydrophobic. The chelating agents which gave hydrophobic precipitates and should therefore exhibit collecting properties are, 8-hydroxyquinoline, 2-methyl-8-hydroxyquinoline, dithizone and Lix 65N.

5.2 Microflotation Tests with Zinc Chelating Reagents

5.2.1 Experimental Materials and Techniques

Microflotation tests were conducted on pure samples of smithsonite, hemimorphite and willemite with zinc chelating

agents as collectors. The experimental procedure was similar to that described in section 2.2. The collecting properties of these reagents on pure calcite were also determined.

Calcite Samples of calcite from Minsterley (Salop) were hand-sorted and ground in a porcelain laboratory mill. The -300+ 150 um fraction was used in the Hallimond tube flotation tests. The purity of the calcite was better than 95%.

Reagents

Chelating Reagents All the zinc chelating reagents were obtained from BDH (Analar grade) and were used as aqueous solutions.

Lix 65N A commercial sample of Lix 65N dissolved in kerosene at approximately 40% V/V was obtained from General Mills Inc. This reagent was used without any previous purification and added as an aqueous emulsion.

Amyl alcohol (50 ppm) was added prior to flotation to ensure a uniform bubble size in the flotation tests.

5.2.2 Results

Hallimond tube tests with chelating agents which formed soluble zinc complexes or alternatively gave rise to hydrophilic precipitates showed that these reagents could not be used as collectors for oxidized zinc minerals. The results obtained with those reagents which formed insoluble, hydrophobic zinc complexes are summarised in Figs. 5.1 to 5.4 inclusive as recovery-pH curves.

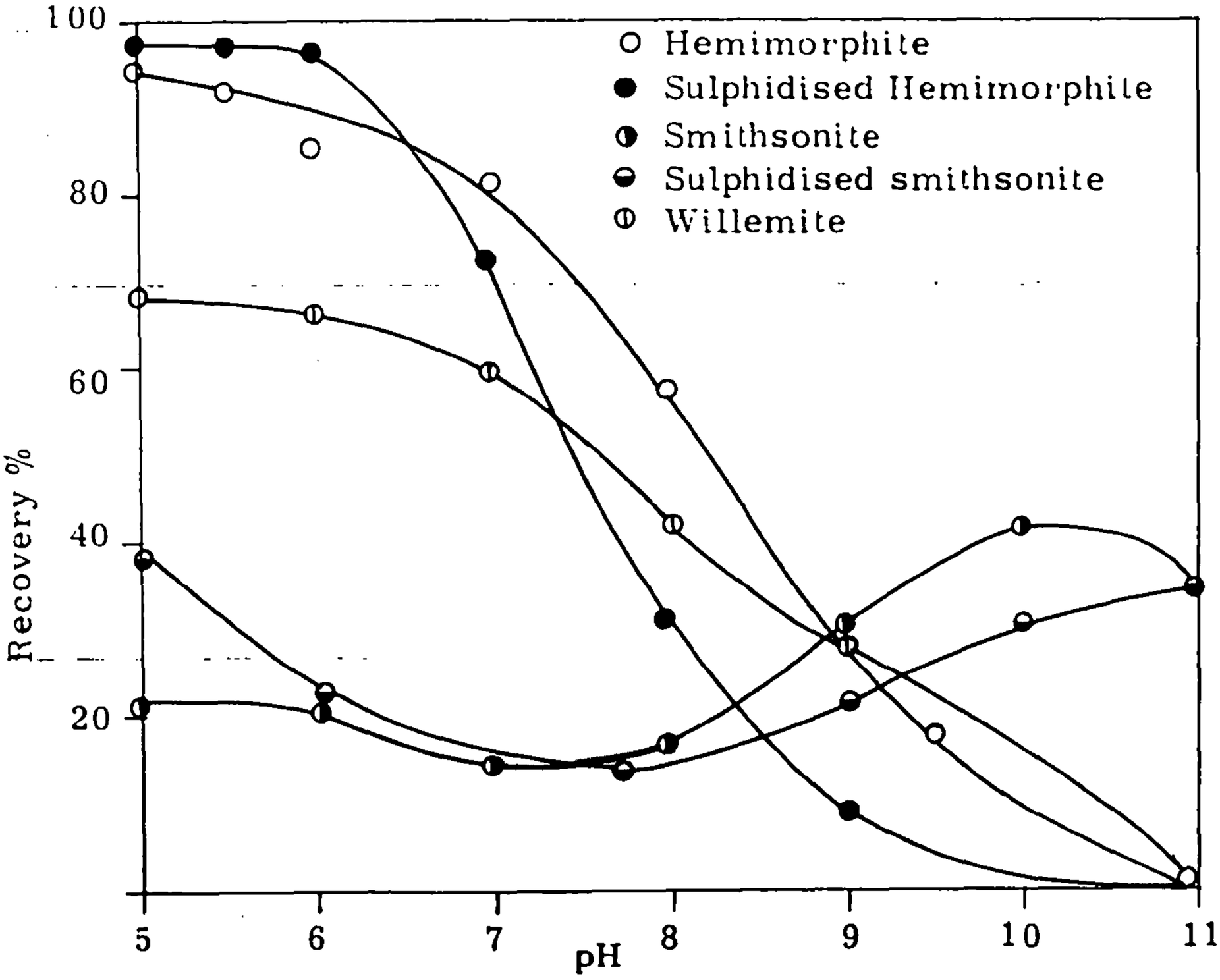


Fig. 5.1 Effect of pH on the flotation of zinc oxide minerals with 8HQ (3.4×10^{-4} M)

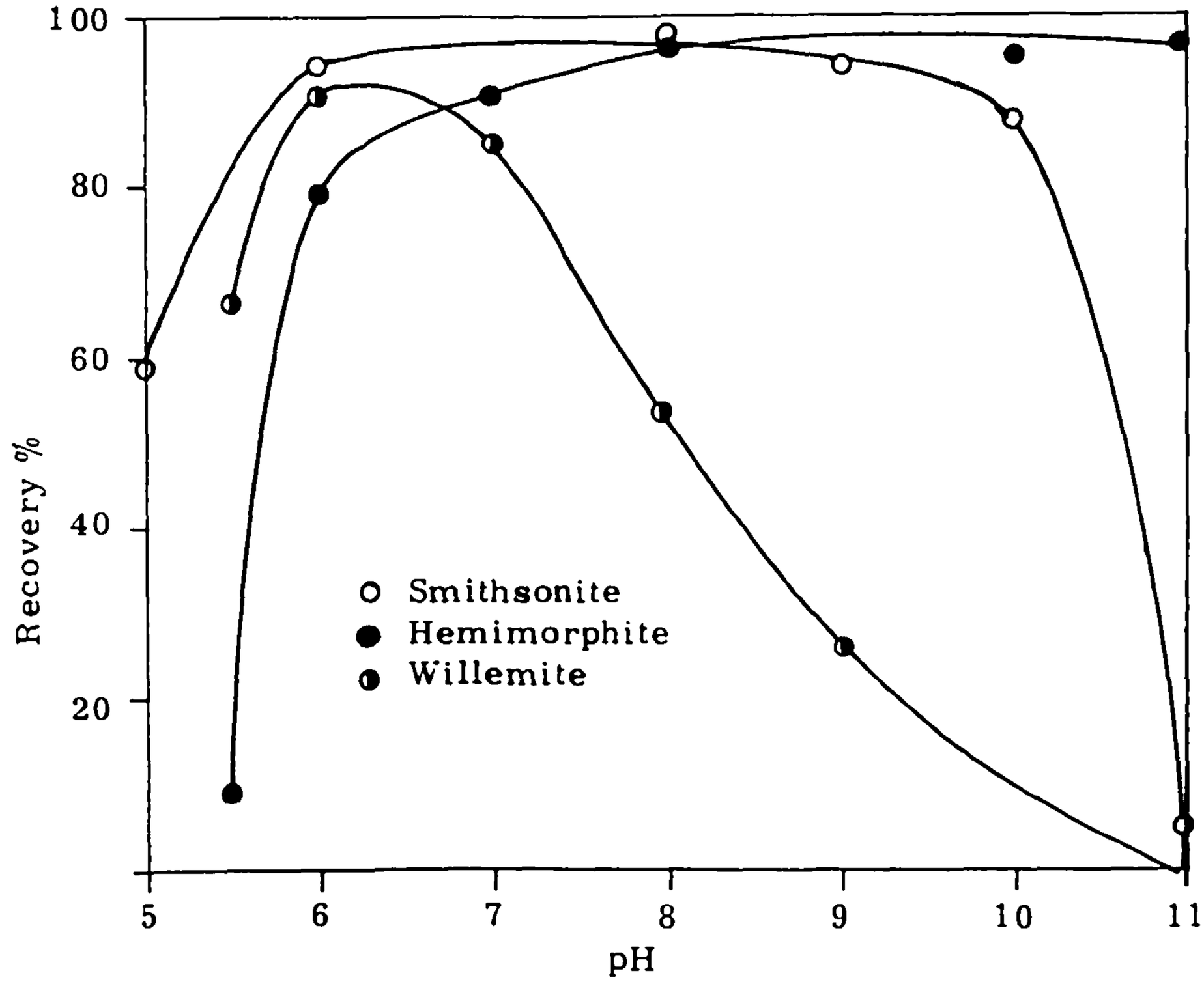


Fig. 5.2 Effect of pH on the flotation of zinc oxide Minerals with 2MHQ (3.4×10^{-4} M)

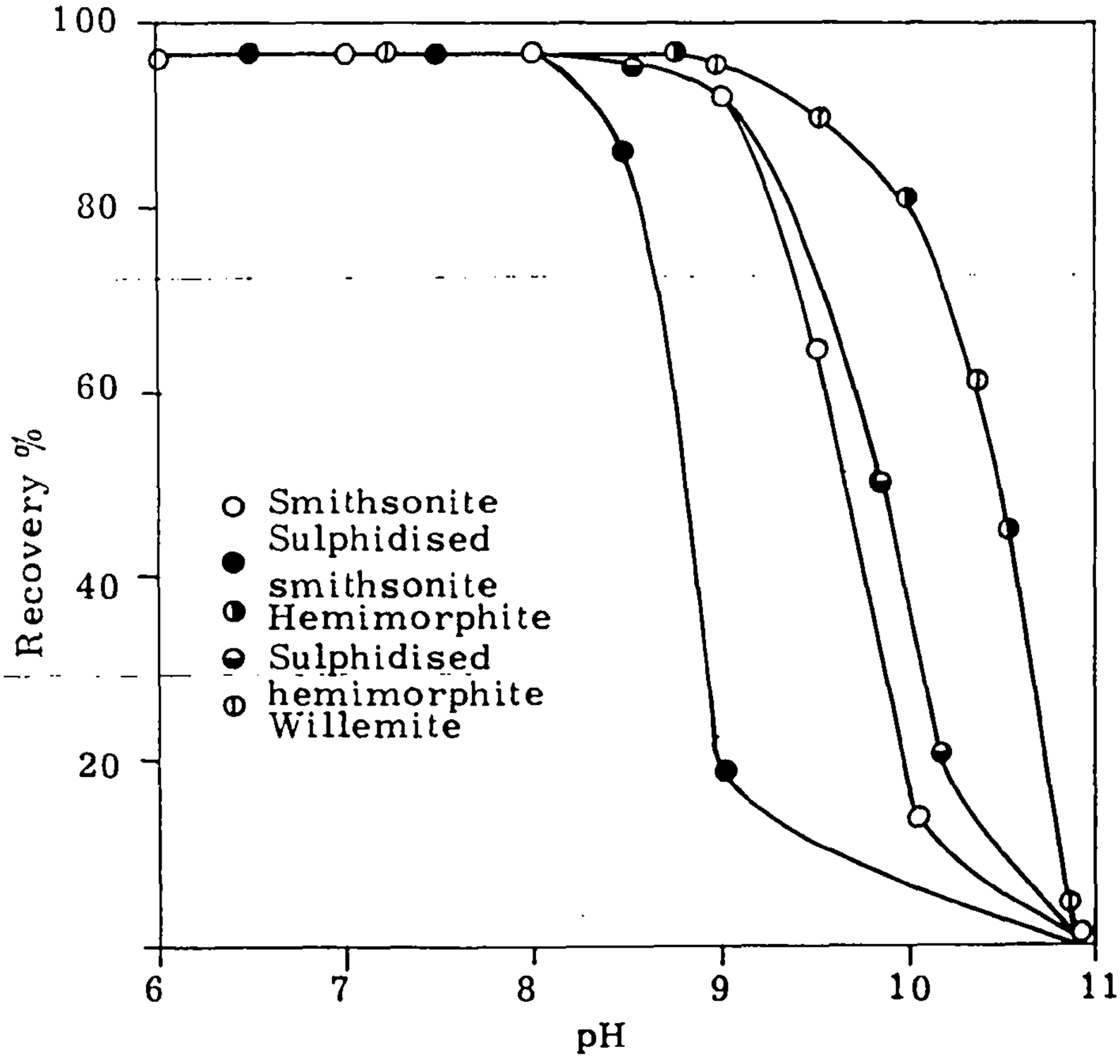


Fig. 5.3 Effect of pH on the flotation of zinc oxide minerals with dithizone ($4.7 \cdot 10^{-5}$M)

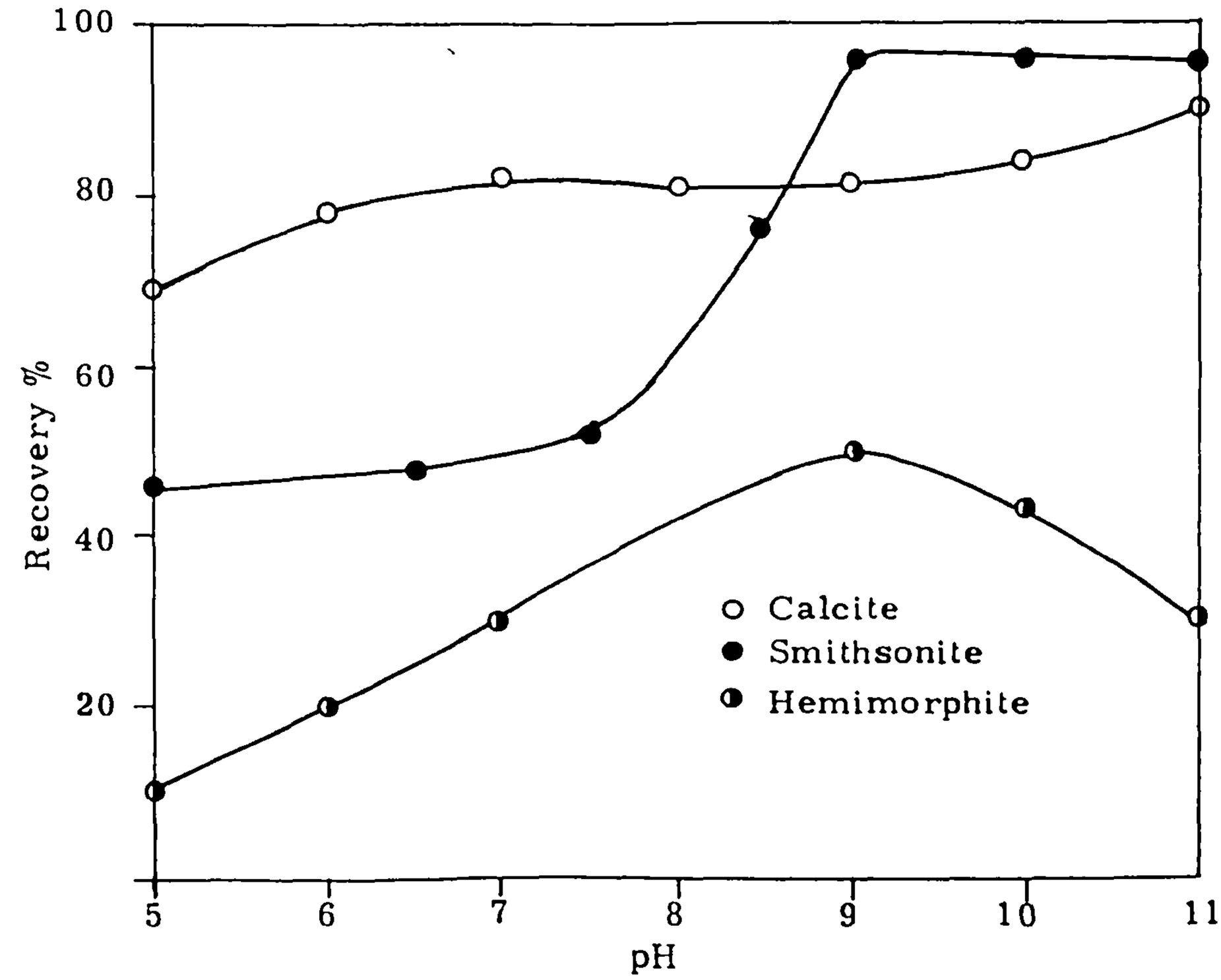


Fig. 5.4 Effect of pH on the flotation of zinc oxide minerals and calcite with Lix 65N (41 ppm)

8-Hydroxyquinoline floated willemite and hemimorphite best at neutral to acid pH values (Fig. 5.1). The flotation of smithsonite was, however, not as pH dependent although there was a tendency for the recovery to increase with pH. Generally the recovery of smithsonite was less than that of the zinc silicate minerals and this was not altered by sulphidising the minerals prior to flotation. Better flotation results were obtained with a collector of 2-methyl-8-hydroxyquinoline (Fig. 5.2) and high recoveries of smithsonite, hemimorphite and willemite were obtained over a wide pH range (6.0 to 11.0). Dithizone exhibited stronger collector properties than 2-methyl-8-hydroxyquinoline and a concentration of 12 ppm was sufficient to give 100% recovery of all three minerals at pH values between 6.0 and 10.0. Sulphidisation moved the recovery-pH curves obtained with dithizone to lower pH values. The effect was quite marked and the pH required to give a 50% recovery of smithsonite and hemimorphite decreased from 10.6 and 9.8 to 9.5 and 9.0 respectively.

Lix 65N (5- nonyl-2-hydroxybenzophenone oxime) showed good collection of smithsonite especially at pH values above 9.0. Hemimorphite also floated under these conditions but the flotation was incomplete. Unlike with the other chelating agents, calcite exhibited considerable flotation with Lix 65N. This chelating agent was not used therefore in further testwork.

Comparison of the Hallimond tube results with Table 5.1 shows that the pH range where flotation was obtained corresponds to the pH range where precipitation of the zinc chelation complex occurred. Flotation tests were not done below pH 5.0 because of the dissolution of the minerals. It was clear, however, that under these conditions a dispersion of zinc chelate was formed in solution which could not then act as a collector.

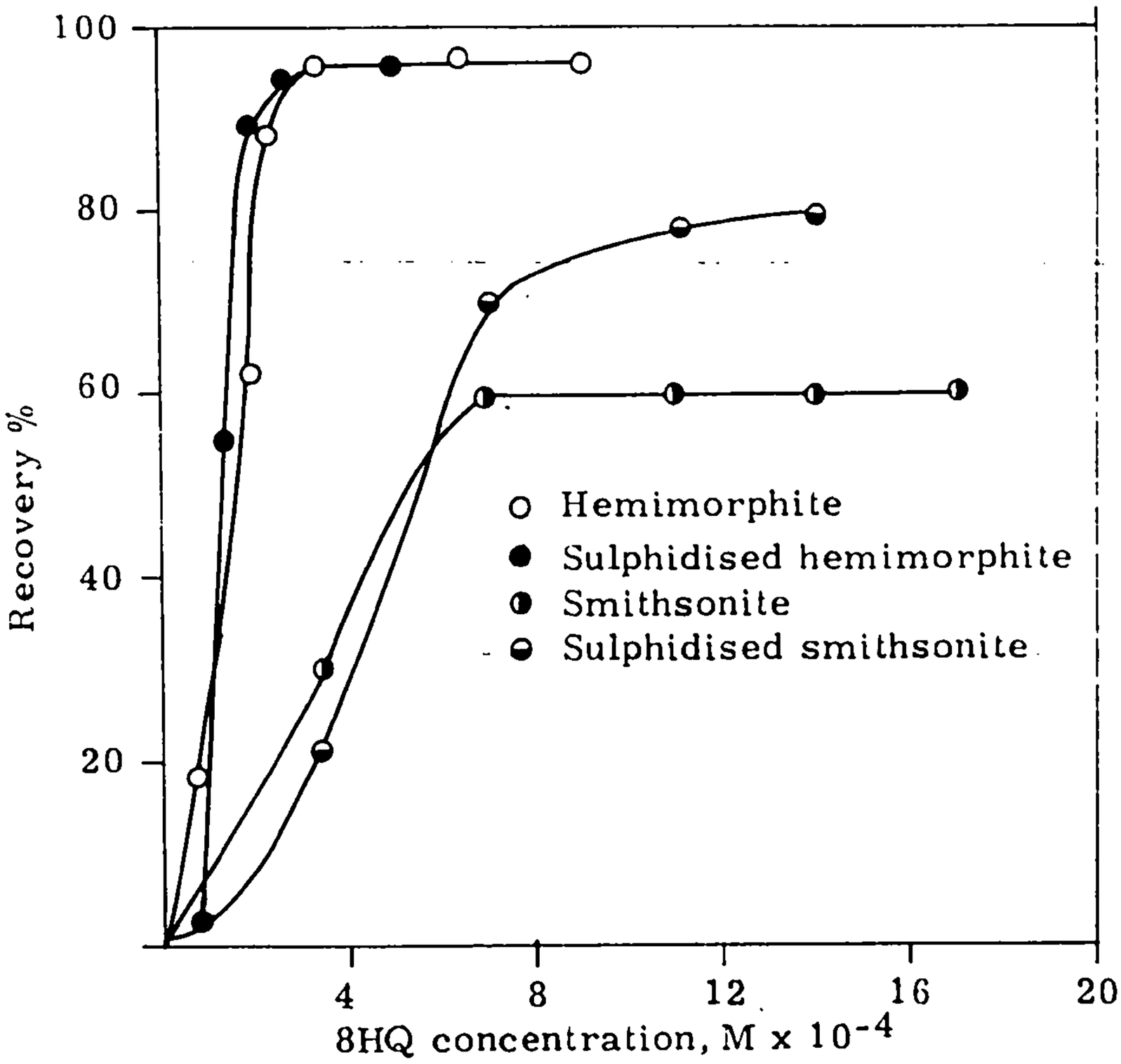


Fig. 5.5 Effect of 8-HQ concentration on the flotation of smithsonite (pH 9.0) and hemimorphite (pH 5.5)

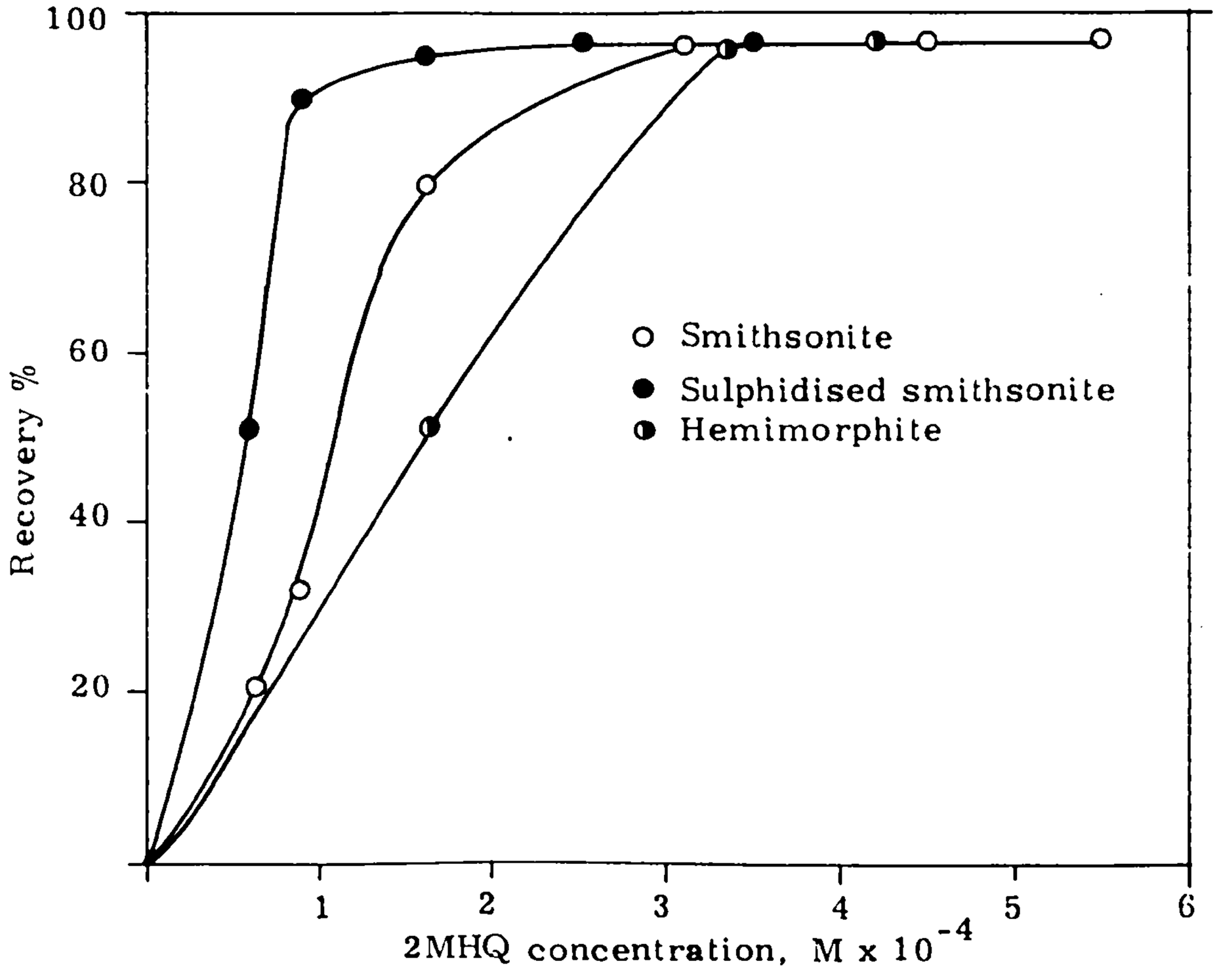


Fig. 5.6 Effect of 2MHQ concentration on the flotation of smithsonite 'pH 9.0) and hemimorphite (pH 8.0)

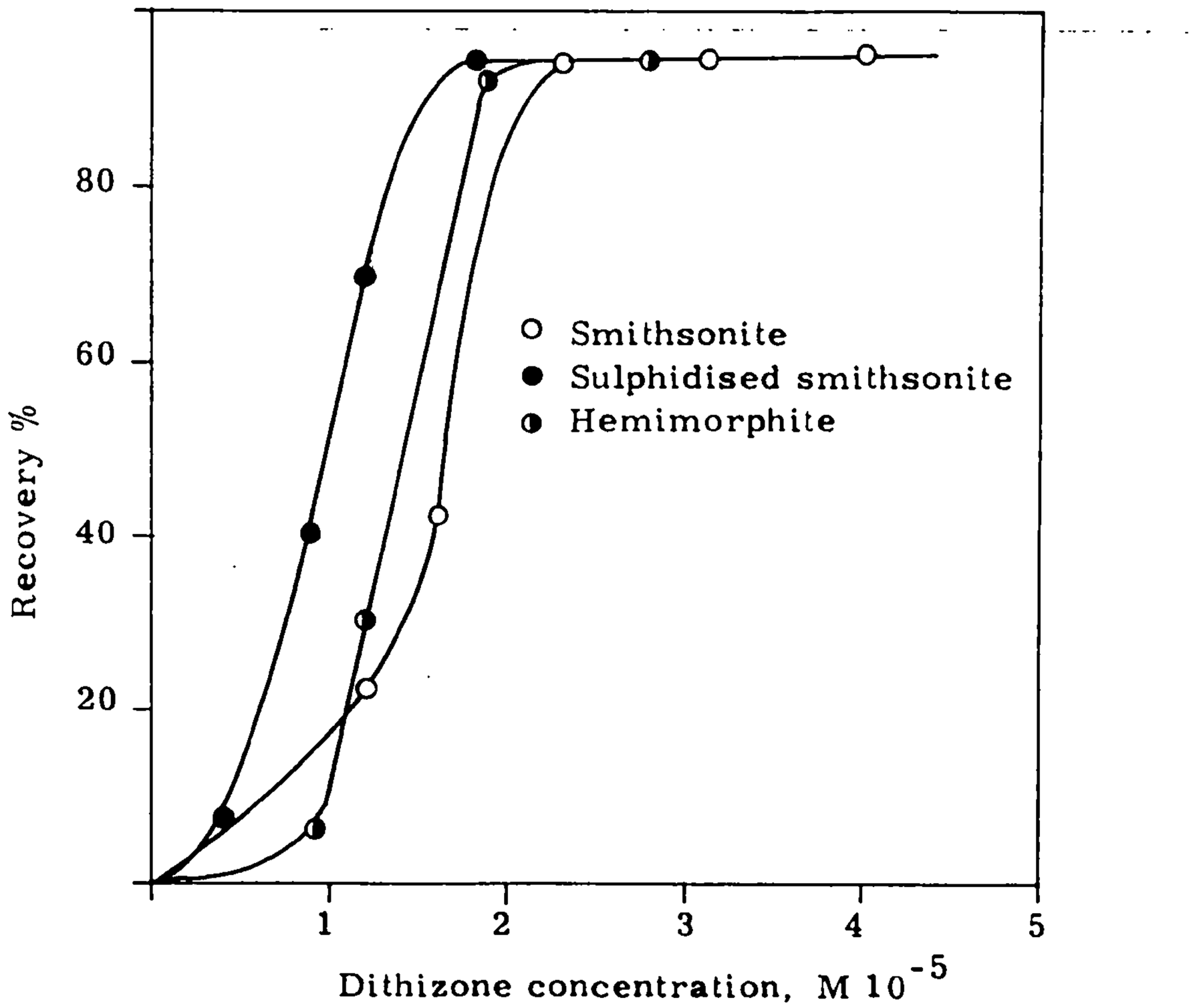


Fig. 5.7 Effect of dithizone concentration on the flotation of zinc oxide minerals at pH 7.5

Flotation tests as a function of chelating agent concentration at the pH values where maximum recoveries were obtained produced the results summarised in Figs. 5.5 to 5.7 inclusive. Increasing the concentration of chelating agent increased the flotation recovery but whereas 100% recovery of all three minerals was obtained with 2-methyl-8-hydroxyquinoline and dithizone the flotation of smithsonite with 8-HQ was incomplete. Dithizone was a stronger collector than 2-methyl-8-hydroxyquinoline which was slightly stronger than 8-hydroxyquinoline. This was demonstrated by the fact that the dithizone concentration required to give 100% recovery of smithsonite was about 10 times lower than that of 2-methyl-8-hydroxyquinoline. Generally, sulphidisation improved the recovery of smithsonite but had little effect on the flotation of hemimorphite.

The results presented in Figs. 5.1 to 5.7 clearly show that chelating agents which form insoluble hydrophobic zinc complexes can act as collectors for smithsonite, hemimorphite and willemite in the Hallimond tube. This suggests that with more knowledge of the properties of the chelating agent and its interaction with the mineral surface it might be possible to suggest collectors more efficient than those currently in use.

5.3 Physico-chemical Properties of the Selected Zinc Chelating Reagents

5.3.1 8-Hydroxyquinoline (8HQ)

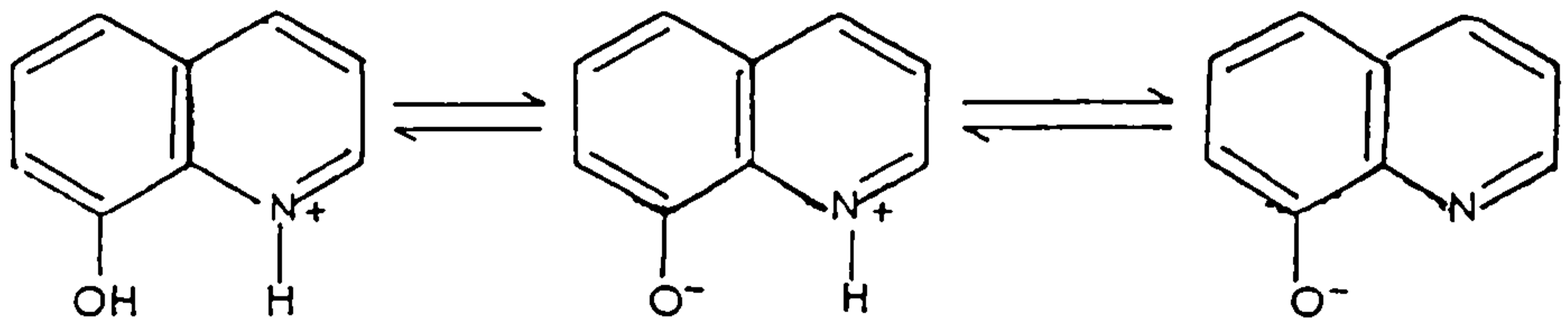
Oxine is an off-white crystalline powder. It is very sparingly soluble in cold water, moderately soluble in ether but readily soluble in absolute alcohol, benzene and chloroform.

It is readily soluble in dilute alkalies and mineral acids forming yellow solutions. 8 HQ solubility values in aqueous solutions are shown in Table 5.2 (81).

TABLE 5.2 SOLUBILITY OF 8 HQ IN AQUEOUS SOLUTIONS

pH	mg of HQ dissolved in 100 ml
3.7	480.0
4.0	248.6
4.8	105.8
5.1	78.3
5.6	59.4
6.9	46.4
7.3	48.3
8.2	58.0
9.1	75.4
10.7	248.6

The 8-hydroxyquinoline molecule is amphoteric and it has been postulated that three different species are formed in solution (81).



8-Hydroxyquinolinium ion ($8H_2Q^+$) | 8-Hydroxyquinoline (8HQ) | 8-Hydroxyquinolinate ion ($8Q^-$)

Thus, the increase of solubility in acidic solutions is caused by the formation of 8-hydroxyquinolinium ion whereas in alkaline solutions 8-hydroxyquinolinate anions are formed. The lowest solubility in water is reached at the iso-electric point at pH 7.4.

The following dissociation constants have been determined for 8-hydroxyquinoline at 25°C (82).

$$K_{HA} = \frac{(H^+)\,(8Q^-)}{(8HQ)} = 10^{-9.66} \qquad 5.1$$

$$K_{H_2A} = \frac{(H^+)(8HQ)}{(8H_2Q^+)} = 10^{-5.00} \qquad 5.2$$

Reaction of 8-hydroxyquinoline with metal ions

Of the seven possible hydroxyquinolines only 8-hydroxyquinoline forms chelate compounds with metal ions. In this compound, the hydroxyl group is so located with respect to the nitrogen atom of the quinoline nucleus that five-membered rings are formed with metals.

8HQ is very unselective in its action reacting with many metal ions, such as Cu^{+2}, Mg^{+2}, Ca^{+2}, Zn^{+2}, Al^{+3}, Pb^{+2}, Fe^{+3} and many more. Usually only one oxidation state of an element forms an insoluble, stable chelate compound because of the oxidizing and reducing action of the 8HQ itself (83).

The stability constants for many of the divalent metal 8-hydroxyquinolinates have been measured in mixtures of dioxane and

water and follow, with minor exceptions, the order of decreasing stability that is common to most chelating agents, i.e. Pd > Cu > Ni > Co > Zn > Cd > Mn > Mg. The stabilities of the 8-hydroxyquinolinates are remarkably high compared to those of the complexes formed with other chelating agents for which data are available, including a number of 8-hydroxyquinoline derivatives and structural analogs.

The solubility product constants of the 8-hydroxyquinolinates as reported by various researchers show very unsatisfactory agreement, possibly because much of the work is based on inexact data on the pH of precipitation. Qualitatively, however, the most stable chelate compounds have the lowest solubility in water. 8-Hydroxyquinolinates are formed through an electrovalent bond to oxygen and a co-ordinate bond to nitrogen. The formation proceeds stepwise, one molecule of oxine reacting with the metal ion to give $M(C_9H_6NO)^{n-1}$, followed by reaction with another 8-HQ molecule to give $M(C_9H_6NO)^{n-2}$, and so on until a neutral compound is obtained.

Two types of divalent metal-8-hydroxyquinolinates have been distinguished; those in which one metal ion reacts primarily with the negatively charged oxygen (zinc, cadmium, magnesium) and those in which primary reaction may possibly be with the covalent nitrogen (cobalt, copper, nickel).

Reaction of 8HQ with zinc ion

Zinc is quantitatively precipitated by 8HQ at pH values above 4.4 up to pH 11.0, as the complex $Zn(C_9H_6NO)_2 \cdot 2H_2O$. Zinc-8-hydroxyquinolinate as well as the majority of the divalent metal oxinates carry two molecules of water at room temperature.

In general, the attachment of water tends to decrease the hydrophobic character of the chelate. The degree of hydration at other temperatures and the temperature required to remove water have been the subjects of much conflicting data in the analytical literature.

It has been demonstrated through investigations using radio-active zinc (84) that the bond between the zinc atom and 8-hydroxy-quinoline is predominantly ionic since the chelate rapidly exchanges its zinc content with soluble zinc salts.

X-ray diffraction studies of zinc-8-hydroxyquinolinate dihydrate (85) have shown a trans-planar arrangement of the two hydroxyquinolinate above the central zinc atom (Fig. 5.8a). However, the anhydrous zinc chelate appears to have a tetrahedral zinc atom (Fig. 5.8b).

Physical properties of the complex. Nassanen et al (86) have studied the equilibrium of zinc-8-hydroxyquinolinate in aqueous solution. The complex formation was studied spectrophotometrically. A value of 8.56 was obtained for log β_1 and 8.90 for log β_2.

5.3.2 2-Methyl-8-hydroxyquinoline (2MHQ)

This compound is sparingly soluble in water but it dissolves in diethyl ether, chloroform, benzene, or dilute acids and alkalis. The solubility of 2MHQ in water was determined by Phillips and Price (87) at 25°C being equal to 2.46×10^{-3}M.

Dissociation Constants of 2MHQ Johnston and Fraiser (88) determined the dissociation constants of this compound. Values of 5.54 and 10.31 were found for pK_{NH} and pK_{OH} respectively (where pK is -log of the ionization constant of the reaction $NH^{+} \rightleftharpoons N + H^{+}$

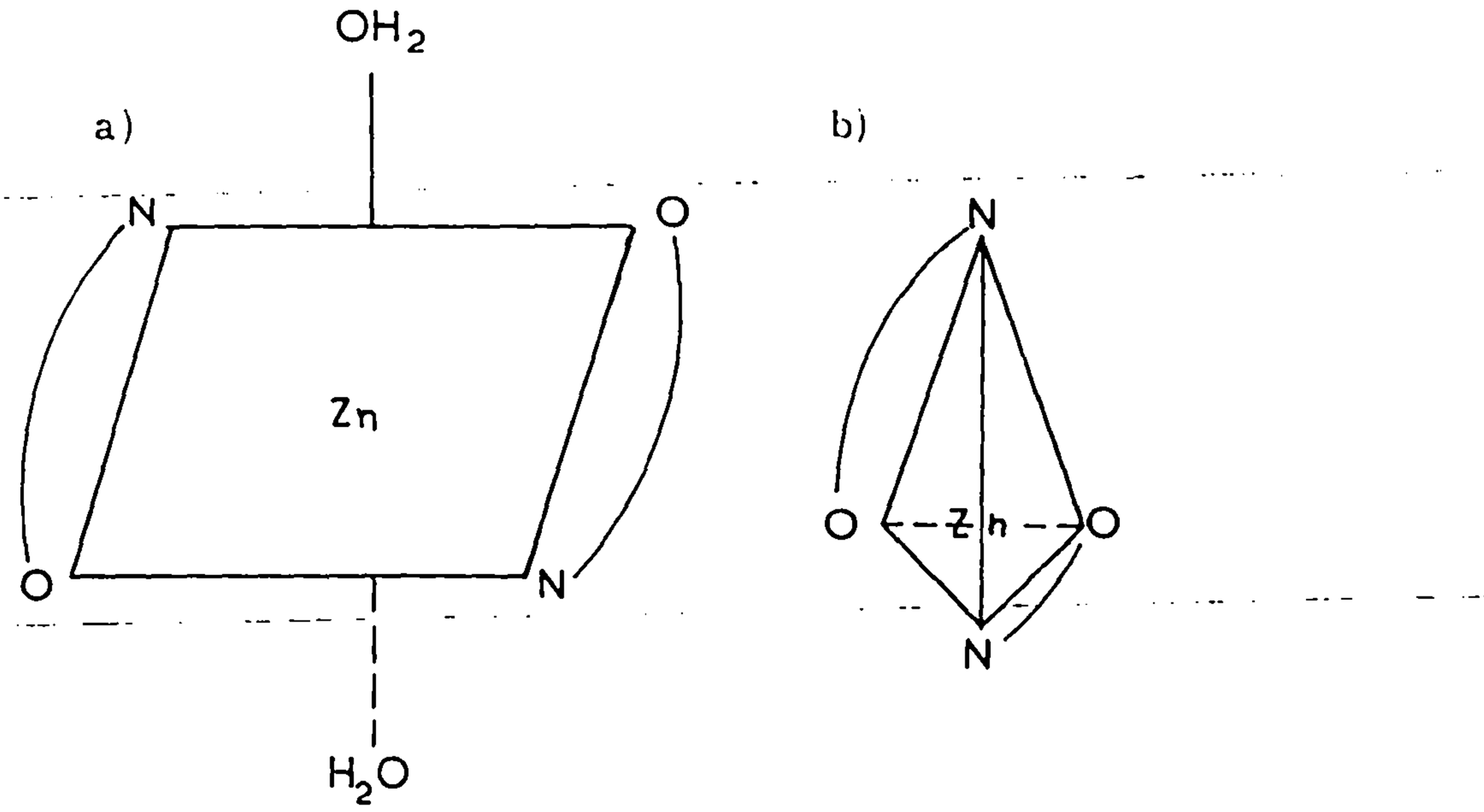


Fig. 5.8 Structure of zinc-8-hydroxyquinolinate

a) dihydrate b) anhydrous

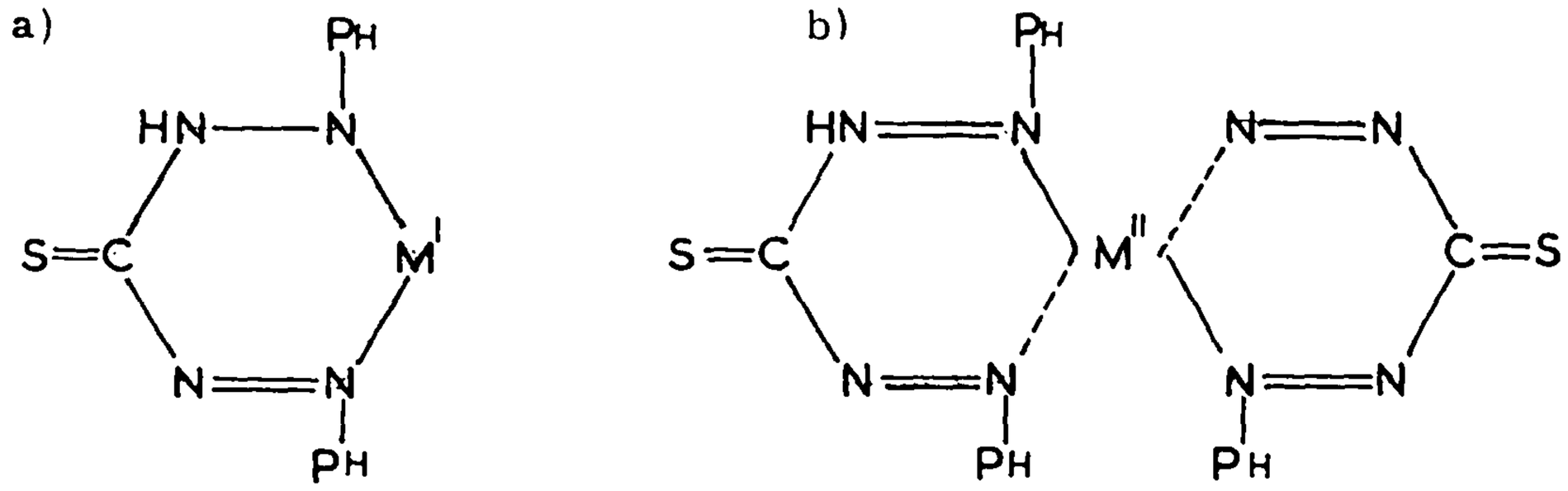


Fig. 5.9 Structure of metal dithizonates

a) univalent metal b) bivalent cation

and pK_{OH} is that of the reaction $R\text{-}O\text{-}H \rightleftharpoons R\text{-}O^{-} + H^{+}$.

Reaction of 2MHQ with metal ions The reagent is similar to 8HQ in its analytical properties but seems to be more selective due to the presence of a methyl group in position 2. In general, the formation constants for 8HQ and 2MHQ show that the chelates of the methyl derivative are somewhat less stable than those of the unsubstituted compound (89). This fact has been attributed to the steric hindrance produced by the methyl group of 2MHQ which prevents the close grouping of the two reagent molecules around the metal ion.

Properties of the Zinc-2-Methyl-8-Hydroxyquinolinate

Phillips and Price (87) using a spectrophotometric technique determined the solubilities of zinc-2-methyl-8-hydroxyquinolinate in the acid pH range. These results are given in Table 5.3.

TABLE 5.3 SOLUBILITIES OF ZINC-2-METHYL-8-HYDROXY-QUINOLINATE

pH	Molarity x 10^4
6.30	0.079
4.24	1.73
4.06	2.40
3.80	5.35
2.38	22.00

5.3.3 Dithizone (H_2Dz)

Pure dithizone is a violet-black crystalline powder with a metallic lustre. It is practically insoluble in aqueous solutions

below pH 7.0 (2×10^{-7} M) but dissolves readily in alkali to give a yellow anion. In aqueous solution dithizone behaves as a monobasic acid.

$$H_2Dz \rightleftharpoons H^+ + HDz^- \qquad 5.3$$

with a dissociation constant K_{HA} of $3.0 \pm 0.2 \times 10^{-5}$ (82). The second hydrogen ion is not removed below pH 12.0. Dithizone is oxidised under weak oxidizing conditions to diphenylcarbodiazone and thereby loses its chelating properties. Solutions of dithizone decompose rapidly if exposed to strong light or to relatively high temperatures.

The reactive group of dithizone can be present in two forms, enol and keto,



enol form keto form

Many heavy metals can replace either one or both hydrogen atoms of dithizone, so forming two different complexes, namely primary (monobasic or 'keto') and secondary (dibasic or 'enol') complexes. Primary dithizonates are preferentially formed in acidic solutions and in the presence of excess dithizone by all the metals which react with dithizone. Fischer (90) assumed that it was the hydrogen of the imino group of dithizone that was replaced by metal; he proposed formulae such as those shown in Fig. 5.9 a and b, where M^I and M^{II} are uni-or bi-valent cations. Since this is equivalent

to assuming a reaction of the reagent in the keto form, the products are also termed keto-dithizonates. If on the other side, the metal is in excess or if the pH is high. some (though not all) of the metals reacting with dithizone give 'enol-complexes'. (See Fig. 5.10 a and b).

For example, copper, silver and mercury give both keto- and enol complexes. The enol-form can be transformed into the keto-form by treatment with acid and dithizone or acid alone can cause disproportionation. However, the primary or enol-complexes have a much greater importance than the secondary ones.

Zinc ion mainly forms primary zinc dithizonate, $Zn(HDz)_2$, which is highly hydrophobic. A study of the structure of this chelate (91) indicates that there are two almost planar dithizonate groups acting as bidentate ligands (Fig. 4.11), tetrahedrally co-ordinated to zinc through sulphur and nitrogen. One phenyl group (A) of each ligand is associated with a chelate ring whereas the other (B) is extended as far as possible from the central atom. with two intervening nitrogen atoms that hold it in the trans-configuration. All the light-atom to light-atom bonds contain some degree of double-bond character and this effectively maintains the phenyl group (B) coplanar with the chelate ring to which it is attached through the two nitrogen atoms. This coplanarity even extends to the phenyl group (A), so that the molecule as a whole can be visualized as two planes through A-zinc-B and A^1-zinc-B^1.

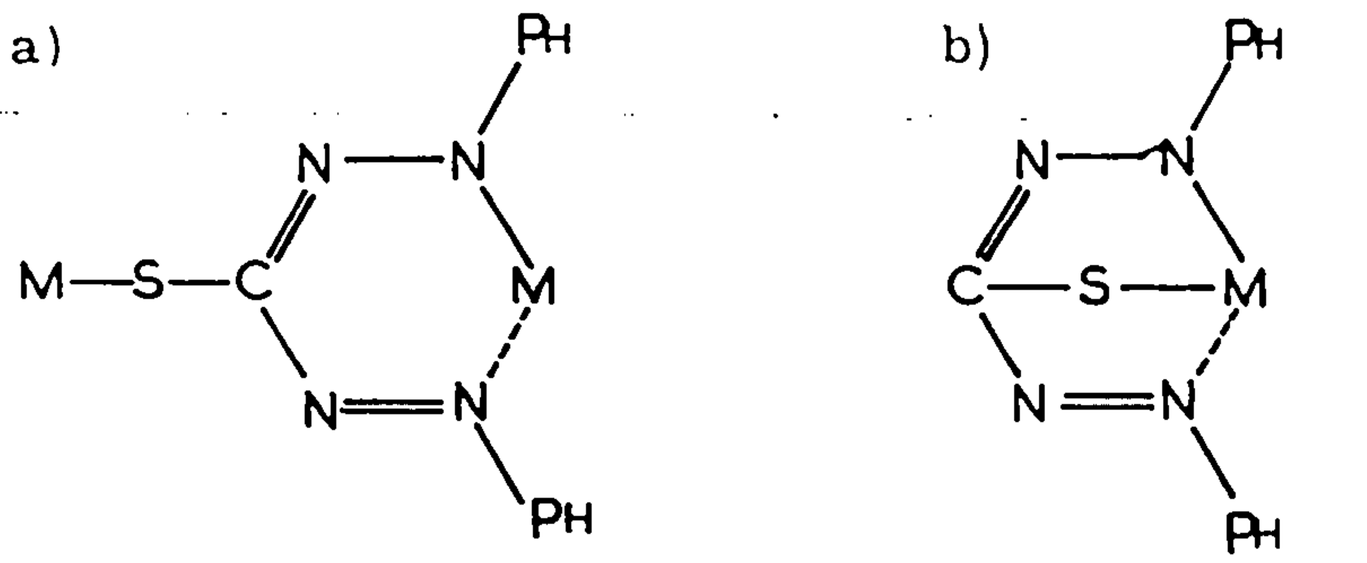


Fig. 5.10 'ENOL' Metallic Chelates

a) univalent metal b) bivalent metal

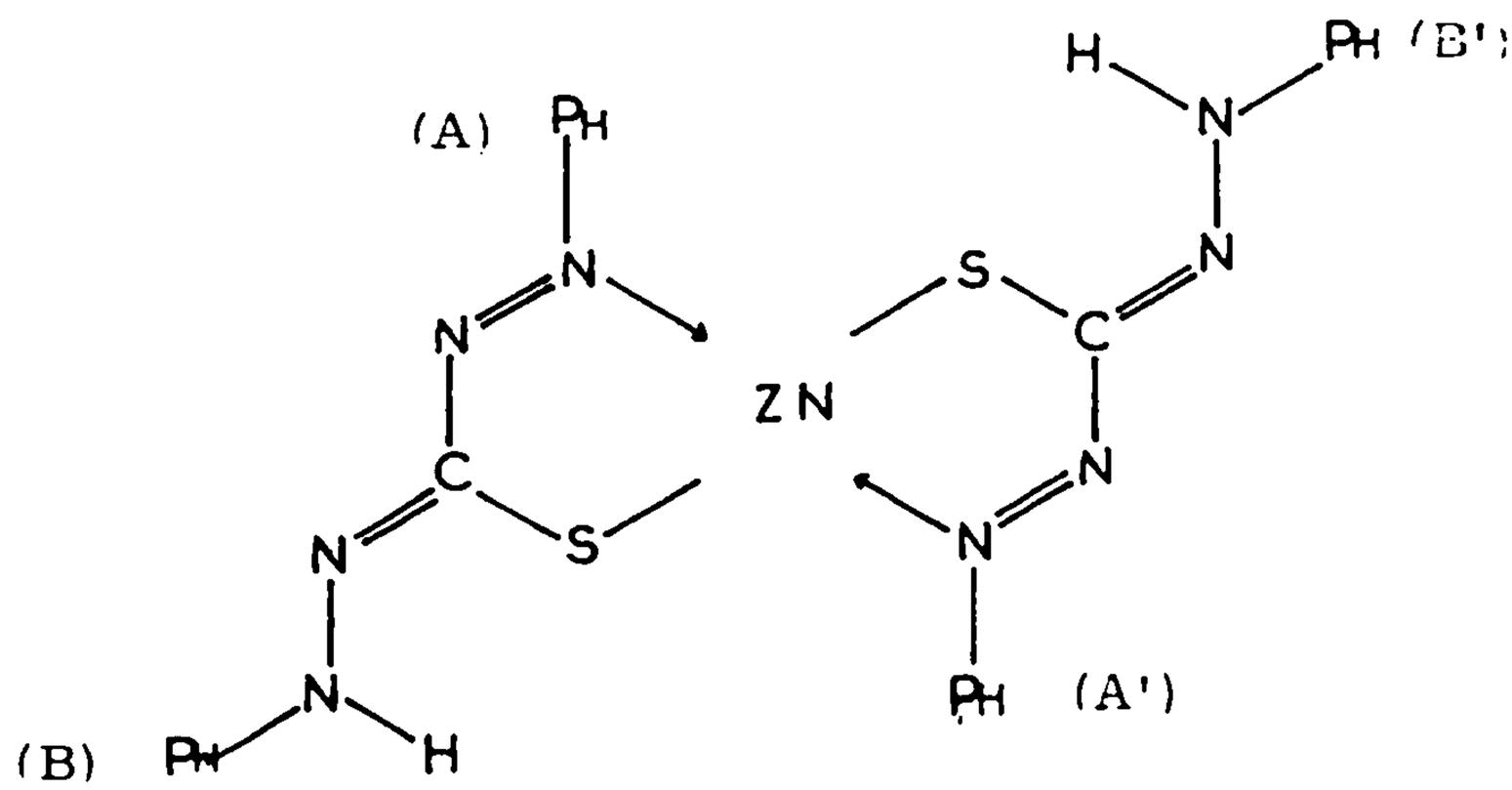


Fig. 5.11 Structure of zinc dithizonate

5.4 Study of the Chemical Reaction Between Zinc Oxide Minerals and Zinc Chelating Reagents

5.4.1 Introduction, Experimental Techniques and Materials

The interaction of the zinc chelating agents with smithsonite, hemimorphite and willemite was studied by measuring the abstraction of chelating agent from solution as a function of time, reagent concentration and pH. Infrared spectrometry was used to identify the surface species and the dispersion of zinc chelate formed in solution (cf. Chapter 6). The object of these studies was to determine the nature of the surface reaction which gives rise to a hydrophobic surface and to determine whether or not the chelating agents which give rise to hydrophilic precipitates are also adsorbed.

Experimental Materials and Techniques

Reagents

All reagents used in this study were of 'Analar' grade. Solutions of HCl and NaOH were used for pH adjustments.

Chelating reagents The chelating reagents described in section 5.2.1 were used. With the exception of dithizone, all of them were used without any previous purification.

Dithizone A commercial sample of dithizone was purified according to the technique described in (82). This technique is based on the insolubility of the oxidation product, diphenylcarbodiazone in aqueous ammonia. 0.5g of dithizone was dissolved in 50 ml of

chloroform and the solution shaken in a separation funnel with four successive 50 ml portions of 1:100 ammonia. The combined aqueous phase was centrifuged to remove droplets of chloroform and then made slightly acid with hydrochloric acid. The precipitated dithizone was extracted with several 15 to 20 ml portions of chloroform. These extracts were washed several times with water and evaporated in a beaker on a water bath at $50^{o}C$ to remove chloroform. The product was dried and stored under vacuum in the dark.

Dithizone solutions were prepared by adding a weighed amount of dithizone to 10 ml of water containing 2 drops of 6N NH_3 to facilitate dissolution. Once dissolved the solution was diluted to the desired volume. The water used to prepare the solutions was boiled for 15 min. to reduce the amount of dissolved CO_2 and then purged with N_2 for 4 hr. to remove oxygen. Fresh solutions obtained by this procedure were made up every day to ensure the absence of oxidised species.

Materials

The smithsonite and hemimorphite samples used were described in section 3.2.3. The willemite sample corresponded to the fraction finer than 105 um and its surface area was 0.59 $m^2 g^{-1}$.

Sphalerite The sphalerite sample from Minsterley, Salop was hand-sorted and ground in a porcelain laboratory mill. The fraction finer than 75 um was deslimed and used in the abstraction tests. The surface area of the sample was 0.14 $m^2 g^{-1}$ and according to its zinc content it consisted of 91% ZnS.

Analysis

8-Hydroxyquinoline and 2-methyl-8-hydroxyquinoline

A direct spectrophotometric method of the determination of both 8HQ and 2MHQ was used. The method is based in the conversion of both reagents to their respective cationic forms (8-hydroxyquinolinium and 2-methyl-8-hydroxyquinolinium ions) by the addition of an acid solution, followed by the measurement of the absorbance of the solutions at 365 and 310 nm respectively (81) (92) (93). At these wavelengths the two cationic molecules absorb strongly.

In each determination 1 ml of 2.2 N HCl solution was added to a 10ml aliquot of the supernatant solution and the absorbance at 365 or 310 nm determined in a Perkin Elmer Model 124 double beam spectrophotometer using 1 cm length quartz cells. Beer's law was obeyed for concentrations below 6.9×10^{-4}M for 8HQ and 3.8×10^{-4}M in the case of 2MHQ.

Dithizone A direct spectrophotometric method was used for the analysis of dithizone (82). In each determination 1 drop of NaOH solution was added to a 5ml aliquot of the supernatant solution to obtain a pH value of 11.0. The absorbance was then measured at 460 nm using 1 cm length glass cells. Beer's law was obeyed for concentrations up to 5.9×10^{-5}M.

Quinaldic acid A direct spectrophotometric method for the determination of quinalidc acid was used. In each determination 1 ml of 2.2 N HCl solution was added to a 10 ml aliquot of the

supernatant solution and the absorbance determined at 322 nm (94). Beer's law was obeyed for concentrations up to 1.44×10^{-4}M.

Method

The amount of chelating agent abstracted in the presence of smithsonite, hemimorphite and willemite was determined by stirring 0.5 g of mineral in 100 ml of solution at different pH values and at various chelating agent concentrations. The residual concentration of chelating agent in the aqueous solution was determined after centrifugation. In those cases where previous sulphidisation was carried out the procedure described in section 3.2.3 was followed.

The abstraction of 2-methyl-8-hydroxyquinoline by sphalerite was determined after different degrees of surface oxidation. The sphalerite samples (3g) were shaken with 100 ml 2MHQ solution at pH 9.0 for 20 hr. Oxidation of the sphalerite was obtained by shaking the samples with 100 ml of H_2O_2 solution at pH 7.0 for 20 hr. Excess oxidizing solution was then removed. the sample washed repeatedly with distilled water and contacted with 2MHQ solutions. Sulphidisation of the sphalerite was carried out in the presence of 4.2×10^{-3}M $Na_2S.9H_2O$ at pH 10.0 for 10h. The samples were used in the abstraction tests after repeated washing with distilled water to eliminate the excess sulphide solution.

5.4.2 Results

5.4.2.1 The Zinc Oxide Minerals/8-Hydroxyquinoline System

The effect of pH on the abstraction of 8HQ by smithsonite, hemimorphite and willemite is summarised in Fig. 5.12. These

results give the impression that after agitation for 1.5 hr. the abstraction of 8HQ by smithsonite and willemite is independent of pH whereas that of hemimorphite decreases with an increase in pH. This is not the case, however, because the results were not obtained at a true equilibrium and given sufficient time the 8HQ was completely consumed by all three minerals. (Equivalent to an uptake of 1.4×10^{-3}; 3.7×10^{-4} and 1.18×10^{-3} mole m^{-2} on smithsonite, hemimorphite and willemite respectively). The results reflect therefore the rate of uptake of 8HQ and indicate that for smithsonite and willemite it was independent of pH whereas for hemimorphite it was not.

In the tests with hemimorphite the solution became yellow and after settlement of the hemimorphite particles a marked Tyndall beam effect was obtained. Similar effects were obtained with smithsonite and willemite after prolonged agitation periods. Analysis of the colloidal suspension showed that the solids contained zinc and 8HQ in the proportions consistent with the formation of the zinc chelate. It would appear therefore that the interaction of 8HQ with the zinc oxide minerals is not an adsorption process but a chemical reaction and that the products of this reaction can be dispersed in the solution. The 'uptakes' referred to in Fig. 5.12 do not therefore refer to 8HQ concentrated at the mineral/water interface but to the amount of 8HQ that has chemically reacted per unit area of solid. Subsequent results are referred to unit area because irrespective of whether the interaction is controlled by a chemical or mass transfer process the reaction rate will be dependent on the surface area.

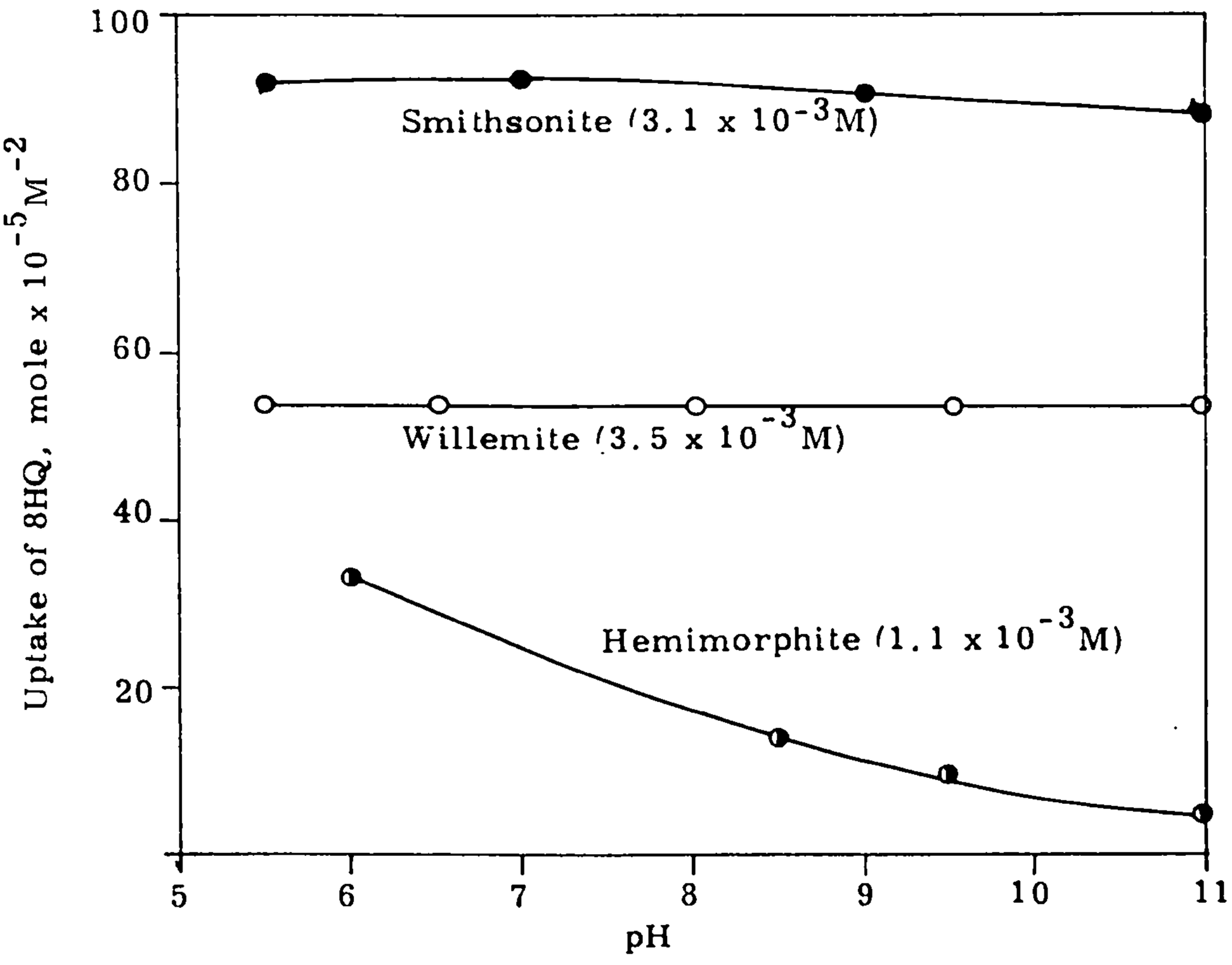


Fig. 5.12 Effect of pH on the abstraction of 8HQ by zinc oxide minerals (Initial concentrations appear in brackets)

The abstraction of 8-hydroxyquinoline by the zinc oxide minerals was determined as a function of time at different initial concentrations of 8HQ. The results obtained with smithsonite at pH 7.6 are shown in Fig. 5.13 a. The abstraction was initially rapid and then slowly decreased with increase in agitation time. Increasing the initial 8HQ concentration increased the abstraction rate and at a given initial concentration the decrease in 8HQ concentration with time followed first order reaction kinetics (Fig. 5.13b). Most of the 8HQ was consumed within 1 hr.

The abstraction of 8HQ by hemimorphite at different initial 8HQ concentrations at pH 6.0 is shown in Fig. 5.14. These results are similar to those obtained with smithsonite except that after 1 hr. there was a tendency for the 8HQ uptake to level off. This does not represent the attainment of equilibrium because after agitation for 2 days all of the 8HQ was consumed. About 40% of the 8HQ was abstracted within the first hour of agitation. This is equivalent to 180 monolayers if it is assumed that the cross-sectional area of the 8HQ molecule is 100 $\mathring{A}^2$ (obtained from the sum of the sectional areas of the benzene and pyridine rings and the OH group) (95) and the uptake is 9.7×10^{-5} mole m^{-2}.

The uptake of 8HQ by willemite was much slower than that by smithsonite and this is demonstrated by comparison of Figs. 5.13 a and 5.15. Similar to smithsonite and hemimorphite, and however, all the 8HQ was consumed after prolonged agitation.

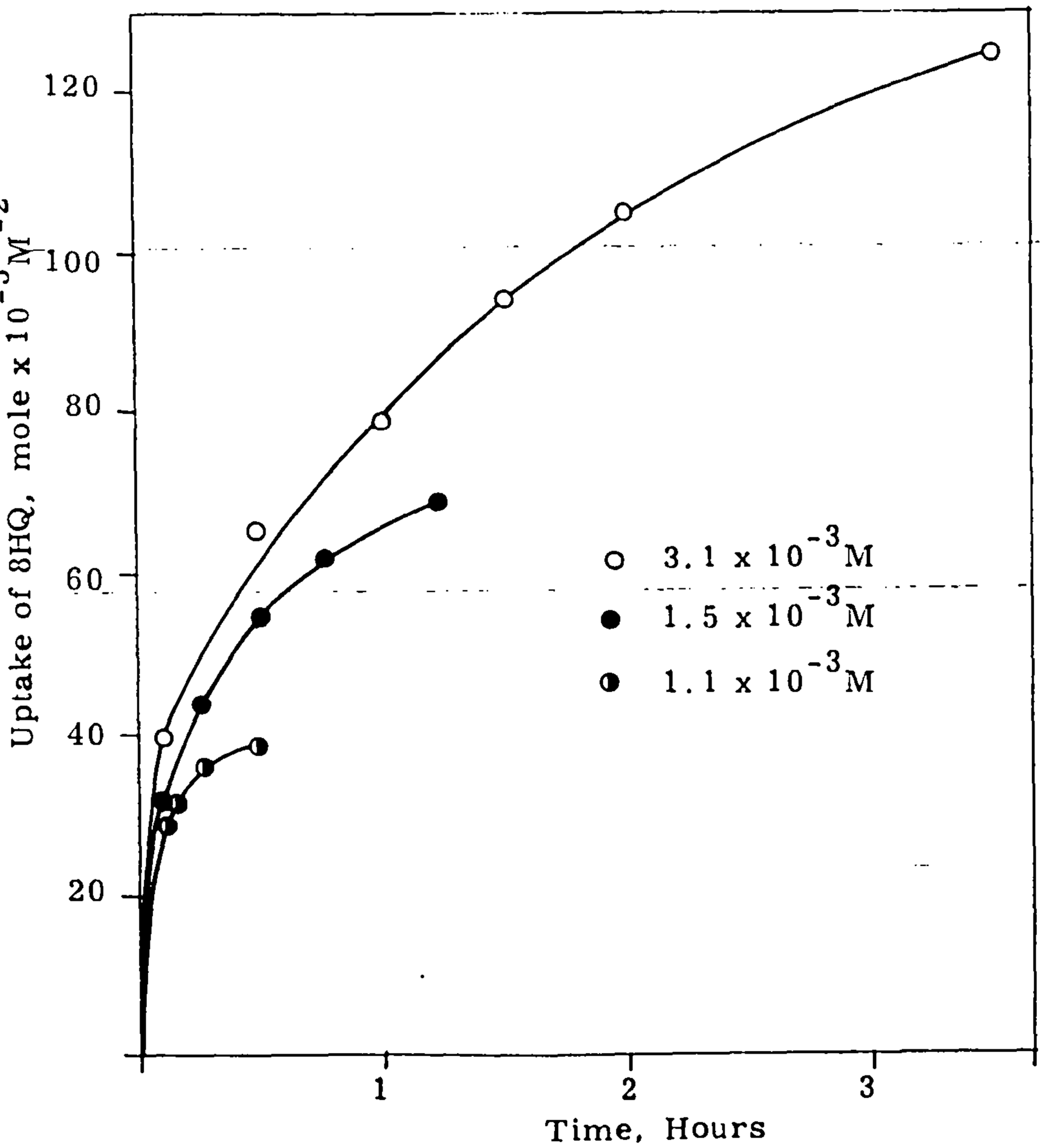


Fig. 5.13 a 8HQ abstraction by smithsonite at different initial concentrations at pH 7.6

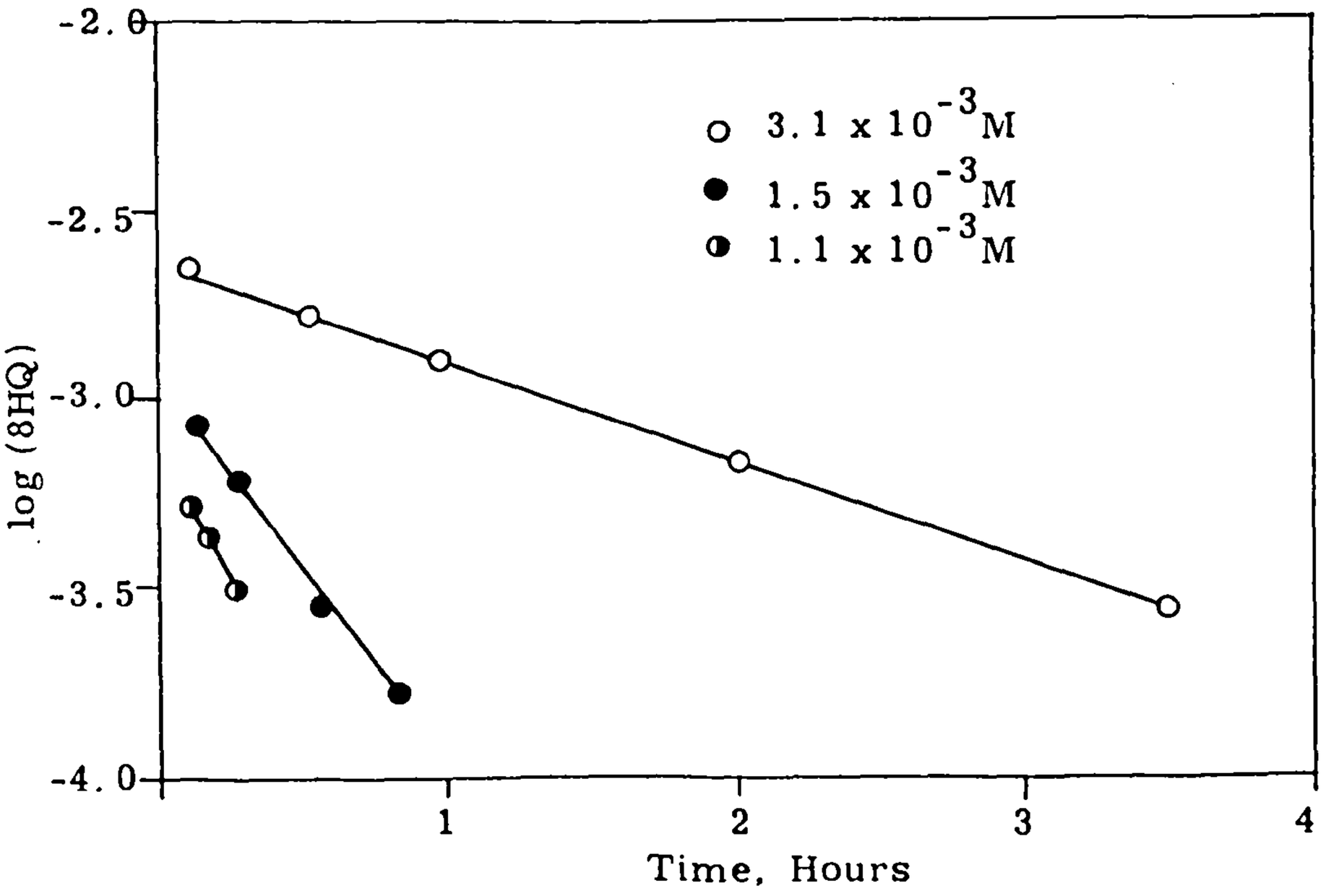


Fig. 5.13 b Change in 8HQ concentration with time at different concentrations of 8HQ

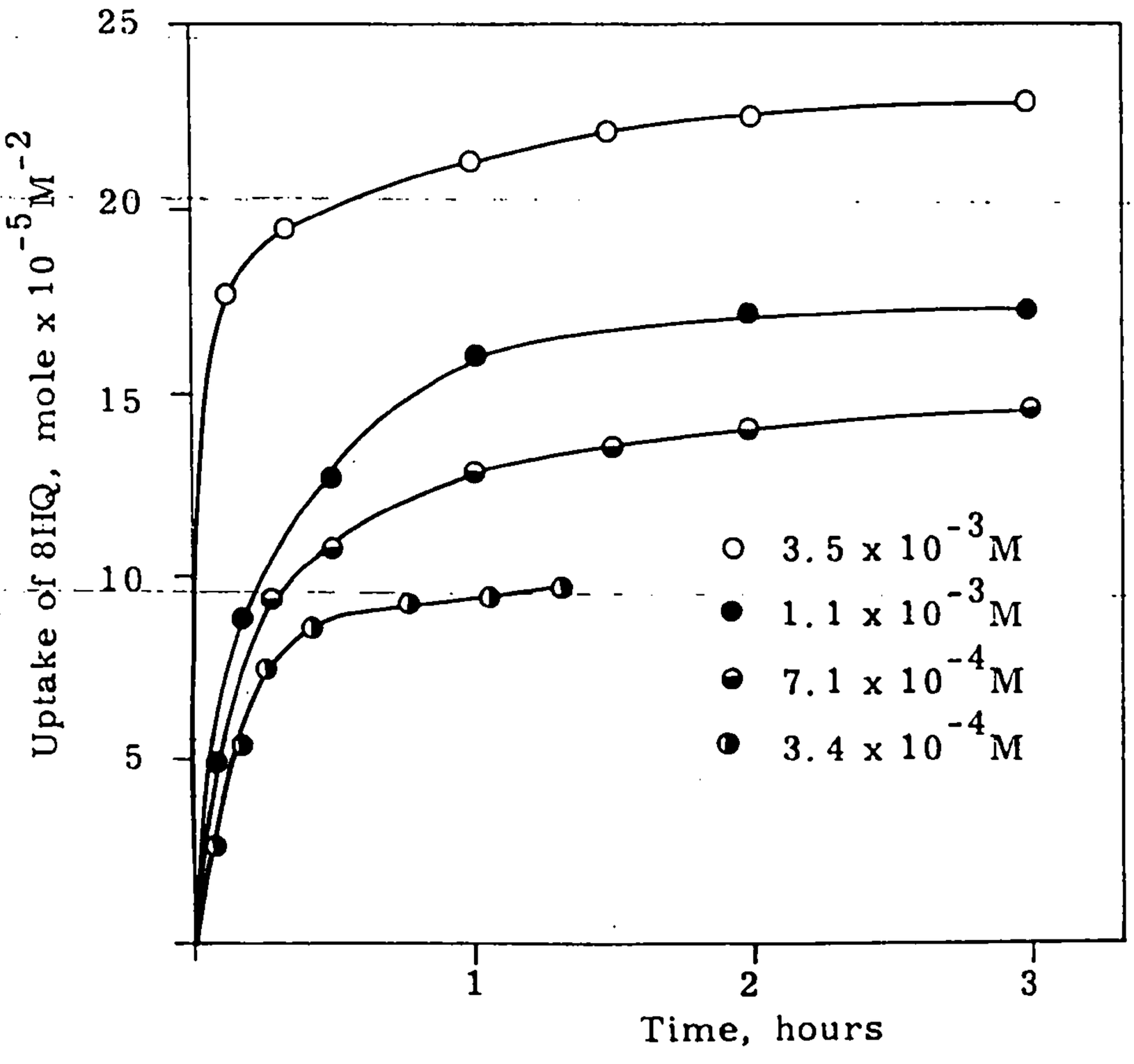


Fig. 5.14 8HQ abstraction by hemimorphite at different initial concentrations at pH 6.0

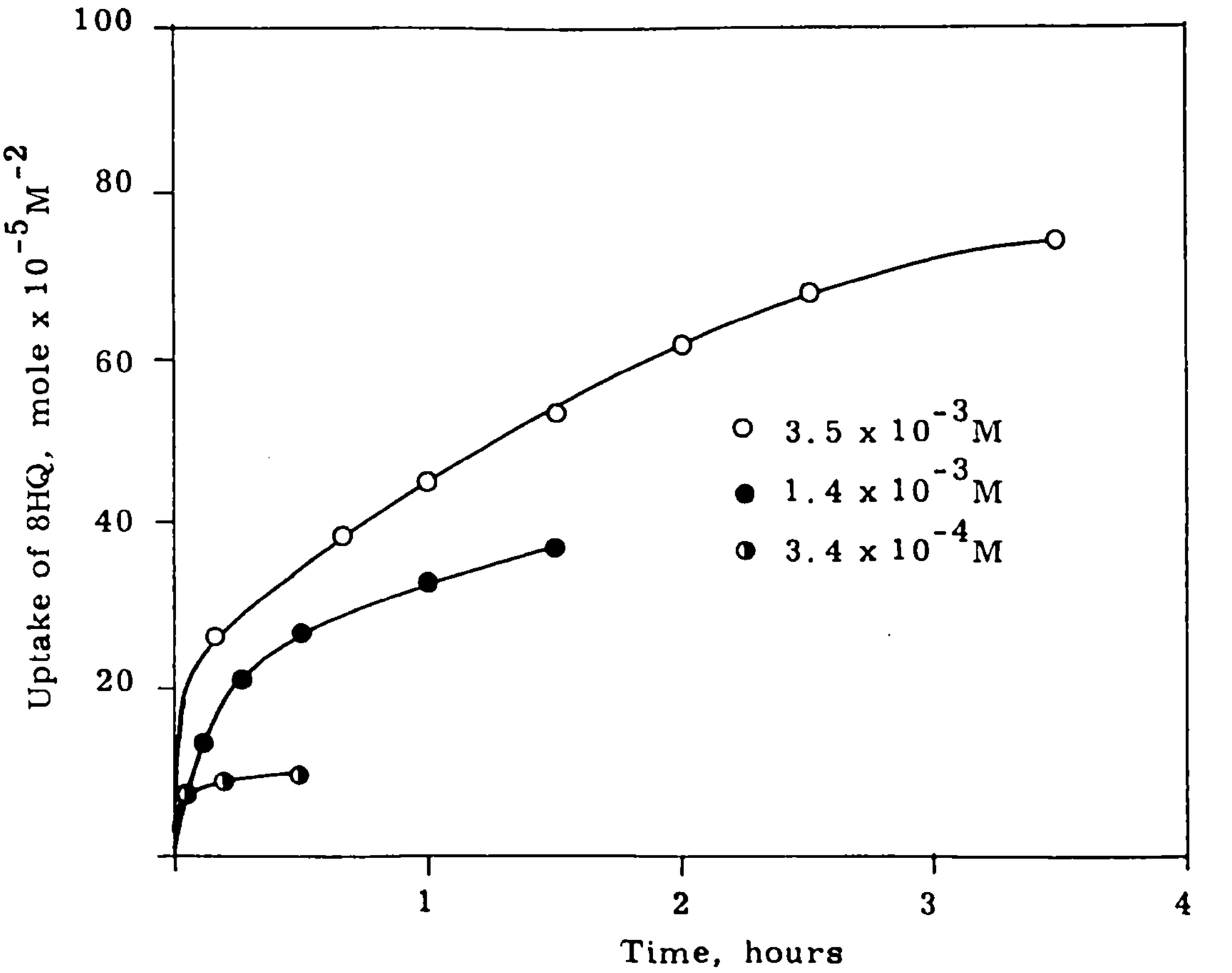


Fig. 5.15 8HQ abstraction by willemite at different initial concentrations at pH 7.0

5.4.2.2 The Zinc Oxide Minerals/2Methyl-8-Hydroxyquinoline System

When smithsonite, hemimorphite and willemite are dispersed in solutions of 2MHQ the concentration of the latter rapidly decreases. Similar to the interaction of 8HQ with smithsonite and willemite the rate of abstraction of 2MHQ is independent of pH. With hemimorphite, however, the rate is very dependent on pH and this is emphasised in Fig. 5.16 where the uptake after 1 hr is plotted as a function of pH. The rate of abstraction of 2-MHQ decreases with an increase in pH. In all cases, however, all of the 2MHQ was abstracted after agitation for a long time.

Smithsonite abstracted 2MHQ at greater rate than did hemimorphite (Figs. 5.17 and 5.18). For example at an initial 2MHQ concentration of 1.1×10^{-3} M complete abstraction was obtained with smithsonite in 30 min. whereas with hemimorphite at pH 6.0 (corresponding to maximum uptake) only 66% was abstracted after 3 hr. Comparison of Figs. 5.13 and 5.14 with 5.17 and 5.18 shows that 2MHQ was abstracted by both smithsonite and hemimorphite at a higher rate than 8HQ. Generally, however, the shapes of the uptake curves were similar in both cases. The rate of uptake of 2MHQ increased with an increase in the initial 2MHQ concentration.

The abstraction of 2MHQ by willemite (Fig. 5.19) was much slower than that obtained by smithsonite but the uptake curves exhibited a similar parabolic shape. Generally the results obtained with willemite and 2MHQ were similar to those with 8HQ (Fig. 5.15) except that the uptake tended to level off more markedly in the latter case.

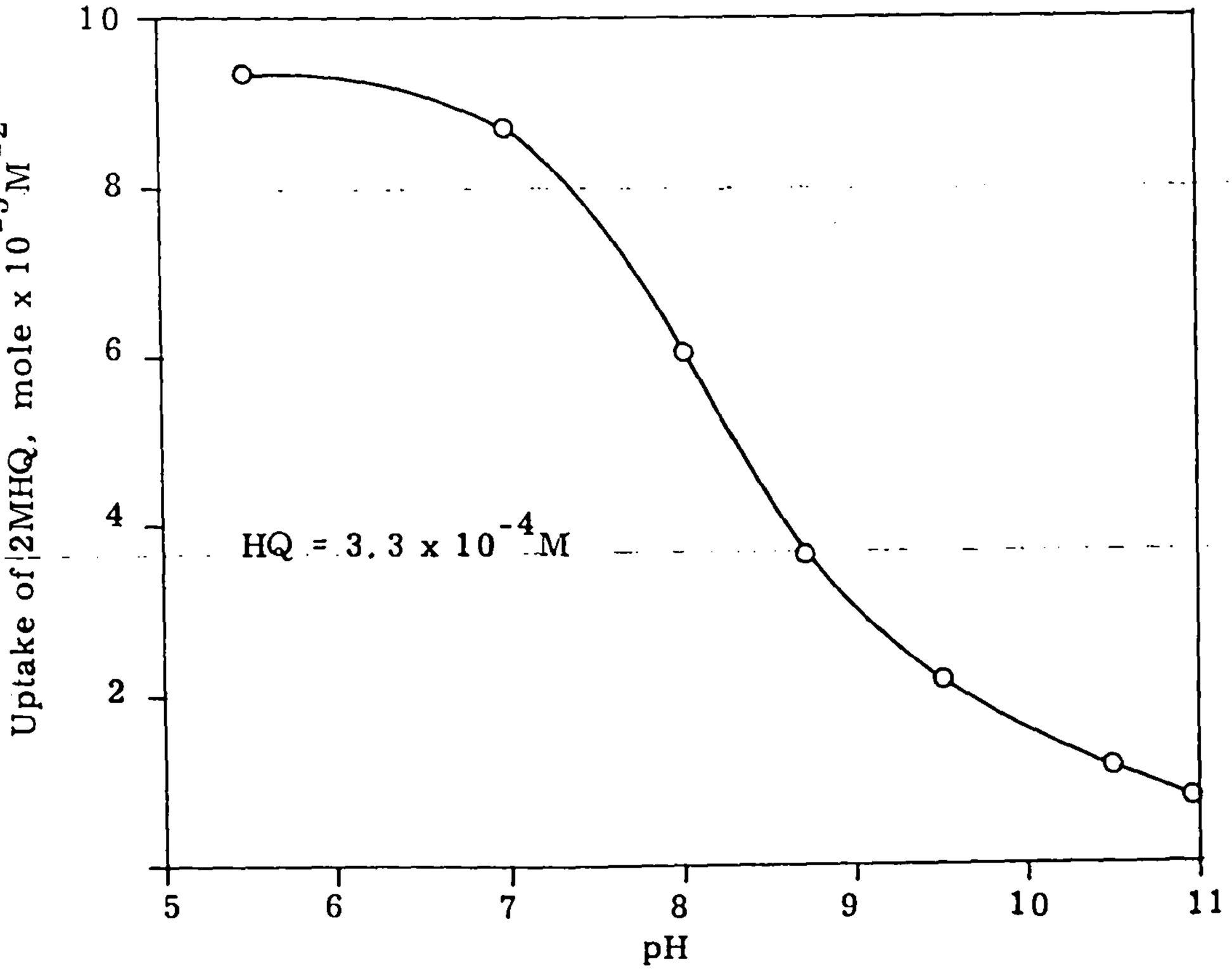


Fig. 5.16 Effect of pH on the uptake of 2MHQ by hemimorphite after 1 h

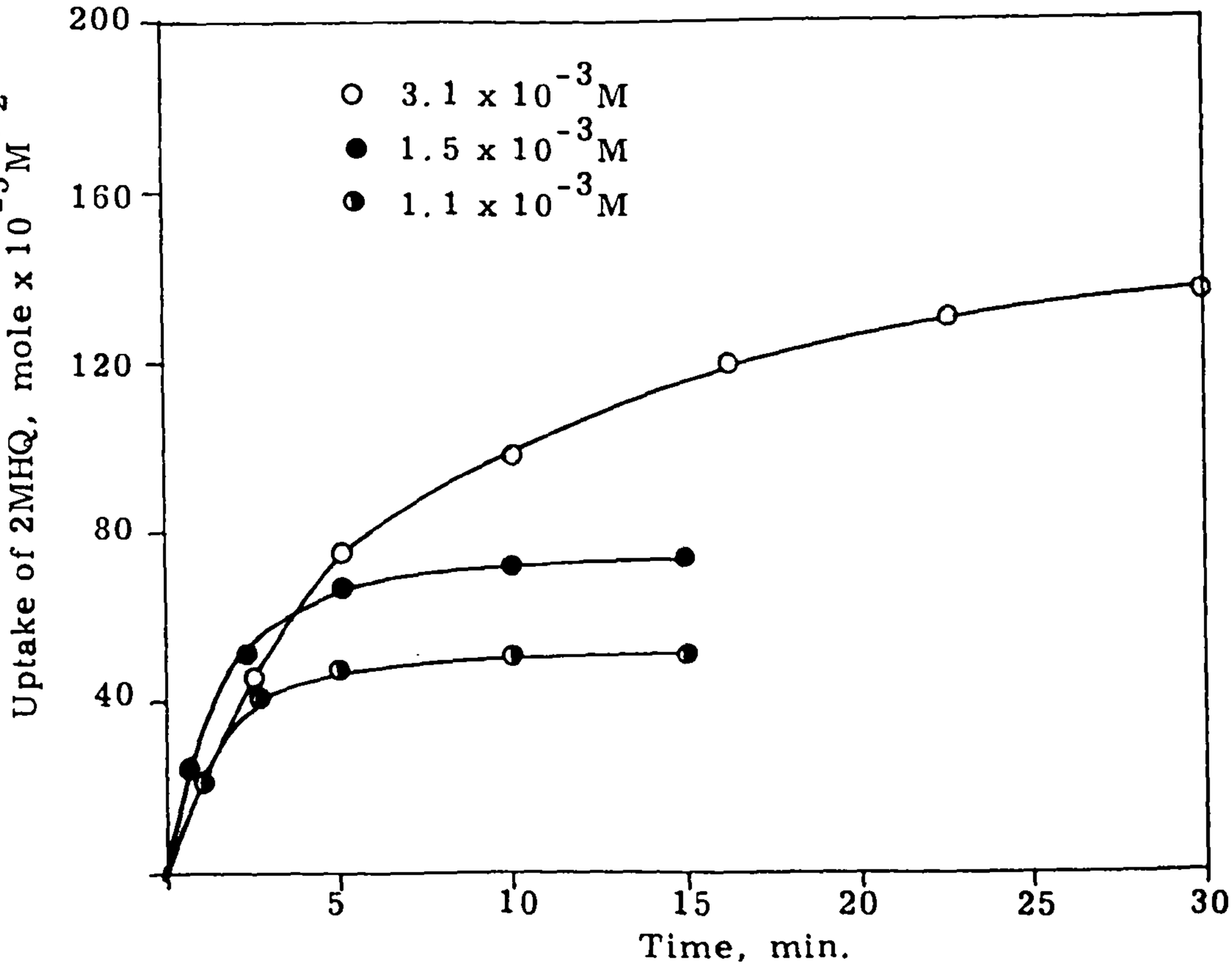


Fig. 5.17 2MHQ abstraction by smithsonite at different initial concentrations at pH 7.6

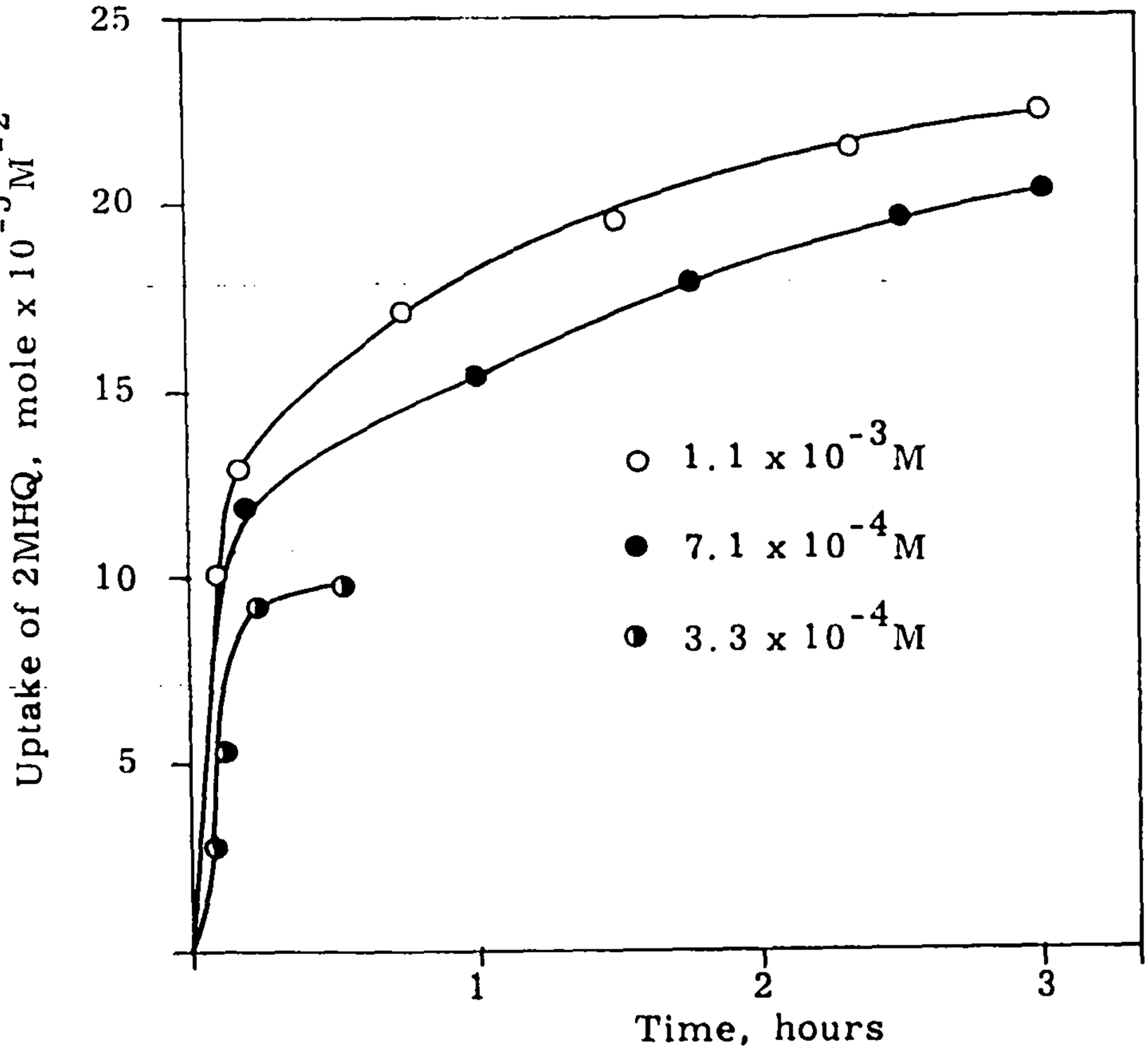


Fig. 5.18 2MHQ abstraction by hemimorphite at different initial concentrations at pH 6.0

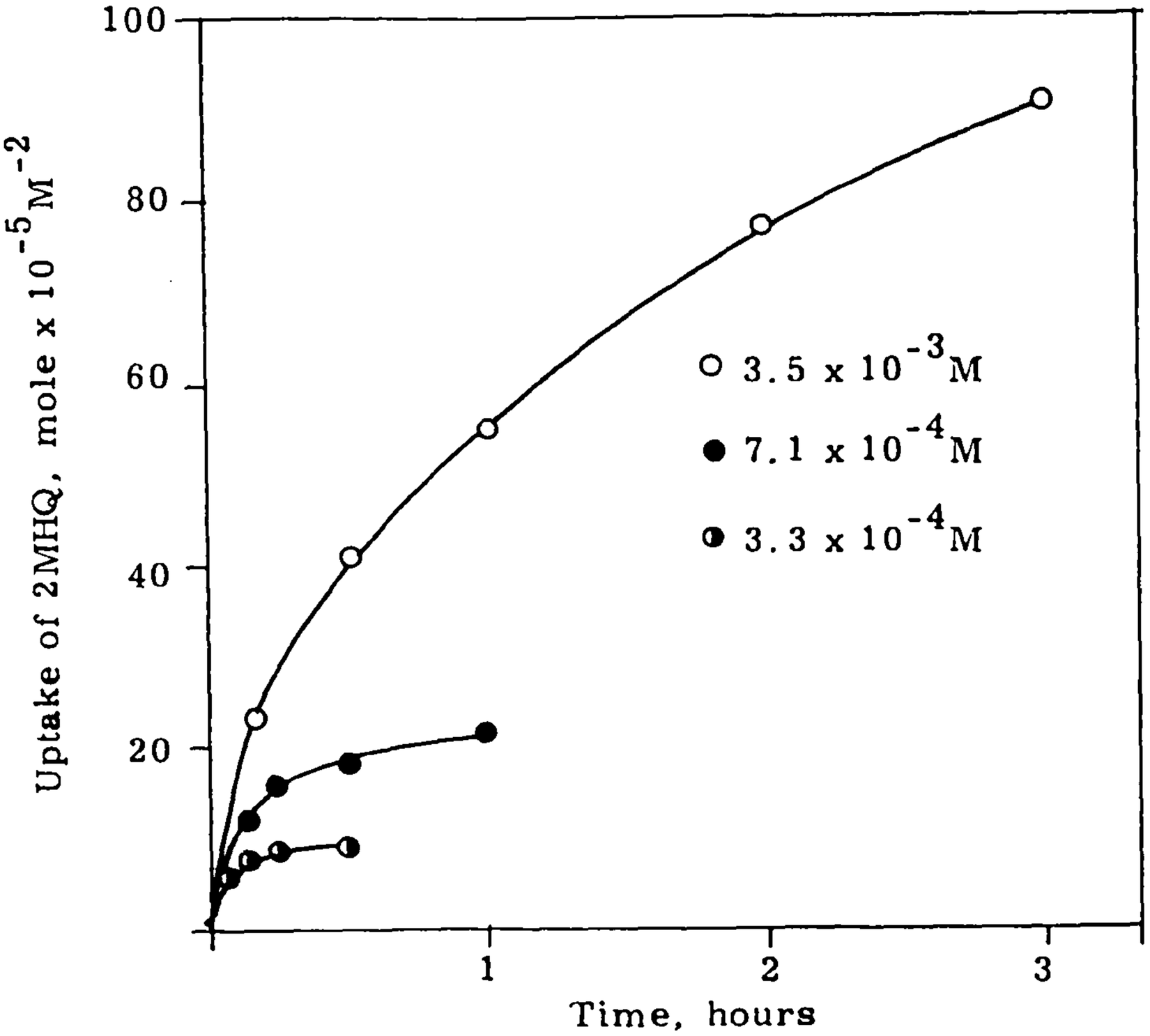


Fig. 5.19 2MHQ abstraction by willemite at different initial concentrations at pH 7.0

With all three minerals a colloidal suspension was formed at the end of the agitation period. The colloid was collected by sedimenting the minerals and filtering the supernatant solution. Analysis showed that the solid contained zinc and 2MHQ in the same proportion as that present in the precipitated zinc chelate.

5.4.2.3 The Zinc Oxide Minerals/Dithizone System

Smithsonite and hemimorphite abstracted dithizone over a wide pH range. In both cases the rate of abstraction was not markedly affected by the pH between pH 6.5 and 9.5 but it decreased markedly at higher pH values. This is demonstrated by the results shown in Figs. 5.20a and b which were obtained after agitation for 30 min. In these tests N_2 was bubbled through the reaction vessel to prevent oxidation of the dithizone.

After 30 min. agitation the abstraction reached a pseudo-equilibrium and it was possible to determine the uptake as a function of residual dithizone concentration (Figs. 5.21 and 5.22). Little can be inferred from the shape of the curves obtained but the results clearly show that the smithsonite was more reactive than the hemimorphite. With prolonged agitation all of the dithizone was abstracted. A study was not made of the willemite-dithizone system.

The reaction of smithsonite and hemimorphite with dithizone produced a reddish-coloured surface layer - presumably of zinc dithizonate. Furthermore a similarly coloured colloidal

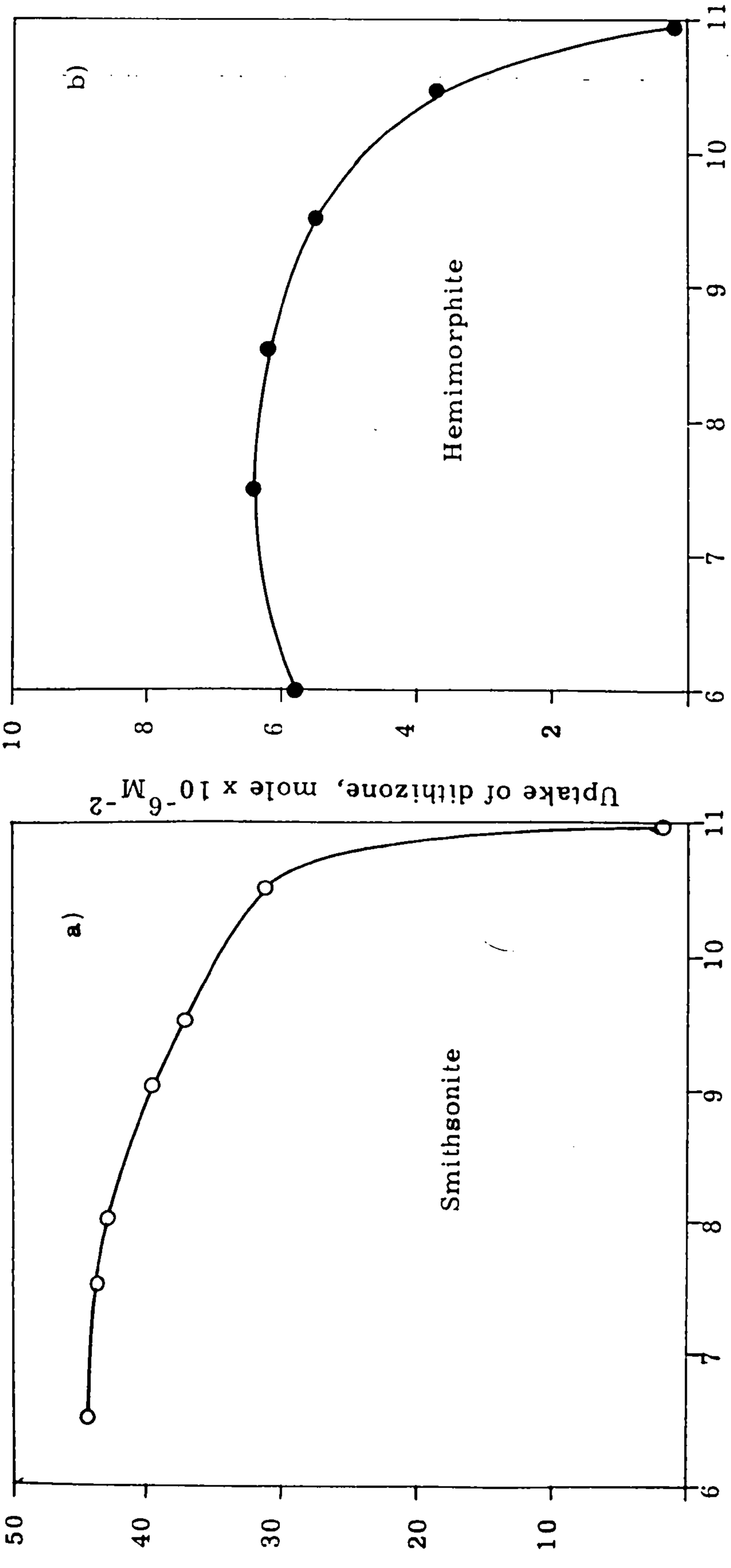


Fig. 5.20 Effect of pH on dithizone uptake by zinc oxide minerals (Dz = 9.8 x 10^{-5}M; time: 30 min)

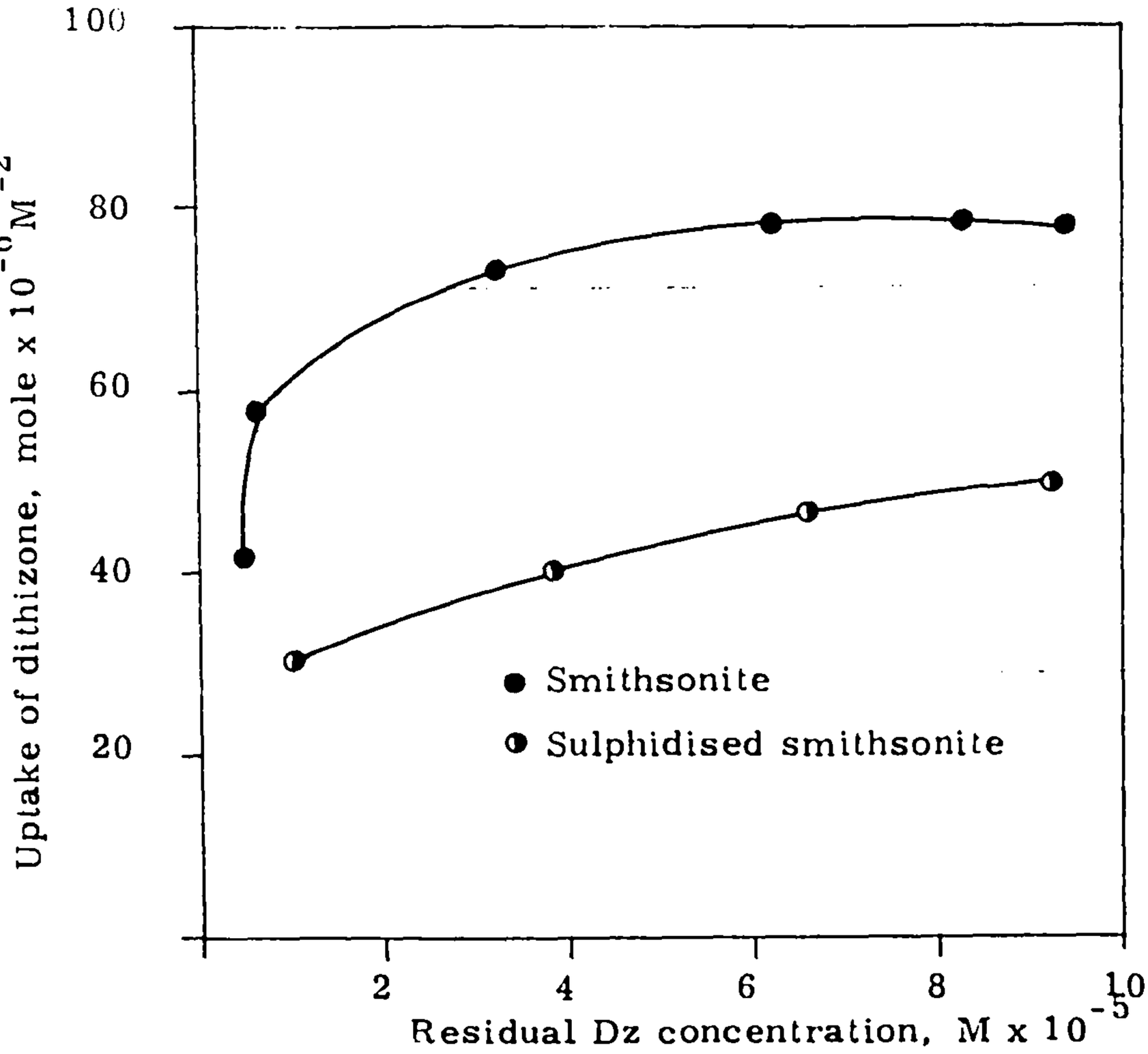


Fig. 5.21 Dithizone abstraction by smithsonite at different initial concentrations at pH 7.6

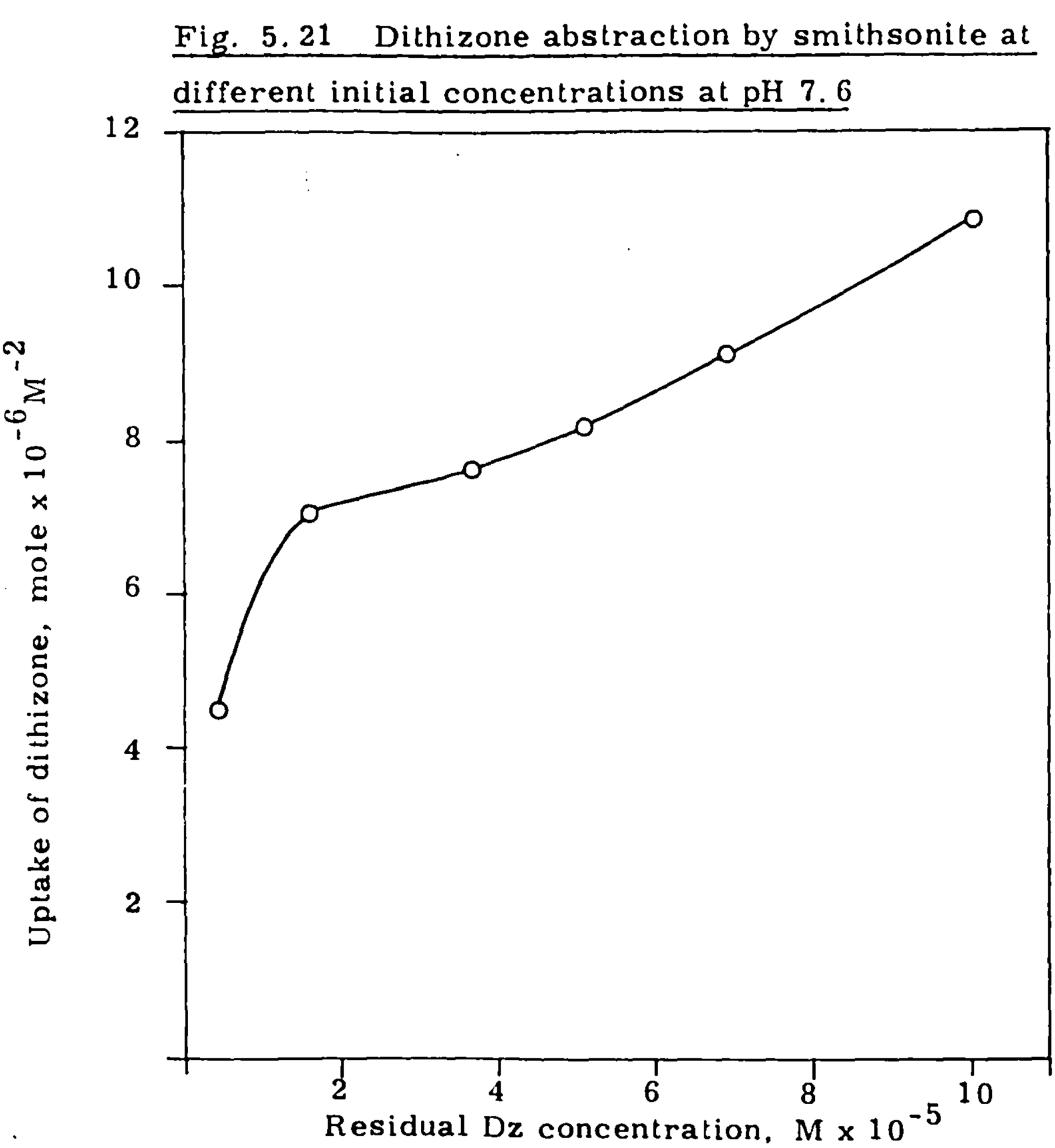


Fig. 5.22 Dithizone abstraction by hemimorphite at different initial concentrations at pH 8.7 after 30 min.

suspension was formed in solution. This colloidal suspension was coagulated with NaCl and then removed by centrifugation. Analysis showed that it contained both zinc and dithizone.

5.4.2.4 The Zinc Oxide Minerals/Quinaldic Acid System

The zinc oxide minerals/quinaldic acid system was investigated because quinaldic acid was one of the chelating agents which forms an insoluble zinc compound but does not have collecting properties. Both smithsonite and hemimorphite abstracted quinaldic acid (Fig. 5.23) to completion but after agitation for 30 min. the smithsonite exhibited higher reactivity than hemimorphite. The rate of abstraction of quinaldic acid decreased with pH but whereas the uptake against pH curve for smithsonite had a convex shape that of hemimorphite was concave. In the pH range 7.0 to 9.0 the abstraction by smithsonite after 30 min. was much greater than that by hemimorphite which decreased to nearly zero.

Similar to the interaction of 8HQ, 2MHQ and dithizone with the zinc oxide minerals the quinaldic acid solution in contact with the minerals contained a colloidal suspension. This colloid contained zinc and quinaldic acid in the ratio 2:1. It can therefore be assumed that the interaction results in the formation of the corresponding insoluble zinc quinaldinate.

5.4.2.5 The Effect of Sulphidisation on the Interaction of 8HQ, 2MHQ and Dithizone with Zinc Oxide Minerals

The results obtained with the zinc oxide minerals clearly show that the interaction with 8HQ, 2MHQ and dithizone proceeds via a chemical reaction in which the corresponding zinc chelate is

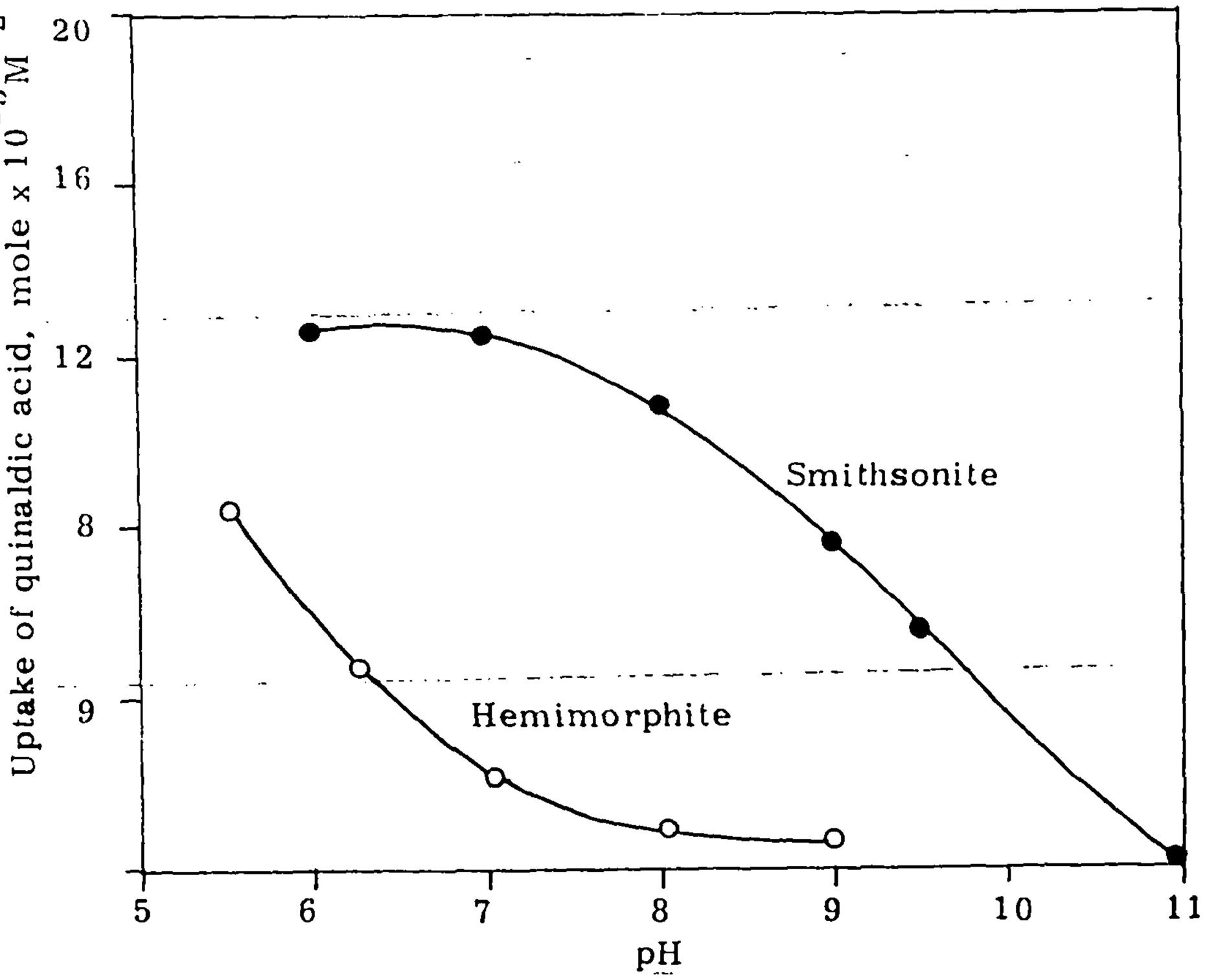


Fig. 5.23 Effect of pH on the uptake of quinaldic acid by zinc oxide minerals (initial concentration 2.9 x 10^{-4} M)

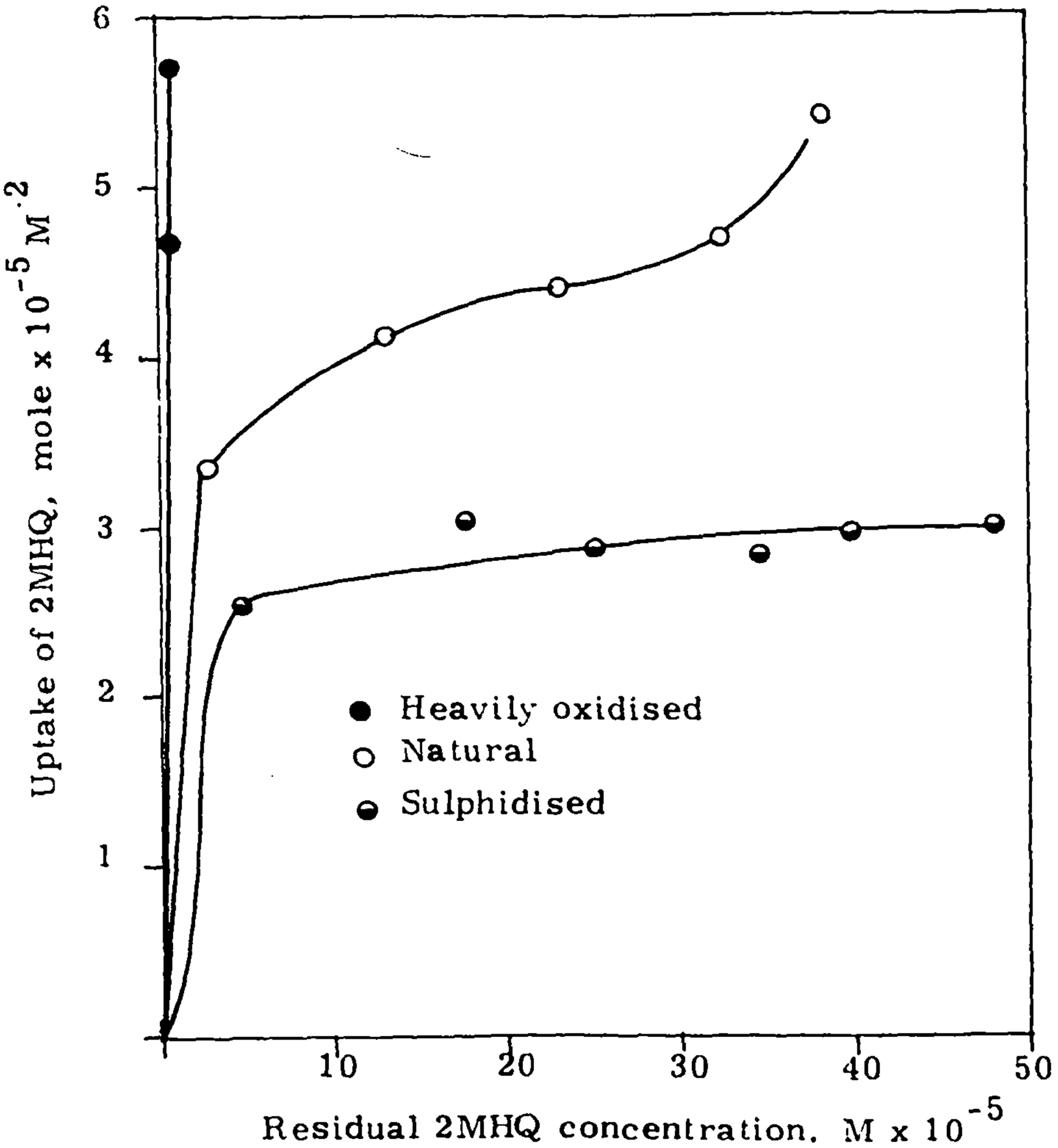


Fig. 5.24 Effect of surface oxidation of sphalerite on the uptake of 2MHQ at pH 9.0 (20 hrs)

formed. Furthermore the zinc chelate does not remain attached to the mineral surface but is detached by the mild shear conditions that were used in the reaction vessel. The detachment of the zinc chelate makes available more mineral surface so that the reaction proceeds until all of the chelating agent is consumed.

Such a mechanism of collector interaction with a mineral is likely to lead to high collector consumption and furthermore a hydrophobic layer which will be readily removed by the shear conditions that prevail in a conventional flotation cell. Indeed, smithsonite particles which originally floated with the chelating agents in the Hallimond tube were rendered non-floatable after agitation for 24 hr.

It follows therefore that if chelating agents are to be used to float zinc oxide minerals some way must be found to reduce the collector consumption and to increase the stability of the hydrophobic layer. Zinc sulphide is more insoluble than zinc oxide minerals and it is therefore possible that by sulphidising the zinc oxide minerals the consumption of chelating agent might be reduced. To determine whether or not zinc sulphide consumed less chelating agent tests were done with sphalerite which had been treated under various oxidising conditions. The results obtained with 2MHQ are shown in Fig. 5.24.

Heavily oxidised sphalerite abstracted 2MHQ rapidly and all of the chelating agent was consumed. A colloid was formed in the supernatant solution. 'Natural' sphalerite abstracted less chelating agent and an apparent equilibrium was established

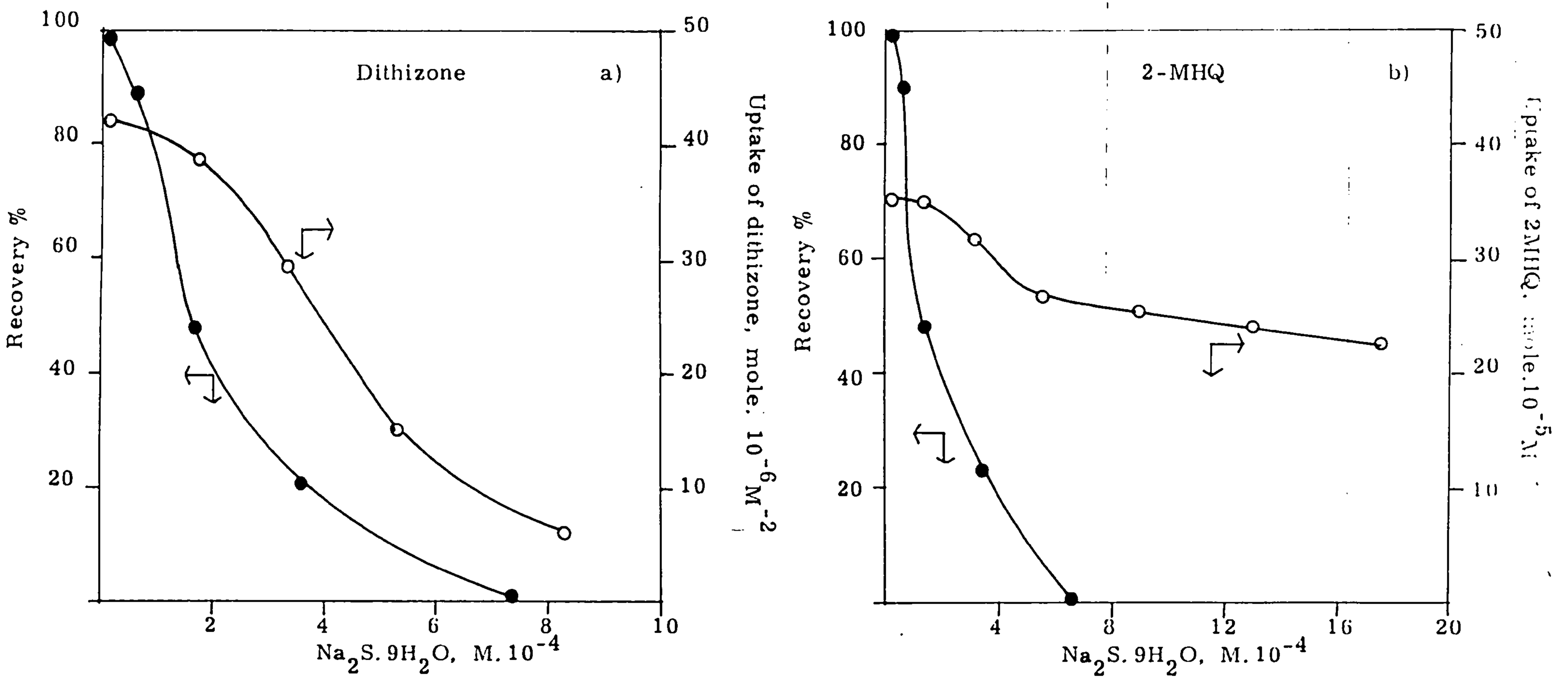


Fig. 5.25 Effect of excess sulphide ions on the flotation and uptake of zinc chelating agent by smithsonite

after about 20 hr. Removal of the oxide sites on the 'natural' sphalerite by sulphidisation considerably reduced the abstraction of 2MHQ further. These results therefore indicate that sulphidisation of the zinc oxide minerals should reduce the consumption of chelating agent.

Tests on sulphidised smithsonite, however, clearly showed that sulphidisation had little effect on the abstraction of 2MHQ despite the fact that during sulphidisation all the sulphide was consumed and that this corresponded to multilayers of ZnS. Consumption of 2-MHQ was only reduced in the presence of excess Na_2S but under these conditions the flotation was depressed. In the case of dithizone previous sulphidisation of smithsonite decreased the rate of dithizone uptake (Fig. 5.21), but longer agitation times produced total consumption of dithizone. The presence of excess sulphide ions also decreased the abstraction of dithizone and similar to the effect with 2MHQ flotation was also depressed (Fig. 5.25).

CHAPTER 6

6 INFRARED STUDIES OF THE ZINC OXIDE MINERALS/ CHELATING AGENT SYSTEM

6.1 Introduction, Experimental Materials and Techniques

The application of infrared spectroscopy to the study of surface chemistry and in particular to mineral flotation research has provided one of the most direct means of observing the interactions and perturbations that occur at the surface during collector adsorption, and of determining the chemical nature of the adsorbed species. However, certain restrictions exist which confine the use of this technique to rather limited spectral regions, and usually not all the absorption bands belonging to an adsorbed molecule can be recorded. This is due, largely, to strong absorption of infrared radiation by the solid adsorbent to which the molecules are bound. Thus the adsorbent may have characteristic infrared absorption bands, and regions of the adsorbate spectrum may be completely obscured since in normal adsorption systems the quantity of adsorbent is far greater than that of adsorbate. As a consequence the assignment of structures is made on the basis of similarities between a relatively few bands in the spectrum of the surface species, and those of the pure compound. At this level doubts arise about the validity of a comparison of the spectra of molecules in unsymmetrical surface environments with those in more uniform surroundings. In a review of this subject, Eischens and Pliskin (96) have demonstrated that such comparisons have produced useful results for a wide variety of adsorption systems. At the present stage, in the

application of the infrared technique to surfaces, a considerable amount of evidence has been obtained in which good correlations exist between the spectra observed and expected surface compounds. Many examples supporting this fact have also been reported for a number of flotation systems. (24) (97) (98).

The aim of this part of the work was to confirm the chemical nature of the products of the reaction between zinc oxide minerals and zinc chelating agents, either on the mineral surface or dispersed in solution. This was qualitatively achieved by comparison with the spectra of pure compounds.

Experimental Materials and Techniques

Preparation of the zinc chelates The zinc chelates were prepared by precipitation from $ZnCl_2$ solutions with stoichiometric amounts of 8HQ, 2MHQ or Dz. The crystals obtained were filtered and thoroughly washed with distilled water until no chelating agent was detected in the filtered solution. Zinc-8-hydroxyquinolinate and zinc-2-methyl-8-hydroxyquinolinate were dried at 110°C for 3 hr. and kept under vacuum. Zinc-dithizonate was dried under vacuum and maintained in dark glass containers to prevent decomposition by the light. The reagents used in the preparation of the chelates were in all cases reagent grade, and with the exception of dithizone which was purified according to the procedure described in section 5.3.3, they were used without further purification.

Mineral samples The -150 um fraction of both smithsonite and hemimorphite was thoroughly deslimed and contacted

with aqueous solutions of the zinc chelating agents at pH 7.6 and 6.0 respectively for 3 hr. After this period the solid was filtered and thoroughly washed with distilled water to eliminate the excess chelating agent solution and then dried under vacuum. The infrared spectra of these collector coated mineral samples were determined. The same procedure was used to obtain the reaction products dispersed in the supernatant solution with the difference that the conditioning treatment lasted 24 hr. In this case the supernatant dispersion was filtered, washed, dried and finally the spectra recorded.

Infrared analysis Discs of the various solid samples were accurately made up with KBr to be 0.3% sample (by weight). The different samples were weighed out and mixed with spectroscopically pure KBr which had been dried at 150^{o}C for 1 hr. The mixture was finely ground in a steel vibratory mill for 1 minute. A 250 mg sample was weighed out and placed in a steel die. The die was evacuated for 10 minutes after which a presure of 10t cm^{-2} was applied for 10 minutes. The pressure was carefully released and the disc placed in a dessicator prior to analysis. A disc of KBr prepared by the same technique was used as a blank.

Equipment The infrared spectra were recorded with a double beam Grubb-Parsons Spectromaster MK. I. A Nernst filament was used as the source of infrared radiation.

6.2 Results and Discussion

Smithsonite like most of the anhydrous carbonates characteristically showed three prominent bands at 1428, 869 and 741 cm^{-1} (Fig. 6.1). These bands are all considered to be caused by the CO_3 groups of the crystal. The spectra coincided with those described for other smithsonite samples (99) (100).

In the case of the infrared spectrum of hemimorphite six well defined bands appear at 1163, 1087, 1010, 926, 826 and 671 cm^{-1} (Fig. 6.2). The bands observed at 1163 and 1087 can be ascribed to the stretching and bending vibrations of the OH groups respectively (101). The band at 1087 cm^{-1} coincides with the frequency of the OH groups in crystalline $Zn(OH)_2$ (102). The different Si-O stretching bands appear in the same region. Thus, the bands at 1087 and 1010 cm^{-1} can be ascribed to the presence of Si-O-Si bands present in the pyrosilicate structure of hemimorphite. The stretching vibration band due to the presence of SiOH groups clearly appears between 917 and 862 cm^{-1}.

After exposure of the zinc oxide minerals to zinc chelating reagents solutions several new bands appeared in the infrared spectra of the minerals. These spectra were therefore compared to those of both zinc chelates and the chelating reagents to establish the identity of the surface species.

The spectra of 8HQ and its zinc chelate are given as spectra a and b in Fig. 6.3. In general the spectra recorded agreed with those reported by several authors (103) (104). The zinc-8-hydroxyquinolinate exhibits the same absorption bands as 8HQ in the 1176-1539 cm^{-1} region with the exception of two new bands at

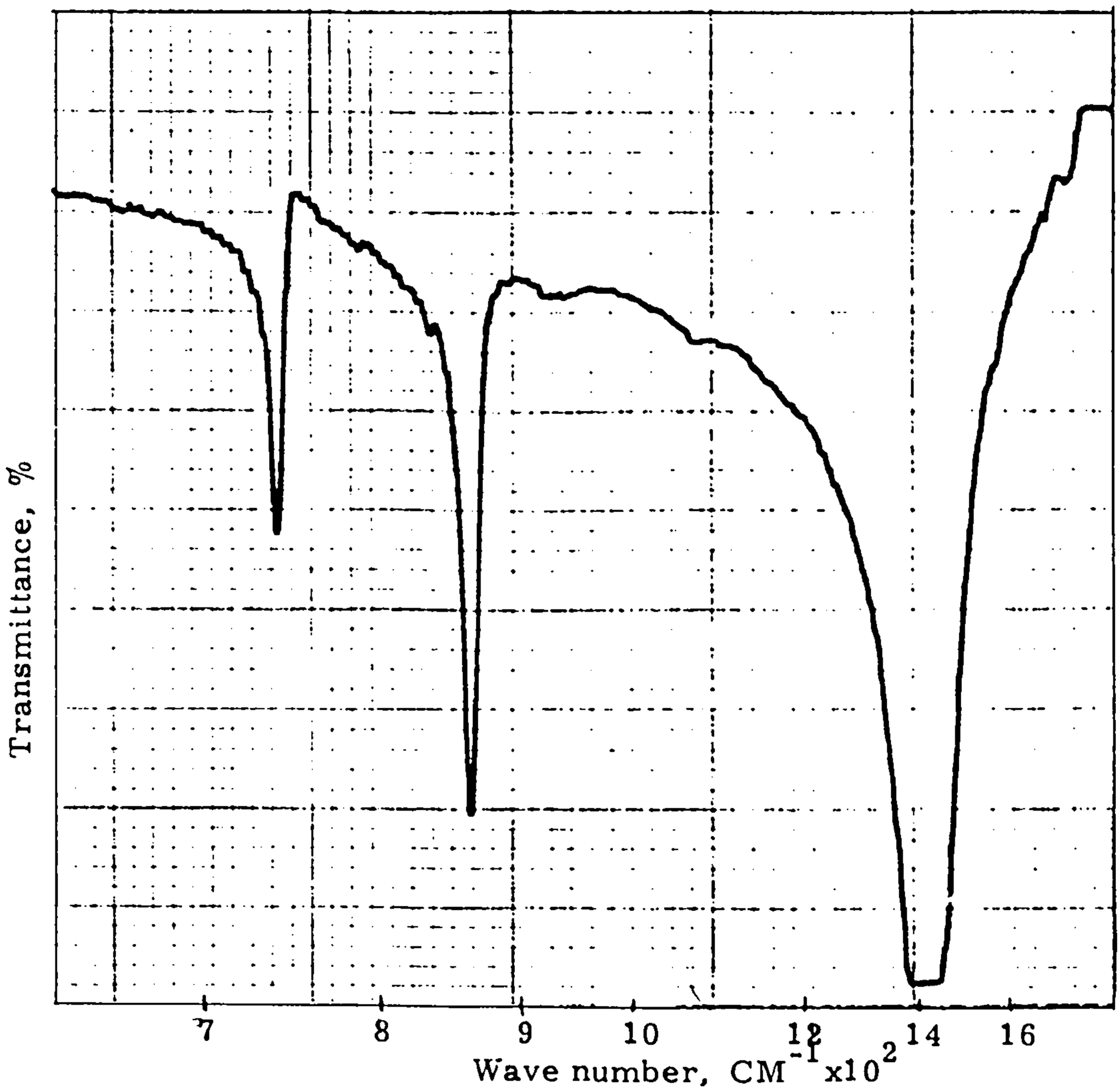


Fig. 6.1 Infrared spectrum of smithsonite

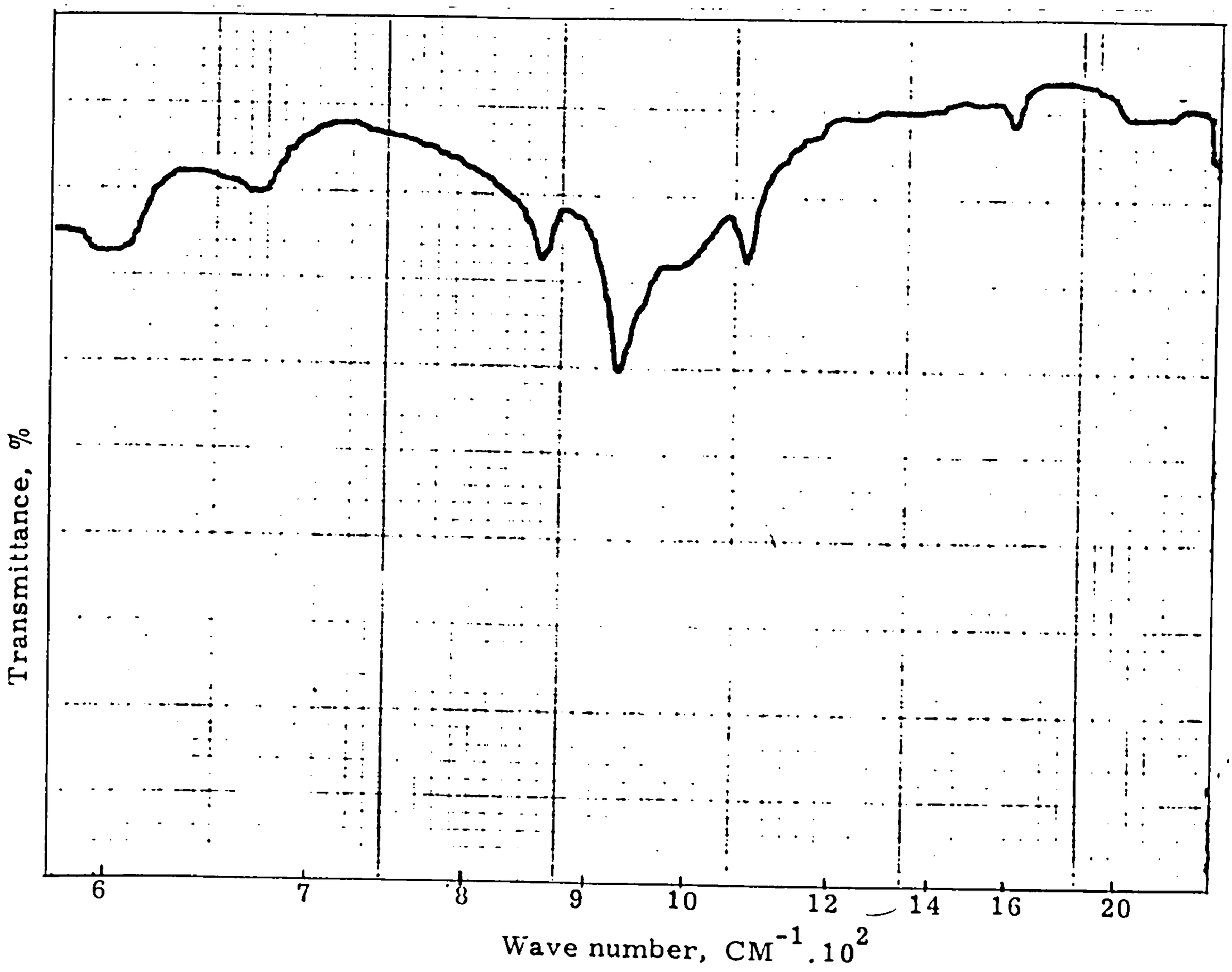


Fig. 6.2 Infrared spectrum of hemimorphite

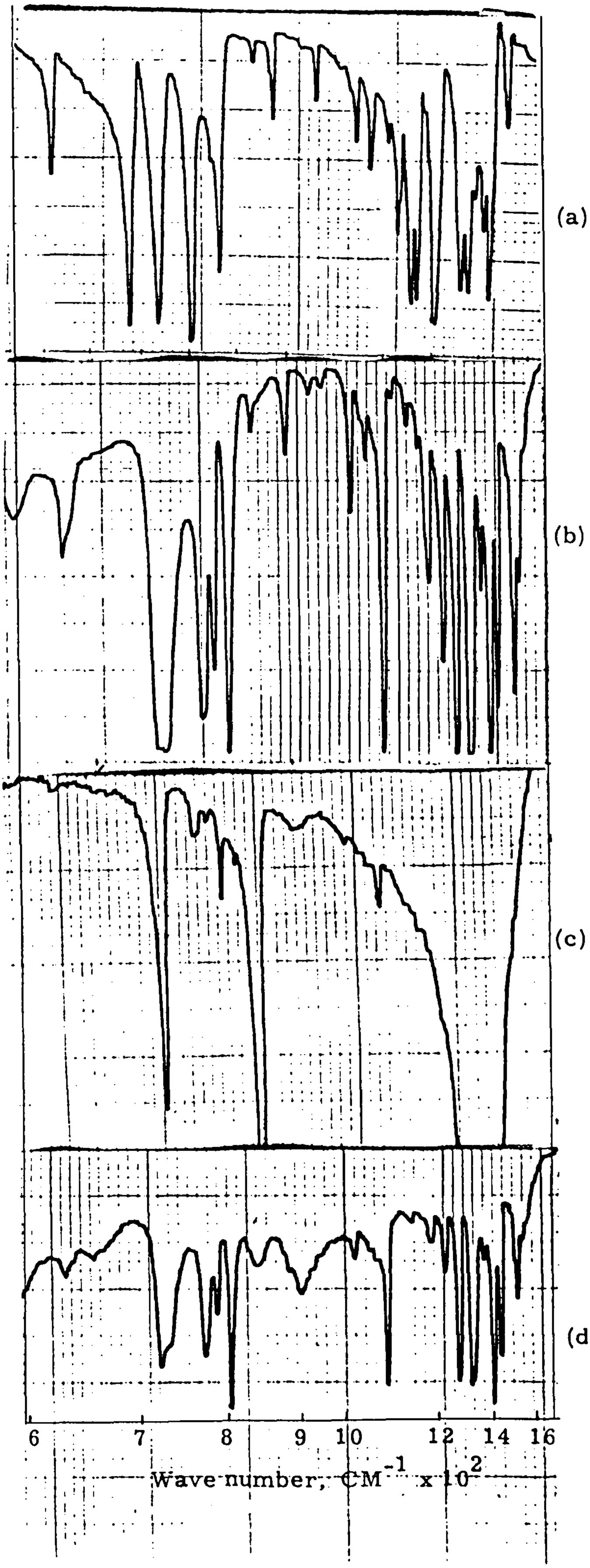


Fig. 6.3 Infrared spectra of (a) 8HQ (b) the zinc chelate (c) smithsonite and (d) hemimorphite after contact with 8HQ solutions

1272 and 1538 cm^{-1} in the case of the zinc chelate. In addition, in the spectrum of the zinc chelate a strong band appears at 1092 cm^{-1}. The latter band appears to be characteristic of a number of metal-8-HQ chelates (103) and it can be used to distinguish between the metal chelate and the 8HQ quite accurately. Which, if any, of the bands in the 8HQ spectrum corresponds to this characteristic band in the chelate spectra is not known. The band at 1092 region occurs near the region commonly assigned to C-O stretching vibrations (between 1205 and 1250 cm^{-1}). This fact, plus the fact that it occurs in the spectra of all the 8HQ chelates suggests that is characteristic of the band between the carbon in position 8 and the oxygen of the hydroxyquinolinate ion. In the 700 to 816 cm^{-1} region there are four strong bands in the 8HQ spectrum which are due to in-plane ring deformation (104). These bands are also present in the zinc chelate but slightly shifted specially the band at 700 cm^{-1} in the 8HQ which becomes a broad band at 730 cm^{-1}.

Bands at 1092, 816 and 781 cm^{-1} are present in spectra of the smithsonite after contact with 8HQ solutions (Fig. 6.3). This indicates that the formation of the zinc-8HQ chelate has occurred on the smithsonite surface. Hemimorphite exhibits several new bands after contacted with 8HQ (Fig. 6.3), and those at 1290, 1092, 816, 781 and 730 cm^{-1} give clear evidence of the formation of the zinc chelate on its surface. The infrared spectrum of the supernatant dispersion formed by reaction of both smithsonite and hemimorphite with 8HQ coincided with that of the bulk zinc-8HQ chelate. The frequencies of the major bands of this system are tabulated in Table 6.1.

TABLE 6.1

ABSORPTION FREQUENCIES (CM^{-1}) OF THE 8HQ/ZINC OXIDE MINERAL SYSTEM

8HQ	Zn-8HQ	Band Assignment	Reference	Smithsonite after reaction with 8HQ	Hemimorphite after reaction with HQ
727	730	ip ring def*	104		730
769	781	ip ring def		781	
800	797	ip ring def			
806	816	op C-H bend		816	816
877	847			1092	1092
962	900				
1047	1025				
1075	1063				
-	1092	diat. vib. C-O group	103		
1149	-				
1177	1212				
1190	1250				
1205	1290				
1205	-				
1351	1351				
1379	1379	Aromatic ring vibrations	105, 106		
1429	-				
1470	1470				
-	1538				
1562	1562				

*The following are used in the table: ip: in-plane; def: deformation, op: out-of-plane, bend.: bending, diat. vib., diatomic vibration.

The spectrum of 2-MHQ showed a similar pattern to that of its zinc chelate, however, the most important difference appears in the 1092 cm^{-1} region (Fig. 6.4). The zinc chelate exhibits a strong band at 1092 cm^{-1} which is not present in the case of 2MHQ. In addition at 735 cm^{-1} the chelate gives a broad strong band that in 2MHQ corresponds to a slightly shifted duplet.

The infrared of both zinc oxide minerals after reaction with 2MHQ showed an absorption band at 1092 cm^{-1} which can be considered as clear evidence that the zinc chelate was present on the mineral surface (Fig. 6.4). In addition, the spectrum of the dispersed solid which was formed during the reaction exactly corresponded to that of the pure zinc chelate. The most important bands of this system are tabulated in Table 6.2.

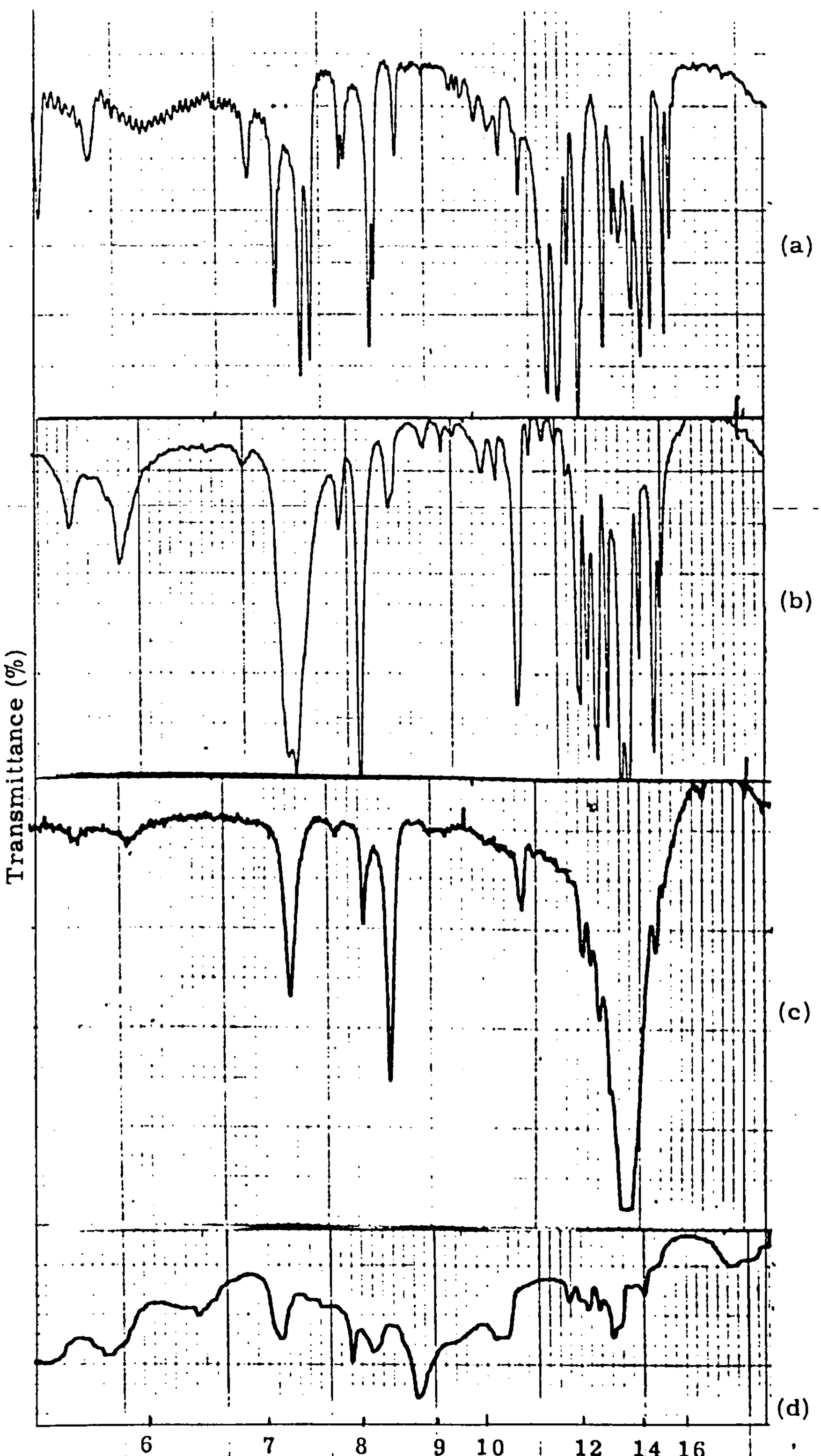


Fig. 6.4 Infrared spectra of: (a) 2MHQ, (b) the zinc chelate (c) smithsonite and (d) hemimorphite after contact with 2MHQ solutions

TABLE 6.2

ABSORPTION FREQUENCIES (CM^{-1}) OF THE 2MHQ/ZINC OXIDE MINERAL SYSTEM

2MHQ	Zn-2MHQ	Band Assignment	Reference	Smithsonite after reaction with 2MHQ	Hemimorphite after reaction with 2MHQ
833	730	ip ring def.	104		735
837	735				
865	784				
1081	830			830	830
1149	869				
-	1092	diat. vib. of C-O group	103	1092	
1220	1265			1265	
1245	1290	Aromatic ring vibrations	105, 106		1290
1316	1316			1316	
1351	1351				1351
1370	1399				
1412	1428				
1481	1481				
1510	-				
1557	1562			1562	

The spectrum of zinc dithizonate was similar to that of dithizone except that some of the bands were shifted. Most of the differences occurred in the C = S absorption region i. e. 1050-1250 cm^{-1} where two well defined triplets occurred in the zinc dithizonate structure (Fig. 6. 5). The absorption spectra of smithsonite and hemimorphite after reaction with dithizone were not significantly different to that of the minerals and it was not possible to ascertain the identity of the surface species. However, the spectra of the colloidally dispersed solid was the same as that of zinc dithizonate which infers that was formed on the mineral's surface.

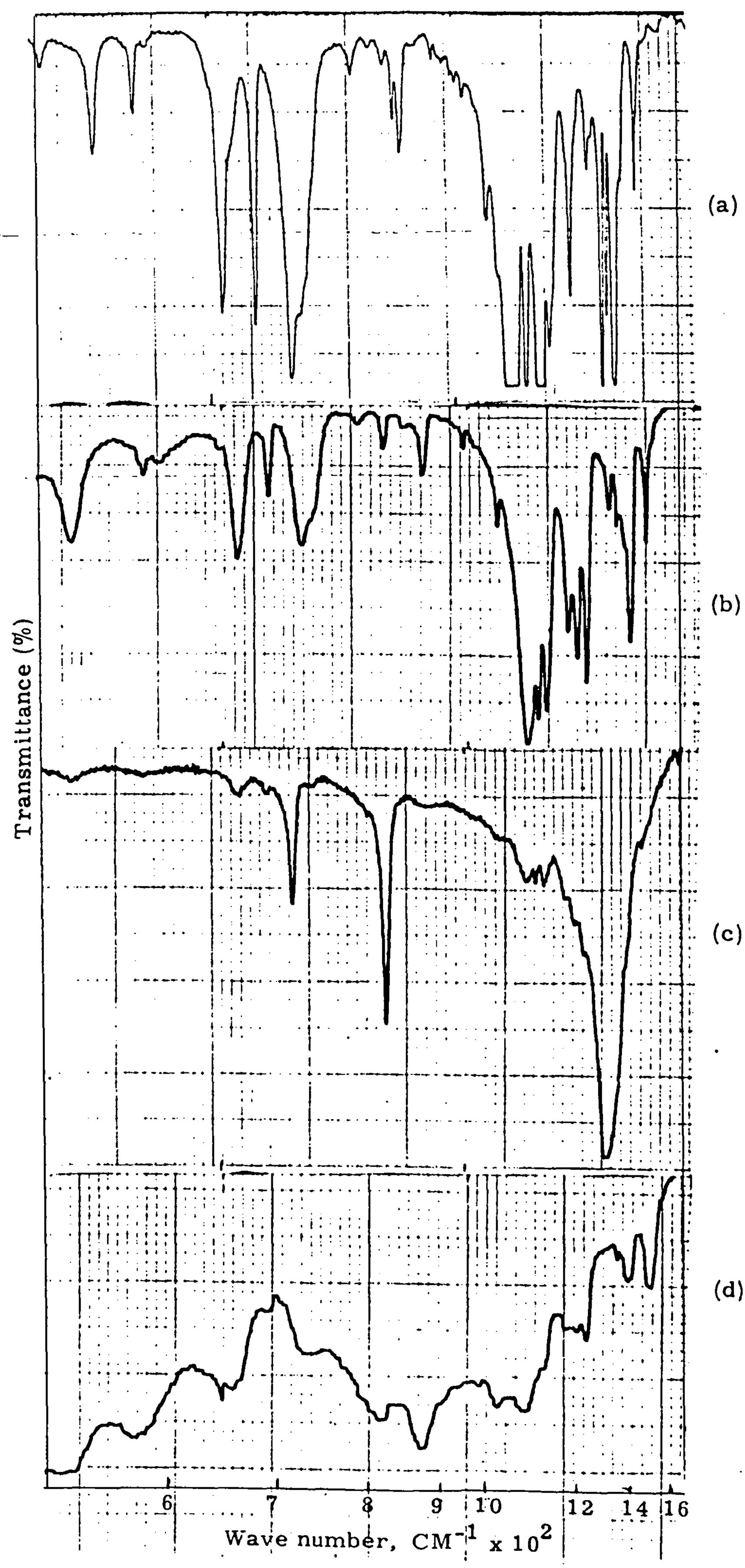


Fig. 6.5 Infrared spectra of: (a) Dz (b) the zinc chelate, (c) smithsonite and (d) hemimorphite after contact with Dz solutions

TABLE 6.3

ABSORPTION FREQUENCIES (CM^{-1}) OF THE DITHIZONE/ZINC OXIDE MINERAL SYSTEM

Dithizone	$Zn(HDz)_2$	Band Assignment	Reference	Smithsonite after reaction with Dz	Hemimorphite after reaction with Dz
707	706	aromatic ring vibrations	106		
746	746				
885	847				
893	909				
1064	1053	C = S Group	106, 107		1136
1136	1136				
1163	1172				
1190	-				
1250	1250				
-	1290				
1325	1325	-C-N-link	107	weak triplet between 1250-1136cm^{-1}	1325
1379	1374				
1424	-				
1449	1472				
1492	1492	S-C = N	107		1472

The results of the infrared studies confirmed that zinc chelate was formed on the zinc oxide mineral surface and some was also colloidally dispersed in the supernatant solution. The results also showed that no detectable chemisorption of chelating agent occurred at the mineral/water interface.

CHAPTER 7

7 GENERAL DISCUSSION

Of all the chelating agents investigated only four functioned as collectors for the zinc oxide minerals in the Hallimond tube and these are 8-hydroxyquinoline, 2-methyl-8-hydroxyquinoline, dithizone and Lix 65N. The latter being an impure solution of 5-nonyl-2-hydroxy benzophenone oxime in kerosene.

The chelating agents floated the minerals under pH conditions where the corresponding insoluble zinc chelates were concentrated at the oil/water interface. From these results and the infrared spectra of the mineral surfaces it can be postulated that the species responsible for producing a hydrophobic surface is a layer of zinc chelate at the mineral/water interface.

The chelating agents exhibited different collecting abilities and if an efficiency series is constructed, based on the concentrations required to give 100% flotation, the result would be

Lix 65N > dithizone > 2MHQ > 8HQ

Lix 65N showed excellent collecting properties for the zinc oxide minerals. Unfortunately its selectivity was low and good flotation of calcium carbonate minerals was obtained under pH conditions where smithsonite also floated. This reagent was therefore omitted from further studies.

The collecting ability of 8HQ for smithsonite was poor and it collected hemimorphite only in a narrow pH range. Introduction of a methyl group in position 2 to give 2-methyl-8-hydroxyquinoline markedly improved the collecting ability for both minerals. This is perhaps surprising because one methyl group does not usually increase the hydrophobicity of a compound by a large amount. However, in this case the methyl group also reduces the hydration of the zinc chelate from two water molecules in the 8-hydroxyquinolinate to one molecule in the 2-methyl-8-hydroxyquinolinate. This effect would also increase the hydrophobic character of the zinc chelate.

Dithizone acted as a stronger collector than 2MHQ and 8HQ. This can be explained by the fact that the introduction of large, voluminous groups such as long alkyl chains or benzene rings reduces the degree of hydration of a chelate and therefore increases its hydrophobicity. Zinc dithizonate contains 4 phenyl groups and is not hydrated. Furthermore it contains two sulphur atoms which have little affinity for water dipoles.

Hydration of the zinc chelate is one of the main reasons why some of the chelating agents which gave rise to insoluble zinc compounds could not function as collectors. Another reason is that the bond between the zinc and those chelating agents possessing acidic groups, e.g. quinaldic and anthranilic acids is highly polar. This bond is therefore a source of hydrophilicity so that if the non-polar group is not sufficiently large a hydrophilic compound results.

Prolonged agitation with those chelating agents which acted as collectors resulted in a loss of hydrophobicity and the formation of the turbid supernatant solution. Infrared and chemical analysis of the colloidal solids demonstrated them to be the different zinc chelates which had been detached from the zinc oxide mineral surface. Similar findings have been described by Nagaraj and Somasundaran [108] who worked on the flotation of copper oxide minerals with Lix reagents. They showed that there was an optimum conditioning time for maximum flotation and that the flotation decreased at longer conditioning times.

The presence of zinc chelate on the zinc oxide mineral surface and colloidally dispersed in the aqueous solution indicates that a heterogeneous reaction takes place between the chelating agent and the zinc surface sites. For smithsonite this reaction can be represented as

$$ZnCO_{3(S)} + 2HA \rightleftharpoons ZnA_{2(S)} + CO_2 + H_2O \qquad 7.1$$

where HA is the chelating agent. Heterogeneous reactions involve many steps which can be summarised as

i) mass transfer of the chelating agents to the mineral surface

ii) adsorption at the mineral surface

iii) chemical reaction at the surface

iv) desorption of the zinc chelate compound

v) mass transfer of the zinc chelate compound away from the solid surface.

Whichever of these is the slowest will be the rate-controlling step. Steps (ii), (iii) and (iv) determine whether or not the overall process is selective and also whether or not the solid is hydrophobic. Obviously if stage (iv) is as rapid as (ii) and (iii) the solid will not remain hydrophobic for very long.

The abstraction of chelating agent by the zinc oxide minerals was dependent on the surface area and also the agitation rate. Dependency on area is consistent with both mass transfer and chemically controlled processes. An increase in abstraction rate with agitation rate, however, clearly indicates that the reaction was controlled by some mass transfer process. The parabolic shape of the uptake-time curves shows that as the reaction proceeded the build-up of an insoluble surface layer of zinc chelate prevented the mass transfer of chelating agent to the mineral surface. It seems probable therefore that the rate-controlling process in the abstraction of chelating agent is the removal or transfer of the reaction product away from the mineral surface.

All of the chelating agent was consumed because as the reaction product was removed from the mineral surface fresh sites became available for attack by the chelating agent. The rate of consumption, however, was dependent on the mineral and the reason must be related to the solubility of the mineral, the availability of surface zinc atoms and its crystallographic form. The exact nature of the relationship is however, not known.

Consideration of the structure of the insoluble zinc chelates shows that van der Waals forces are the main intermolecular forces present in these compounds with the exception of zinc-8-hydroxyquinolinate dihydrate where there is also the possibility of hydrogent bonding (109). The underlying mineral, however, has a polar surface which strongly interacts with water dipoles. This leads to the conclusion that the forces responsible for the adhesion of the insoluble zinc chelate to the mineral surface must be weak. The removal of the hydrophobic layer by mild shear is, therefore, not surprising.

In addition to a chemical reaction at the mineral/water interface with the chelating agent there is the possibility that some chelating agent is removed via reaction with soluble zinc. High chelating agent consumption by this route is, however, unlikely because considerable amounts of insoluble zinc chelate were found at the mineral/water interface by infrared spectrometry. Furthermore insoluble zinc chelate formed by precipitation in solution is unlikely to contribute to the hydrophobicity of the minerals at any stage during the conditioning process unless the mineral and precipitate surfaces are oppositely charged. The latter is unlikely in the presence of excess chelating agent and at high pH values.

Chemical reaction between the chelating agent and the zinc mineral will of course occur if the reaction product is more stable than the reactants. In this case for the reaction to proceed the zinc chelate must be more insoluble than the zinc mineral or zinc hydroxide. Comparison of the calculated solubilities of smithsonite, zinc hydroxide and the zinc chelates (Fig. 7.1 and

Appendix I) at different pH values shows that the zinc chelates are more insoluble than smithsonite. It is reasonable to assume that similar conclusions would be obtained with hemimorphite and willemite. Thermodynamically, therefore, spontaneous conversion of the zinc oxide minerals to the zinc chelate should occur when the minerals are immersed in aqueous solutions of the chelating agent.

The 'conventional' collector oleic acid should form zinc oleate when contacted with smithsonite and the other zinc oxide minerals. This is demonstrated by the position of the zinc oleate solubility curve relative to that of smithsonite and zinc hydroxide in Fig. 7.1. In practice, however, it is found that the reaction is incomplete and that the hydrophobic surface formed is much more stable than that obtained with the chelating agents. Similar conclusions are obtained if the interaction between fatty acids and the salt-type minerals is considered.

The reasons for the difference between the fatty acid and chelating agent systems are probably related to the structuring produced in the long chain carboxylate layer of hydrophobic bonding and the possibility of chemisorption. Several authors (25) (110) argue that a chemisorbed layer is formed when oleic acid interacts with minerals such as calcite and others (111) (112) have shown that the carboxylate uptake is consistent with the formation of calcium carboxylate. The evidence is, however, not conclusive. The interaction by hydrophobic bonding between a chemisorbed layer and carboxylate which has chemically reacted with the mineral cation

—·—·— Smithsonite
——— Zinc hydroxide
..... Zn-oleate
— — — Zn-8-hydroxyquinolinate
— — — — — Zn-2-metyl-8-hydroxyquinolinate
—·—·— Zn-dithizonate

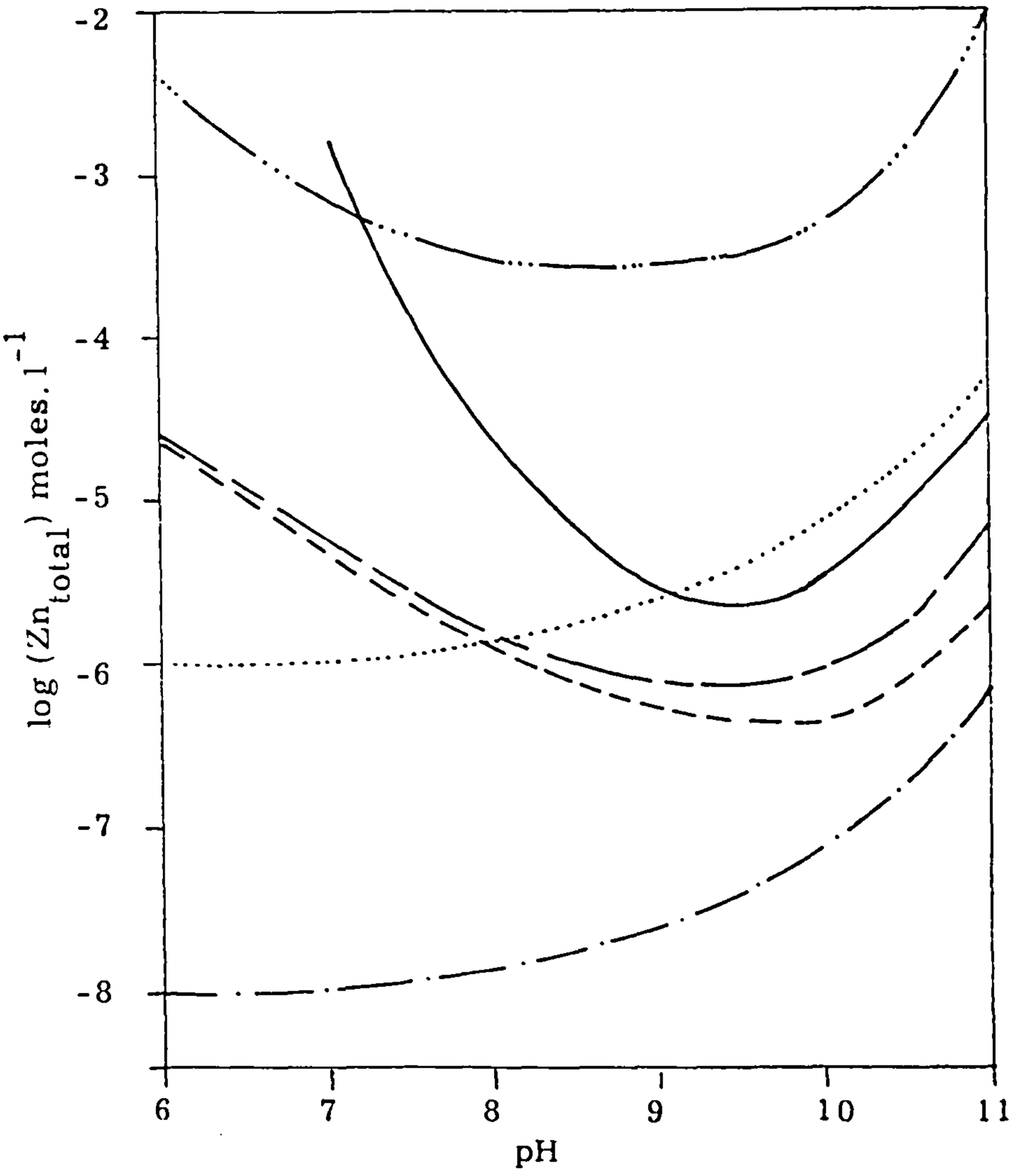


Fig. 7.1 Solubility diagram of the different chelates

would provide a mechanism by which the reacted material is bound to the surface. In the absence of a chemisorbed layer, however, the hydrophobic bonding contribution from the alkyl chains of the carboxylates must be the main reason for the stability of the carboxylate layers. No evidence was obtained in the present work that chelating agents were chemisorbed on the zinc oxide minerals.

Sulphidising the zinc oxide minerals should reduce the uptake of chelating agent because zinc sulphide is more stable than the zinc chelates. It follows therefore that results obtained with sphalerite should reflect those obtained from sulphidised zinc oxide minerals. This, however, was not the case.

The abstraction of 2MHQ decreased with the level of oxidation of the sphalerite surface but even after sulphidisation the amount consumed was equivalent to 43 monolayers. This is rather surprising and suggests that the sphalerite surface rapidly oxidises on immersion in water to produce sites at which the chelating agent can react. Additionally some chemisorption might also occur at -ZnS sites. The zinc chelate coating on sulphidised sphalerite was stable and unlike with the zinc oxide minerals no colloidal dispersion was observed in solution. This further suggests that chemisorption of the chelate might be involved.

Sulphidisation of the zinc oxide minerals did not result in a significant reduction in the abstraction of chelating agent except in the case of dithizone. This is surprising and suggests

that freshly sulphidised zinc oxide minerals are liable to immediate oxidation on removal of excess sulphide ions. Evidence that this was the case was demonstrated by the detection of sulphur oxyanions in the solution by ultra-violet spectrophotometry.

In summary a limited number of chelating agents can be used to render zinc oxide minerals hydrophobic. These reagents interact by a heterogeneous reaction which gives an insoluble, hydrophobic zinc chelate as one of the reaction products. Mild shear conditions remove the hydrophobic layer from the mineral surface so that it is no longer floatable. Although sulphidisation reduces the solubility of the minerals and the dosage of chelating agent required to give good flotation, the consumption of chelating agent is still very high.

CHAPTER 8

8 FLOTATION OF A SYNTHETIC ORE WITH ZINC CHELATING REAGENTS

8.1 Experimental Materials and Techniques

Synthetic ore The ore sample used was similar to that in Chapter 2.

Reagents Dithizone, 8- hydro xyquinoline and 2-methyl-8-hydroxyquinoline (Analar grade) were obtained from BDH and used without any previous purification. The dithizone was added as a solution in acetone. Dowfroth 250 was used as frother. All the solutions were freshly prepared before use.

Experimental Techniques

Batch Flotation Tests All the flotation tests were conducted under the same experimental conditions as those described in Chapter 2. The ore was ground for 7 min. and the product was 95% finer than 150 um. The average grade of the synthetic ore was $17 \pm 0.1\%$ Zn. In those tests where the ore was sulphidised prior to flotation, sodium sulphide was added before the collector solution or kerosene emulsion containing the collector. Sulphidisation times of 30 min. at pH 10.0 were used to ensure the total consumption of sulphide ions, since excess sulphide ions act as a depressant. All sulphidisation tests were carried out with 600 gt^{-1} of $Na_2S.9H_2O$. Conditioning times of 10 minutes were used with the collector solution.

8.2 Results

The effect of pH on the flotation of the synthetic ore is shown in Fig. 8.1. The best concentrate grade was obtained between pH 10.0-10.5, but despite the high dosages of dithizone used, recoveries were low. From this curve a flotation pH of 10.0 was chosen for all future experiments. Increasing the dithizone dosage to 2 Kg t^{-1} increased the zinc recovery to 42% and this is reflected in the results in Table 8.1. Attempts to increase the recovery by the addition of a collector of emulsified dithizone in a non-polar oil (kerosene) and by sulphidising the sample prior to collector addition only met with partial success. Addition of the collector emulsion produced a slight increase in recovery at collector dosages of 0.50 and 1.0 Kg t^{-1}. At lower dosages however, the kerosene suppressed the froth so that a lower recovery was obtained. Sulphidisation of the ore prior to collector addition also increased the zinc recovery, although not substantially (see column 3 in Table 8.1). The joint action of sulphidisation followed by the addition of emulsified collector demonstrated the best results.

8-Hydroxyquinoline and 2-methyl-8-hydroxyquinoline were not effective collectors of zinc oxide minerals.

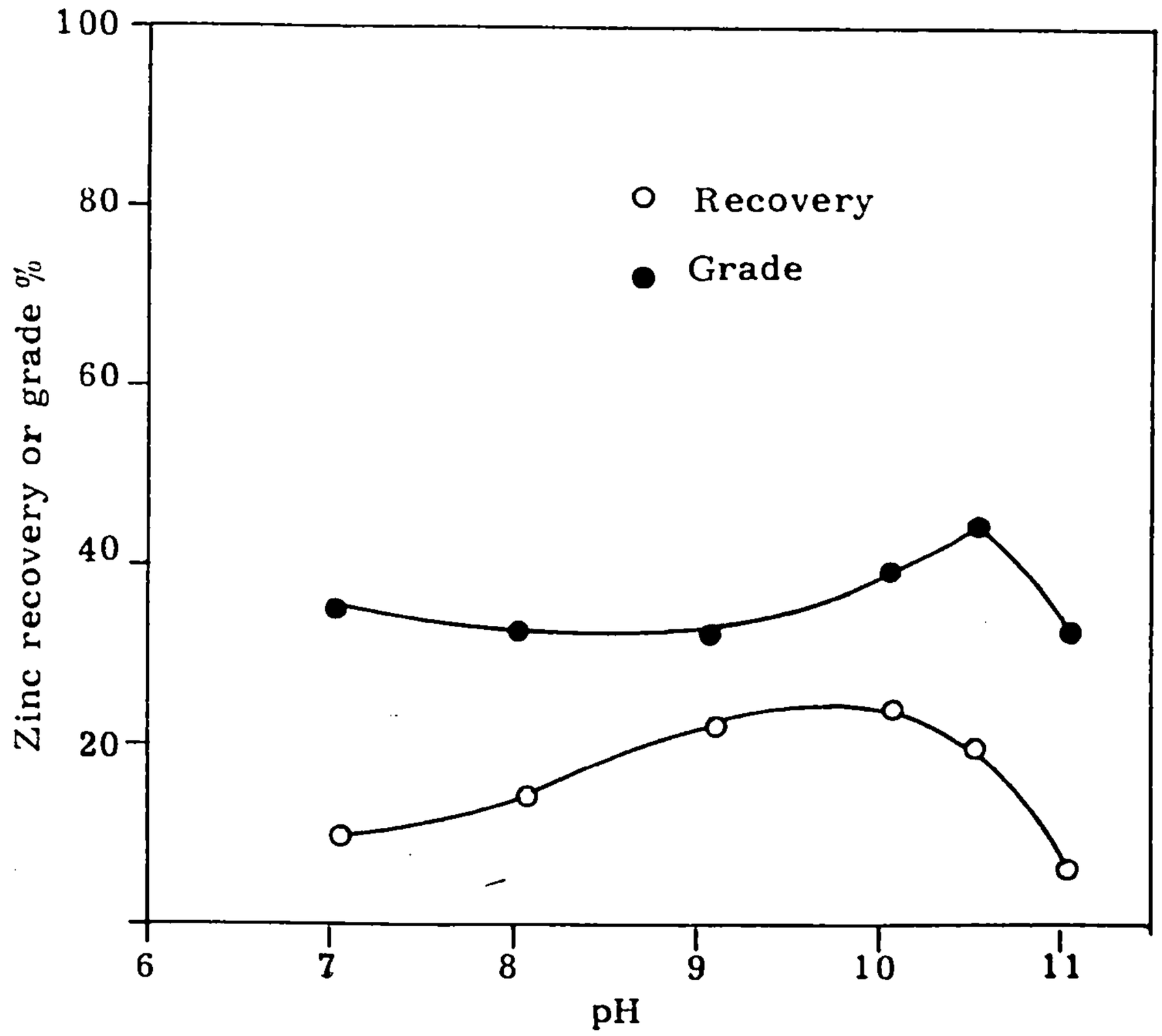


Fig. 8.1 Effect of pH on the flotation of zinc oxide minerals with dithizone

TABLE 8.1 FLOTATION OF ZINC OXIDE MINERALS WITH DITHIZONE UNDER DIFFERENT CONDITIONS

Dithizone dosage Kg t^{-1}	1		2		3		4	
	Grade	Recovery	Grade	Recovery	Grade	Recovery	Grade	Recovery
0.20	36.2	14.4	43.3	8.6	37.2	26.0	37.1	24.0
0.50	31.0	17.0	38.3	24.8	36.0	25.0	37.7	37.7
1.00	38.7	28.0	32.5	29.1	38.7	35.3	34.8	47.0
2.00	41.8	42.0	32.5	40.0	37.0	40.0	34.9	52.0

Columns:

1 , Flotation of the zinc ore with dithizone

2 Flotation of the zinc ore with an aqueous emulsion containing kerosene (1kg t^{-1}) and dithizone

3 Flotation of the zinc oxide minerals with dithizone after a previous sulphidisation step

4 Joint action of sulphidisation and kerosene emulsion on the flotation with dithizone.

Discussion

The flotation results obtained with the chelating agents emphasize that although dithizone and 2MHQ are selective toward zinc oxide minerals in the Hallimond tube they cannot be used as collectors in a conventional laboratory cell. The collector layer of zinc chelate on the minerals is weakly attached so that under the shear conditions that prevail in a cell i.e. high agitation rate and high pulp density the collector layer is removed. This was specially true with 2MHQ.

Attempts to improve the stability of the collector layer or to reduce the consumption of chelating agent by sulphidising the minerals and adding a non-polar oil were only partially successful. Furthermore reducing the shear in the cell by reducing the impeller speed only slightly improved the recovery with dithizone. It would, therefore, appear that flotation with chelating agents containing a small hydrophobic group is not likely to be successful.

If the chelating agents are to be used to float zinc oxide minerals a method must be found to improve the stability of the collector layer and to reduce reagent consumption. Clearly sulphidisation is unsuccessful although bulk zinc sulphide is more insoluble than the appropriate zinc chelate. A possibility might be to increase the size of the hydrophobic group in the chelating agent so that hydrophobic bonding exists within the collector layer. However, too great an increase would result in a loss of selectivity because the reagent would behave like a long chain electrolyte.

CHAPTER 9

9 SUMMARY AND CONCLUSIONS

The flotation of the zinc oxide minerals, smithsonite, willemite and hemimorphite with zinc chelating agents has been studied and the results have been compared to those obtained with conventional collectors. Measurements have been made of the solubility of the zinc oxide minerals, their electrokinetic characteristics and their interaction with dodecylamine and various zinc chelating agents. The nature of the collector layer on the zinc minerals has been investigated.

As a result of these studies the following conclusions can be made:

1 Zinc oxide minerals are readily floated with conventional-type collectors such as oleic acid and long-chain alkylamines but the selectivity is poor.

2 The most selective conventional-type collectors are the long-chain alkylamines after a sulphidisation step, however, the concentrate grades are still not good.

3 The solubility of zinc oxide minerals in aqueous solutions increases in the order hemimorphite, willemite and smithsonite, and the zinc content in solution is dependent on the initial pH value. Equilibrium is established after about 7 days.

4 The zinc oxide minerals are amphoteric and they consume OH^- ions at high pH values and H^+ ions at low pH values. An equilibrium pH is attained within 1 day and is independent of the initial pH but dependent on the mineral. Equilibrium pH values for smithsonite, hemimorphite and willemite are 7.6; 8.7 and 7.0 respectively.

5 The abstraction of H^+ and OH^- ions by zinc oxide minerals can be attributed to the different dissolution mechanisms at high and low pH values and also to the adsorption of these ions at the mineral/water interface.

6 Smithsonite tends to hydroxylate at pH values above 9.0 to form a surface similar to that of hydrozincite. This probably accounts for the solubility being lower than that theoretically predicted.

7 Sulphidisation decreases the solubility of smithsonite, the soluble zinc content being reduced below 1 ppm. The solubility of sulphidised smithsonite is independent of the initial pH but, unlike unsulphidised smithsonite, the equilibrium pH is not. Sulphidisation does not have a marked effect on the solubility of hemimorphite.

8 All three zinc oxide minerals exhibit negative electrophoretic mobilities between pH values of

5.5 and 11.0. This probably due to the preferred adsorption of anionic species such as, OH^-, $Zn(OH)_3^-$ and $Zn(OH)_4^{-2}$ than that of cationic ones i.e. Zn^{+2}, $Zn(OH)^+$ and H^+.

9 Sulphidisation of the zinc oxide minerals increases their negative electrophoretic mobilities, especially in the case of smithsonite. This is associated with two effects: specific adsorption of sulphide ions into the electrical double layer and chemical reaction of sulphide ions with the zinc sites on the mineral surface.

10 Both smithsonite and hemimorphite consume HS^- ions via a heterogeneous chemical reaction. The former being much more reactive than the latter.

11 In the presence of dodecylamine the negative electrophoretic mobility of the zinc oxide minerals is reduced to zero and then made positive. The adsorption is consistent with the generally accepted theory of long chain electrolytes adsorption by oxides and silicates.

12 Sulphidisation increases the adsorption of amine by the zinc oxide minerals because of an increase in coulombic attraction between the amine and the sulphidised surface.

13 8-Hydroxyquinoline, 2-methyl-8-hydroxyquinoline, dithizone and Lix 65N function as collectors for the zinc oxide minerals in the Hallimond tube.

These reagents correspond to those which react with zinc ions to form hydrophobic zinc chelates, as determined by two-liquid flotation tests.

14 Chelating agents which form soluble zinc complexes or give rise to hydrophilic precipitates do not function as collectors for zinc oxide minerals.

15 The chelating agents which function as collectors exhibit different collecting abilities depending on the degree of hydration of their respective zinc chelates. Their collecting efficiency increases in the order 8HQ, 2MHQ, dithizone, Lix 65N. Lix 65N is, however, unselective and also collects calcium minerals.

16 The chelating agents which function as collectors interact with the zinc oxide minerals by a heterogeneous chemical reaction. The product of this reaction is the insoluble zinc chelate which remains loosely attached to the mineral surface. Excessive shear, however, detaches the layer which gives rise to a loss of hydrophobicity and the presence of colloidal zinc chelate in the supernatant solution. The driving force for the reaction is that the solubilities of the zinc chelates are lower than that of the zinc oxide minerals.

17 The zinc oxide minerals consume all the chelating reagent from solution but the rate of consumption is

dependent on the mineral. The consumption rate increases in the order: hemimorphite, willemite and smithsonite.

18 'Fresh' sphalerite reacts with 2MHQ to give multilayers of zinc chelate which are firmly held to the surface.

19 Previous sulphidisation of zinc oxide minerals does not result in a significant reduction in the abstraction of zinc chelating reagent possibly because of the rapid reoxidation of the sulphidised layer when immersed in water.

20 Under the shear conditions that prevail in a laboratory flotation cell the chelating agents give rise to good concentrate grades but poor recoveries. It would therefore appear that chelating agents cannot be used to float zinc oxide minerals unless some way is found to increase the stability of the collector layer and to reduce the reagent consumption.

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APPENDIX I SOLUBILITY CALCULATIONS OF THE DIFFERENT ZINC CHELATES

1 Solubility of Zinc-8-hydroxyquinolinate, ZnA_2

To determine a mathematical equation which gives account of the solubility of zinc-8-hydroxyquinolinate the following equilibria must be considered.

$$ZnA_{2(s)} \rightleftharpoons Zn^{+2} + 2A^- \qquad A.1$$

$$K_s = (Zn^{+2})(A^-)^2 = 10^{-21.23} \qquad A.2$$

Depending on the pH Zn^{+2} ions can undergo hydrolysis according to equations 3.16-3.19. Therefore, the dissolution of zinc-8-hydroxyquinolinate (S) can be described by the following equation

$$S = (Zn^{+2}) + (ZnOH^+) + (Zn(OH)_3^-) + (Zn(OH)_4^{-2}) \qquad A.3$$

and substituting from equations 3.16 to 3.19

$$S = (Zn^{+2})\,(1 + \beta_1(OH^-) + \beta_3(OH^-)^3 + \beta_4(OH^-)^4) \qquad A.4$$

The dissolution of ZnA_2 releases 8-hydroxyquinolinate anions (A^-) which in turn undergo hydrolysis as follows.

$$HA \xrightleftharpoons{H_2O} H^+ + A^- \qquad K_{HA} = 10^{-9.66} \qquad A.5$$

$$H_2A \rightleftharpoons H^+ + HA \qquad K_{H_2A} = 10^{-5.00} \qquad A.6$$

The solubility of zinc-8-hydroxyquinolinate can also be described by the sum of the different 8-hydroxyquinoline species in solution.

$$S = (HA) + (H_2A^+) + (A^-) \qquad A.\ 7$$

From equations A. 5 and A. 6.

$$S = (A^-)\left(1 + \frac{(H^+)}{K_{HA}} + \frac{(H^+)^2}{K_{HA}\cdot K_{H_2A^+}}\right) \qquad A.8$$

and

$$(A^-) = \frac{S}{1 + \frac{(H^+)}{K_{HA}} + \frac{(H^+)^2}{K_{HA}\cdot K_{H_2A^+}}} \qquad A.9$$

Substituting in equation A.2.

$$(Zn^{+2}) = \frac{K_s}{S^2}\left(1 + \frac{(H^+)}{K_{HA}} + \frac{(H^+)^2}{K_{HA}\cdot K_{H_2A^+}}\right) \qquad A.10$$

Introducing equation A. 10 in equation A. 4 gives an expression for the solubility of zinc-8-hydroxyquinolinate as a function of the pH.

$$S^3 = K_s\left(1 + \frac{(H^+)}{K_{HA}} + \frac{(H^+)^2}{K_{HA}\cdot K_{H_2A^+}}\right)^2 \left(1 + \beta_1(OH^-) + \beta_3(OH^-)^3 + \beta_4(OH^-)^4\right)$$

$$A.11$$

2 Solubility of zinc-2-methyl-8-hydroxyquinolinate, $Zn(MA)_2$

Similar to zinc-8-hydroxyquinolinate, a mathematical expression describing the variation of the solubility of $Zn(MA)_2$ with pH can be obtained. In this case the following equilibria are considered.

$$Zn(MA)_{2(s)} \rightleftharpoons Zn^{+2} + 2MA^- \qquad A.12$$

$$K_s = (Zn^{+2})(MA^-)^2 = 10^{-22.72} \qquad A.13$$

$$HMA \xrightleftharpoons{H_2O} H^+ + MA^- \qquad K_{HMA} = 10^{-10.31} \qquad A.14$$

$$H_2MA^+ \rightleftharpoons H^+ + HMA \qquad K_{H_2MA^+} = 10^{-5.54} \qquad A.15$$

The solubility of $Zn(MA)_2$ is given by the following equation,

$$S^3 = K_s \left(1+\frac{(H^+)}{K_{HMA}} + \frac{(H^+)^2}{K_{HMA}\cdot K_{H_2MA^+}}\right)^2 \left(1 + \beta_1(OH^-) + \beta_3(OH^-)^3 + \beta_4(OH^-)^4\right) \qquad A.16$$

3 Solubility of Zinc Dithizonate, $Zn(HDz)_2$

In the case of zinc dithizonate no experimental solubility product constant value was found in the literature, however, a theoretical value can be obtained by using the following equation.

$$(Zn^{+2})\,(HDz^{-})^{2} = K_s = K^{2}_{H_2Dz} / \beta_2 = 10^{-24.09} \qquad A.17$$

where K_{H_2Dz} is the dissociation constant of dithizone and its value is $10^{-4.52}$. β_2 corresponds to the overall formation constant of the zinc dithizonate and is equal to $10^{15.05}$.

Thus, the theoretical expression of the solubility of zinc dithizonate at different pH values is given by

$$S^3 = K_s\left(1+\frac{(H^+)}{K_{H_2Dz}}\right)^2\left(1 + \beta_1(OH^-) + \beta_3(OH^-)^3 + \beta_4(OH^-)^4\right) \qquad A.18$$

4 Solubility of Zinc Oleate, $Zn(Ol)_2$

The solubility of zinc oleate is calculated by the following expression

$$S^3 = K_s\left(1 + \frac{(H^+)}{K_{HOl}}\right)^2 \left(1 + \beta_1(OH^-) + \beta_3(OH^-)^3 + \beta_4(OH^-)^4\right) \qquad A.19$$

where K_s is the solubility product constant of zinc oleate and is equal to 10^{-18}. K_{HOl} is the dissociation constant of oleic acid which is equal to $10^{-5.02}$.