

THE ACTION OF SODIUM SILICATE
ON THE FLOTATION OF SALT-TYPE
MINERALS WITH OLEIC ACID.

A thesis submitted for the degree of
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by

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To my parents

ABSTRACT

A study has been made of the depression of the fatty acid flotation of fluorite, barite and calcite with sodium silicates of different silica to soda ratios. The investigation included measurements of the solubility and electrokinetic properties of the minerals in the presence of oleic acid and sodium silicate. The results obtained have been critically compared with those quoted in the literature and the mechanism of oleate and silicate adsorption has been elucidated.

The solubility of the minerals followed that predicted by solution equilibria data. Sodium oleate decreased the dissolution rate of calcite and fluorite by forming a layer of calcium oleate on the minerals' surface. Sodium silicate decreased the solubility of the minerals because of the adsorption of silicate species.

The IEP of barite and fluorite occurred at pH 4.5 and 9.5, respectively and calcite was negatively charged over the pH range studied (pH > 9.0). Sodium oleate and sodium silicate increased the negative electrophoretic mobility of the minerals at high concentrations at pH 10.0.

Oleic acid was abstracted by the minerals by a chemical reaction resulting in the formation of a new phase of calcium or barium oleate. The flotation recovery of the minerals closely followed the amount of oleate abstracted by the minerals. Maximum flotation and abstraction of oleate occurred at pH values 7 - 12 and 9 - 12 for barite and calcite/fluorite, respectively. Sodium silicate depressed the flotation of fluorite and barite at pH values above 9 and below 7 and that of calcite in the pH region 8 - 12. This corresponded to the conditions where sodium silicate reduced the abstraction of oleate.

The adsorption of silica on calcite, barite and fluorite is

considered to be through interaction of the Si(OH)_4 and SiO(OH)_3^- species with the cationic surface sites resulting in the formation of a surface calcium or barium silicate. Carbonate interacts with the same cationic sites and so in the presence of excess carbonate the adsorption of silica by barite and fluorite is reduced. The addition of aluminium chloride increased the adsorption of silica species on calcite and barite. Precipitation of aluminium hydroxide on the mineral surface and the formation of aluminosilicate ions at pH values below and above 9, respectively, are suggested as reasons for the increased silica adsorption.

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CHAPTER 1. PRESENT KNOWLEDGE ON THE FLOTATION OF SALT-TYPE MINERALS

1.1. Introduction

Salt-type minerals are characterised by solubilities which are higher than most oxides and silicates but lower than simple salt minerals like halite and sylvite. Minerals in this category include calcite, barite, fluorite, apatite, and scheelite. Separation of these minerals by flotation, when they occur together, is difficult because of similarities in their surface chemical properties. Fatty acids and their alkali soaps are commonly used as collectors but without the addition of modifying agents little or no selectivity is obtained.

Although the literature on the flotation of salt-type minerals is voluminous there is still much that is unknown about the interaction of the various reagents with the minerals. This is especially true with regard to the use of modifying agents such as quebracho and sodium silicate. Why selectivity is obtained when these reagents are added has not been adequately investigated.

1.2. Properties of salt-type minerals

1.2.1. Crystal structure

The general formula of salt-type minerals is given by M_xA_y , where M represents a cation of valence y and A an anion of valence x. The

most common minerals are salts of alkaline earth metals and in these M can be Ca^{2+} , Mg^{2+} , Ba^{2+} , Sr^{2+} etc. and A one of the following anions: F^- , SO_4^{2-} , CO_3^{2-} , WO_4^{2-} , PO_4^{3-} . The carbonates of iron and manganese also belong to this group.

The simplest structure is possessed by fluorite. In fluorite, CaF_2 , which is crystallized in the cubic system, the calcium ions are located at the corners and face centres of the cube unit cell while the fluoride ions are located at the centres of each cubelet that results from the eight-fold division of the unit cell. Each calcium ion is, therefore, coordinated to eight neighbouring fluoride ions at the corner of a cube and each fluoride ion is, in turn, coordinated to four calcium ions. This structure with a unique 8:4 coordination, is characterised by the most probable cleavage occurring along the (111) plane located between two fluoride layers. The unit cell of fluorite is given in fig. 1.1a.

The crystal structure of carbonates, sulfates, tungstates, and phosphates is more complex than that of fluorite. In this case, the cations are ionically bonded to anionic radicals which, in turn, are composed of more than one metallic or non-metallic species strongly bonded to each other by mixed ionic and covalent forces. Calcite, the most common of the carbonates, possesses a rhombohedral structure with the calcium ions located at the corners and the carbonate ions at the centre and edges of the unit cell (fig. 1.1b).

Sulphates and tungstates are characterised by tetrahedral coordination of the hexavalent ions with the oxygen of SO_4^{2-} or WO_4^{2-} . The difference between the two species is that the coordination of SO_4^{2-} is symmetrical whereas that of WO_4^{2-} is not. Barite, BaSO_4 , possesses an orthorhombic structure with the cations in twelve-fold coordination

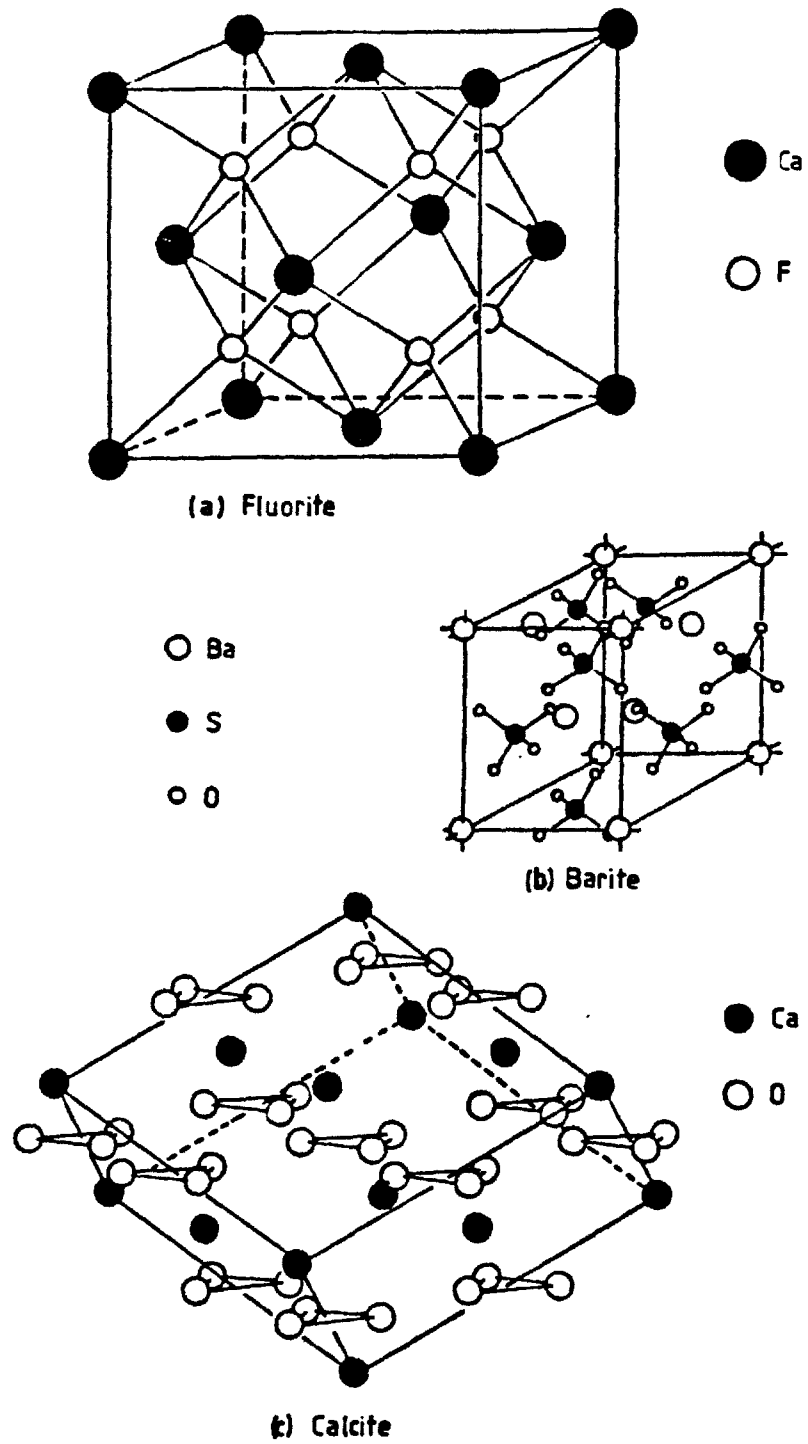


Fig. 1.1. Crystal structure of (a) fluorite (1),
(b) barite (2) and (c) calcite (3).

with the oxygen of the sulphate groups (fig. 1.1c). The cleavage occurs along the (001) and (201) planes.

The crystal structure of phosphates is much more complex mainly due to the extensive substitutions of the components of the crystal lattice by many ions. In spite of their complexity phosphate minerals have been studied in detail because of their commercial as well as biological relevance, and their crystal structure has been well established (4,5).

The surface properties of these minerals must in some way reflect the composition of the mineral and the crystal structure. The arrangement of atoms in the cleavage planes of fluorite (111), calcite (10T1) and barite (001) is given in fig. 1.2. The distribution of the uncompensated charges is more uniform in the case of fluorite than the other two minerals and this results in a stronger electrostatic field on the surfaces of the latter two minerals. The surface energy is lower on the cleavage planes than it is on the other planes. Thus, in the case of fluorite, values of 543 and 1082 erg/cm² have been obtained for the (111) and (110) planes respectively (7). Variations in the surface energy result from any perturbation of the periodic pattern of the crystal lattice produced by the presence of lattice defects or impurities or even the abrupt ending and rearrangement of the lattice at the surface.

Deviations of the crystal lattice from the ideal structure can be estimated by electrophysical methods. Parameters such as Fermi level or concentration ratio of the charge carriers, p/n , have been found to reflect such deviations and have been correlated with the flotation and electrostatic response of certain minerals. Plaksin et al (8) and Carta et al (9, 10) have studied the flotation of calcite,

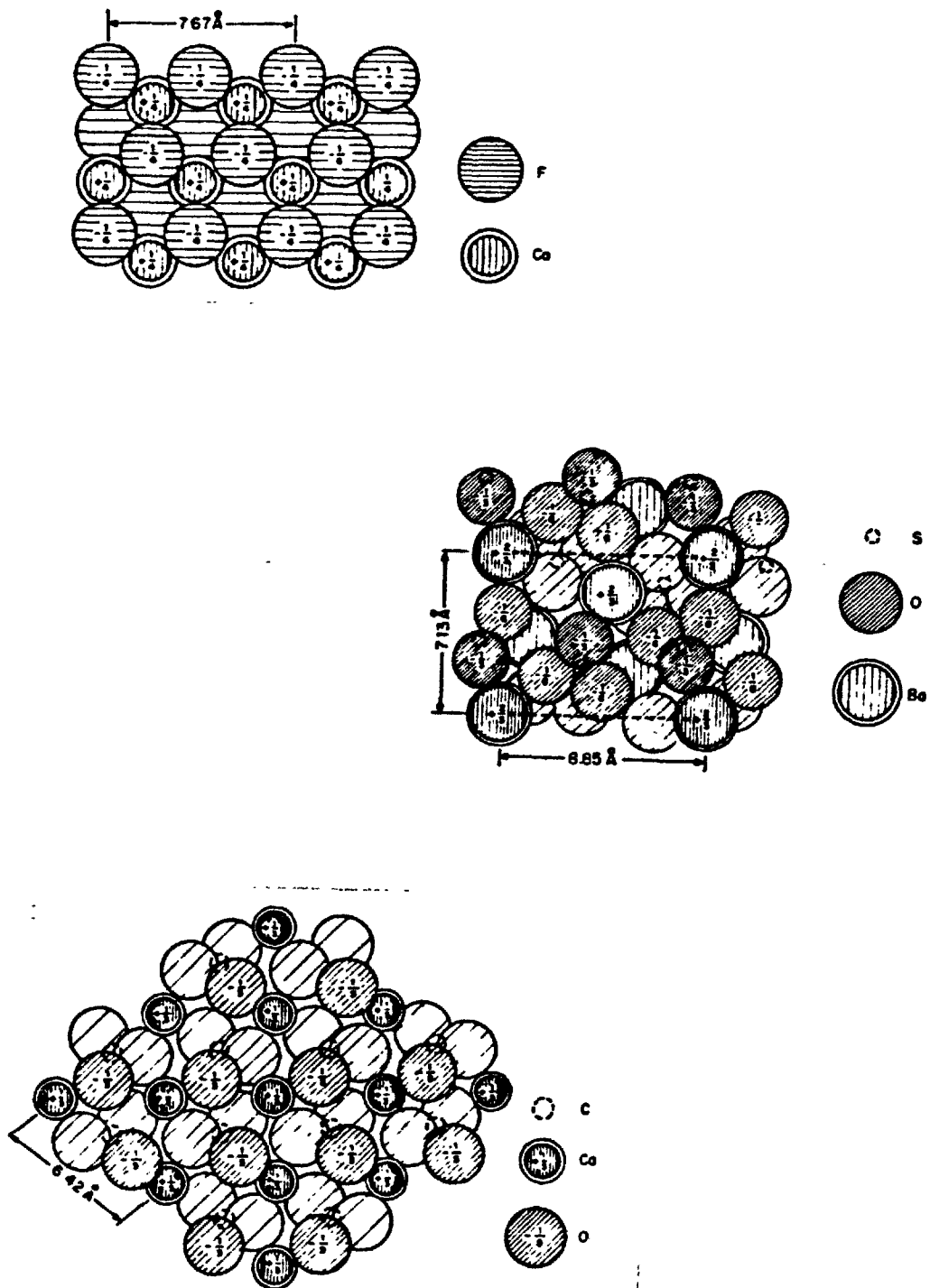


Fig. 1.2. Surface structures of (a) fluorite (111),
(b) barite (001) and (c) calcite (10T1) faces, (6).

barite and fluorite after subjecting the minerals to such treatments as X-ray or γ -irradiation, ionic bombardment, heating, dry or wet grinding and grinding in the presence of oxidising agents (e.g. H_2O_2). The latter authors showed that in the anionic flotation of these minerals with sodium oleate separation of fluorite from barite and the latter from calcite was easily achieved after heating the minerals in the absence of the collector. This was attributed to the fact that the Fermi level of the p-type semiconductor barite increases while that of the n-type semiconductors calcite and fluorite decreases on heating thus promoting the adsorption of the collector anion.

1.2.2. Solubility

The solubility of minerals in water is of considerable importance from the point of view of flotation because it is the predominant factor which determines both the composition of the aqueous phase and the charge characteristics of the solid/liquid interface.

The dissolution of solids, such as the salt-type minerals, can be represented by an equilibrium of the type:



for which the equilibrium constant, K_{sp} , known as the solubility product is given by:

$$K_{sp} = a_{M^{y+}}^x \cdot a_{A^{x-}}^y = \gamma_{M^{y+}}^x \cdot \gamma_{A^{x-}}^y [M^{y+}]^x [A^{x-}]^y \quad (1.2)$$

where a represents the activities, square brackets the concentrations in moles l^{-1} and γ the activity coefficients. For simple salts the solubility can be taken as equal to the concentration of the cation or anion in solution and can, therefore, be calculated from the solubility product. For complex salts, however, complexation and hydrolysis of one of the ions has a marked effect on the solubility. It is probable

that in a number of determinations of the solubility products of the salt-type minerals not all the reactions have been considered, neither have the effects of ionic strength and the particle size. This would account for the wide range of solubility products quoted in the literature. To illustrate this point, data for some salt-type minerals is given in Table 1.1.

Table 1.1. Solubility products of some salt-type minerals

Mineral	Formula	K_{sp}	Ref.
Aragonite	CaCO_3	6.3×10^{-9}	(12)
Barite	BaSO_4	$1.1-15.0 \times 10^{-10}$	(12)
Calcite	CaCO_3	$4.7-6.6 \times 10^{-9}$	(11), (12)
Fluorite	CaF_2	$4.0-17.0 \times 10^{-11}$	(11), (12)

Other factors which can affect the solubility of some minerals are grinding and the presence in solution of ions which can undergo reaction with the cation or anion. It is well known that when calcite is dry ground the surface can be converted to calcium oxide with the evolution of CO_2 (13). Partial transformation into aragonite and vaterite (14 - 16) has also been reported. Furthermore, it has been shown that in the presence of dissolved CO_2 the surface of fluorite can be converted to calcium carbonate at alkaline pH values (17 - 21).

The solubility of the salt-type minerals at different pH values can be calculated and allowance made for the hydrolysis of the cation and anion. The equilibria involved in the dissolution of calcite are as follows:

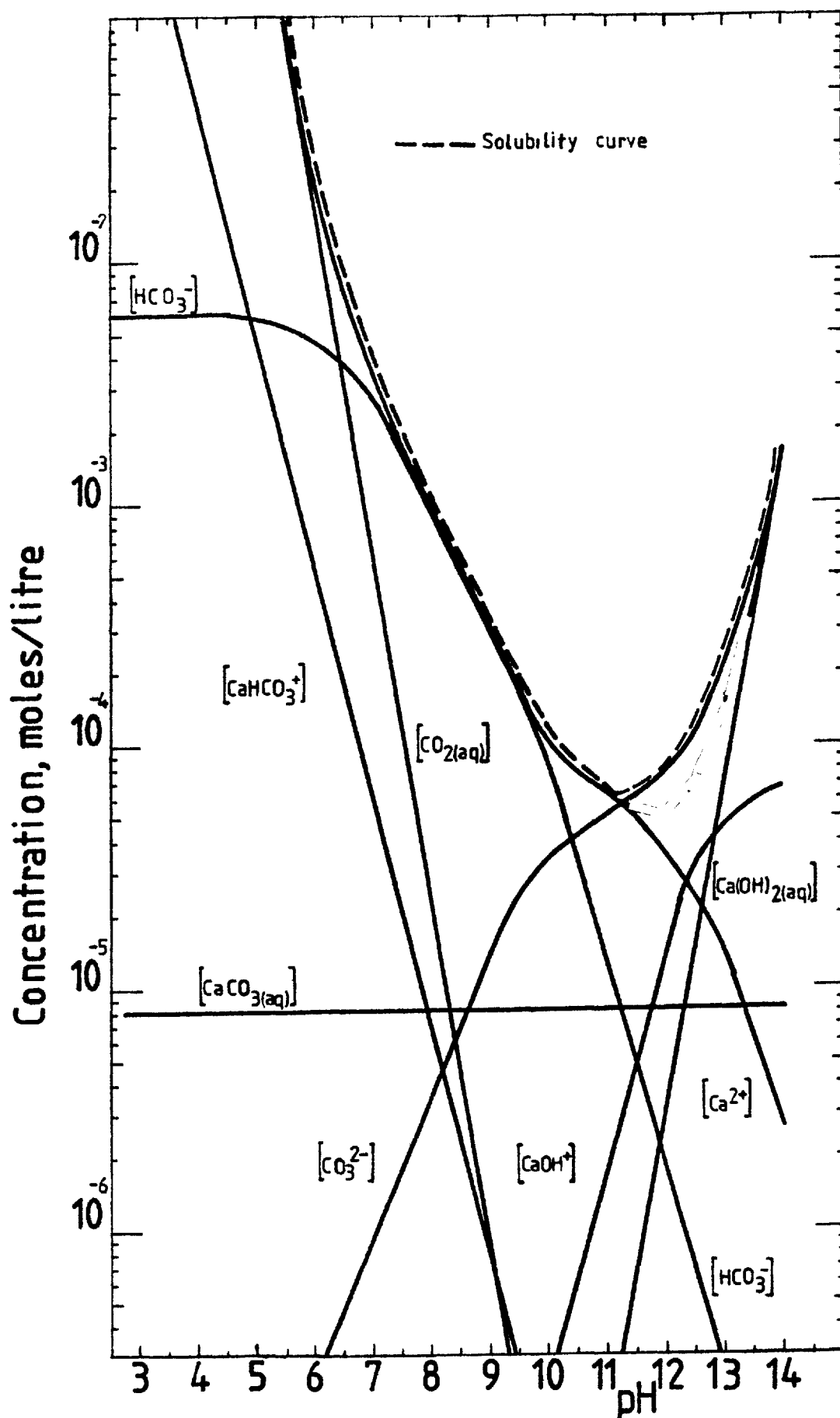


Fig. 1.3. Distribution of calcium and carbonate species in a solution saturated with calcite and solubility of calcite as a function of pH (system closed to the atmosphere, $p_{\text{CO}_2} = 0$).

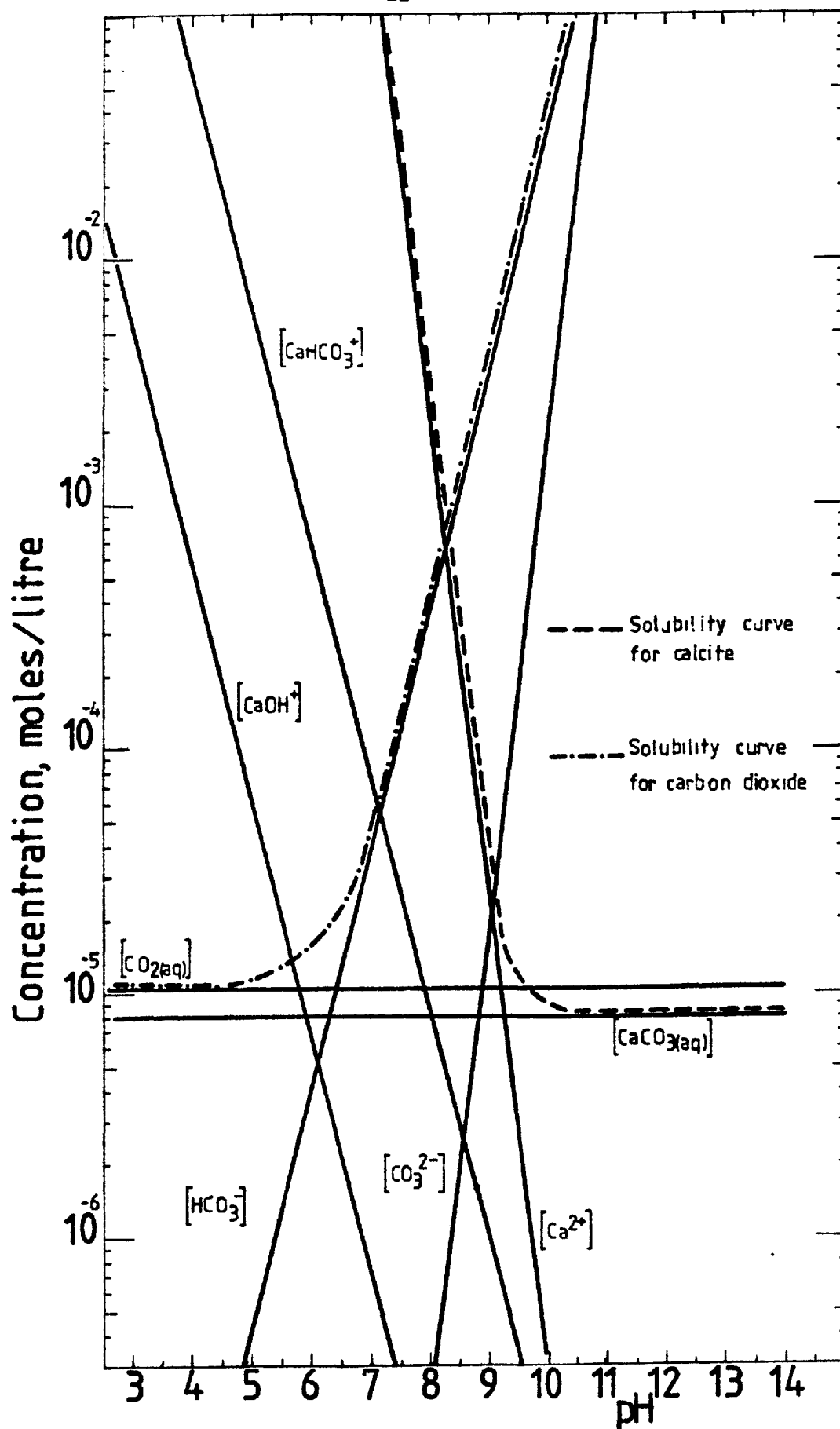
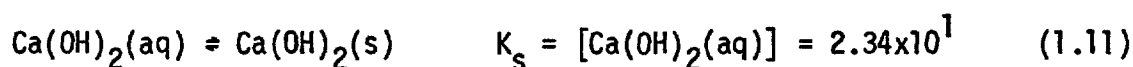
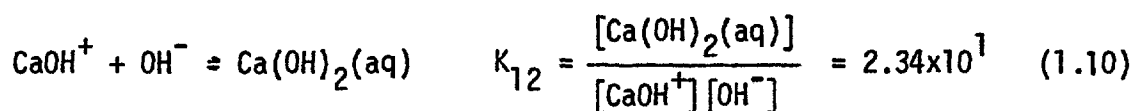
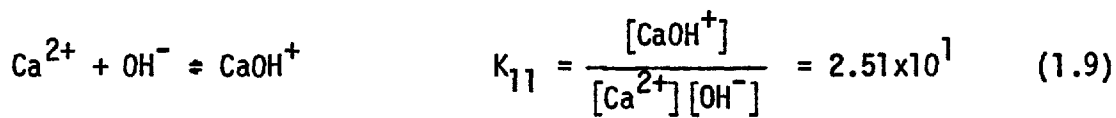
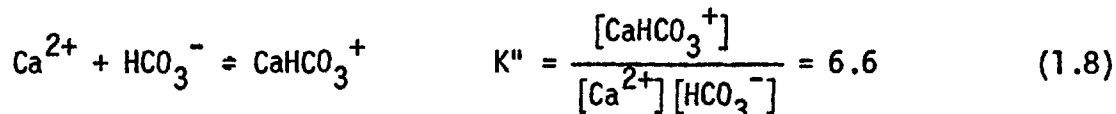
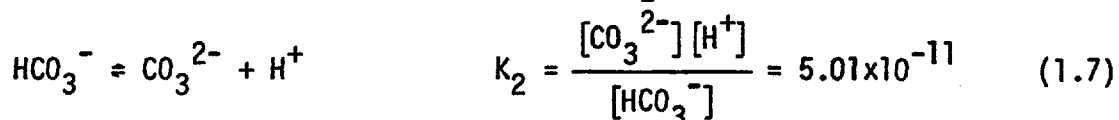
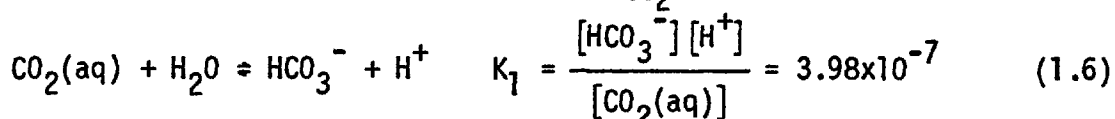
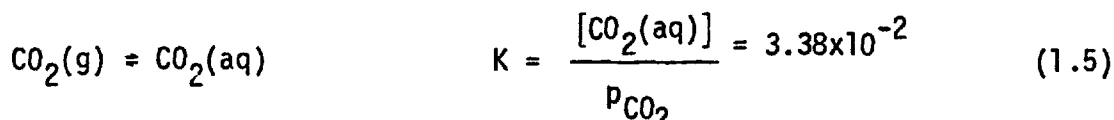
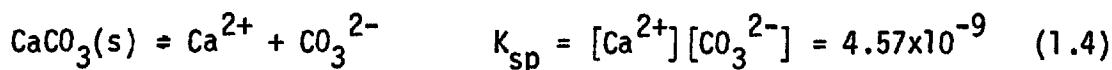
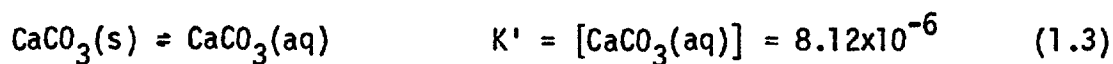


Fig. 1.4. Distribution of calcium and carbonate species in a solution saturated with calcite and solubility of calcite and carbon dioxide as a function of pH (system open to the atmosphere, $p_{CO_2} = 3 \times 10^{-4}$ atm).

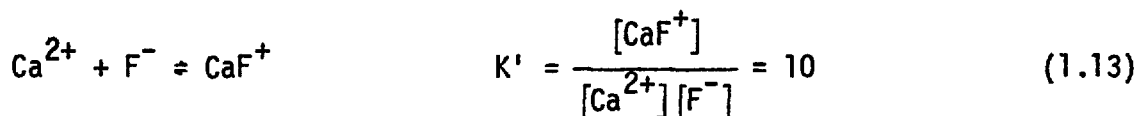
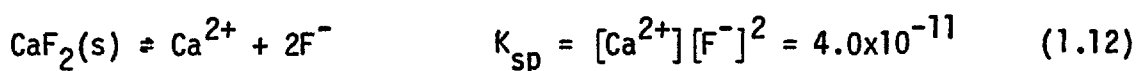


The equilibrium constants were obtained from refs. 11, 12 and 22. In a closed vessel with no space above the liquid equilibrium (1.5) does not apply and by using the rest of the equilibria and the appropriate mass and charge balances the solubility and distribution diagram shown in fig. 1.3 is obtained. Under these conditions calcite exhibits a minimum solubility at pH 11.5 and above this value the solubility increases because of the formation of calcium hydroxy species. Below pH 11.5 the formation of bicarbonate and soluble carbon dioxide increases the solubility.

In an open vessel calculation of the solubility becomes rather

indeterminate since the partial pressure of CO_2 above the solution determines the amount of soluble CO_2 . The air currents above the vessel, the rate of reaction, and the geometry of the vessel will all affect p_{CO_2} at the surface of the solution. True equilibrium will be reached only when the soluble CO_2 is in equilibrium with the partial pressure of CO_2 in the atmosphere ($10^{-3.5}$ atm). Reference to equilibrium (1.5) and fig. 1.3 shows that this is obtained at a pH of approximately 8.3. The escape of CO_2 from the solution will produce a higher solubility than that obtained in a closed vessel, at pH values below 8.3. Above this value the increased solubility of CO_2 , due to the formation of HCO_3^- and CO_3^{2-} ions, will exert a common ion effect so that a lower calcite solubility is obtained. These effects are demonstrated qualitatively in fig. 1.4. To make these calculations it was assumed that the soluble CO_2 was that in equilibrium with a fixed $p_{\text{CO}_2} = 10^{-3.5}$ atm according to equilibrium (1.5).

The distribution and solubility diagram for fluorite is shown in fig. 1.5. Between pH 5 and 11 the solubility of CaF_2 can be predicted from the solubility product assuming that the mineral is a simple salt of a strong acid and strong base. At pH values below 5, however, the F^- hydrolysis to form HF and HF_2^- and this increases the solubility. The HF concentration exceeds that of F^- at pH values below 3. An increase in solubility at pH values above 12 is obtained because of the formation of calcium hydroxy species. The equilibria used to obtain this diagram are (11, 12):



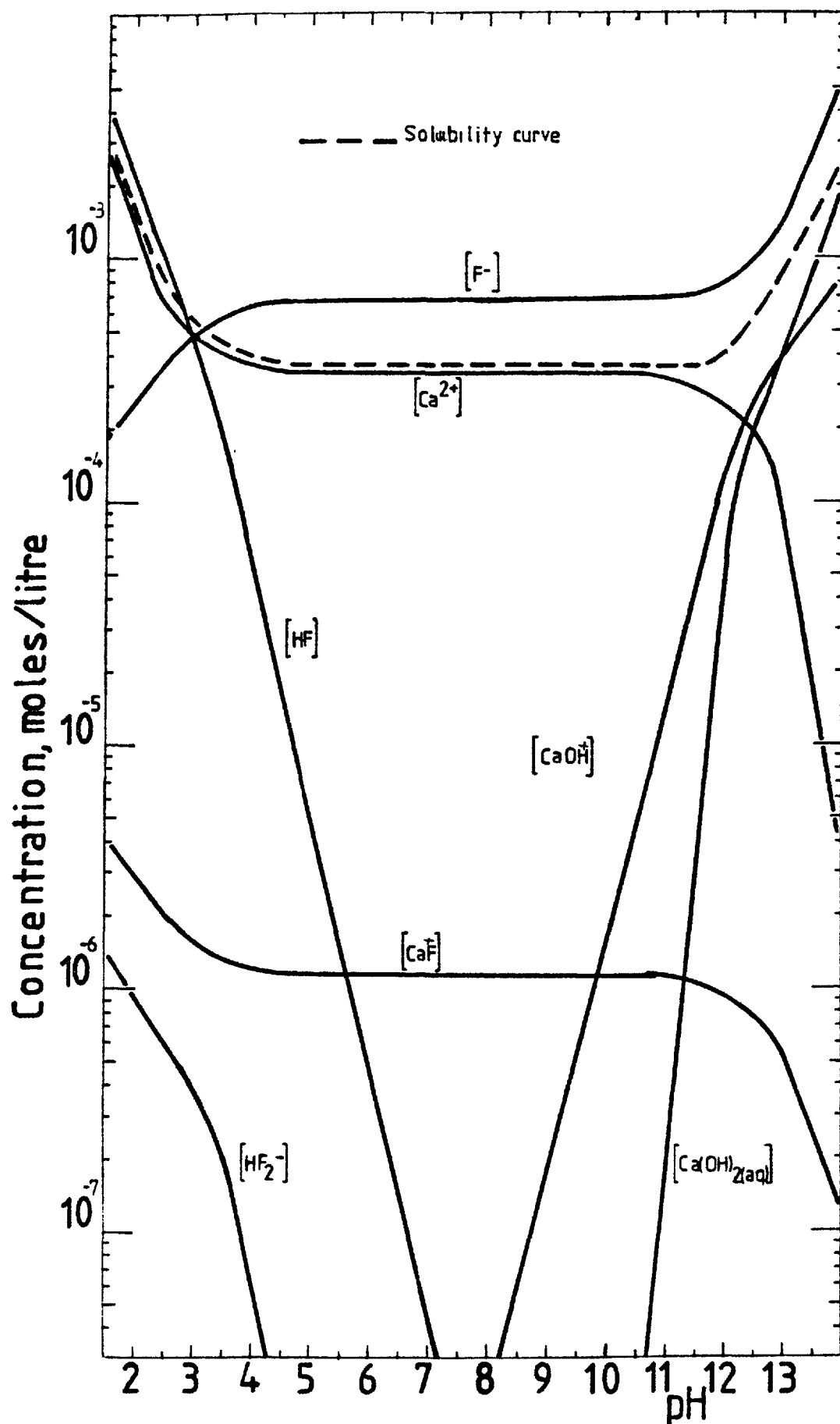


Fig. 1.5. Distribution of calcium and fluoride species in a solution saturated with fluorite and solubility of fluorite as a function of pH ($p_{CO_2} = 0$).

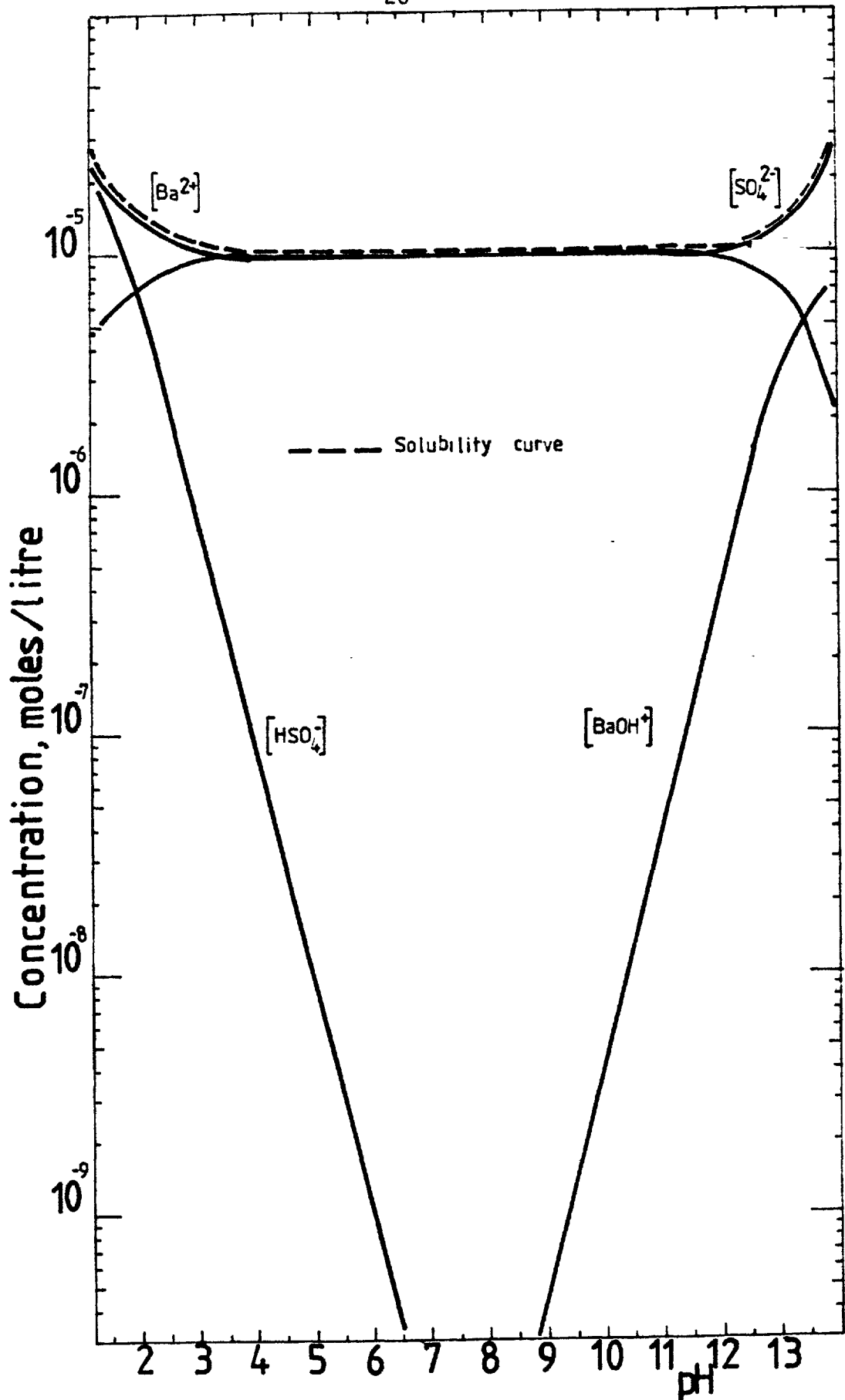
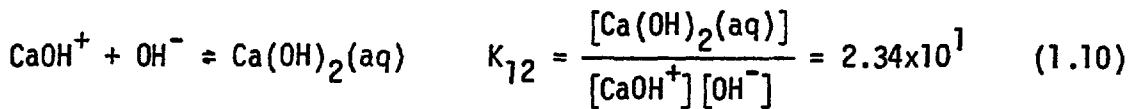
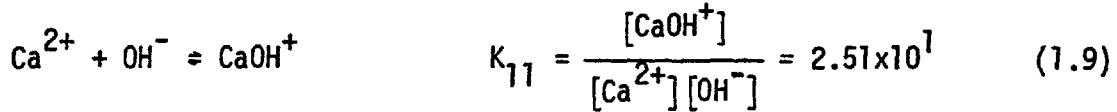
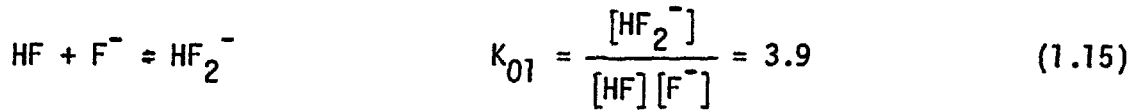
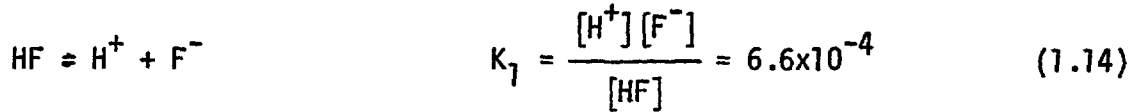
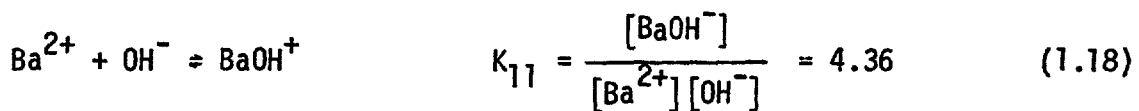
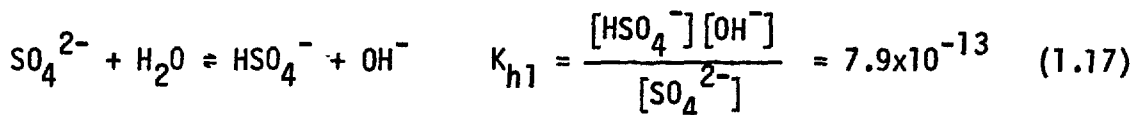
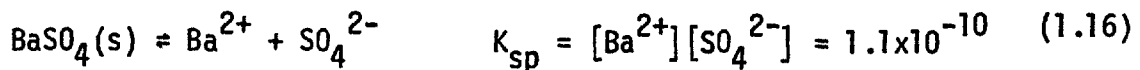


Fig. 1.6. Distribution of barium and sulphate species in a solution saturated with barite and solubility of barite as a function of pH ($p_{CO_2} = 0$).



In saturated solutions of barite the solubility is independent of pH over a wide pH range because the Ba^{2+} and SO_4^{2-} ions only undergo hydrolysis at high and low pH values, respectively. Thus in the pH range 3 to 12 the solubility can be calculated from the solubility product assuming BaSO_4 to be a salt of a strong base and strong acid. The equilibria involved are (12, 23):



1.2.3. Surface charge

When a mineral is immersed in an aqueous solution its surface acquires a charge due to either dissociation of surface groups or the preferential adsorption of ions. The presence of the surface charge gives rise to the well known electrical double layer (24, 25). Ions responsible for the surface potential are termed potential determining, PDI, and for the salt-type minerals they are the ions which make up

the crystal lattice (26, 27). For oxides and silicates H^+ and OH^- ions are potential determining (27 - 29).

The surface potential, ψ_0 , cannot be measured directly but it can be calculated from the Nernstian expression:

$$\psi_0 = \frac{kT}{ze} \ln \frac{a}{a_0} \quad , \quad V \quad (1.19)$$

where k : Boltzmann constant, $1.380 \times 10^{-23} \text{ J/}^\circ\text{K}$
 T : absolute temperature, $^\circ\text{K}$
 z : valence of the PDI, ($e = 1.602 \times 10^{-19} \text{ C}$)
 a_0, a : activity of the PDI at the PZC and under the conditions studied, respectively.

The negative logarithm of the PDI activity corresponding to zero charge on the surface is known as the point of zero charge or PZC. The PZC for each mineral is unique and various theoretical attempts have been made to relate it to the properties of the atoms which make up the mineral (30, 31). Experimentally the PZC corresponds to the concentration at which the net adsorption of PDI is zero. Potentiometric titrations can be used to determine the PZC when H^+ and OH^- ions are potential determining. An estimate of the PZC can be obtained by determining the concentration of PDI at which the zeta potential is zero. This condition is called the iso-electric point (IEP) and it equals the PZC when there are no specific adsorption effects. The zeta potential is the only potential in the electrical double layer which can be measured by electrokinetic methods and it corresponds to that situated at a zone of shear in the liquid near the solid surface. Generally the zeta-potential is assumed to approximate to that of the Stern plane which is the position of closest approach of hydrated counter ions to the solid surface.

Studies of the zeta-potential and electrical double layer characteristics of minerals are difficult to interpret because the surface potential is very dependent on such factors as origin of the mineral, the presence of trace impurities sample preparation and ageing. These factors account for the wide variability in PZC and IEP data quoted in the literature (6, 29).

Although the potential determining ions for the ionic solids and salt-type minerals are generally assumed to be those which make up the crystal lattice considerable attention has been focussed, in the literature, on the effect of pH on the zeta-potential. The reasons for this are that the ions which make up the salt-type minerals are subject to hydrolysis which is pH dependent and furthermore pH controls the degree of ionisation of many of the reagents used in the flotation process.

Studies of the effect of pH on the zeta-potential of barite have been made by Fuerstenau et al (32) who obtained an IEP at pH 8.0. This value is, however, rather high compared to that obtained by Plitt and Kim (33), and other workers (34 - 36), at a pH of 5.3. The effect of Ba^{2+} and SO_4^{2-} ions on the zeta-potential of barite appears to have been little studied and that information which is available relates to poorly defined experimental conditions (35, 36).

Although many studies have been made of the electrokinetic properties of calcite there is no general agreement on the IEP with respect to pH or indeed whether it is possible to determine the IEP. The reason for this controversy is that calcite is very soluble at pH values below 9.0 where the IEP is expected, and most of the determinations have been made under non-equilibrium conditions. Somasundaran and Agar (37) showed that the pH at the IEP shifted with the time of equilibration and they

drew attention to the problems of measuring the zeta-potential under these conditions. They also suggested that the IEP occurred in the pH range 8.0 to 9.5 but no exact value was given.

Some authors consider that the zeta-potential of fluorite is positive at all pH values (38, 39) whereas others consider that under similar conditions fluorite is negatively charged (40). Choi (41) determined an IEP at pH 7.0 which is some three pH units lower than that obtained by Fuerstenau et al (42) and Miller and Hiskey (21). The latter authors also determined the effect of Ca^{2+} and F^- ions and showed that whereas increasing the Ca^{2+} concentration made the zeta-potential more positive, or less negative, increasing the F^- concentration had little effect.

The zeta-potential of scheelite has been measured recently, in various electrolyte environments, by Arnold and Warren (43). The mineral was found to be negatively charged throughout the pH region. It reversed sign at relatively high concentrations of Mg^{2+} ions ($1 \times 10^{-3} \text{M}$) and above pH 10.0. The introduction of the constituent ions, Ca^{2+} and WO_4^{2-} , into the solution did not significantly change the zeta-potential, though, both are potential determining ions for this mineral. Fuerstenau et al (42) measured the zeta-potential of scheelite by a streaming potential technique and found that it was negatively charged at all pH values but less so at pH 7 - 8 than at the other pH values. Similar results were obtained by O'Connor (44) and Atademir et al (45).

The behaviour of apatite is much more complex. It was pointed out by Saleeb and Bruyn (46) that the concentration of any two ions which make up the crystal can be varied independently without changing the solubility product. If the concentrations of the three potential determining ions i.e., Ca^{2+} , PO_4^{3-} , OH^- (or F^-), are plotted on three mutually perpendicular axes a 'solubility' surface can be constructed. On this surface a curve

containing an infinite number of points of zero charge can be located. A series of PZC values is given by the authors for various types of synthetic apatites. For natural apatite, partially saturated with fluoride, Somasundaran (47, 48) obtained an isoelectric point at pH 4.0 which shifted towards a final value of 6.0 with equilibration. H^+ , OH^- , and PO_4^{3-} were found to have a major role as potential determining species but the changes in zeta-potential due to addition of Ca^{2+} and F^- ions was also significant. Similar conclusions have been reached by Smani et al (49) who obtained isoelectric points of apatites between pH 3.8 and 4.9.

1.3. Reagents used in the flotation of salt-type minerals

1.3.1. Thermodynamics of adsorption

Thermodynamic aspects of collector adsorption can be obtained from experimentally determined adsorption isotherms and two different approaches have been used.

Fuerstenau (50, 51) has assumed that the adsorption density of ions in the Stern plane is given by the Stern-Grahame equation:

$$\Gamma_s = 2 r C \exp \left(- \frac{\Delta G_{ads}^0}{RT} \right), \quad (\text{moles/m}^2) \times 10^3 \quad (1.20)$$

where r : ionic radius of the adsorbed ion, m

C : bulk concentration of the adsorbed ion, moles/l

R : gas constant, 8.31439 J/mole. $^{\circ}K$

T : absolute temperature, $^{\circ}K$, and

ΔG_{ads}^0 : free energy of adsorption, J/mole

The term ΔG_{ads}^0 is the driving force of adsorption and is considered to be made up of a number of contributing terms:

$$\Delta G_{ads}^0 = \Delta G_{elec}^0 + \Delta G_{HM}^0 + \Delta G_{CH_2}^0 + \Delta G_h^0 + \Delta G_{solv}^0 + \Delta G_{CHEM}^0 + \quad (1.21)$$

where	ΔG^0_{elec}	: electrostatic contribution ($= z_{\pm} F \psi_{\delta}$)
	ΔG^0_{HM}	: association of the hydrocarbon chains at the interface
	$\Delta G^0_{CH_2}$	: interaction of the hydrophobic chain direct with the surface
	ΔG^0_h	: hydrogen bonding
	ΔG^0_{solv}	: hydration or dehydration of the adsorbate or adsorbent upon adsorption
	ΔG^0_{CHEM}	: covalent bond formation between adsorbate and adsorbent.

All terms, except the electrostatic one, give rise to specific adsorption and can be taken as specific adsorption free energy, ΔG^0_{spec} . The adsorption can be either physical or chemical depending on the type of bond formed between adsorbed ions and the surface. Physical adsorption includes adsorption by coulombic attraction and Van der Waals forces whereas in the case of chemisorption a covalent bond is formed between the adsorbate and adsorbent.

Cases et al (52 - 56) studied the adsorption of n-alkyl-ammonium chlorides and sodium oleate on various minerals and they found the adsorption isotherms to exhibit two well defined regions. The first, with a coverage less than a monolayer, had a finite slope and was attributed to bi-dimensional condensation on a nonhomogeneous surface while the second one, with an infinite slope, was considered to be due to condensation on a homogeneous surface, i.e., the first adsorbed layer. They considered this to be the case when the normal interaction energy between the adsorbent and adsorbate was electrostatic in nature (biotite-alkyl-ammonium chlorides). In contrast, if the chemical work is the predominant factor (magnesite-sodium oleate), three-dimensional condensation of

collector on the mineral was proposed.

In both approaches, the association of collector ions on the surface to form two-dimensional aggregates called hemi-micelles, is considered to take place above a certain collector concentration.

1.3.2. Collectors used in salt-type mineral flotation other than fatty acids

Although fatty acids are used extensively in the flotation of salt-type minerals many investigations have been made with other anionic collectors and also cationic collectors (57, 58 - 61). Dobias (62) studied the adsorption characteristics of sodium dodecylsulphate, sodium dodecylsulphonate and primary and quarternary amines on apatite, barite and fluorite and proposed that while anionic surfactants are adsorbed due essentially to their interaction with crystal lattice cations as well as specific adsorption in the Stern layer, the cationic reagents are adsorbed by electrostatic attraction for negatively charged sites. The formation of a bi-layer of sodium dodecylsulphate on the barite surface has been reported by Cuming and Schulman (63). The orientation of the second layer was assumed to be with the polar groups towards the liquid because a hydrophilic surface was obtained at high collector concentrations. The mechanism of adsorption of this collector on barite was considered to be the formation of a salt between the lattice cations and alkyl sulphate.

Hanna and Saleeb and Hanna (64, 65) observed that the adsorption of sodium di-2-ethylhexylsulphosuccinate (Aerosol OT) on calcite, precipitated CaCO_3 and tricalcium phosphate corresponded to that required for the formation of a bi-layer on the surface. Chemisorption resulting in the formation of a salt between the surfactant anions and the calcium species on the surface, was proposed as the mechanism of formation of the

first layer while inter-chain cohesion was suggested as a possible explanation for the formation of the second layer. Flotation and contact angle data were consistent with the formation of a bi-layer and the postulated adsorption mechanisms.

Fuerstenau and Miller (66) have postulated the formation of calcium sulphonate on the calcite surface because of the similarity between the results obtained in the presence of sodium dodecyl sulphonate and those with fatty acids. The formation of a fatty acid soap in the latter case was indicated by an infrared technique. A similar mechanism has been proposed by Shergold (67) for the adsorption of sodium dodecyl sulphate on fluorite.

In contrast to the above reports, Mukai et al (68), Choi (41), Somasundaran and Agar (37) considered the adsorption of alkylsulphonate and sulphates on fluorite, scheelite, calcite and apatite to be the result of electrostatic attraction between the collector and mineral, under conditions where the minerals were positively charged.

The flotation of barite with sodium dodecyl benzene sulphonate at alkaline pH values and in the presence of iron oxides was attributed by Arafa et al (69) to the formation of the complex $\text{Fe}(\text{RSO}_3)_2\text{OH}$, which is adsorbed on the barite surface. The formation of specific compounds between the dodecyl phosphate anion and the calcite surface has been shown to take place by Seth et al (70) using infrared analysis. Under the same conditions apatite did not form such compounds and it was considered that this was due to the common occurrence of phosphate in both the apatite and collector.

Cases et al (56) consider that the adsorption of n-alkylammonium chlorides on calcite and phosphate oolites is coulombic at adsorption densities below a vertically-oriented monolayer, and that above monolayer

adsorption proceeds through interaction of the hydrocarbon chains. A similar mechanism has also been proposed by Saleeb and Hanna (71) and Mishra (72) for the adsorption of amines on calcite.

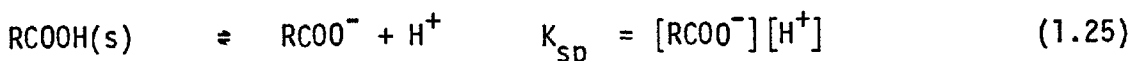
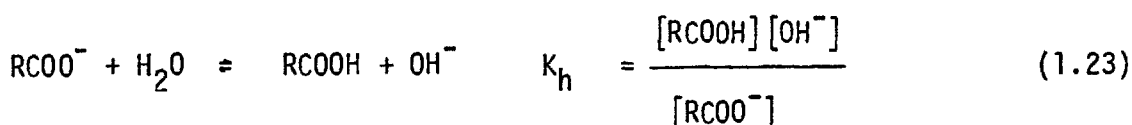
Solnyshkin (73) and Kuzkin et al (74) attribute the adsorption of amines to the formation of complex compounds such as amine carbonates followed by physical adsorption of the neutral molecules in the diffuse double layer which results in multilayer formation. In addition, Levinskii (75) considers that the hydrolysis of amine soaps is a further source for the amine molecules in the diffuse part of the double layer. Recently, Arnold et al (76) showed that the co-adsorption of neutral molecules of dodecylammonium chloride on scheelite was necessary for good flotation. They found that the recovery was lowered when the pH was reduced below about 10 but excellent flotation was obtained even at about pH 7 by adding dodecanol together with dodecylammonium chloride. With the completely ionic trimethyldodecylammonium chloride the recoveries were poor and independent of pH. The role of the neutral amine molecules in flotation of hematite and quartz has been found by Kulkarni and Somasundaran (77 - 79) to be important. These authors assume that ionomolecular complexes are formed between the neutral and ionised amine in solution and these complexes then adsorb at the mineral/water interface. Data supporting this mechanism is, however, not available.

1.3.3. Oleic acid-sodium oleate as collectors for salt-type minerals

a. Aqueous chemistry of oleic acid: Carboxylic acids and their soaps with alkaline metals are usually employed as collectors for the flotation of salt-type minerals. Oleic acid or its sodium salt, sodium oleate, is the most widely used collector of this type. Some of the

properties of these compounds will be briefly reviewed in the following paragraphs.

Oleic acid is a colorless liquid with a low melting point ($\approx 14^{\circ}\text{C}$). It is an unsaturated fatty acid with 18 carbon atoms in the alkyl chain and one double bond occurring between the 9th and 10th carbon atoms and is of the cis-form. The area covered by the carboxylic group is equal to $20.5\text{\AA}^2$ (80). Oleic acid has a low solubility in water, at room temperature, and because of this it is used in the form of sodium oleate, which is soluble at high pH values. Sodium oleate hydrolyses and forms neutral oleic acid molecules when the pH is decreased. The equilibria involved are:



The solubility product, K_{sp} , of oleic acid is $5 \times 10^{-13} \text{ M}^2$ (81, 82) and combining this value with $K_a = 2 \times 10^{-5}$ (83, 84) it can be shown that the solubility of neutral oleic acid is $K = 2.5 \times 10^{-8} \text{ moles l}^{-1}$ and that the hydrolysis constant $K_h = K_w/K_a = 5 \times 10^{-10}$. The solubility-pH curve for an oleic acid-saturated solution is shown in fig. 1.7. In fig. 1.8 the logarithmic concentration diagrams are given for two different initial concentrations of oleic acid, i.e. 5×10^{-3} and $5 \times 10^{-5} \text{ M}$. At the higher oleic acid concentration precipitation occurs at pH values below 10 and

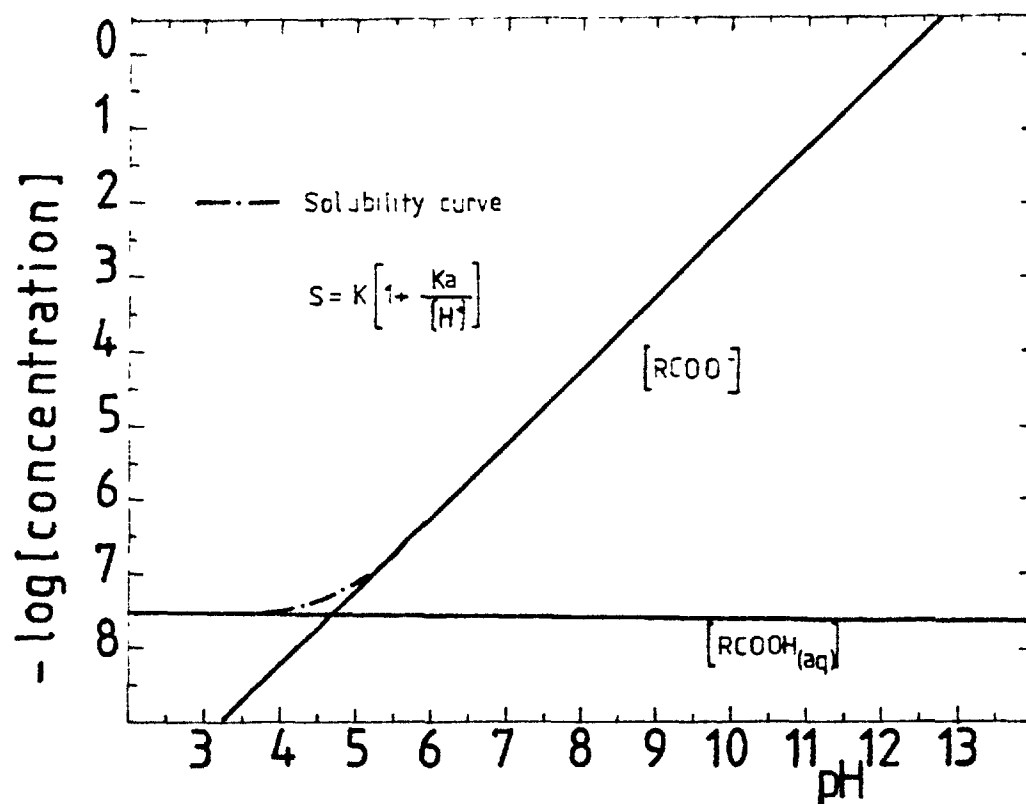


Fig. 1.7. Solubility of oleic acid as a function of pH.

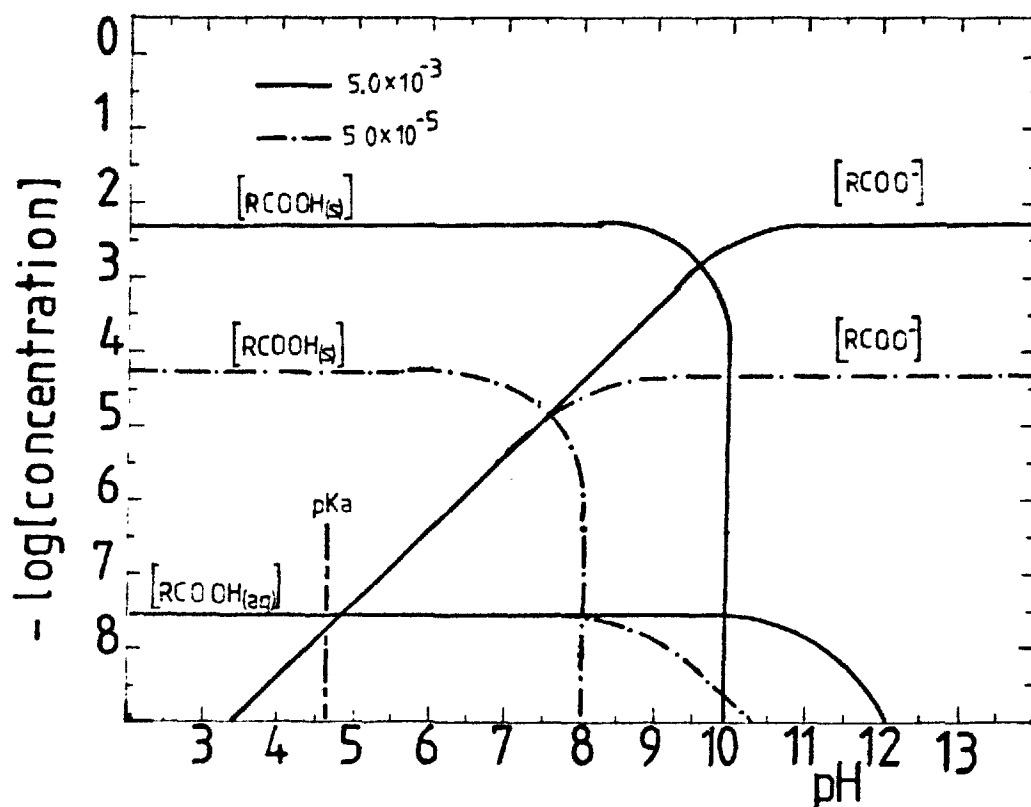


Fig. 1.8. Logarithmic concentration diagram at two sodium oleate concentrations.

at the lower concentration below pH 8.0.

Conductivity and surface tension results obtained by Zimmels and Lin (85) showed that in a fatty acid soap solution the association of the surfactant molecules is discontinuous and that there is a central critical micelle concentration, CMC, with secondary association concentrations distributed on both sides of this value. The values given for sodium oleate solutions are $1.7-1.9 \times 10^{-4}$ and $4-6 \times 10^{-4}$ M and are called pre-CMCs since they occur at concentrations lower than $2.1-2.3 \times 10^{-3}$ which is the CMC reported for sodium oleate.

b. Mechanism of adsorption of oleic acid: A number of authors have proposed that oleate chemisorbs on fluorite (86, 118), barite and calcite (87, 88) to form a surface metal carboxylate and displacement of the mineral anion. Evidence for this mechanism has been obtained by infrared spectrometry which unfortunately suffers from the disadvantage that some of the observed spectral changes could be the result of the sample preparation technique used rather than the oleate adsorption. Peck and Wadsworth (87) showed that maximum chemisorption occurred at about pH 9.0. As the pH decreased the chemisorption decreased but the physical adsorption of oleic acid molecules increased. Sodium oleate was physically adsorbed at high pH values. Flotation recovery was proportional to the amount of oleate that had been chemisorbed.

Berlinskii et al (89, 90) and Berger et al (91) showed that sodium oleate or oleic acid can physically adsorb on the chemisorbed layer, the former being readily removed by washing. Predali (92, 93) argues that the adsorption of fatty acids by dolomites is by chemisorption. He considers, however, that the fatty acid molecule is adsorbed at low pH values because of induced dipole effects. Plitt and Kim (33) reject the view of chemisorption of fatty acids on barite and they consider that the

collector species, i.e. neutral molecules or ions at low and high pH values, respectively, are adsorbed because of the tendency of the hydrocarbon chain to be removed from water. The adsorbed collector species lie parallel to the surface and form multilayers of which the outer part is mobile and can easily be detached.

It has been suggested that coulombic adsorption of oleate occurs on apatite and calcite (94) under conditions where the minerals are positively charged. Fuerstenau and Miller (66), however, have shown by infrared spectrometry that when fatty acids adsorb on calcite a chemical reaction occurs and that the calcium soap is formed. The distinction is, therefore, made between the chemisorbed layer of surface calcium carboxylate suggested by Peck et al (87) and multilayers of calcium soap.

All the above mechanisms mainly seek to explain the adsorption of the first layer of fatty acids on minerals. Multilayer adsorption on salt-type minerals has been found to exist by almost all the investigators and different explanations have been given (80, 89 - 91). Direct salt precipitation is proposed by Du Rietz (82). Russian authors (95) failed to find any correlation between the solubility of the mineral and precipitation of the metal salt but this is probably due to the use of incorrect solubilities for the minerals. Fuerstenau and Miller (66) found that there is a correlation between the amount of fatty acid required for the flotation of calcite and the solubility of the corresponding calcium soap. Recently, Atademir (96) attributed the 'adsorption' of fatty acids on calcite and scheelite to the precipitation of the calcium soaps on the surface. The collecting ability of these reagents, therefore, depends on the amount of soap precipitated on the surface and the strength with which the precipitate is held to the surface.

1.3.4. Modifying reagents

The separation of salt-type minerals by flotation in the absence of modifying agents is difficult to achieve. Modifiers are added to improve the selectivity and they achieve this either by promoting the adsorption of collector on a mineral or group of minerals or by rendering the mineral hydrophilic even in the presence of collector. Modifiers that prevent flotation are termed depressants and they act either by preventing collector adsorption or by adsorbing with the collector in such a way that the surface remains hydrophilic.

Depressants which have been suggested for the separation of the salt-type minerals are numerous and they range from inorganic ions such as silicates, sulphates, phosphates and polyvalent metal ions to the large complex organic molecules typified by starch and quebracho. Probably, the most important reagent is, however, sodium silicate (water glass) which is used not only to depress silicate gangue minerals but also to improve the selectivity between the salt-type minerals.

1.3.5. Sodium silicate in the flotation of salt-type minerals

The data obtained in early investigations of the effect of sodium silicate on salt-type mineral flotation cannot be interpreted because the experimental conditions were not adequately defined. A brief review of more recent data is given below.

Eigeles (97) found a decrease in the flotation of calcite and fluorite with sodium oleate in the presence of sodium silicate and that the adsorption of oleate was reduced. Sodium carbonate was used as a pH modifier but unfortunately it was shown that carbonate obscures the effect of sodium silicate (98 - 101). Kholomovskaya and Skobeev (98) reported the importance of carbonate to effect selectivity in the flotation of calcite-

phosphorite mixtures. They found that in the presence of carbonate, phosphorite adsorbed more silicate than calcite and the amount adsorbed was a function of the temperature and the pulp density. The presence of collector decreased the silicate adsorption. Berlinskii (102) found that the adsorption of sodium silicate on calcite and scheelite increased with silicate concentration. This was indicated by the increase in the zeta-potential of the mineral surfaces. Rinsing with water and increasing the temperature resulted in a decrease in the amount of sodium silicate adsorbed on calcite but not on scheelite. The adsorption of silica gel on the surface of apatite and scheelite, calcite, scheelite and apatite from sodium silicate solutions was studied by Cheng (103) and Solnyshkin (73), respectively, using infrared methods. They suggested that silica gel, $\text{SiO}_2 \cdot x\text{H}_2\text{O}$, and water glass were adsorbed in the diffuse layer of apatite. Sodium carbonate decreased the amount adsorbed on apatite and scheelite and changed the composition of the double-layer which consisted of adsorbed sodium silicate in the form of $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ molecules. In the case of calcite a silicate compound with a fibrous structure was adsorbed which contained non-saturated silicon atoms. They considered the effect of sodium carbonate to be not due to an exchange reaction between CO_3^{2-} and SiO_3^{2-} ions but to a decrease in the hydrolysis of water glass at higher pH values. Furthermore, the amount of silica gel on the surface of scheelite was decreased due to the formation of soluble sodium tungstate in alkaline medium.

Glembotskii et al (104, 105) attributed the decrease of the electrokinetic potential of celestite in the presence of water glass to the adsorption of HSiO_3^- and SiO_3^{2-} ions in the diffuse part of the double layer. The proposed mechanism, however, seems to be incorrect since adsorption of negatively charged species on a negatively charged surface

cannot decrease the zeta-potential unless the adsorption is specific.

Contrary to the above investigators, Nikiforov and Skobeev (106) showed that the depression action of water glass on calcium minerals increased in the presence of soda. The difference found between Na_2CO_3 and NaOH was attributed to a change in the water glass structure in solution as well as on the mineral surface. Infrared studies (107) of acidified ($\text{pH} \approx 1$) water glass on fluorite, showed that water glass strongly depressed this mineral with the formation on the surface of an open-chain polymer (siloxane polymeric silicic acid). When the same mineral was treated with alkaline water glass, it resulted in the formation of weak Si-OH groups on the surface due to the disintegration of Si-O-Si by OH^- ions. Nikiforov and Skobeev (107) and Berlinskii (108, 109) have reported the strong depressing effect of acidic water glass on calcite and this was attributed to the formation of highly polymeric anions with a branched structure on the surface of this mineral. The effect of time was also investigated. A decrease in the contact time of calcite and scheelite with the water glass solution reduced the amount of reagent adsorbed on scheelite.

It is reported that the efficiency of sodium silicate as a depressant increases with the soda to silica ratio (110). However, interpretation of the literature is made difficult because many investigators have not included details of the sodium silicate used in their experiments. Sollenberger and Greenwalt (111, 112) studied the role of the ratio and found this to be important only above $\text{pH } 7.0$ and at high concentration of silicates. Fuerstenau et al (42) studied the influence of sodium silicate on the flotation of calcite, fluorite, apatite and scheelite. They consider that with a ratio of $\text{SiO}_2:\text{Na}_2\text{O}$ of 1.6 the depression of calcite can be attributed to silicate anion adsorption and that the adsorption is chemical

in nature. With ratios greater than 2, the adsorption of colloidal silica is responsible for the depression and the adsorption is physical. High concentrations of sodium silicate do not affect the flotation response of apatite and scheelite while fluorite is depressed at high pH values. Berlinskii (113) also showed that chemisorption and physical adsorption of alkaline and acidic sodium silicate with a ratio of 2.6:1, respectively, occurred on scheelite, powellite, apatite and calcite using an infrared technique. It has been found that sodium silicate is more effective as a depressant when it is added with salts of polyvalent cations or used at elevated temperatures. The favorable effect of aluminium salts has been reported by a number of workers (95, 114 -117). Thus, the separation of fluorite from calcite is improved by simultaneous addition of aluminium salts and sodium silicate (115). This is attributed by Abeidu (117) to a decrease in adsorption of oleate on calcite due to competition between the collector species and the anion $\text{Al}_2\text{SiO}_3(\text{OH})_6^{2-}$. In addition to aluminium, salts of zinc or chromium have also been found to improve the selectivity in fluorite-calcite systems (102, 108). Iron salts depress the flotation of calcite, in calcite-scheelite systems, and decrease the amount of sodium silicate needed, while their effect in the celestite-anhydrite system is negligible (105).

1.4. Aims of the project

The objectives of this project were to investigate, under well defined experimental conditions, the interaction between sodium silicate solutions and the salt-type minerals barite, calcite and fluorite in the presence and absence of oleic acid, to determine the effect of sodium silicate on the flotation of these minerals with oleic acid and to elucidate the effect of polyvalent cations. The project was divided into a number of stages:

1. A study of the solubility and electrical double layer characteristics of the minerals as a function of pH and in the presence of various electrolytes including sodium silicate and oleic acid.
2. Measurement of the effect of sodium silicates with different silica to soda ratios on the Hallimond tube flotation of the minerals with oleic acid.
3. A study of the solution equilibria properties of sodium silicates at the concentration levels and pH values used in the flotation tests.
4. Determination of the mechanism of adsorption of oleic acid and sodium silicate, on the minerals, both in the presence of each other and on their own.
5. Determination of the effect of aluminium ions on the flotation and adsorption properties of the minerals in the presence of oleic acid and sodium silicate.

CHAPTER 2. MATERIALS AND EXPERIMENTAL METHODS

2.1. Materials

2.1.1. Minerals

Selected samples of high-purity minerals were supplied by R.F.D. Parkinson and Co., Shepton Mallet, Somerset. The fluorite was from Weardale, Co. Durham, the calcite, described as fluorescent calcite, was from Minsterley, Salop, and the barite was from Sandgate Beds, Fullers Earth, Nutfield, Surrey. Hand picked samples were hand ground in an agate mortar. The products were dry-sieved and the -0.300+0.150 mm and -0.150 mm fractions were collected. The -0.300+0.150 mm fraction was used in flotation tests while the -0.150 mm fraction was used in adsorption measurements. Both fractions were stored in glass containers in a vacuum desiccator. A semi-quantitative XRF analysis of the samples gave the results given in Table 2.1.

2.1.2. Reagents

Fluka 'purum', ≥ 95 per cent, oleic acid was used throughout. A stock sodium oleate solution was prepared by saponification of the oleic acid for several hours at 60°C with an excess of NaOH. The resulting solution had a concentration 5.0×10^{-3} M and a pH of approximately 11.0. The solution was kept in an amber glass bottle and fresh solutions were

Table 2.1. XRF analysis of mineral samples

Mineral	Major >5%	Intermediate 5-0.5%	Minor 0.5-0.05%	Trace <0.05%
Barite	Ba, S	Al	Sr, Ca, Ti	Fe, Zn
Calcite	Ca	-	Al, Si, Mn, Fe	Zn, Y
Fluorite	Ca, F	-	Al, Si	Mn, Fe, Y, Ba

made up every 5 days. Ageing the solutions for a long time resulted in the formation of a white precipitate.

The sodium silicates used had silica to soda ratios varying from 1.00:1 to 3.41:1. The silicates with ratios 1.65:1, 2.07:1, 2.94:1 and 3.41:1 were provided by Crosfield Chemical Co. and those with ratios of 2.56:1 and 1.00:1 were obtained from Hopkin-Williams and BDH, respectively. With the exception of the silicate with a ratio of 1.00:1 all were supplied as concentrated viscous liquids which were readily soluble in water. The silicate with a 1.00:1 ratio was in the form of hydrated soluble pellets with the given chemical formula of $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$, and the name sodium metasilicate. The silicates were used without further purification. Some of the characteristics of these silicates obtained from the suppliers are given in Table 2.2.

Aged sodium silicate solutions were prepared by making up $1.0\text{--}13.64 \times 10^{-3}$ M SiO_2 solutions at the required pH value and storing them in plastic containers for up to 34 days. Fresh solutions were prepared every day.

All other chemicals used in this work were of Analytical grade except where otherwise stated.

Table 2.2. Physical properties and composition of sodium silicates

Supplier	Grade	S.G. at 20°C/20°C	Mean wt. ratio SiO ₂ :Na ₂ O	Mean Mol. ratio SiO ₂ :Na ₂ O	Mean Na ₂ O, %	Mean SiO ₂ , %	Mean total solids, %	pH
Hopkin and Williams	-	-	0.96	1.00	29.22	28.28	-	-
Crosfield	H120	1.60	1.60	1.65	17.98	28.75	46.7	13.5
"	120	1.60	2.00	2.07	16.07	32.15	48.2	13.0
BDH	-	1.50	2.47	2.56	12.50	31.00	43.5	-
Crosfield	96	1.48	2.85	2.94	11.20	31.95	43.2	12.1
"	1	-	3.30	3.41	6.57	21.70	51.1	11.6

2.2. Experimental methods and techniques

2.2.1. Flotation tests

Flotation tests were carried out in a modified Hallimond tube containing a long sample arm to minimize errors caused by mechanical 'carry over'. Conditioning and flotation times of 3 and 1.5 min were used, respectively. HCl and NaOH were used to modify the pH.

A sample of 1 g of the mineral to be tested was conditioned with 200 ml solution containing sodium oleate and sodium silicate at the required pH in a beaker. At the end of the conditioning the suspension was transferred to the Hallimond tube and agitated with a magnetic stirrer. Nitrogen at a constant flowrate was passed through the suspension.

The pH values quoted in the results are those obtained at the end of the conditioning period. No significant difference was obtained between these values and those at the end of flotation, except at neutral pH values, where differences of ± 0.5 pH units were sometimes obtained especially in experiments with calcite.

2.2.2. Solubility studies

The solubility determinations were carried out by equilibrating 1 g of mineral (-0.150 mm) with 100 ml of the appropriate solution for 6 days in Erlenmeyer flasks. Preliminary experiments showed that equilibrium was established at the end of this period. Plastic containers were used in all tests involving fluorite. In the studies with calcite and fluorite nitrogen saturated, CO_2 -free double distilled water was used and the solutions were kept under a nitrogen atmosphere. CO_2 -free water was produced by bubbling nitrogen through the doubly distilled water for at least 5 hours. Such precautions were assumed to be unnecessary with barite. At the end of the equilibration time samples were taken,

centrifuged and analysed for mineral cation and, where appropriate, anion.

2.2.3. Electrokinetic measurements

The electrophoretic mobility of fluorite, barite and calcite was measured with a Rank Bros. MK II microelectrophoresis instrument. Small amounts of mineral were added to the required solutions and conditioned for 10 min prior to measurement of the electrophoretic mobility. Except where the variable investigated was pH, the pH was kept constant by the addition of small amounts of HCl and NaOH. The aged sodium silicate solutions used in these tests were prepared by diluting more concentrated solutions, adjusting the pH to that required and then leaving them for 34 days. Small changes in pH were noted during this time and the most pronounced changes occurred with the dilute solutions.

2.2.4. Adsorption measurements

1. Oleate - Preliminary adsorption tests showed that the adsorption of oleate at the mineral/water interface was a rapid process. In further tests, therefore, 0.1 g of the appropriate mineral powder was shaken with 100 ml of the reagent solution in 100-ml Erlenmeyer flasks for 30 min. After agitation, half of the solution was used for pH measurements, while the remainder was used to determine the equilibrium oleate concentration after removal of the solids by centrifugation. The amount of oleate adsorbed was determined from the difference between the initial and the equilibrium oleate concentration.

The mineral samples used in these tests were prepared by grinding the -0.150 mm fraction of each mineral in an agate mortar to - 45 μm . The specific surface areas obtained by a single point technique using a

Quantachrome Monosorb apparatus were 3.3709, 2.9296 and 0.8423 m²/g for barite, calcite and fluorite, respectively. At least two independent measurements were made on each mineral.

2. Silicates - Preparation of the mineral samples: A portion of the -45 µm calcite, barite and fluorite was further ground in a stainless steel mortar for about 20 min. A stainless steel mortar was used to minimise silicon contamination of the samples which might arise from the use of an agate mortar. Small amounts of each mineral were ground and stored in plastic containers in a vacuum desiccator. The surface area of each batch was measured prior to its use and the results obtained are summarised in Table 2.3. Impurity content of the samples is shown in Table 2.4.

Table 2.3. Surface area of the mineral samples used for silica and/or aluminium adsorption determinations, m²/g

Mineral Sample	Barite	Calcite	Fluorite
1	1.8673	3.3465	0.8238
2	2.3990	4.6125	-
3	-	3.7541	-
4	-	2.50	-

Procedure: 100 ml of the sodium silicate solution was prepared with CO₂-free double distilled water. The pH of this solution was adjusted to the predetermined value and 50 ml of this final solution was pipetted into a 50-ml Erlenmeyer flask containing 10.0 g of the mineral to be studied (30.0 g were used in the case of barite). The

Table 2.4. Quantitative analysis of the impurities in the minerals used for silica and/or aluminium adsorption determinations

Mineral Element	Fluorite	Barite	Calcite
Pb	0.07%	-	-
Fe	0.48%	≈260ppm	0.72%
S	<≈150ppm	-	-
Zn	-	-	-
Al	-	-	-
Mn	< 0.05%	-	2.2 %

rest of the solution was kept in a plastic bottle for determination of the amount of silica initially added (reference solution).

The flasks were agitated by shaking for 15 hrs after which the suspensions were centrifuged in 100-ml Teflon tubes for 30 min at a speed of 3000 rpm. The clear liquid was transferred to polypropylene beaker, the pH was measured and its silicon content was determined. The amount of silica adsorbed was found by subtracting the equilibrium from the initial silicate concentration. The initial concentration was determined at the same time as the equilibrium concentration.

3. Aluminium ions - The mineral samples and procedures used in the determination of aluminium adsorption, both in the presence and absence of sodium silicate, were similar to those used in the silicate adsorption tests.

2.3. Analytical methods

2.3.1. Calcium determination

The calcium concentration in solution was determined by atomic absorptiometry. Standards were prepared by dilution of a master solution, containing a known amount of $\text{Ca}(\text{NO}_3)_2$, supplied by BDH. Initially small amounts of F^- , CO_3^{2-} and Na^+ were added to the standards at levels similar to those encountered in the sample solutions, but it was found that this was unnecessary and was discontinued. Fresh standards were prepared.

2.3.2. Sulphate determination

The determination of low amounts ($< 1.0 \times 10^{-5}$ moles/l) of sulphate in solution is difficult and a general method is not available. This is mainly because many of the ions which might be present with the sulphate interfere with the determination of the sulphate.

Recently, Stephen (119) has proposed a new method for the determination of small amounts of sulphate in solution by nephelometry. It is based on the precipitation of sulphate by 2-amino-perimidine hydrochloride and measurement of the light scattering of the suspension with a nephelometer. While sulphate can be determined in the presence of other anions without any difficulty, when the latter are present in small amounts, the determination becomes impossible at higher concentrations due to the lack of specificity of the reagent. The permitted impurity varies from anion to anion and for chloride it is about 500-1000 ppm. In the present studies it was found that oleate and silicate ions interfered at much lower concentrations ($< 1.0 \times 10^{-5}$ M) so that the method could not be used under these conditions. In the absence of other ions, except chloride, the method could be applied and gives excellent results with sulphate concentrations as low as 2.0×10^{-6} moles/l. The procedure used was as follows:

Reagents: 0.5 g of 2-amino-perimidine hydrochloride (supplied by Koch-Light) was dissolved in 100 ml warm double distilled water and the hot solution was filtered and stored in an amber-coloured glass bottle. A new solution was prepared every two days.

A stock potassium sulphate solution was prepared by dissolving 18.14 mg of freshly dried A.R.-grade salt in 1 l of distilled water. This solution had a sulphate concentration equal to 10 ppm or 1.04×10^{-4} M and was used for calibration purposes.

Apparatus: An "EEL" nephelometer comprising an EEL nephelometer head and EEL Unigalvo Type 20 (Evans Electroselenium Ltd., Essex, England) was used. Test tubes provided with the instrument were used for holding the suspensions in the nephelometer.

Procedure: Between 1.0 and 5.0 ml of a standard sulphate solution was added to five 10-ml volumetric flasks and the total volume made up to 5 ml by the addition of distilled water. To each volumetric flask was added 4 ml of the 2-amino-perimidine hydrochloride solution. After diluting the contents to the mark the solutions were mixed by inverting the flasks and then left to stand for about 5-10 min. Each suspension was transferred to the nephelometer tube and the light scattering measured after setting the zero reading on a blank solution and the sensitivity to give a reading of about 80% f.s.d. for the most concentrated sulphate solution. Distilled water and the reagent solution gave the same readings at this sensitivity, but the reagent solution was used as a blank throughout. The readings were stable and reproducible provided that the suspension was shaken prior to each measurement. The calibration curve obtained is given in Fig. 2.1.

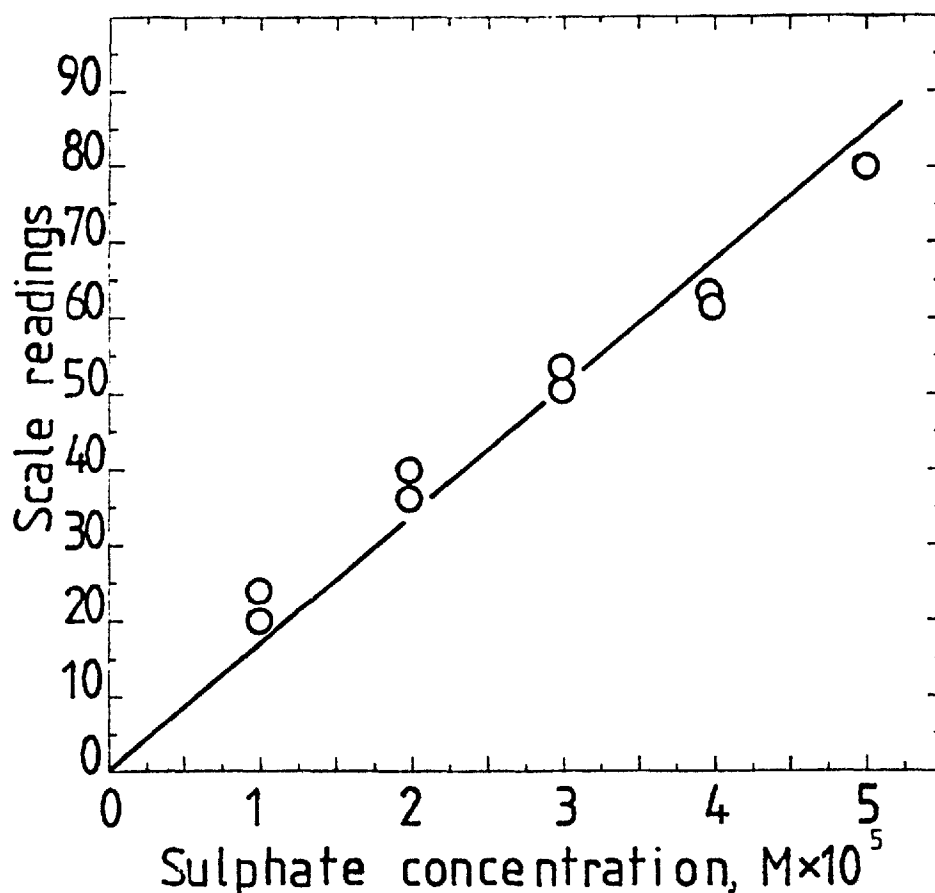


Fig. 2.1. Calibration curve for the determination of sulphate ions in solution.

2.3.3. Fluoride determination

The fluoride concentration of the solutions was measured with an 'Orion' fluoride-ion selective electrode (model 94-09) in combination with a saturated calomel reference electrode and a 'Pye' model 290 pH meter with expanded scale.

Reagents: A stock sodium fluoride solution was prepared by dissolving 0.5525 g of freshly dried A.R.-grade salt in 500 ml of distilled water. This solution had a fluoride concentration equal to 500 ppm or $2.631 \times 10^{-2} M$ and was used for calibration purposes.

The TISAB buffer (total ionic strength adjustment buffer) was prepared

as described by Frank and Ross (120). Briefly the procedure was as follows: In a 1-l beaker was placed approximately 500 ml distilled water and 57 ml of glacial acetic acid, 58 g of sodium chloride, and 0.30 g of sodium citrate were added. The beaker was placed in a water bath and a solution of 5 M sodium hydroxide was added until the pH was between 5.0 and 5.5. The solution was left to cool, poured into a 1-l volumetric flask and distilled water was added to the mark.

The use of TISAB in the determination of fluoride by an ion selective electrode is essential because (1) it buffers the solution avoiding hydroxyl interference, (2) it provides citrate ions which complex aluminium and thus releases the fluoride as a free ion, and (3) it provides a constant ionic strength.

Calibration: Fluoride standards were prepared by pipetting the predetermined amount of fluoride solution into an 100-ml volumetric flask and diluting to the mark. The following procedure is similar to that described by Shergold and Selve (121). A 25 ml volume of each fluoride standard solution was pipetted into a 100-ml polypropylene beaker and this was followed by the addition of 25 ml of TISAB. The solution was agitated by a 'Teflon'-covered magnetic follower. The electrode system was then placed in the gently agitated solution and after 10 min the potential was measured. Measurements of the electrode potential were always made in ascending order of fluoride ion concentration and the reason for this is that the electrode takes time to stabilize after reading a high fluoride concentration. By plotting the measured potential as a function of the logarithm of the fluoride ion concentration a calibration curve was obtained. A new calibration curve was plotted prior to each series of measurements due to slight variations, which can be attributed to fluctuations in the ambient temperature, and the electrode potential.

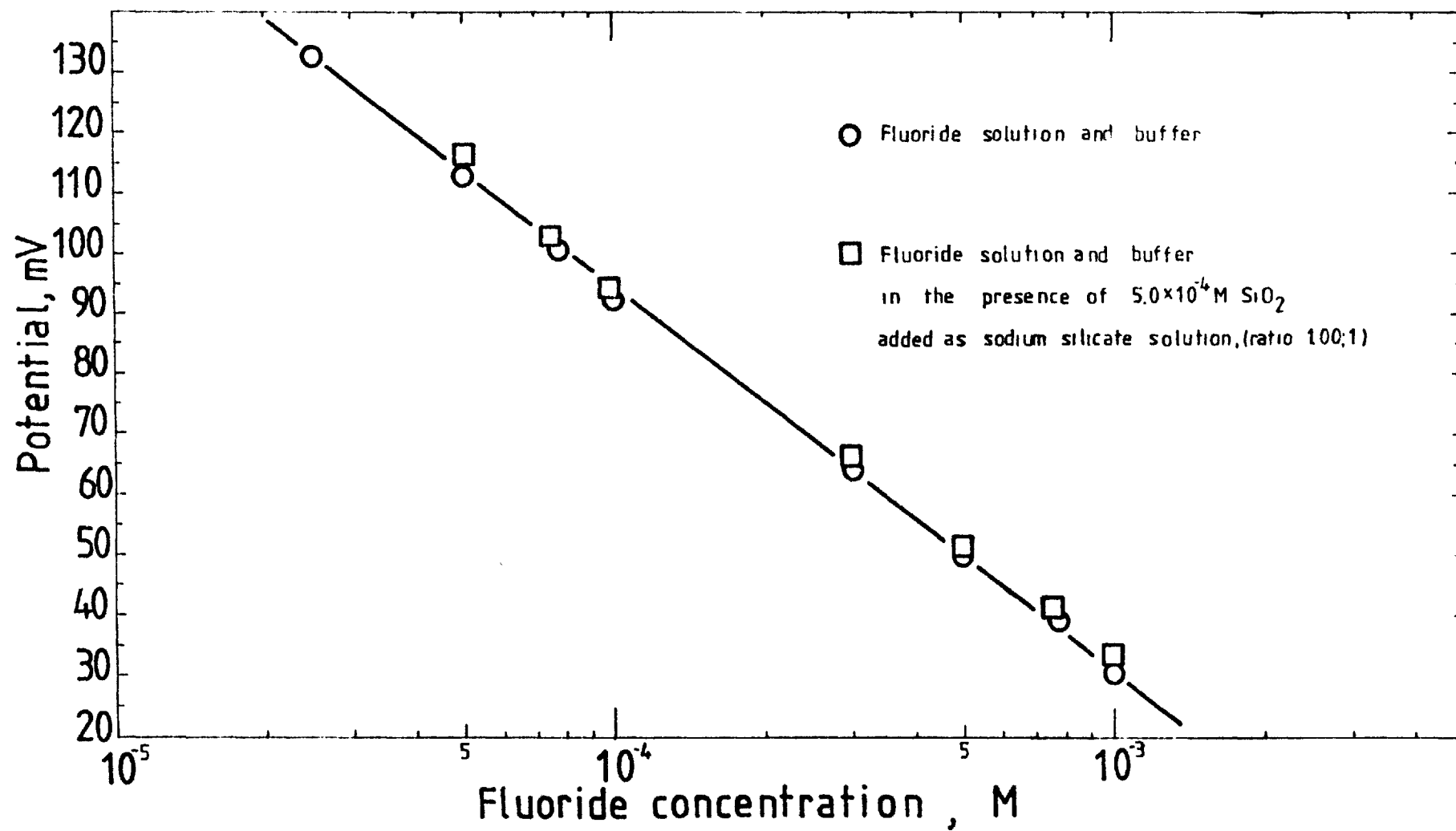


Fig. 2.2. Calibration curve for fluoride determination with an ion-selective electrode.

One of these curves is shown in Fig. 2.2. In the same figure the points obtained in the presence of 5.0×10^{-4} M SiO_2 (added as sodium silicate) are also given. It is clear that silicates do not interfere with fluoride determination and that excellent straight lines were obtained in both cases in the fluoride concentration range 1.0×10^{-5} - 3.0×10^{-3} M.

2.3.4. Oleate determination

The method used for the determination of oleate was that of Gregory (122) for anionic surfactants. The solution containing the oleate was reacted with a copper-triethylenetetramine complex in an alkaline medium of monoethanolamine and the resulting complex was extracted into a cyclohexane-isobutanol mixture. Addition of diethylammonium diethyldithiocarbamate to the solution of extracted complex produced a colour which was determined with a Perkin-Elmer 124 double beam spectrophotometer.

Reagents: Copper-triethylenetetramine - 25 g of copper(II) nitrate trihydrate was dissolved in 125 ml of water and stirred slowly into a solution containing 16.25 g of triethylenetetramine in 125 ml water. 250 ml of water was added and the whole was diluted with water to 1 l.

Isobutanol-cyclohexane extractant - 200 ml of isobutanol was mixed with 800 ml cyclohexane.

Diethylammonium diethyldithiocarbamate solution - 0.2 g of diethylammonium diethyldithiocarbamate was dissolved in 10 ml of isobutanol. This solution was prepared freshly every 2 days.

Procedure: 5 ml of the copper-triethylenetetramine solution was added to 25 ml of the oleate solution contained in the extracting tubes, followed by exactly 10 ml of isobutanol-cyclohexane extractant. The tubes were inverted rapidly 100 times and after the phases separated the organic layer transferred into a dry test tube and two drops of the diethylammonium

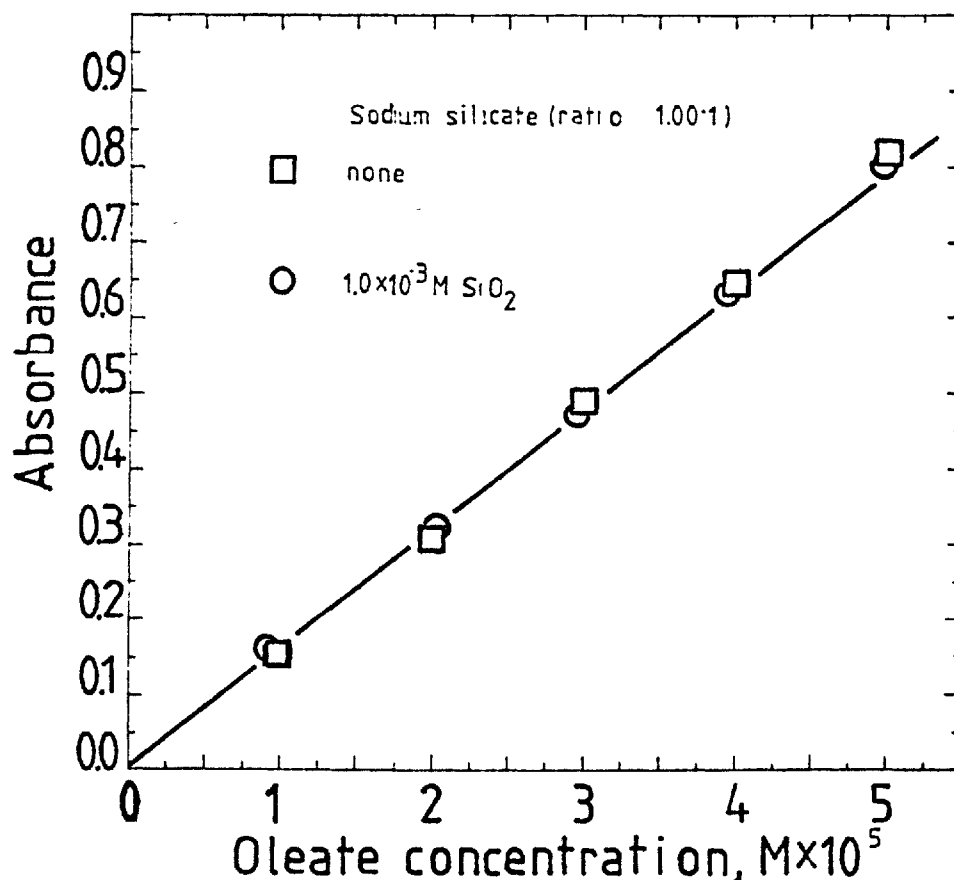


Fig. 2.3. Calibration curve for the spectrophotometric determination of oleate in the absence and presence of sodium silicate.

diethyldithiocarbamate solution were added. After standing for 15 min in the dark the absorbance of each sample was measured against the extractant blank in 10-mm cells at a wavelength of $435 \text{ m}\mu$. The calibration curve thus obtained is shown in Fig. 2.3.

It has been reported (122) that silicates added as water glass decrease the absorbance of the oleate solution. For this reason the calibration curve was determined in the presence of 1.0×10^{-4} and $1.0 \times 10^{-3} \text{ M SiO}_2$. The results have been plotted in the same figure and indicate that at these levels sodium silicate does not interfere with the oleate determination.

2.3.5. Silicon determination

The total amount of silica in solution was determined by using a spectrophotometric technique. The method was based on the formation of the yellow molybdosilicic acid and measurement of the absorbance of the solution. A Perkin-Elmer 200 double beam spectrophotometer was used. Depending on the concentration of silica in solution two different methods were used as described below.

1. Spectrophotometric determination of dissolved silica based on α -molybdosilicic acid formation - The silicon-containing solution was reacted with an ammonium molybdate solution while the pH was kept constant at 4.2 by adding a sodium acetate-acetic acid mixture. Under these conditions only the α -acid is formed (123).

Reagents: Sodium acetate-acetic acid buffer - To 50 ml of 2 M acetic acid was added 50 ml of 2 M sodium acetate.

Ammonium molybdate 10% - 10 g of ammonium molybdate was dissolved in hot water and diluted to 100 ml.

Procedure: The sample or standard solution was added to a 50-ml volumetric flask and diluted to about 40 ml. 2 ml of the buffer and 2 ml of the ammonium molybdate solutions were added and the whole was diluted to the mark. The pH was checked and the solution was left for 15 min at 20°C. The absorbance of this solution was measured against a blank solution, prepared using the same procedure, at 400 m μ in 10-mm glass cells. The calibration curve thus obtained was linear in the concentration range 0.0 to 7.0×10^{-4} M SiO₂, and is shown in Fig. 2.4.

2. The spectrophotometric determination of silicic acid in dilute solution - The method is that proposed by Garrett and Walker (124), and it is based on the formation of the molybdosilicic acid by reacting the silicon containing solution with sodium molybdate. Both the α - and β - forms

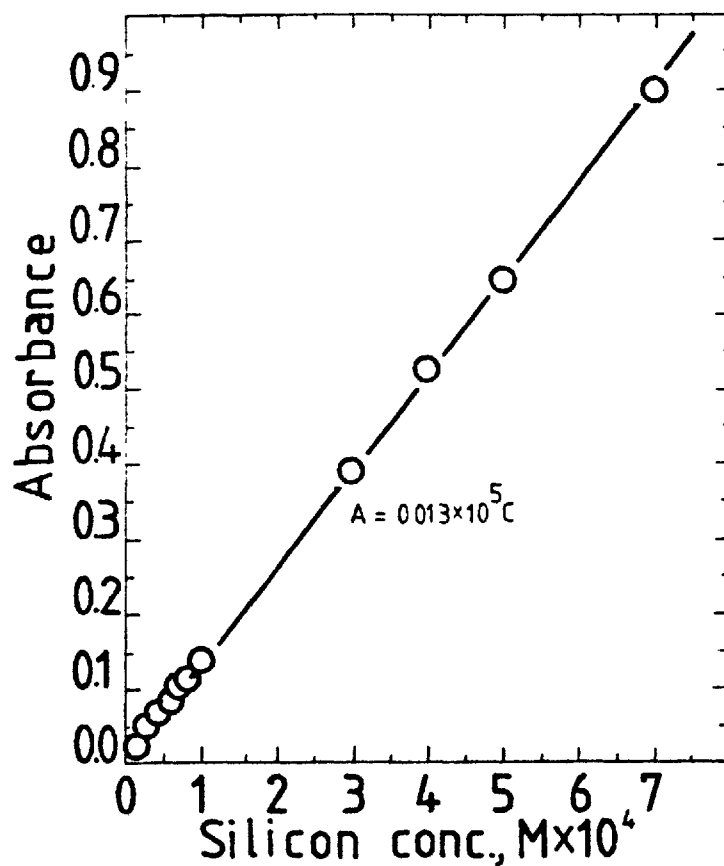


Fig. 2.4. Calibration curve for spectrophotometric determination of dissolved silica based on α -molybdosilicic acid at 400 mμ.

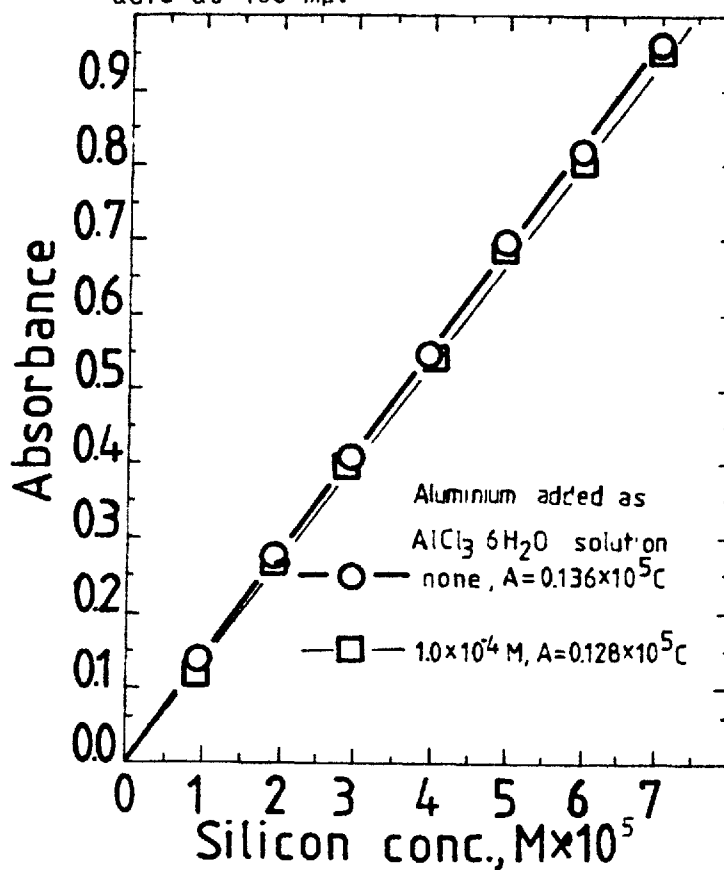


Fig. 2.5. Influence of aluminium ions on the spectrophotometric determination of silica at 329 mμ.

of the molybdosilicic acid are formed, and the absorbance of the solution can be measured at the wavelength of 329 $m\mu$ where the extinction coefficients of the two forms are equal. The measurement is, therefore, independent of the form of the acid. The conditions can be varied widely and the determination can be made in solutions having pH values up to 4.6.

Reagents: Sodium molybdate, stock solution, 5×10^{-1} M - 2.098 g sodium molybdate dihydrate were dissolved in 100 ml distilled water.

All the working solutions, i.e. 2.5×10^{-2} M sodium molybdate and 10^{-1} M hydrochloric acid were prepared by diluting 5 ml of the appropriate stock solution to 100 ml.

Procedure: The pH of the sample or standard solution was adjusted to be between 4.0 to 8.0 and an appropriate amount of the solution was pipetted into a 50-ml volumetric flask with 5 ml of each of the 10^{-1} M acid and 2.5×10^{-2} M molybdate solutions. After standing for 40 min the solution was diluted to 50 ml and the absorbance measured at 329 $m\mu$ in 10-mm quartz cells against a blank solution prepared in a similar way but without silicate.

The Beer's law was obeyed and a linear calibration curve was obtained, at concentrations up to 8.0×10^{-5} M SiO_2 (Fig. 2.5). In both procedures sodium metasilicate was used for the preparation of the silicon standards. A similar calibration curve was, however, obtained when standards were prepared by fusion of pure crystalline quartz with sodium peroxide. All solutions, standards and reagents, were kept in plastic containers.

It is well known that silicon can form stable complexes with fluoride ions especially at low pH values. The results presented in Table 2.4 show, however, that fluoride ions do not interfere with the determination of silicon, at least at the concentration levels used.

The effect of soluble aluminium on the spectrophotometric determination

2.5. Influence of fluoride ion on silicon determination

SiO ₂ taken, M	SiO ₂ found (without any addition), M	SiO ₂ found (1x10 ⁻³ M NaF added), M	SiO ₂ found (1x10 ⁻³ M NaF, 2x10 ⁻³ M boric acid), M
4x10 ⁻⁵	4.20x10 ⁻⁵	4.16x10 ⁻⁵	4.14x10 ⁻⁵
8x10 ⁻⁵	8.45x10 ⁻⁵	8.34x10 ⁻⁵	8.36x10 ⁻⁵

of silicon was studied. At a total aluminium concentration of 1.0×10^{-4} g-atoms/l there was a small reduction in colour and the determined silicon concentration was 3.8% less than the calculated value. The aluminium concentration in the final solution used for silicon determination was, however, less than 2.0×10^{-5} g-atoms/l and its effect was, therefore, considered to be negligible.

The relative error in the silicate determinations was less than $\pm 2.0\%$ but at low silicon concentration ($< 1.0 \times 10^{-5}$ M SiO₂) it increased to about $\pm 7\%$.

2.3.6. Aluminium determination

The total amount of aluminium in solution was determined by a spectrophotometric method based on the formation of a coloured complex with pyrocatechol violet at pH 6.0-6.1 (125).

Reagents: 1,10 phenanthroline, 0.1% w/v - 50 g (± 0.5 g) of hydroxylammonium chloride was dissolved in 400 ml of water. This solution was transferred to a 500-ml volumetric flask, 0.5 g (± 0.005 g) of 1,10-phenanthroline hydrate was added and the solution was diluted to the mark.

Catechol violet, 0.0375% w/v - 0.075 g (± 0.001 g) of catechol violet was dissolved in approximately 15 ml of water. The solution was

transferred to a 200-ml volumetric flask and diluted to the mark. The reagent solution was stored in a glass bottle in a refrigerator. No spore growth was observed.

Hexamine buffer, 30% m/v - 150 g (± 0.5 g) of hexamine was dissolved in approximately 350 ml of water, the solution was filtered and transferred to a 500-ml volumetric flask. 8.4 ml (± 0.1 ml) of ammonia solution (sp. gr. 0.880) was added and the whole was diluted to the mark.

Standard aluminium solution - Two standard aluminium solutions were prepared, one by using an aluminium wire (99.9%) and the other by using $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (99.999%). In the first case 0.4212 g of aluminium was dissolved in 20 ml hydrochloric acid (sp. gr. 1.18) and diluted to 1 l (final concentration: 1.56×10^{-2} g-atoms Al/l). In the second case 0.37581 g of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 8.72 ml hydrochloric acid (sp. gr. 1.18) and diluted to 1 l (final concentration 1.55×10^{-3} g-atoms Al/l). All the above solutions were stored in polyethelene bottles except where otherwise stated.

Calibration: A standard aluminium solution with concentration equal to 7.80×10^{-5} g-atoms Al/l was prepared by diluting the more concentrated solution. The acidity was maintained at 0.1 M by the addition of HCl. Between 0.0 and 5.0 ml of a standard aluminium solution was added to eight small polyethelene bottles and the total volume was made up to 35 ml by the addition of the appropriate amount of 0.1 M hydrochloric acid solution. This was followed by 1 ml (± 0.1 ml) of 1,10 phenanthroline solution, 2 ml (± 0.05 ml) of catechol violet solution and 10 ml (± 0.1 ml) of the hexamine buffer solution. The absorbance of the solution was measured at 585 μ in 10-mm glass cells, against a blank, between 10 and 20 min after adding the hexamine buffer.

Analysis of samples: 5.0 ml of the solution to be analysed was

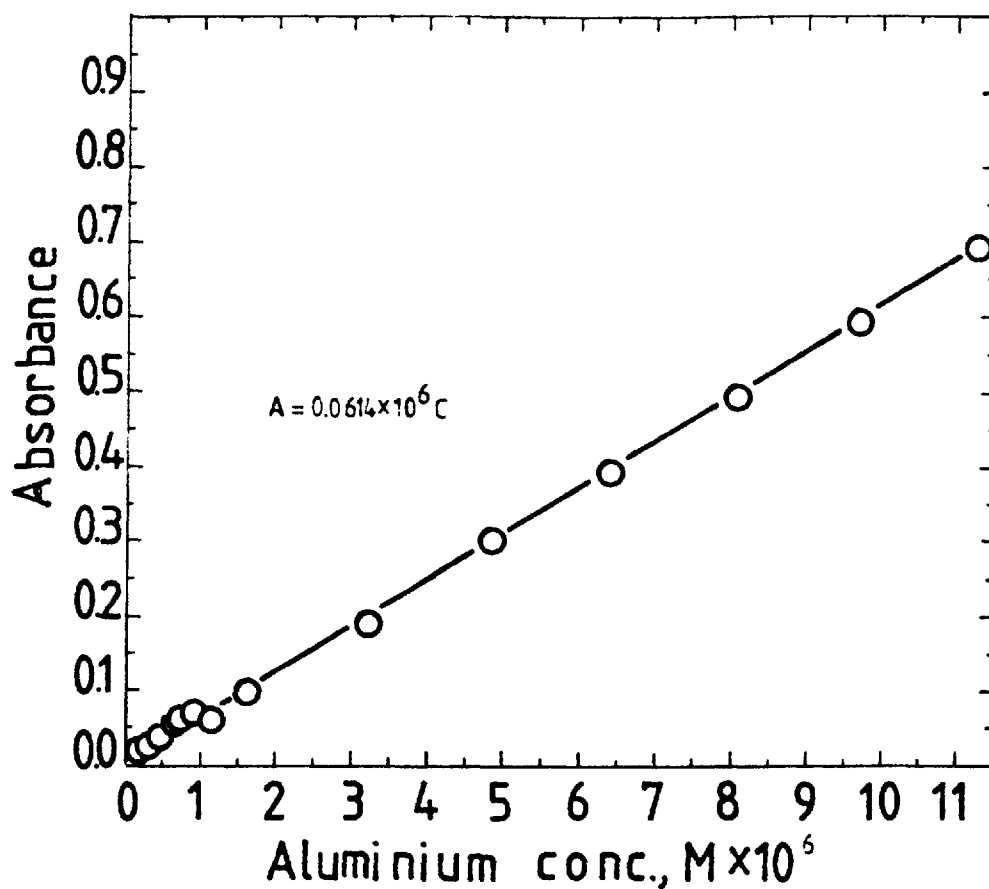


Fig. 2.6. Calibration curve for aluminium determination at 585 mμ.

pipetted into a polyethelene bottle containing 30.0 ml of 0.116 M hydrochloric acid solution. The solution was left to stand for about 6 h and then its aluminium concentration was determined. Absorbance readings were converted to concentrations by the calibration curve shown in Fig. 2.6 or by using a value for the extinction coefficient equal to 61.4×10^3 l/mol.cm.

CHAPTER 3. SOLUBLE SILICATES

3.1. Introduction - Terminology

In this chapter a brief review of the chemistry of aqueous sodium silicate solutions is given with special emphasis on dilute solutions. The behaviour of silicate solutions is to a large extent dependent on the solubility of silica. Unfortunately, despite the large amount of literature on this subject, there is no generally accepted value because of the uncertainty of the structure of the silicate solutions. To avoid ambiguity, the following terms will be used in reference to the various forms of silica:

Silica:- This is a general term and refers to any form of silicon dioxide, crystalline or amorphous.

Crystalline silica:- Quartz, tridymite and cristobalite.

Amorphous silica:- This refers to any form of silica lacking crystal structure and includes the following:

1. Silica sol - This is colloidal silica dispersed in water. Depending on the pH of the medium the particles may be uncharged or have a low charge (at pH less than 4.50) or be negatively charged (at pH above 7.0). In the former case the viscosity of the sols increases with time while in the latter (pure silica sols) it remains constant or decreases with time. Silica sols may contain high concentrations of SiO_2 . In

these systems a stabilizer reagent is added to prevent gelation or aggregation (small amounts of alkali, etc.).

2. Silica gels - This term includes all the amorphous forms of silica which result after flocculation or gelation of silica sols, ranging from the dense, hard, impervious mineral opal to the extremely light, porous, synthetic product "aerogel". The degree of hydration ranges from almost anhydrous SiO_2 to soft gelatinous masses containing 100 parts of water per part of silica.

In addition to the above the following terms are used:

1. Monosilicic or monomer silicic acid - This refers to the formula $\text{Si}(\text{OH})_4$ and is the only form in which silica exists in its saturated solution, i.e. in solutions at equilibrium with solid silica, at pH values lower than 9.0.

2. Polysilicic acids - These are silicic acids containing two or more atoms of silicon per molecule.

Salts of the above acids are called (mono-) silicate and polysilicates and their ions exist in highly alkaline solutions. Monosilicic acid and generally the low molecular weight forms of silica in solution (disilicic acid) react with an ammonium molybdate solution in less than ten minutes while the higher homologues react more slowly.

3. "Active" silica - This is any silica in molecular or colloidal form in aqueous solution which is in such a state of polymerisation that when diluted with sodium hydroxide solution to a pH of 12.0 and an SiO_2 concentration of 0.02% ($\approx 3.3 \times 10^{-4}$ M) at 30°C , depolymerizes substantially completely to monomer in less than 100 min.

4. Polymerization-Depolymerization - Polymerization involves the condensation of silanol groups to form siloxane bonds ($2-\overset{|}{\underset{|}{\text{Si}}}\text{OH} \rightarrow -\overset{|}{\underset{|}{\text{Si}}}-\text{O}-\overset{|}{\underset{|}{\text{Si}}}- + \text{H}_2\text{O}$) while depolymerization results in the formation of monomeric forms of silica

in solution through the breaking down of the siloxane bonds.

5. Silicate ions - This refers to all ions existing in a silicate solution, including monomers and/or polynuclear species.

6. Colorimetric silica - total silica - The amount of silica available for colorimetric determination is called "colorimetric" silica and may be less or equal to the "total" silica present which is determined gravimetrically.

3.2. Solubility of silica in water

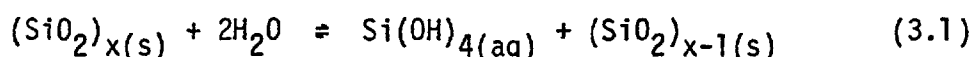
3.2.1. Co-ordination number of silicon

It is well known that silicon exhibits four fold co-ordination in many of its oxygen bearing compounds. However, it would appear that under certain conditions five and six fold co-ordinated silicon is possible. Weyl (126) suggested that the co-ordination number (c.n.) of silicon in aqueous solution in the presence of OH^- ions was 6. He concluded this from the similarity in size of the F^- and OH^- ions, the existence of the SiF_6^{2-} ion and the fact that F^- substitutes for OH^- in natural silicates. Raman studies by Early et al (127) and extensive work by Ingri and Lagerström (128 - 9), however, failed to prove this.

Recently Ganeyev (130) postulated that the formation of silicate ions with a c.n. of 5 and 6 in acid, neutral and alkaline solutions is feasible. Furthermore, the existence of ions with a c.n. of 6 in alkaline solutions has been proved by NMR Si^{29} spectroscopy (130). In view of the controversy over the conditions under which a c.n. of 6 is obtained, a c.n. of 4 is assumed in the rest of this thesis (131). This assumption simplifies the presentation of the reactions which occur in aqueous solutions.

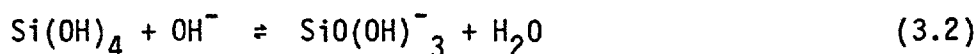
3.2.2. Solubility of silica in water

It was suggested by Aoki (132) that silica dissolves in water forming a true solution up to a certain concentration which can be defined as the "solubility of amorphous silica". Since his work the solubility of various forms of silica has been extensively studied by many workers and a summary of the results can be found in the work of Iler (126) and Krauskopf (133). The dissolution of silica in water proceeds according to the reaction:



where $(\text{SiO}_2)_x$ represents any form of silica. This reaction is catalyzed by OH^- ions and for some forms of silica it is extremely slow. The slowness of the dissolution reaction probably accounts for the differences in solubility values reported in the earlier literature.

The work of Alexander et al (134) was an advance on previous studies because the solubility of amorphous silica was determined under conditions of true equilibrium. Both unsaturated and supersaturated solutions were used and the same equilibrium value was obtained. The solubility of three forms of silica was studied and the final concentration in solution was the same and equal to 0.012 - 0.014% or $1.99 - 2.33 \times 10^{-3}$ M SiO_2 . The solubility of silica was constant in the pH region 8.0-5.0 and slightly increased at lower pH values. Above pH 9.0 the solubility of silica increased due to the formation of silicate ions, while the concentration of $\text{Si}(\text{OH})_4(\text{aq})$ remained constant. The amount of silica which can exist in solution at high pH values has not yet been definitely established (135). The conversion of $\text{Si}(\text{OH})_4$ into silicate ions at high pH values can be explained on the basis of the equilibrium:



The work of Alexander was followed by a series of publications in which the solubility of different forms of silica was studied under various equilibrium conditions (136 - 50). At this point it must be emphasized that the equilibrium between amorphous silica and dissolved silica is metastable because the stable form of solid silica at room temperature and pressure is α -quartz. Krauskopf (133) reported a value of $1.67\text{--}2.34 \times 10^{-3}$ M SiO_2 for the solubility of amorphous silica and Greenberg and Price (136) found that the equilibrium value for colloidal silica was not markedly affected by ionic strength up to 0.1 M NaCl. Jørgensen (145), however, obtained a slightly lower equilibrium value at 77.7 mg SiO_2 /l (or 1.36×10^{-3} M SiO_2) for the solubility of amorphous silica in 1 M NaClO_4 solutions. The effect of sodium or perchlorate ions on the formation of the solubility-defining layer, i.e. a disturbed layer on the surface of the particles of amorphous silica, may be the reason for such a discrepancy.

The values obtained for the solubility of various forms of silica in water are given in a recent review by Volosov et al (151).

The solubility of silica increases slightly at low pH values, possibly because of the formation of a complex between the acid used and silica. Sadek (152) and Elmer (138) found increases in the presence of hydrochloric and nitric acid, respectively. With hydrofluoric acid the increase can be attributed to the formation of SiF_6^{2-} ion. Solubility increases are also obtained in the presence of hydroxy-organic compounds such as citric acid, tartaric acid, acetone and alcohols (153). Although these effects have been known for some time reliable data is not available because no systematic studies have been made.

The solubility of silica decreases in the presence of certain metal cations. Iler (154 - 5) reported that even trace amounts of aluminium

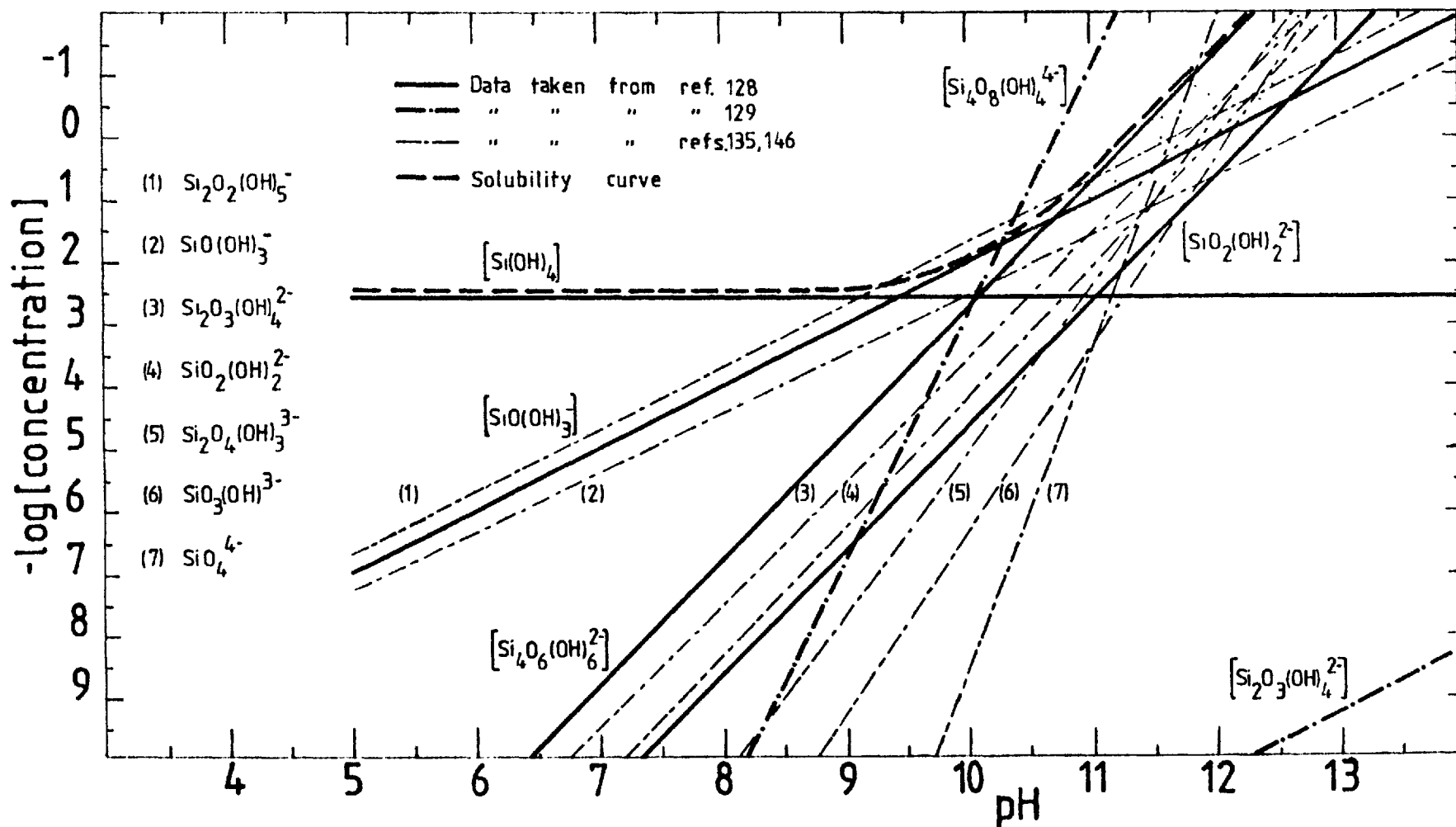


Fig. 3.1. Theoretical solubility and distribution diagram of the various silicate species in an aqueous solution saturated with respect to amorphous silica at 25°C (solubility curve was drawn using data taken from ref. 128).

reduced the solubility of silica considerably. The reason has not been adequately explained.

The concentration of the possible silica species in equilibrium with solid silica is shown in Fig. 3.1 as a function of pH. The constants used are those of Ingri (last column of Table 3.1). To obtain this diagram the concentration of Si(OH)_4 was assumed to be constant over the whole pH region.

The concentration of silicate species reported by a number of other researchers is also given in this diagram for comparison. Their data are represented by the dashed lines (135, 156). The formulae of the various silicate species is that proposed by Ingri for mononuclear or polynuclear hydroxo complexes. Species given in other form have been re-written according to this nomenclature to avoid ambiguity. The dotted area in the figure is that in which stable polynuclear species may exist along with monomeric ones, in considerable amounts.

3.3. Aqueous chemistry of sodium silicate

3.3.1. Sodium silicate

Before considering the behaviour of silicate solutions, a brief reference will be made to the soluble glasses from which the soluble silicates are prepared commercially. The term sodium silicate refers to a whole family of chemicals which consist mainly of sodium oxide and silicon dioxide in various proportions and their composition is expressed by the general formula: $\text{Na}_2\text{O} \cdot r\text{SiO}_2$. The index r is usually called "modulus" or "ratio" of the sodium silicate. The commercial sodium silicates are prepared by fusion of a mixture of sand and soda ash at high temperatures. The resulting glass is dissolved in water under controlled conditions of temperature and pressure. The mixture thus

obtained is referred to as soluble sodium silicate (157).

Most of the commercially available sodium silicates are not true chemical compounds but complexes of definite sodium silicate and either silica or alkali. Harman (158) concluded from conductivity, transfer number, activity coefficient, hydrolysis, osmotic activity, freezing-point, phase relation and diffusion experiments that there are only two simple definite sodium silicate salts: Na_2SiO_3 (and its hydrates $\text{Na}_2\text{SiO}_3 \cdot 6\text{H}_2\text{O}$, $\text{Na}_2\text{SiO}_3 \cdot 2.5\text{H}_2\text{O}$) and $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$. These two silicates correspond to ratios 1:1 (metasilicate) and 2:1 (disilicate). Silicates with higher ratios are not considered to be true compounds but mixtures of the two. The crystal structure of these two silicates is not completely known. According to Jamieson (159 - 60), Glasser et al (161) and Brekhunets et al (162) the crystal structure of "sodium metasilicate enneahydrate" contains isolated $\text{H}_2\text{SiO}_4^{2-}$ groups, and no condensed silicate ions, in contrast to anhydrous Na_2SiO_3 which contains $(\text{SiO}_3)_n$ chains. Alexander (163) claimed however, that the silicate ions in crystalline metasilicate are monomeric, because monosilicic acid is formed on reaction with acid, which is consequently partially polymerized in an aqueous solution of this salt. Sodium disilicate is supposed to have the same structure as the minerals of the mica group.

The structure of sodium silicates with ratios ranging from 1.16:1 to 7.74:1 was studied by Lentz (164). They were found to contain SiO_4 , Si_2O_7 , Si_3O_{10} , $(\text{SiO}_3)_4$, and polysilicate structures. The ratio of sodium silicate determines the type of silicate ions existing in solution. Thus, silicates with a ratio less than 2.0:1 give mainly monosilicate and disilicate ions. This has been confirmed by light scattering studies (165 - 7) as well as by using the ammonium molybdate method (168 - 9). Sodium silicates with higher ratios give highly polymerized silicate ions

in solution. O'Connor (165), using the molybdate method concluded that in aqueous solutions of sodium silicates with ratios higher than 2.0:1 the silicate ions are present as two dimensional polymeric anions. He based his view on the fact that non-cyclic silicic acids depolymerize rapidly (< 5 min) while the polysilicic acids derived from these polysilicate ions require up to several hours for complete depolymerization.

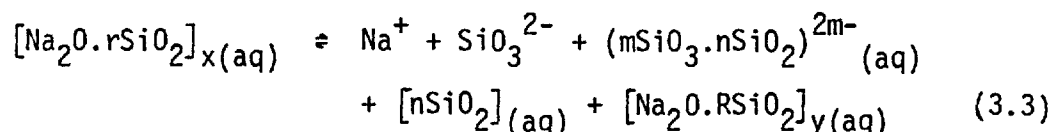
The number-average molecular weight of polysilicate ions which exist in a 2M SiO_2 sodium silicate solution with ratio 3.3 was found to be approximately 200 (170). Polysilicic acid prepared from a solution of 3.3 ratio sodium silicate (0.33 M SiO_2) had a number-average molecular weight of about 280. From these data and the assumption that the polysilicate ions vary between the dimer and 20-mer, it is inferred that the 3-mers are the predominant species in these sodium silicate solutions.

3.3.2. Chemistry of dilute aqueous sodium silicate solutions

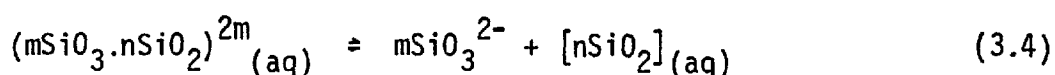
A dilute sodium silicate solution is generally defined as a solution which contains less silica than that corresponding to the solubility of amorphous silica. However, it can also include solutions which are slightly supersaturated. One of the basic problems with dilute solutions is that the structure of the silica species is not known. This problem also applies to concentrated solutions, but with dilute solutions it is more pronounced because many of the indirect techniques used to determine average molecular weights or average numbers of silicon atoms per ion only apply in concentrated solutions.

A very comprehensive study of aqueous sodium silicate solutions with ratios varying from 1:1 to 1:4 under alkaline conditions has been carried out by Harman (158). He studied the properties of sodium silicate solutions in concentrations varying from 1×10^{-3} M up to 2 M. These

concentrations are, however, somewhat higher than those normally associated with dilute solutions. The equilibria given for equilibrated solutions of sodium silicate are:



and in more dilute solutions further depolymerization takes place

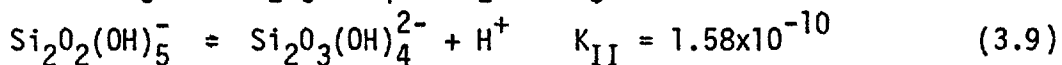
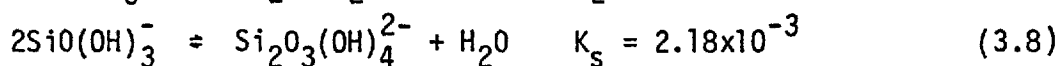


In the above reactions square brackets represent colloidal particles.

Harman concluded that in a 1×10^{-2} M SiO_2 sodium silicate solution with a ratio 4:1, 34% of the total silica was in the form of undissociated monosilicic acid and 14% in the form of ions or ionic micelles (particles having a negative charge), while at a concentration of 7×10^{-3} M SiO_2 , 75% of silica was in these two forms. The rest of the silica, in both cases, was in colloidal form. In a sodium silicate solution with a concentration 1×10^{-2} M SiO_2 and ratio 3:1, 40% of the total silica was in colloidal form. In more concentrated solutions at higher ratios than 2:1 all the silica was present in colloidal form. He also concluded the equilibria represented by the above equations show a tendency to proceed from right to left with increasing ratio at any one concentration and with increasing concentration at any one ratio. In dilute solutions of these silicates Harman suggested that uncharged silica in the form of H_2SiO_3 (equivalent to $\text{Si}(\text{OH})_4$) or simple hydrated silica occurred. Sodium silicates with ratios higher than 2:1 exhibited properties characteristic of colloidal electrolytes with a micelle of the composition $(\text{mSiO}_3 \cdot \text{nSiO}_2)^{2m-}(\text{aq})$ where $(m + n)/n$ equals r , i.e. the ratio of the sodium silicate.

For a dilute sodium silicate solution where colloidal silica is not present the dissolution process, at high pH values, results in the formation of sodium and silicate ions. As the pH of the solution is reduced and because silicic acid is a weak acid, silicate ions hydrolyse and form neutral molecules of silicic acid. The concentration of each ionic species present will be a complicated function of the pH.

The equilibria involved in the first steps of the neutralization of a silicate solution were first studied by Roller and Ervin (135). To interpret their experimental data they assumed that association took place even in dilute alkaline solutions (SiO_2 concentration between 1.05×10^{-5} and 6.9×10^{-4} M and pH values from 12.62 to 11.11, respectively), and resulted in the formation of disilicate ions. The equilibrium constants were determined:



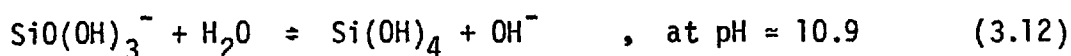
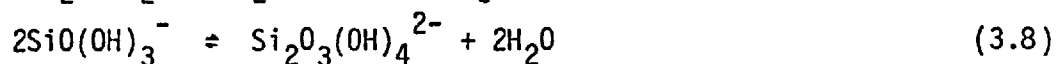
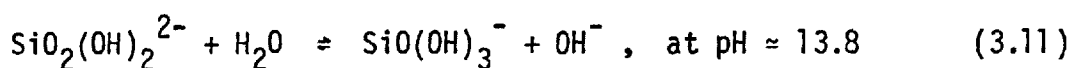
The above equations permit calculation of equilibria involving monomeric and dimeric forms of the silicate ions, but give no indication of the next stage in the formation of ions of still higher molecular weight.

The pH at which disilicate ions essentially disappear, as the pH is reduced, can be calculated using the above data:

$$\frac{[\text{H}^+][\text{Si}_2\text{O}_3(\text{OH})_4^{2-}]^{1/2}}{[\text{Si(OH)}_4] 2.18 \times 10^3} = 1.58 \times 10^{-10}, \quad \log \frac{[\text{Si}_2\text{O}_3(\text{OH})_4^{2-}]^{1/2}}{[\text{Si(OH)}_4]} = \text{pH} - 8.1$$

According to this equation, if $[\text{Si(OH)}_4]$ is stable in aqueous solution then

the pH of a 1.0 M sodium silicate solution would have to be reduced to 7.5 to convert 95% of the disilicate ions to the free non-ionized acid. However, due to the high rate of polymerization of $\text{Si}(\text{OH})_4$ and its subsequently reduced concentration in solution, the disilicate ion actually disappears at a much higher pH. Jander (126) reported that this takes place at pH 10.9. Briefly, the neutralization of a sodium silicate solution (1 M) may be represented as follows:



Further neutralization results in the polymerization of silicic acid. Greenberg (171) and Greenberg and Sinclair (172) calculated the ratio of the concentration of singly ionized to that of un-ionized silicic acid, i.e. the ratio $[\text{SiO}(\text{OH})_3^-]/[\text{Si}(\text{OH})_4]$ assuming that in dilute solutions and at pH values above 10.5 the only silicate ions which exist are the monomeric ions $\text{SiO}(\text{OH})_3^-$ and $\text{SiO}_2(\text{OH})_2^{2-}$. At pH 10.5, 9.5 and 8.0 the ratios obtained were 5:1, 1:1, 1.6:10 and 1.6:100. Obviously between pH 8 and 10.5 the concentration of the silicic acid molecule and silicate ions is significant although both are dependent on pH.

Lagerstrom (129) studied the equilibria in silicate solutions in 0.5 m NaClO_4 (molality, i.e. moles/1000 g water) at 25 and 50°C, and in 3 m NaClO_4 at 25°C. He used a potentiometric titration method which permits determination of the average number of silicon atoms per unit charge in a polynuclear ion. The silica concentration was varied between 1.0×10^{-3} to 2.0×10^{-1} m and the pH was in the 10.0 to 13.5 region. He explained the data obtained in 0.5 m NaClO_4 in terms of the species $\text{Si}(\text{OH})_4$, $\text{SiO}(\text{OH})_3^-$, $\text{SiO}_2(\text{OH})_2^{2-}$ and $\text{Si}_4\text{O}_6(\text{OH})_6^{2-}$. The data in 3 m NaClO_4

Table 3.1. Equilibrium constants for silicate reactions

Reaction	Constant	Ref. 129			Ref. 128
		I=0.5/NaClO ₄ 50°C	I=0.5/NaClO ₄ 25°C	I=3/NaClO ₄ 25°C	I=0.5/NaCl 25°C
$\text{H}_2\text{O} = \text{OH}^- + \text{H}^+$	K_w	12.97	13.73	14.03	13.70±0.02
$\text{Si}(\text{OH})_4 + \text{OH}^- = \text{SiO}(\text{OH})_3^- + \text{H}_2\text{O}$	K_1	- 3.84	- 4.27	- 4.60	- 4.29±0.05
$\text{SiO}(\text{OH})_3^- + \text{OH}^- = \text{SiO}_2(\text{OH})_2^{2-} + \text{H}_2\text{O}$	K_2	- 1.06	- 1.17	- 1.32	- 0.99±0.05
$\text{Si}(\text{OH})_4 + 2\text{OH}^- = \text{SiO}_2(\text{OH})_2^{2-} + 2\text{H}_2\text{O}$	β_2	- 4.90	- 5.44	- 5.92	- 5.28±0.15
$4\text{Si}(\text{OH})_4 + 2\text{OH}^- = \text{Si}_4\text{O}_6(\text{OH})_6^{2-} + 6\text{H}_2\text{O}$	β_{24}	-13.38	-14.89	-	-15.03±0.20
$4\text{Si}(\text{OH})_4 + 4\text{OH}^- = \text{Si}_4\text{O}_8(\text{OH})_4^{4-} + 8\text{H}_2\text{O}$	β_{44}	-	-	-23.64	-
$2\text{Si}(\text{OH})_4 + 2\text{OH}^- = \text{Si}_2\text{O}_3(\text{OH})_4^{2-} + 3\text{H}_2\text{O}$	β_{22}	-	-	- 9.94	-
$\text{Si}(\text{OH})_4 = \text{SiO}(\text{OH})_3^- + \text{H}^+$	$*K_1$	9.13	9.46	9.43	9.51±0.05
$\text{SiO}(\text{OH})_3^- = \text{SiO}_2(\text{OH})_2^{2-} + \text{H}^+$	$*K_2$	11.91	12.56	12.71	12.94±0.15
$\text{Si}(\text{OH})_4 = \text{SiO}_2(\text{OH})_2^{2-} + 2\text{H}^+$	$*\beta_2$	21.04	22.02	22.14	22.12±0.15
$4\text{Si}(\text{OH})_4 = \text{Si}_4\text{O}_6(\text{OH})_6^{2-} + 4\text{H}_2\text{O} + 2\text{H}^+$	$*\beta_{24}$	12.56	12.57	-	12.37±0.20
$4\text{Si}(\text{OH})_4 = \text{Si}_4\text{O}_8(\text{OH})_4^{4-} + 4\text{H}_2\text{O} + 4\text{H}^+$	$*\beta_{44}$	-	-	32.48	-
$2\text{Si}(\text{OH})_4 = \text{Si}_2\text{O}_3(\text{OH})_4^{2-} + \text{H}_2\text{O} + 2\text{H}^+$	$*\beta_{22}$	-	-	18.13	-

was explained assuming equilibria between the three mononuclear species mentioned and $\text{Si}_2\text{O}_3(\text{OH})_4^{2-}$ and $\text{Si}_4\text{O}_8(\text{OH})_4^{4-}$. The equilibria and equilibrium constants used by this author are given on Table 3.1.

Ingri (128) continued the work of Lagerström and studied the equilibria in silicate solutions in 0.5 m NaCl. The data obtained covers total silicate concentrations from 2.5×10^{-3} to 8.0×10^{-2} m and pH values between 10.0 and 13.5, and was explained assuming the existence of the polynuclear species $\text{Si}_4\text{O}_6(\text{OH})_6^{2-}$ together with $\text{Si}(\text{OH})_4$, $\text{SiO}(\text{OH})_3^-$ and $\text{SiO}_2(\text{OH})_2^{2-}$. The equilibrium constants reported by this author are also given in Table 3.1.

Both Ingri and Lagerström agree that, in the concentration range studied, the equilibria with polynuclear species were rapidly obtained provided that clear solutions free of colloid or precipitate were studied.

Aveston (173) studied the hydrolysis of sodium silicates with ratios between 0.96:1 and 1.56:1 by an ultracentrifugation technique. The degree of polymerization was found to increase rapidly with increase in ratio and concentration. The existence of a series of polynuclear species in addition to the monomers and tetramers was also proposed.

Recently, Bilinskii and Ingri (174) studied the equilibria in very dilute silicate solutions (3.2×10^{-4} - 1.32×10^{-3} M SiO_2) and at pH values as low as 8.50. They concluded that under these conditions $\text{SiO}(\text{OH})_3^-$ was the only silicate ion present. The equilibrium constant for the reaction



was determined and found to be $10^{-9.46 \pm 0.02}$ ($= *K_1$).

Using the equilibrium constants given by Lagerström for 0.5 m NaClO_4 medium at 25°C the logarithmic distribution diagram for 1×10^{-3} M SiO_2 solution was constructed (Fig. 3.2). It can be clearly seen that

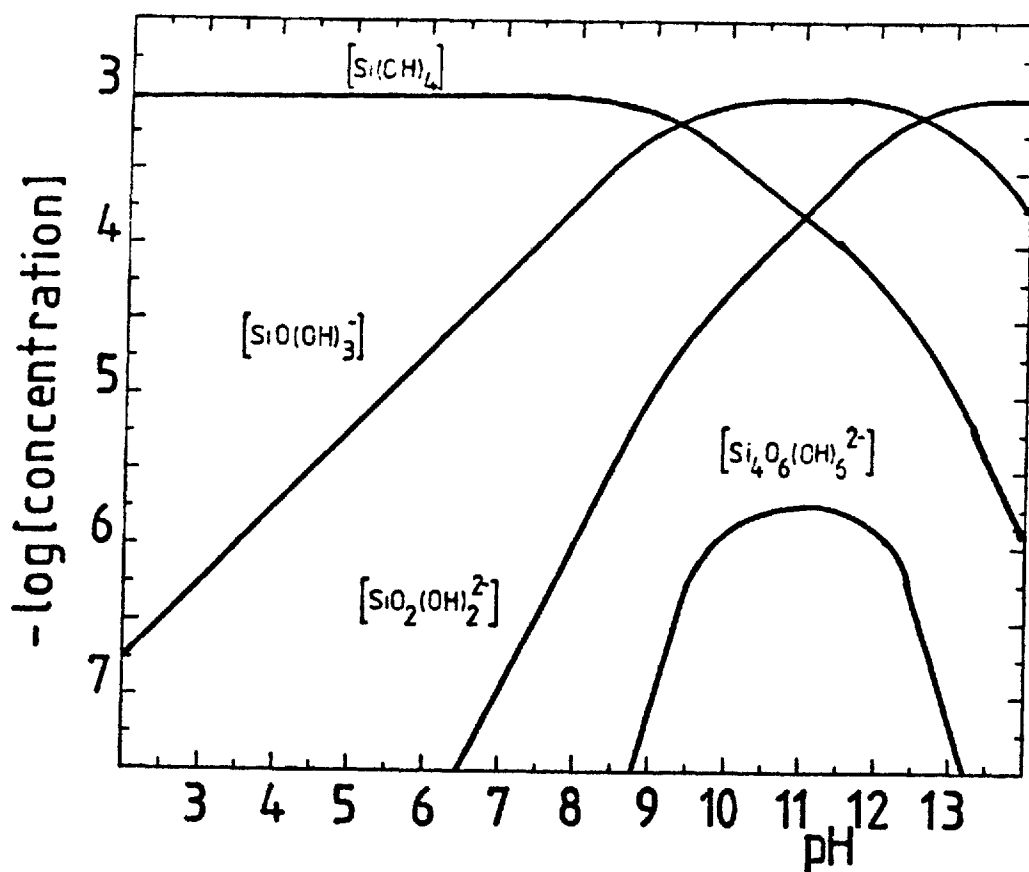


Fig. 3.2. Logarithmic concentration diagram for $1 \times 10^{-3} \text{ M}$ SiO_2 solution (constants taken from ref. 129)

$\text{Si}(\text{OH})_4$ predominates at pH values below 9.0, $\text{SiO}(\text{OH})_3^-$ between 9.5 and 12.5 and $\text{SiO}_2(\text{OH})_2^{2-}$ at pH values above 12.5. $\text{Si}_4\text{O}_6(\text{OH})_5^{2-}$ does not predominate at any pH but between pH 10.0 and 12.0 its concentration reaches a maximum.

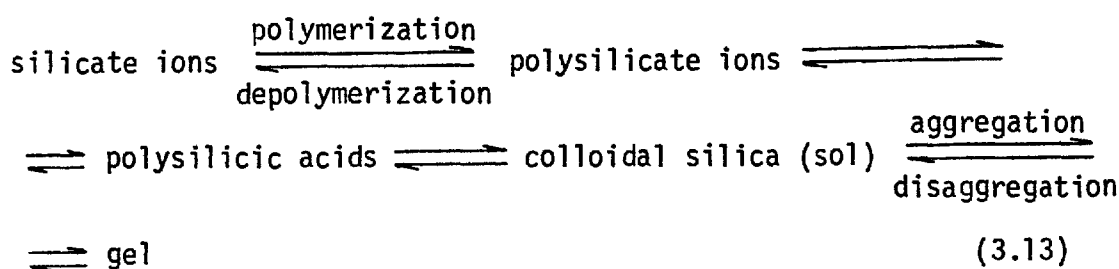
In their studies on the solubility of various forms of silica in aqueous solutions Kopeikin and Mikhailov (146) supported the ideas of previous investigators. They found that silica at $\text{pH} \leq 7$ is in the form of undissociated $\text{Si}(\text{OH})_4$ while noticeable dissociation starts at $\text{pH} \geq 8$. At pH 10 and 11 most of the silica in solution is represented by $\text{SiO}(\text{OH})_3^-$ ions whereas at pH 12.0 it is present in the form of three simple ions $\text{SiO}(\text{OH})_3^-$, $\text{SiO}_2(\text{OH})_2^{2-}$ and SiO_4^{4-} in equal amounts. They

suggested that dimeric ions are formed in noticeable amounts (> 1% of the total SiO_2) starting at pH 8.0. The $\text{Si}_2\text{O}_3(\text{OH})_4^{2-}$ is the predominant type of dimer at pH 10 - 11. They also concluded that higher polynuclear species were present but in smaller amounts.

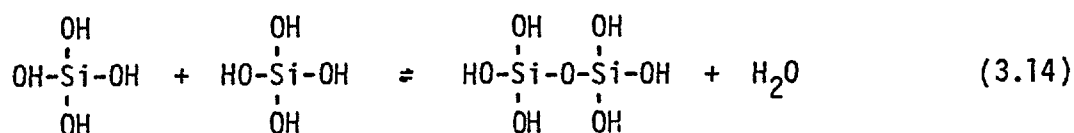
Finally, the dissociation constants of silicic acid together with the solubility of various forms of silica at elevated temperatures and pressures has been measured by a great number of researchers and a detailed review is given by Ryzhenko (175) and Volosov et al (151).

3.3.3. Polymerization-Depolymerization

When the concentration of silica in solution exceeds the value given for the solubility of amorphous silica polymerization of silica takes place. In the reverse case, when the silica concentration is reduced to that below the solubility, depolymerization occurs. The overall polymerization/depolymerization process can be represented as follows:

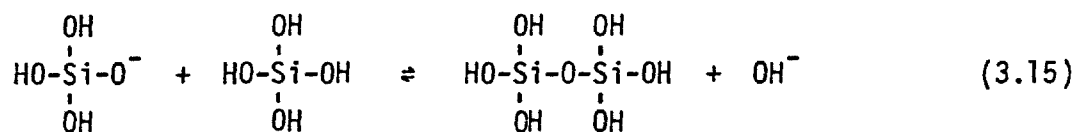


The polymerization of silica results in the formation of siloxane bonds by condensation of silanol groups and can be represented by:



The rate of reaction depends on the silica concentration and temperature as well as the pH. The effect of the pH on the rate of polymerization

has been studied extensively. First, it is well known that the rate is very slow at low and high pH values (126, 176). In acidic media the polymerization rate is so slow that supersaturated solutions, with respect to monosilicic acid, can exist for a long period of time(126). The polymerization rate in the pH region 4 to 10 has been measured by various methods but the value given for the maximum rate of polymerization varies considerably. Greenberg (177 - 8) and Greenberg and Sinclair (172) reported that the rate was at a maximum at pH 8.6 and the following polymerization reaction was proposed:



According to them this mechanism is consistent with the following information on the reaction:

1. No reaction takes place at high pH values where the solutions consist mainly of silicate ions which would tend to repel each other and any polysilicic acid formed would be expected to depolymerize.
2. The reaction takes place slowly, if at all, at low pH values where the concentration of un-ionized silicic acid is high. At very low pH the reaction may go by a different mechanism and,
3. The reaction proceeds at a maximum rate in the pH range 8 - 9. In this range the concentration of silicic acid and the singly ionized form are both significant.

Goto (179) and Okamoto et al (180) studied the rate of polymerization in the pH range 7.0 to 10.0. The reaction rate constant at various pH values was calculated on the assumption that the polymerization reaction was third order with respect to the concentration of molecular silica. It was found that the rate constant increased linearly with pH which

indicates that the polymerization proceeds more rapidly at higher pH values. Brady et al (181) have concluded, however, from light-scattering measurements that the optimum pH for rapid polymerization is about 8.0. Similar values have been obtained by Richardson et al (182) and Iwasaki (183). Bechtold (184) reports a maximum polymerization rate at slightly lower pH values.

Recently, Kitahara (140) studied the polymerization of silicic acid obtained by hydrothermal treatment of quartz. His results were in a good agreement with those already reported (180, 184) for sodium silicate solutions. The rate of the polymerization of silicic acid showed a maximum at about pH 7.5. A second and third order polymerization reaction was proposed at pH values below and above pH 7.5, respectively. The activation energy was estimated to be 9.8 kcal/mol at 25°C.

Both polymerization and aggregation were considered by Iler (126) to be catalyzed by OH^- and F^- ions. The minimum rate of polymerization was obtained at around pH 2 to 3 (185). At low pH values the polymerization process was catalyzed by H^+ and F^- ions (even when they were present in trace amounts) and a third order reaction was obtained. At higher pH values the process was catalyzed by OH^- ions. The same author claimed that polymerization in the presence of OH^- and F^- takes place by an intermediate increase of the co-ordination number from 4 to 6. This has been shown, however, not to be the case (172).

The structure of the polymer species formed depends on the pH. At around pH 2 to 3 chainlike or open-branched polymers are initially produced. Such polymers may be defined as having a certain molecular weight, but can scarcely be considered as being "particles" of SiO_2 . On the other hand, in alkaline solutions, polymers form in which there are internal condensation and crosslinking to give particles with an interior consisting

essentially of silicon and oxygen atoms, with hydroxyl groups attached to silicon only around the outside.

Similar views have been put forward by Markhasev and Sedlitskii (186). According to them, in a sodium silicate solution, $\text{Na}_{2n}\text{Si}_m\text{O}_{n+2m}$, three different groups of polymeric species exist and their structures depend on the n:m and O:Si ratios:-

1. the fibrelike ($\approx 20\overset{\text{O}}{\text{\AA}}$ cross section), with anionic complexes containing more than 50 SiO_4 groups, and a n:m ratio less than 1/4 and an O:Si ratio between 2-2.5.

2. the colloidal solutions ($10\text{-}20\overset{\text{O}}{\text{\AA}}$ particle size), with anionic complexes consisting of 5-50 SiO_4 groups and a n:m ratio between 1/4 - 5/6 and O:Si ratio between 2.25-3.2 and,

3. the true sols (particle size less than $10\overset{\text{O}}{\text{\AA}}$), with an anionic complex consisting of 4 or less SiO_4 groups and a n:m ratio greater than 5/6 and O:Si between 3.2-4.

The presence of some ions, salts and organic compounds influence the polymerization rate of silicic acid. The effect of F^- ions was mentioned above. Ghost et al (153) studied the polymerization rate in the presence of alcohols and found that it decreased.

Polymerization/depolymerization processes are reversible. On dilution, therefore, polysilicic acids depolymerize to monosilicic acid, but the rate of reaction is very slow.

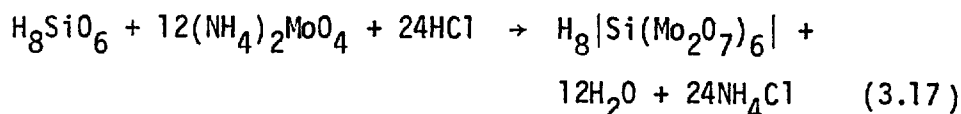
3.3.4. Reaction of molybdate ions with silicic acid/silicate ions

An important reaction of silicic acid and silicate ions is that with molybdate ions. This reaction has found considerable use in the quantitative determination of low concentrations of silica and also in the determination of the different forms of soluble silica. Silicic

acid forms yellow heteropoly acids with molybdate, vanadate and tungstate via the co-ordinatively unsaturated acid H_8SiO_6 (187). The reactions involved can be summarized as



and



The reaction has been studied in more detail by Strickland (188) who concluded that there are two forms of silicomolybdic acid, namely the α - and β -forms. Evidence for a third form γ - acid is not strong (187). Which form predominates is dependent on the pH and a low pH favours the β -form which converts slowly to the α -form on standing.

A variety of different methods have been used for the determination of silicon based on the molybdate reaction. It is generally agreed that the reaction rate is different for the various forms of silica in solution, although precise reaction times have not been established.

Some authors (187) believe that monomeric silica reacts with molybdate ions in less than 75 s, while the dimeric form reacts within 10 min. Higher polynuclear species react at an even slower rate due to the intermediate depolymerization. Generally the rate of the reaction between silica and molybdate ions depends on the concentration of the reacting substances, temperature, pH, type of the acid used to adjust the pH, and the presence of some organic compounds (acetone, ethanol).

Another method, for studying the forms of silica in solution, is that used by Merril and Spencer (189 - 90). They studied the colour changes of a solution of pinacyanol chloride ($\approx 1 \times 10^{-5} \text{M}$) by adding different amounts of sodium silicate (ratio 3.3:1) and sodium hydroxide.

In the presence of colloidal matter, the initial blue solution of the dye shifts to a red colour (concentration of $\text{SiO}_2 \approx 0.33\text{M}$).

3.4. Study of sodium silicates used in the present work

3.4.1. General

In the preceding paragraphs an attempt was made to review the information available on the aqueous chemistry of silica and especially that referring to dilute solutions. It is clear from this review that there is considerable controversy over the forms of soluble silica and furthermore that the properties of silicate solutions are dependent on the initial material and procedure used to prepare them. In view of these uncertainties a study was made of the sodium silicate solutions used, in the present work, to attempt to identify the forms of soluble silica present. The ammonium molybdate method was used.

3.4.2. Experimental

The procedure used was that given by Chow and Robinson (191). The solution under study was reacted with 4.0 ml of 10% ammonium molybdate solution and 0.2 ml of 18N sulphuric acid solution. Soon, or 5 min after, adding the reagents the absorbance of the solution was measured. In the former case the change in the absorbance was followed for up to 30 min (no detectable changes occurred after this time), while, in the latter case only, the readings at 5 min were taken. The amount of silica reacted in 5 min was considered to represent the monomeric silica present, and it was determined from a calibration curve constructed by the dilution of a $1 \times 10^{-2}\text{M}$ sodium silicate solution with ratio 1:1, aged for more than two months at pH ≈ 12 so that all the silica was colorimetrically available. Absorbance measurements were

made at a wavelength of 430 mμ with 0.5-cm quartz cells and a Perkin Elmer 124 Double Beam Spectrophotometer. The Beer's law was valid at least up to 3×10^{-3} M SiO_2 , and the extinction coefficient was 758 litres moles⁻¹ cm⁻¹.

At this point it is of interest to note that Chow and Robinson recommend the use of 2 ml of 10% ammonium molybdate solution. This is, however, not enough for the completion of the reaction at the high silicon concentrations used. If it is assumed that the molar ratio of Mo:Si must be at least 12:1. 4 ml of the ammonium molybdate solution was, therefore, used in the present study.

3.4.3. Forms of silica in solution at various concentrations and pH values

Whenever fresh sodium silicate solutions were tested they were prepared by diluting a stock solution with a concentration of 1.0×10^{-2} M with respect to sodium silicate. The total silica concentration of these solutions varied between 1.0×10^{-2} and 3.4×10^{-2} M SiO_2 depending on the ratio of sodium silicate used. These stock solutions were prepared every day prior to their use, and exhibited pH values between 10.5 and 11.5. The lowest pH corresponded to the silicate with a ratio of 3.41:1.

The stock solutions (1.0×10^{-2} M) sodium silicate) were prepared by dilution of the supplied, concentrated sodium silicate solution in which most of the silica was present in polymeric form. It was, therefore, necessary to determine the extent of polymerization in the stock solutions. Direct measurements of the absorbance of the stock solutions were not possible because the concentration was above the range suitable for the

molybdate method. The following procedure was, therefore, used. A predetermined amount of stock solution was pipetted into a 50-ml flask, the reagents added, and the resulting solution diluted to the mark. The absorbance of the solution was then measured as a function of time; the first measurement being made within 30 s of dilution. Comparison of the concentrations determined from the absorbance values with the initial total silicate concentration gave an estimation of the amount of polymeric silica present. It can be assumed that this value will be less than the degree of polymerization in the stock solution because some depolymerization will occur during dilution.

With the exception of sodium silicates with ratios higher than 2.56:1 and at concentrations above $1.5 \times 10^{-3} \text{M SiO}_2$, where up to 10% polymeric silica was obtained, the solutions contained only monomeric silica. The maximum concentration of silica in monomeric form in equilibrium with amorphous silica at pH 10.5 is $2.69 \times 10^{-2} \text{M SiO}_2$. This value can be obtained either by calculation using the data in Table 3.1 or from Fig. 3.1. A $1 \times 10^{-2} \text{M}$ solution of 3.41:1 sodium silicate contains $3.4 \times 10^{-2} \text{M SiO}_2$ which suggests that up to 20% of the SiO_2 must be present in a polymeric form. This value is somewhat higher than the 10% polymerized silica suggested by the dilution experiments. The reasons for this discrepancy may be attributable to the detection of lower molecular weight polymers by the analytical technique or, more likely, rapid depolymerization during the dilution stage.

Although the results obtained do not give quantitative information on the degree of polymerization in the stock solution they do show that in the concentration range used in the flotation studies etc. only monosilicate species are present.

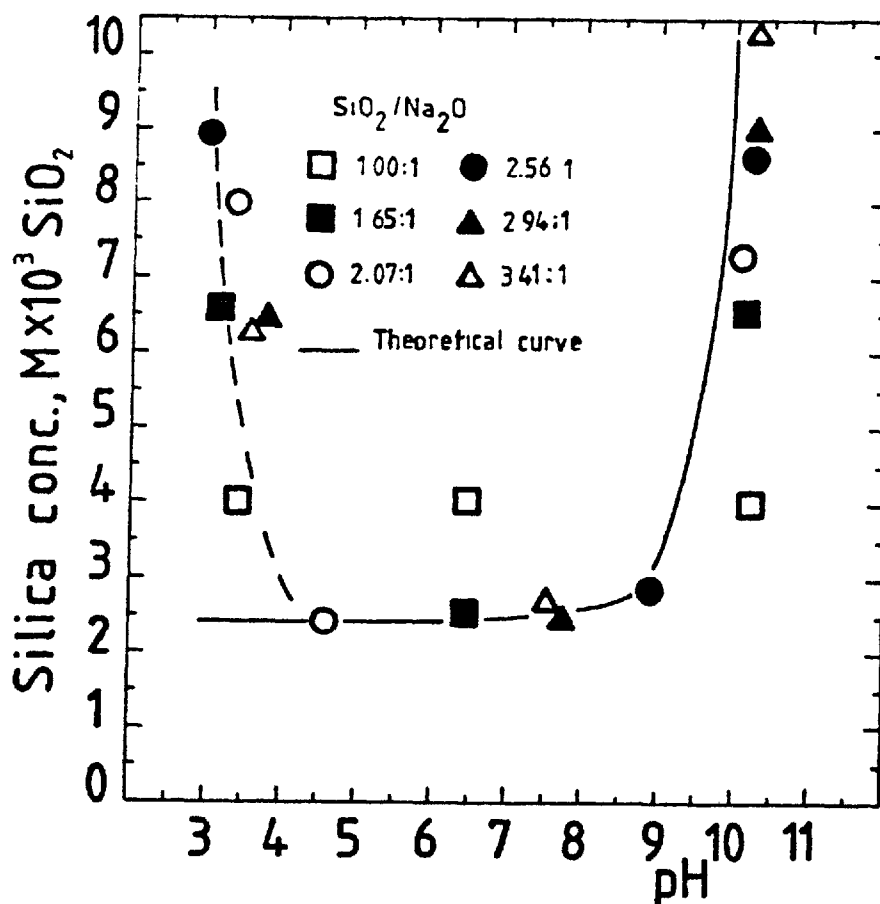


Fig. 3.3. Equilibrium concentration of silica in solutions containing various initial amounts of silica after ageing for 34 days.

Aged sodium silicates were tested. Three solutions of each silicate were prepared at a concentration of $4.0 \times 10^{-3} \text{M}$ and at various pH values and left to age for 34 days. At the end of this time the pH was measured and the amount of monosilicate determined with the method described above. The results obtained are summarized in Table 3.2 and Fig. 3.3. The latter shows the equilibrium silica concentration as a function of pH and it demonstrates that at pH values above 4.5 the experimental points fall on the curve representing the solubility of amorphous silica, at 25°C , although no solid silica

Table 3.2. Amount of monomeric silica present in the aged sodium silicate solutions

Ratio 1.00:1			Ratio 1.65:1			Ratio 2.07:1		
pH	Initial con, M SiO ₂	Final con, M SiO ₂	pH	Initial con, M SiO ₂	Final con, M SiO ₂	pH	Initial con, M SiO ₂	Final con, M SiO ₂
10.2	4.0×10^{-3}	4.0×10^{-3}	10.1	6.5×10^{-3}	6.5×10^{-3}	10.1	8.2×10^{-3}	7.2×10^{-3}
6.4	"	"	6.4	"	2.5×10^{-3}	4.7	"	2.4×10^{-3}
3.5	"	"	3.2	"	"	3.3	"	7.9×10^{-3}
Ratio 2.56:1			Ratio 2.94:1			Ratio 3.41:1		
pH	Initial con, M SiO ₂	Final con, M SiO ₂	pH	Initial con, M SiO ₂	Final con, M SiO ₂	pH	Initial con, M SiO ₂	Final con, M SiO ₂
10.3	10.2×10^{-3}	8.6×10^{-3}	10.3	11.7×10^{-3}	9.0×10^{-3}	10.3	13.6×10^{-3}	10.4×10^{-3}
8.9	"	2.8×10^{-3}	7.8	"	2.4×10^{-3}	7.6	"	2.6×10^{-3}
3.0	"	8.9×10^{-3}	3.8	"	6.4×10^{-3}	3.6	"	6.3×10^{-3}

was detected. This means that solutions with concentrations above the solubility were supersaturated and contained polymeric species. The discrepancy observed with the 1.00:1 ratio sodium silicate at pH 6.4 can be attributed to the low rate of polymerization of silica in this pH range and at relatively low initial concentrations. Below pH 4.5 the equilibrium silica concentration increased as the pH was decreased. This was surprising because the solubility of silica at these pH values is expected to remain constant or at least to increase only slightly. An increase in the solubility of silica at low pH values (<2) has been predicted by Alexander et al (134) and verified experimentally by Brown et al (139). This behaviour was attributed to the presence of fluoride and the formation of complexes with HCl etc. However, this is unlikely, in the present studies, because the increase in silica concentration occurred at pH values below 4.0. The polymerization of silica proceeds slowly in the pH range 2 to 5 (126, 176, 192 - 3). It is, therefore, probable that the reason for the results obtained at low pH values is that equilibrium was not established even after 34 days. In other words, under these pH conditions the ageing effect is very slow so that the monosilicate concentration of solutions produced by dilution does not appear to change. The reasons why precipitation of silica does not occur and the mechanism of stabilization of the monosilicic acid is not known.

3.4.4. Polymerization rate of silica prepared from a sodium silicate with ratio 2.07:1

In this series of experiments the polymerization rate of silica was studied at various pH values and at a constant initial silicate concentration equivalent to $8.2 \times 10^{-3} \text{ M SiO}_2$. The sodium silicate with

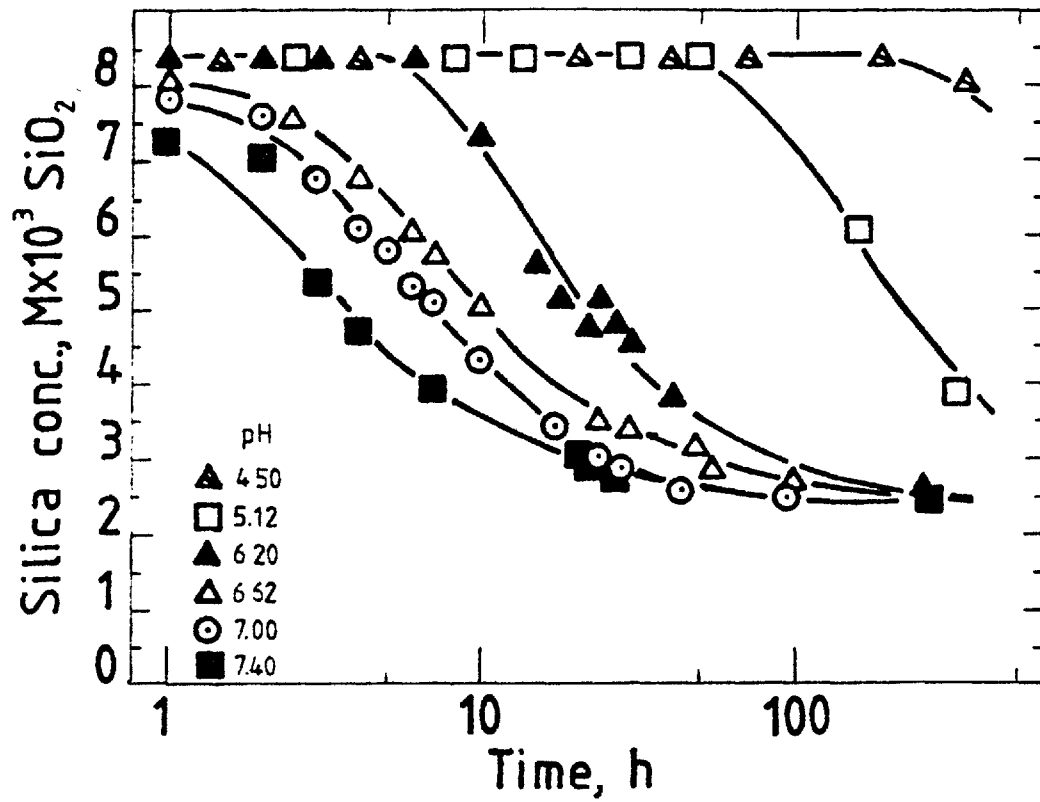


Fig. 3.4. Changes in the concentration of monomeric silica in the acid solution.

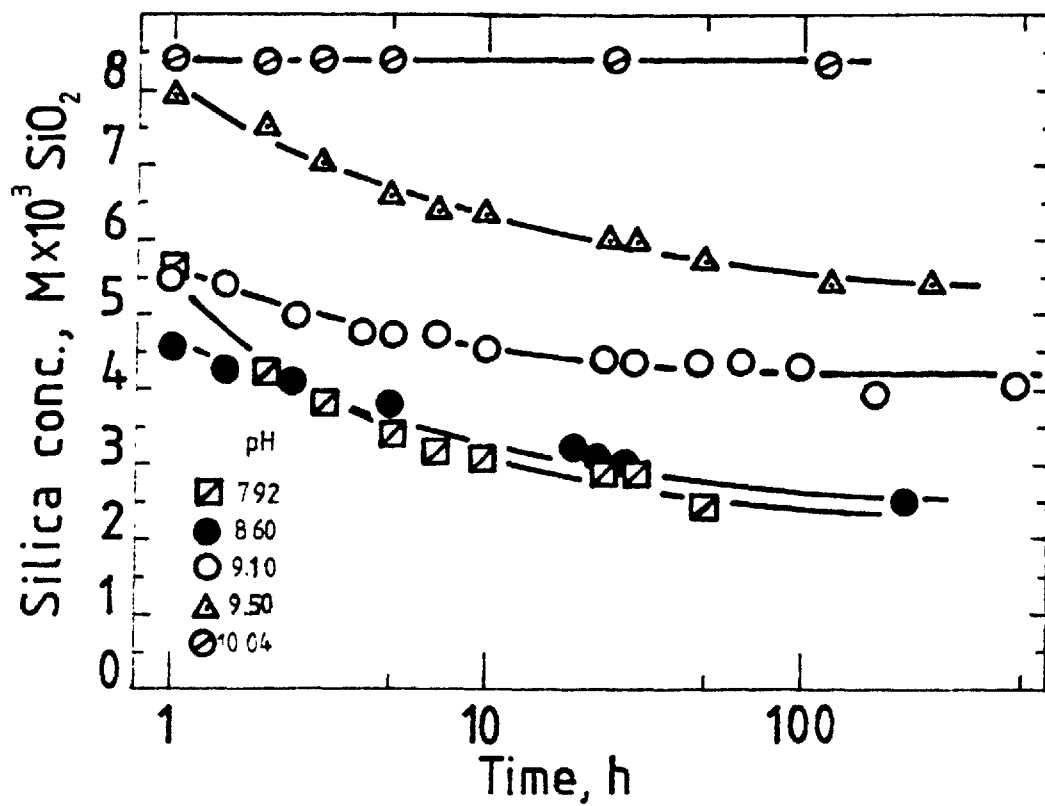


Fig. 3.5. Changes in the concentration of monomeric silica in the alkaline solution.

a ratio of 2.07:1 was used. The pH was adjusted with HCl or NaOH to the required value and then the solution was stored in a polyethelene bottle. At regular time intervals the monomeric silica content of each solution was determined and the pH was checked and minor adjustments made if necessary. The changes in concentration were followed up to 20 days, after which all the solutions appeared to have attained equilibrium. All of the silica in the freshly prepared solutions was monomeric.

The change in concentration of monomeric silica with time at different, but constant, pH values is shown in Fig. 3.4 and 3.5 for pH values above 7.9 and below 7.4, respectively. The data at various pH values in the pH range 5.1 to 10.0 fits the following equation:

$$-\frac{dC}{dt} = K_n(C-C_e)^n \quad (3.18)$$

where

C : concentration of monomeric silica at time t , (moles/litre)

C_e : solubility of amorphous silica at 25°C, (moles/litre)

and K_n , n constants.

At pH values below 7.9 the reaction is of the second order ($n=2$), whereas above 7.9 it is of the third order ($n=3$).

Using equation (3.16) and the experimental data obtained in this work, the numerical values of the constant K_n were calculated at the pH of the experiments. In these calculations a C_e value of $2.4 \times 10^{-3} M$ SiO_2 was used at pH values below 8.0. For pH values above 8.0 C_e was assumed to be the equilibrium value found in the present work. This assumption is reasonable because the earlier work showed that these solutions had reached equilibrium. The values thus obtained are plotted in Fig. 3.6 and 3.7 as a function of pH. K_2 and K_3 are the rate constants for the second and third order reactions,

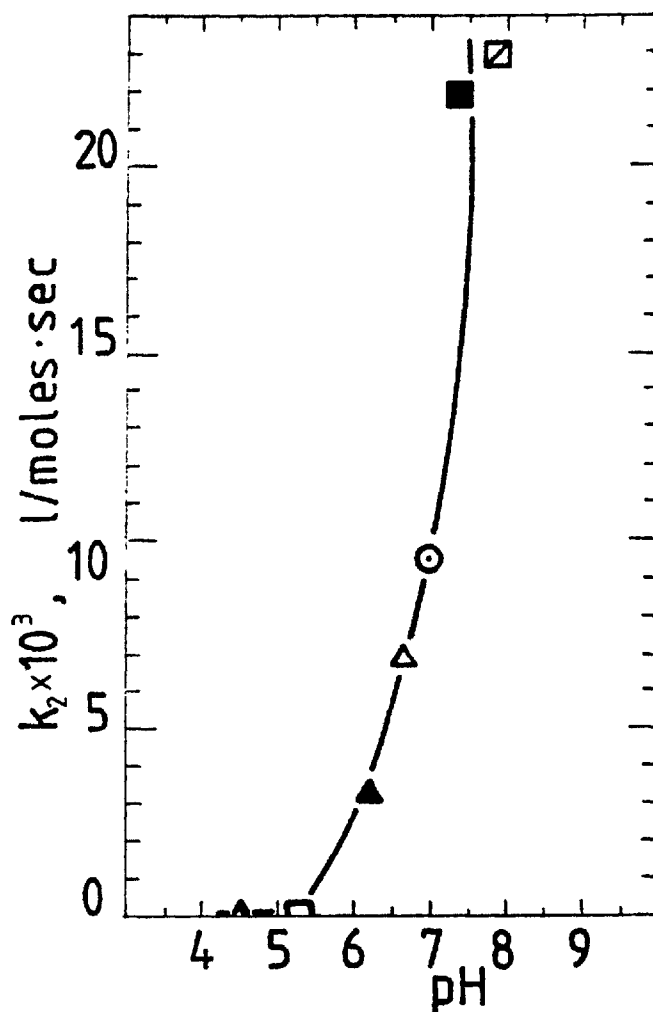


Fig. 3.6. Values of the polymerization constant, k_2 , of silicic acid at various pH values (symbols as in Fig. 3.4).

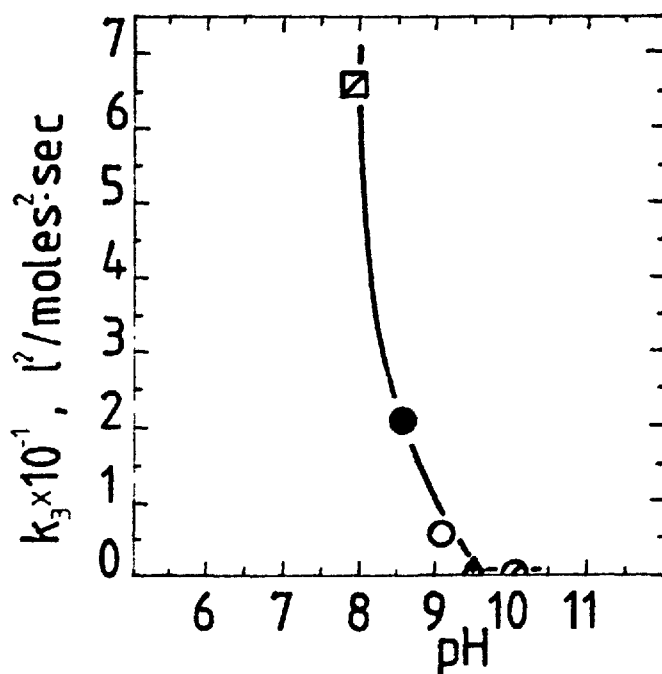


Fig. 3.7. Values of the polymerization constant, k_3 , of silicic acid at various pH values (symbols as in Fig. 3.5).

Kitahara (140).

Finally, in Fig. 3.8 a sketch, describing the mode of preparation of sodium silicate solutions used in the studies with salt-type minerals, is given. The (P) area in this figure corresponds to the polymerization domain. Sodium silicate solutions outside this area are stable. Polynuclear (stable) species are present in considerable amounts only in solutions with compositions in the dotted area. The concentration of the sodium silicate solutions during ageing was within the limits of area (A), while their concentration, after dilution, fell within the area (B). Dilutions were carried out at constant pH. It is evident that the concentration of some of the solutions fell within the insolubility domain during ageing. The presence of some polymeric silica is, therefore, to be expected but the amount is likely to be small because of the depolymerization which occurs rapidly at such concentrations (10^{-2} - 10^{-3}) and the fact that no polymeric species could be detected with the ammonium molybdate method in the dilute solutions.

The dashed lines (1) and (2) demonstrate the preparation of fresh sodium silicate solutions. The composition of these solutions was always outside the insolubility domain with the exception of solutions prepared from sodium silicates with ratios 2.94:1 and 3.41:1, at concentrations of 2.9×10^{-3} and 3.4×10^{-3} M SiO_2 , and at pH values below 8.5 and 9.0, respectively.

3.5. Conclusions

1. The aqueous chemistry of dilute sodium silicate solutions can be satisfactorily described by the solubility diagram of amorphous silica in water at 25°C.

2. Due to the slow rate of polymerization of silica at low

concentrations, solutions slightly oversaturated with respect to amorphous silica can remain stable for a long period of time without precipitation occurring.

3. Fresh sodium silicate solutions, prepared by dilution are free of polymeric species with the exception of those with concentrations greater than $1.4 \times 10^{-3} \text{ M SiO}_2$ and a ratio above 2.56:1. The polymeric silica in these solutions does not exceed 10% and its presence is attributable to the non-equilibrium conditions.

4. Aged sodium silicate solutions, at concentrations between 4.0×10^{-3} and $13.6 \times 10^{-3} \text{ M SiO}_2$ and at pH values below 10.3 contain polymeric silica species; the exact amount being dependent on the initial concentration and the pH.

5. Solutions with pH values between 4.60 and 8.95 and concentrations of 6.5×10^{-3} to $13.6 \times 10^{-3} \text{ M SiO}_2$ attain equilibrium within 34 days. The silica content of the solutions is $2.4 \pm 0.3 \times 10^{-3} \text{ M SiO}_2$ and this is in a monomeric form.

6. Solutions with SiO_2 concentrations between 4.0×10^{-3} and $13.6 \times 10^{-3} \text{ M}$ and with pH values below 4.6 are not under equilibrium conditions because their content in monomeric silica was always more than the value given for the solubility of amorphous silica at 25°C .

7. The polymerization of silica is a second and third order reaction at pH values below and above 8.0, respectively.

8. The maximum rate of polymerization occurs at pH 8.0.

CHAPTER 4. SOLUBILITY OF BARITE, CALCITE AND FLUORITE

4.1. Solubility of all three minerals as influenced by the pH

4.1.1. Barite

The sulphate concentration in a solution saturated with barite at different pH values is shown in Fig. 4.1. Barium could not be determined because a suitable technique for determining low barium concentrations is not available. The sulphate concentration was independent of the pH in the range studied and was equal to $3.0 \pm 0.4 \times 10^{-5}$ moles/litre. This value compares well with that determined from the solubility product (1.04×10^{-5} moles/litre) assuming that the activity coefficients are unity and that BaSO_4 behaves as the salt of a strong base and strong acid. The effect of SO_4^{2-} and Ba^{2+} hydrolysis on the concentration of SO_4^{2-} was not observed because it occurs outside the pH range studied, i.e. below pH 2 and above 13, respectively (see Fig. 1.6).

4.1.2. Calcite

The solubility of calcite in water at different pH values was determined by measuring the total calcium concentration. The results obtained in a closed vessel with no CO_2 present are shown in Fig. 4.2. At high pH values (>11.5) the solubility was low but as the pH decreased

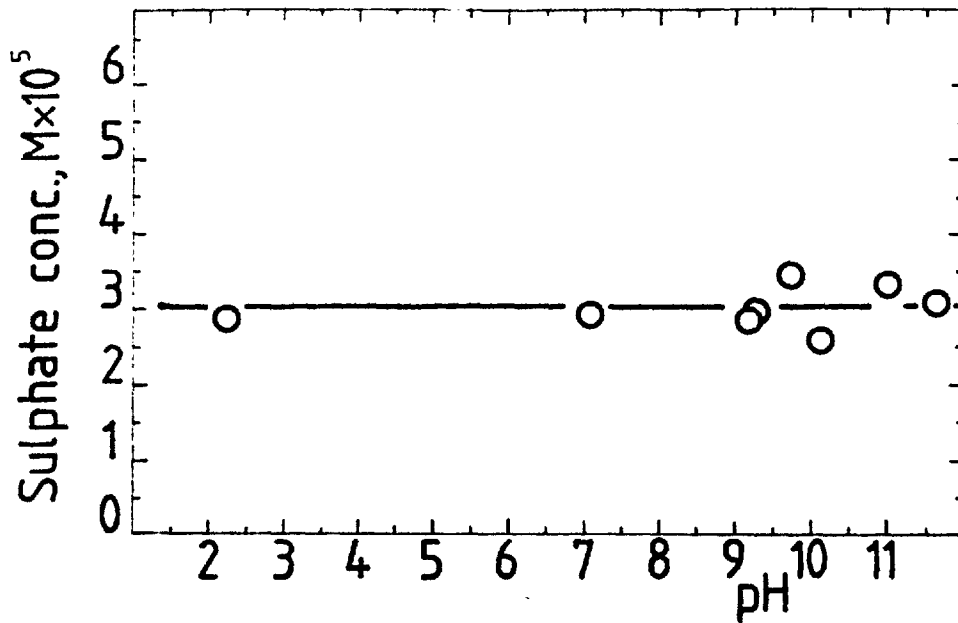


Fig. 4.1. Concentration of sulphate, in a solution saturated with barite, at various pH values.

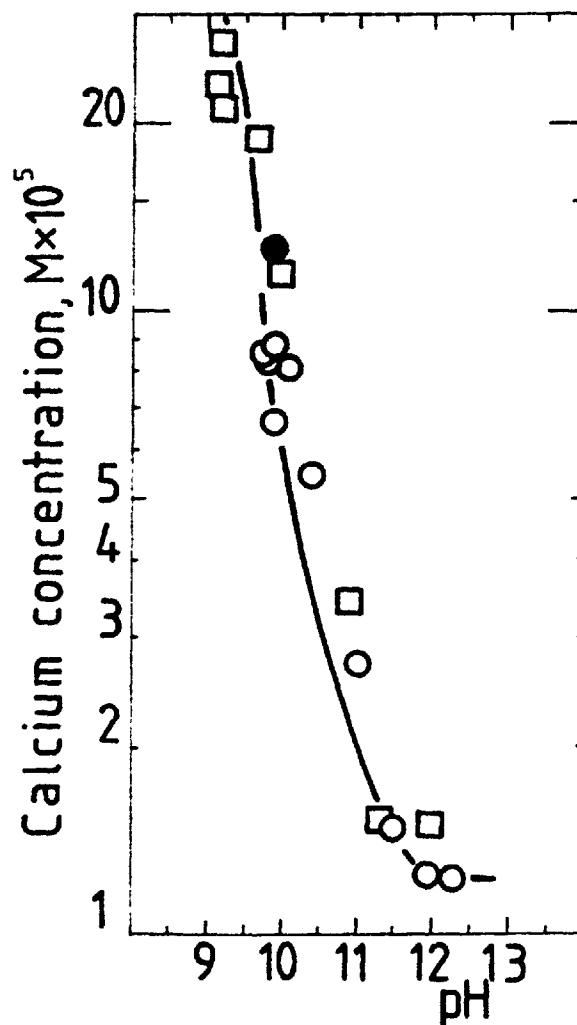


Fig. 4.2. Concentration of calcium in solution saturated with calcite, at various pH values (Calcite: $\circ$ rinsed with water after grinding, $\square$ non-rinsed calcite, $\bullet$ theoretical value).

hydrolysis of the carbonate ion occurs and the solubility increased markedly. Equilibrium pH values below 9.8 were not obtained because this value represents the buffering pH for the system.

The curve of Fig. 4.2 is in excellent agreement with the theoretical one which is given in Fig. 1.3. The only deviations noticed are those at high pH values (>11.0) but they are small and can be attributed to the experimental error. At these pH values the concentration of calcium in solution is near the lower limit of the detection of the analytical method, i.e. $1.0 \times 10^{-5} \text{M}$.

4.1.3. Fluorite

Both the fluoride and calcium concentrations were determined in saturated solutions of fluorite. The results obtained at different pH values are shown in Fig. 4.3. Comparison of Fig. 4.3 with the theoretical concentrations, calculated assuming a solubility product of $4.0 \times 10^{-11} \text{ moles}^3/\text{litre}^3$ (Fig. 1.5), shows a fairly good agreement. The actual value of the solubility product, calculated from the experimental data, is $7 \pm 1 \times 10^{-11} \text{ moles}^3/\text{litre}^3$.

At pH values below neutral the fluoride concentration was double that of calcium but at higher pH values the dissolution was apparently non-stoichiometric. At these pH values the calcium concentration was slightly less than half of the concentration of fluoride. However, the difference is of the same order as the experimental error and is probably not significant.

4.2. Influence of carbonate species on the solubility

4.2.1. Barite

The theoretical solubility of barite shown in section 1.2.2 was

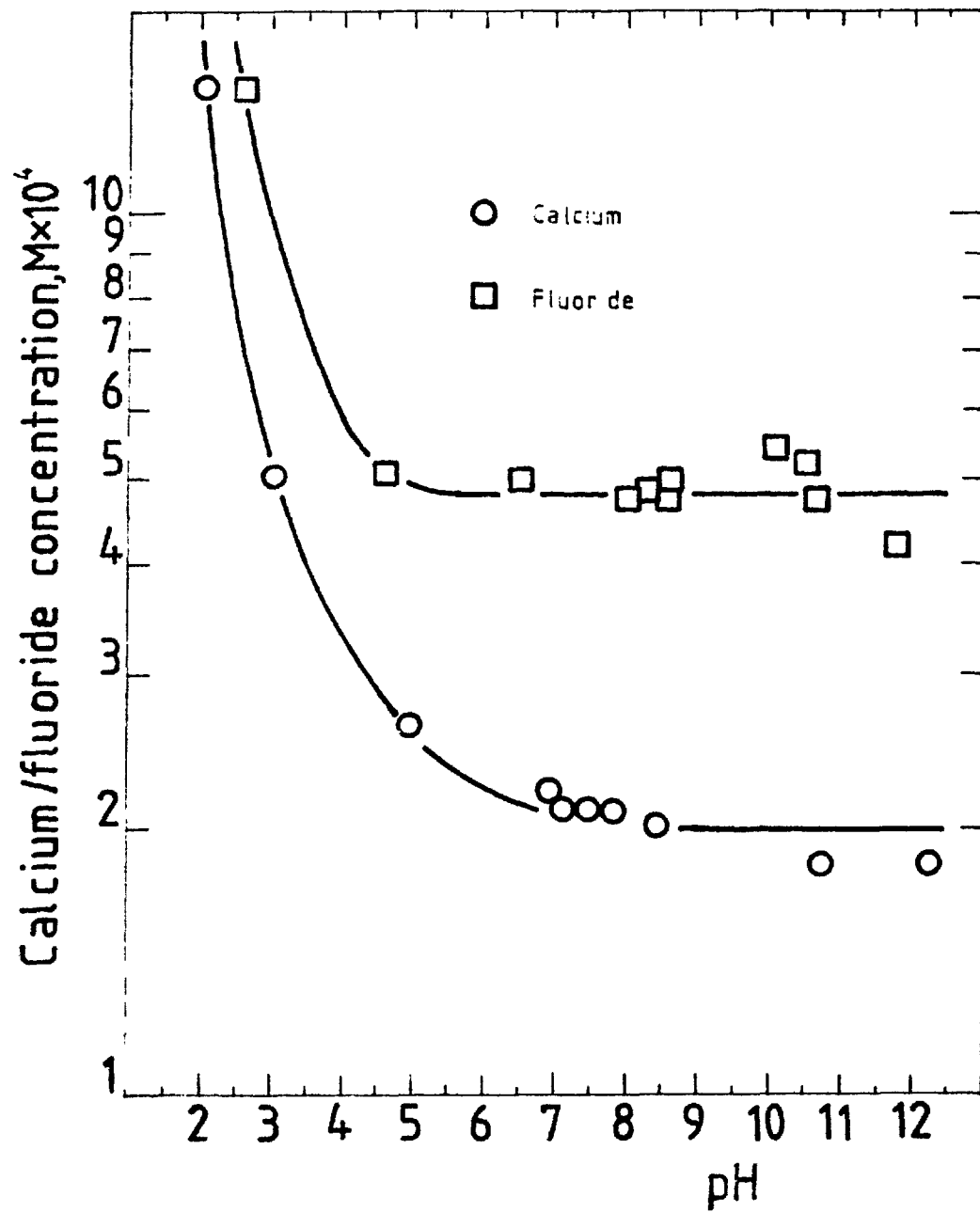
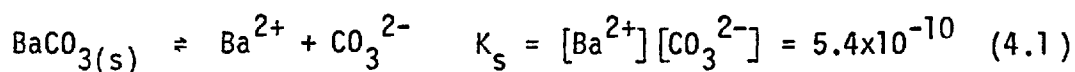


Fig. 4.3. Fluoride and calcium concentration, in saturated suspensions of fluorite, at different pH values.

calculated assuming the absence of CO_2 . If CO_2 is present then there is the possibility that barium carbonate will be precipitated according to the equilibrium:



It can readily be shown, using equilibria (1.5) to (1.7) that in a system open to the atmosphere barium carbonate should form at pH values above 8.69. The solubility measurements in the present work were determined in the absence of CO_2 and its effect was, therefore, not observed.

The kinetics of the carbonation reaction are not known but it is reasonable to assume that if the carbonate in solution is increased, i.e. by the addition of sodium carbonate, barium carbonate will form more rapidly. The same effect on the kinetics of the reaction is also expected by an increase in the pH. Whether or not the reaction takes place on the barite surface or in solution has not been determined.

4.2.2. Fluorite

The solubility of fluorite in the presence of carbonate species has been determined by Bahr (17 - 20) who concluded that calcium carbonate was formed on the fluorite surface and thereby reduced the solubility. Unfortunately no attempt was made to control the pH and the pH at which this phenomenon occurs was not given. Miller and Hiskey (21) showed that calcium carbonate was present in the infrared spectra of fluorite conditioned at pH values above 8.0. However, this cannot be taken as proof of the carbonation reaction because of the sample preparation technique used and possible contamination with atmospheric carbon dioxide.

In the present work the carbonation reaction was studied by

determining the calcium and fluoride concentrations in saturated suspensions of fluorite containing added sodium carbonate. The results obtained at a total carbonate concentration of 6.0×10^{-3} M are shown in Fig. 4.4. At pH values below 8.6 the solubility of fluorite was approximately similar to that obtained in the absence of carbonates (Fig. 4.3), the slight increase being the result of the effect of an increase in ionic strength on the solubility. Above this pH value the calcium concentration decreased abruptly whereas that of fluoride increased. In fact the calcium concentration decreased to 1.7×10^{-5} M at pH 10.5 and above, and this value corresponds to that in equilibrium with calcite under the same conditions.

Calculations using equilibria (1.3) to (1.7) show that in a solution saturated with fluorite and atmospheric carbon dioxide, i.e. $p_{\text{CO}_2} = 3.16 \times 10^{-4}$ atm, calcium carbonate should form at pH values above 8.6. This is the value at which calcium and fluoride concentrations deviated from that expected for fluorite on its own. Both the theoretical and experimental data, therefore, indicate that the formation of calcium carbonate is favoured at pH values above 8.6.

Precipitation of calcium carbonate in solution does take place and this is indicated by the constancy of the product $[\text{Ca}^{2+}][\text{F}^-]^2$. Indeed, at any pH, the values calculated for this quantity are the same and within experimental error equal to the solubility product of fluorite. On the other hand, formation of the calcium carbonate on the fluorite surface is likely to occur together with precipitation in solution. This is supported by the fact that the concentration of both calcium and fluoride attains a constant value at high pH values (>10), which is higher and lower, respectively, than the calculated value assuming that precipitation of calcium carbonate takes place only

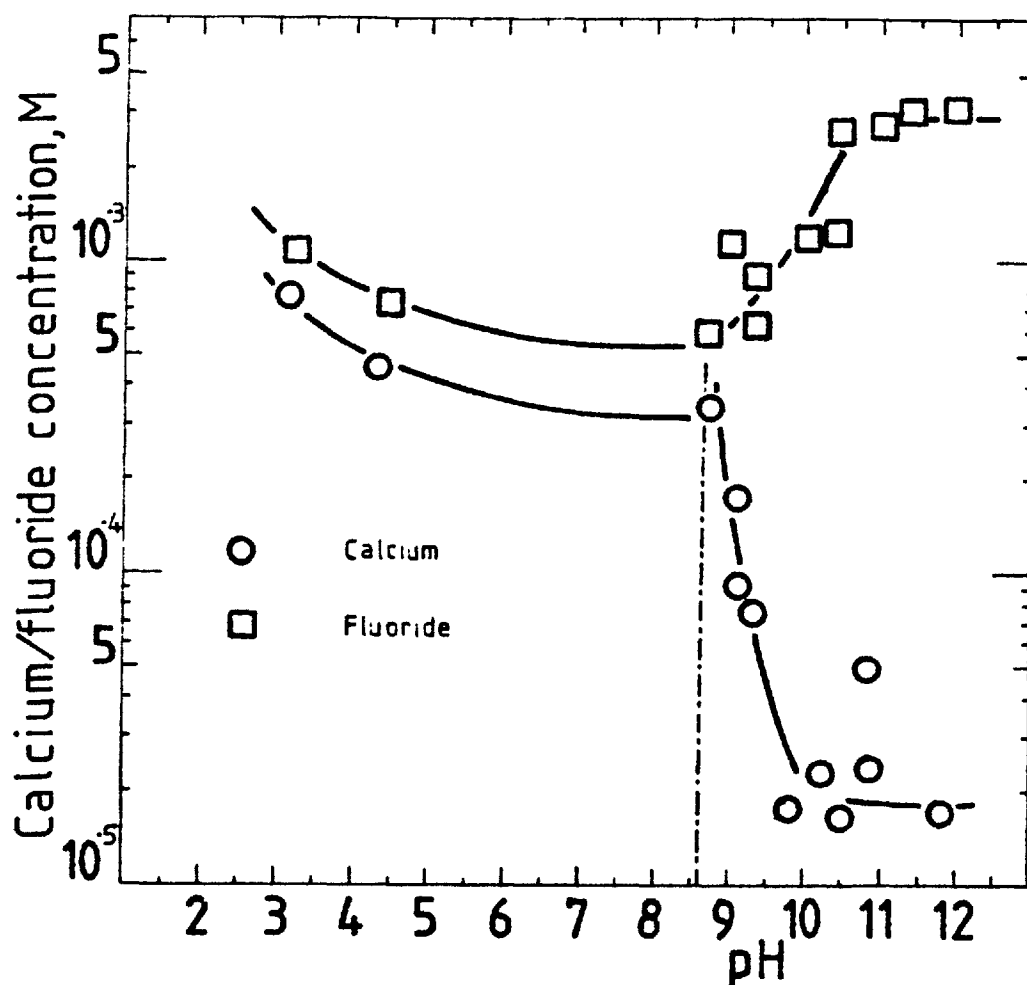


Fig. 4.4. Calcium and fluoride concentration, in saturated fluorite suspensions containing 6×10^{-3} M Na_2CO_3 , as a function of pH.

in solution, and the reaction proceeds to completion.

It is evident that if carbonation of the fluorite surface does occur then the rate and the extent of the reaction will be greater at high pH values and carbonate concentrations. Separate tests conducted at pH values 9.0 and 10.5 and at various concentrations of total carbonate species (added as sodium carbonate) showed that the concentration of calcium and fluoride rapidly assumed constant values.

4.3. Effect of oleate ions on solubility

To examine the effect of oleate concentration on the solubility of calcite and fluorite a series of experiments was conducted in which the minerals were equilibrated with various oleate solutions. The results are shown in Figs. 4.5 and 4.6 for calcite and fluorite at pH 10.0 ± 0.1 and 9.6 ± 0.2 , respectively. Generally the concentration of soluble calcium in equilibrium with both minerals decreased at high oleate concentrations. Surprisingly, the fluoride concentration decreased.

Values quoted in the literature for the solubility product of calcium oleate are contradictory (194 - 7). An apparent solubility product, based on the concentrations of calcium and oleate species, was determined in the present work by a nephelometric technique. A value of 7.4×10^{-15} moles³/litre³ was obtained which is close to that quoted by Du Reitz (82) at 3.98×10^{-16} moles³/litre³. Whichever value is correct does not change the conclusion that, under the conditions of the tests represented by Figs. 4.5 and 4.6, calcium oleate should be stable.

If calcium oleate is precipitated in solution the equilibrium concentrations of fluorite and calcite lattice ions should be such that they satisfy the relations:

$$[\text{Ca}^{2+}][\text{F}^{-2}] = K_{\text{sp1}} \quad (4.2)$$

and

$$[\text{Ca}^{2+}][\text{CO}_3^{2-}] = K_{\text{sp2}} \quad (4.3)$$

respectively. In other words, the concentration of the lattice anions i.e. CO_3^{2-} and F^{-} ions, should increase whereas the concentration of calcium should decrease. Reference to Fig. 4.6 shows that this was not the case and that both the calcium and fluoride concentration

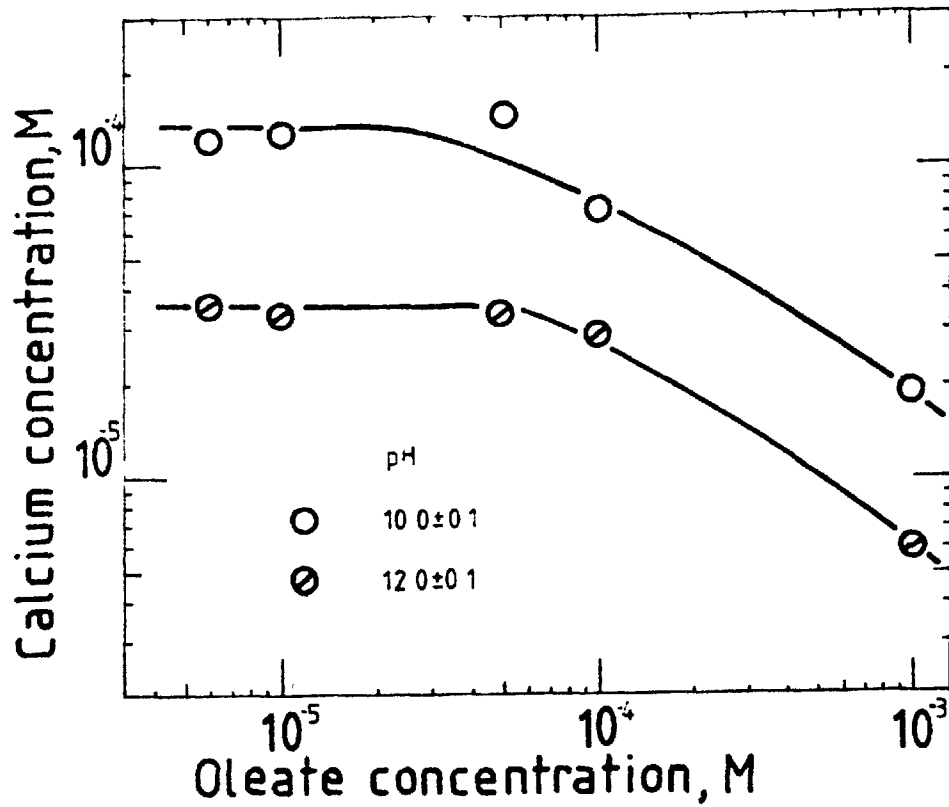


Fig. 4.5. Calcium concentration in solutions containing calcite, as a function of total oleate concentration.

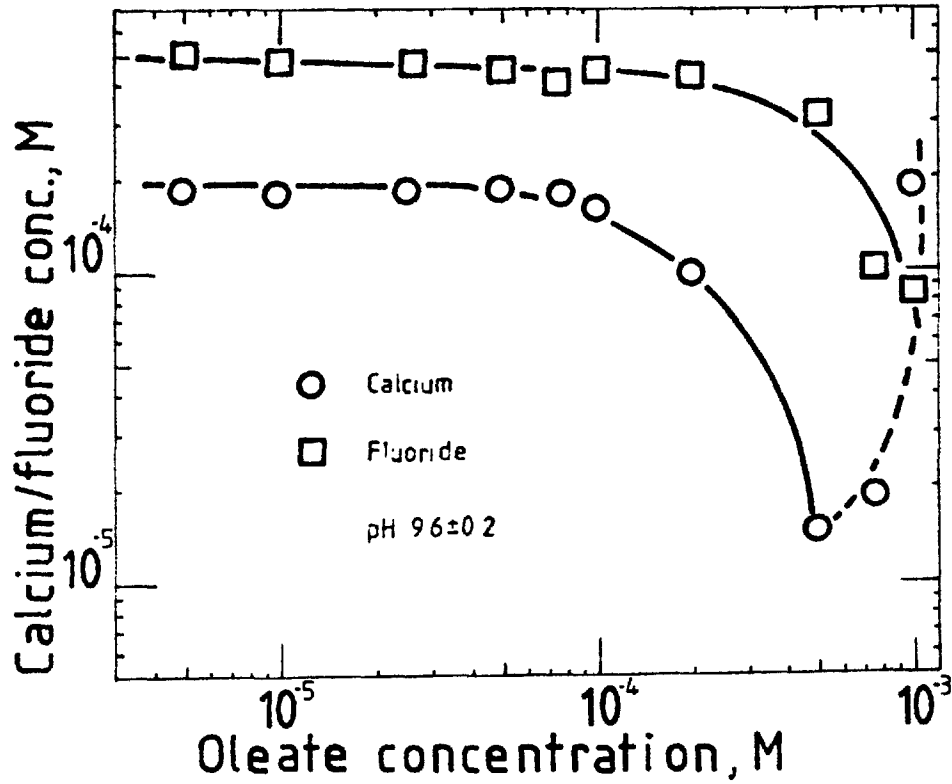


Fig. 4.6. Calcium and fluoride concentration, in saturated fluoride suspensions, as a function of total oleate concentration.

decreased continuously.

The above results suggest that a calcium oleate layer is formed on the surface of the minerals which effectively prevents their dissolution and the attainment of equilibrium.

At oleate concentrations above 5.0×10^{-4} M the concentration of calcium in a suspension containing fluorite increased. Three independent determinations carried out at these concentration levels showed that this effect is real and that was not due to an experimental error. In Fig. 4.6 the points obtained in one test are shown. In these solutions the particles of fluorite formed a stable suspension and a clear supernatant could not be obtained even after prolonged centrifuging. The same phenomenon, i.e. the formation of a stable colloidal suspension, has been reported by Matijević et al (198) and Paterson and Salman (199) and was ascribed to the formation of either a particulate calcium oleate or to the stabilization of the mineral particles by the excess oleate through adsorption of the oleate ions in the double-layer of calcium oleate surrounding the particles of the mineral. Both contentions are likely to occur under the conditions of Fig. 4.6. They are consistent with the fact that the fluoride concentration was found to decrease with increasing oleate concentrations. Although some colloidal particles could be present in the solutions used to measure the fluoride concentration these would not interfere with the determination of the latter (section 2.3.3).

4.4. Effect of silica on the solubility

The effect of silicate on the solubility of calcite and fluorite was investigated. In Figs. 4.7 and 4.8 the results obtained at various concentrations of silica, added as sodium silicate, are shown. In these

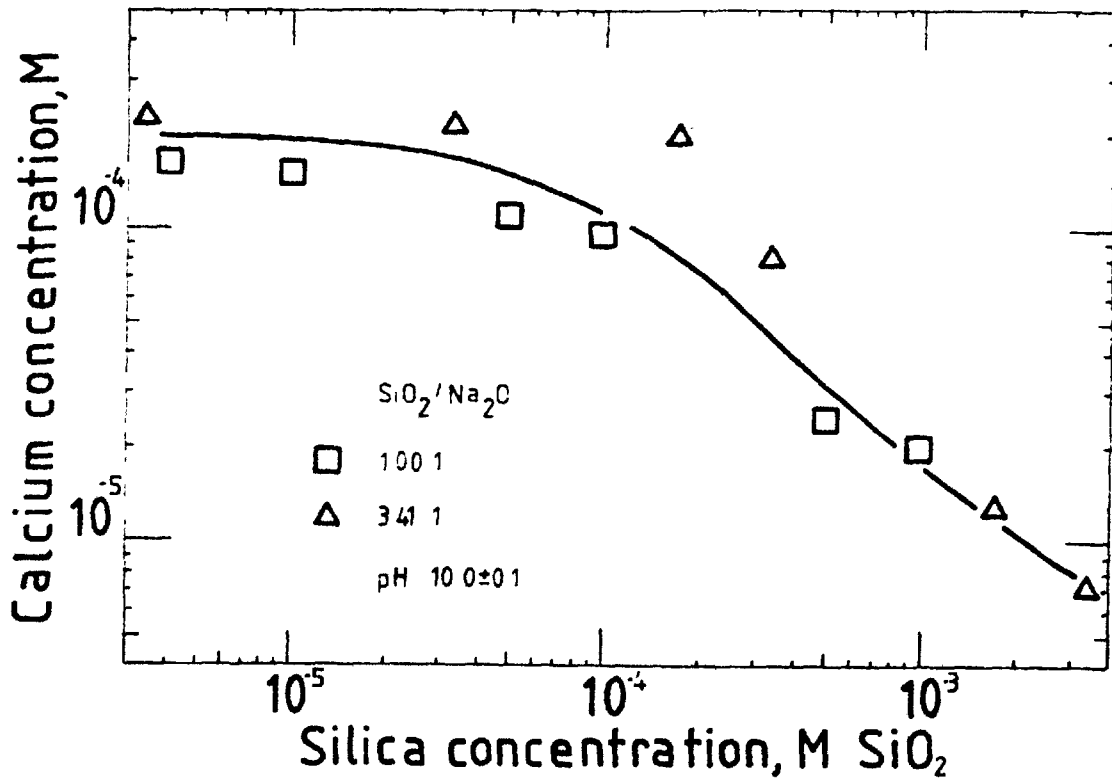


Fig. 4.7. Calcium concentration as a function of SiO_2 concentration in suspensions saturated with calcite.

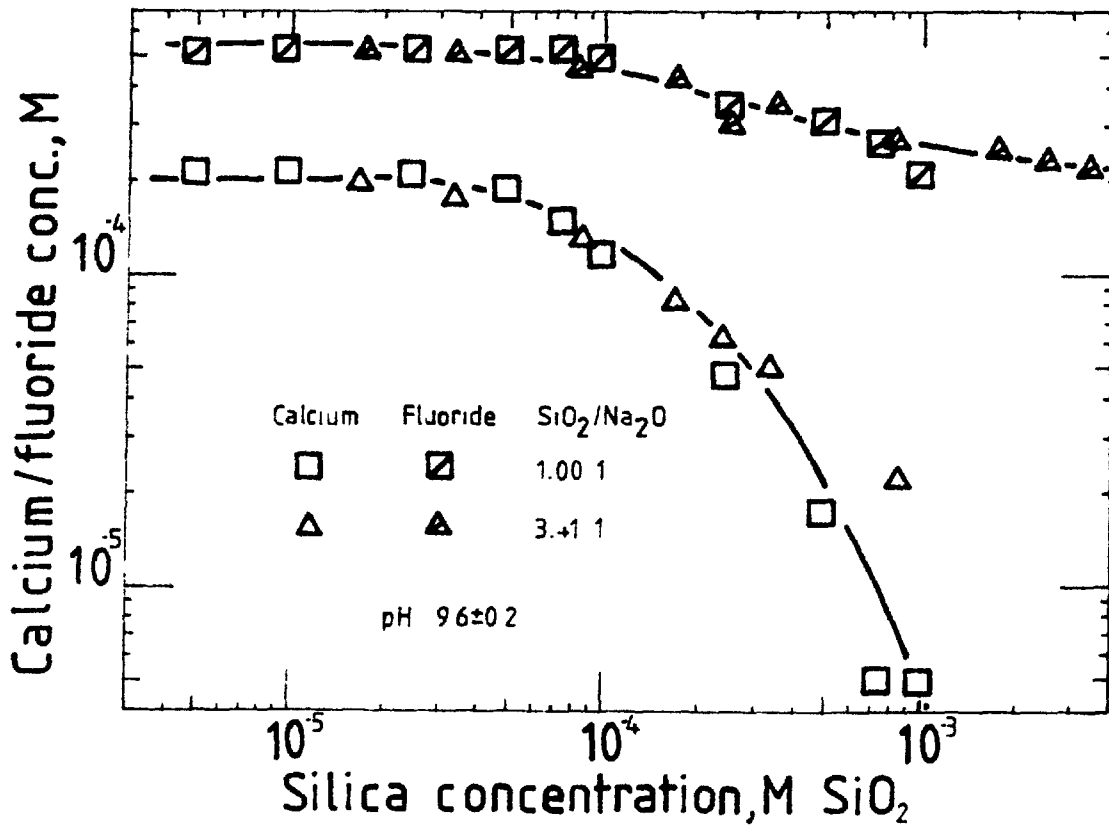
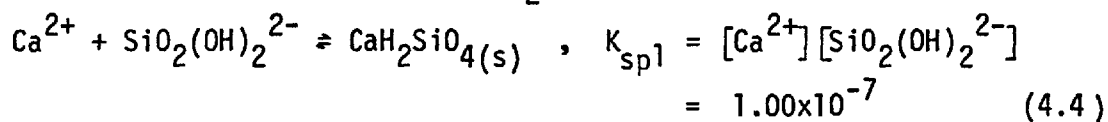


Fig. 4.8. Calcium and fluoride concentration as a function of SiO_2 concentration in suspensions saturated with fluorite.

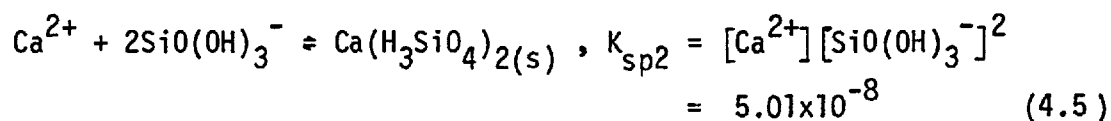
tests the pH was kept constant at 10.0 ± 0.1 and 9.6 ± 0.2 for calcite and fluorite, respectively. Two different sodium silicates with ratios 1:1 and 3.41:1 were used and the points in Figs. 4.7 and 4.8 have been plotted against the silica concentration, expressed as moles SiO_2 per litre. No differences in the behaviour of these two silicates were found. At silica concentrations above 1.0×10^{-4} M SiO_2 the concentration of calcium in equilibrium with both calcite and fluorite decreased considerably so that it was too low to be measured in solutions containing more than 1.0×10^{-3} M SiO_2 . The fluoride concentration decreased much less markedly than that of calcium in fluorite suspensions.

The system $\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ has been extensively studied by a number of investigators (200 - 6) because of its importance in the cement industry and a detailed review is given by Steinour (207) and Brunauer (208). Calcium oxide and SiO_2 can form a series of colloidal, hydrated compounds in which the CaO to SiO_2 molar ratio varies widely. These hydrates are formed in relatively concentrated CaO and SiO_2 solutions and at high pH values (>9.0), and they dissolve rapidly when the pH is reduced.

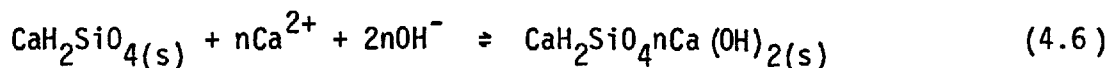
According to Greenberg (203 - 4) the following equilibria occur in a solution saturated with $\text{Ca}(\text{OH})_2$ and containing silicate species:



and



Evidence for reaction (4.5) is not conclusive. A reaction of the type:



has also been proposed (205). The final form of the precipitate will be dependent on the pH and the relative amounts of CaO and SiO_2 .

In the present work it was found that more than 2.45×10^{-3} M SiO_2 was required to form a precipitate, detected with a nephelometric technique, in a solution containing 5.0×10^{-3} M Ca^{2+} at pH 12.0. At lower pH values the precipitate rapidly disappeared. It would appear, therefore, that the decrease in calcium concentration demonstrated in Figs. 4.7 and 4.8 cannot be attributed to the bulk precipitation of calcium silicate. A possible reason for the behaviour is that silica adsorbs at calcium sites on the mineral surface to form a calcium silicate-fluoride layer. Equilibrium between this compound and the solution would be dependent on the concentrations of Ca^{2+} , F^- and silicate species which means that if the silica concentration is increased the product of the Ca^{2+} and F^- concentrations should decrease. An alternative explanation is that the adsorption of silica inhibits the dissolution of both calcium and fluoride ions.

CHAPTER 5. ELECTROKINETIC STUDIES

5.1. Introduction - The electrical double layer at the solid/liquid interface

When a solid and liquid phase are brought into contact, e.g. dispersion of mineral particles in an aqueous solution, there is often a transfer of charge carriers so that the solid acquires a surface charge. This charge is compensated in the adjacent solution by the same number of carriers with an opposite charge. The surface charge and the counter charge comprise an electrical double layer. The electrical potential in the liquid (ψ) decreases exponentially from ψ_0 , the surface potential, with distance from the surface (x).

Gouy and Chapman independently have derived an equation relating the potential with distance which simplifies to:

$$\psi = \psi_0 e^{-kx} \quad , \quad \text{at } \psi_0 \ll 25\text{mV} \quad (5.1)$$

and

$$\psi = \frac{4kT}{ze} e^{-kx} \quad , \quad \text{when } \psi_0 \text{ is large} \quad (5.2)$$

where $1/k$ is referred to as the "thickness of the double layer" and is a function of the ionic strength. These equations were derived assuming:

1. that the double layer is flat

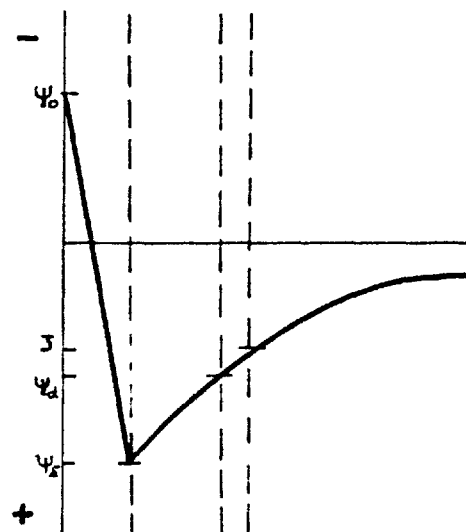
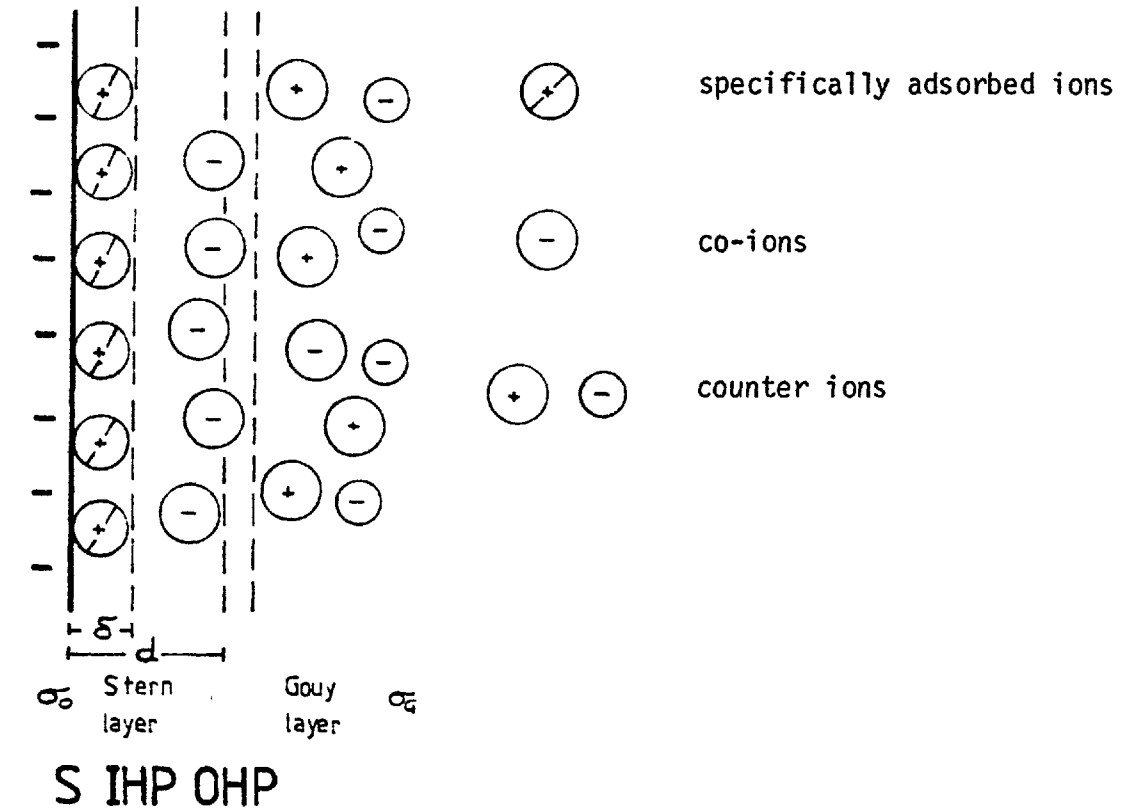
2. the dielectric constant does not change with surface potential and distance from the surface
3. ions are point charges, and
4. the work done to move an ion from bulk solution into the double layer is against coulombic forces only.

The Gouy-Chapman theory of the diffuse double layer suffers from a number of defects and in recent years most of the assumptions made have been challenged and modified. The most notable defect is the assumption of point charges which leads to the calculation of absurdly high ionic concentrations near to the charged surface. Stern (209) introduced a correction for the finite size of the ions in the first ionic layer adjacent to the charged surface. He also considered the possibility of specific ion adsorption giving a compact layer of counter-ions attached to the surface by electrostatic and van der Waals forces. The total double-layer, according to Stern, is, therefore, divided into two parts, a compact (Stern) layer and diffuse layer, the two layers being in equilibrium.

Grahame (210) modified the Stern theory and divided the Stern layer into two planes called the Inner and Outer Helmholtz planes. The former represents the centre of charge of chemisorbed ions and the latter the locus of nearest approach of hydrated counter-ions.

Generally the Gouy-Chapman theory can be used to calculate the potential in the diffuse double-layer if the Stern potential (ψ_δ) is substituted for ψ_0 in the relevant equations. A schematic representation of the Stern-Grahame model of the double-layer is shown in Fig. 5.1, along with the potential drop across the double-layer for the special case of specific adsorption of cations.

The sign and magnitude of the Stern potential is of considerable



1. Non specific adsorption

$$\sigma_0 = -\sigma_G$$

2. Specific adsorption

$$\sigma_0 = -(\sigma_{IHP} + \sigma_G)$$

- a. finite adsorption

$$|\sigma_{IHP}| < |\sigma_0|$$

- b. superequivalent adsorption

$$|\sigma_{IHP}| > |\sigma_0|$$

Fig. 5.1. Model of the double layer at the solid/solution interface and for the case of specific adsorption of cations.

importance in colloid chemistry, because it is one of the parameters which controls the stability of the colloidal dispersions. In spite of its great importance this parameter can not be measured directly and its value is generally assumed to be approximately the same as the electrokinetic or zeta-potential which is the potential at plane of shear situated just outside the Stern plane.

Various methods are available for the measurement of the zeta-potential of mineral particles but the most widely used is that of microelectrophoresis. This method measures the electrophoretic mobility of the charged particles suspended in a solution under an applied electric field. The mobilities obtained can be either used as such, or converted to zeta-potentials using the Helmholtz-Smoluchowski equation:

$$\frac{u}{E} = \frac{\epsilon \zeta}{4 \pi \eta} \quad (5.3)$$

where

u : electrophoretic velocity, m/s

E : strength of the applied field, V/m

ϵ : permittivity, Cb/V.m

η : viscosity, N.s/m²

The quantity u/E represents the electrophoretic mobility and in S.I. its units are m²/V.s. Usually, viscosity is expressed in P and the electrophoretic mobility in cm²/V.s. In that case the right hand side of eq (5.3) should be multiplied by 10⁻⁴.

Equation (5.3), however, has limited use and for a spherical particle, it is only valid when $ka \gg 1$, where a is the radius of the particle. For low values of ka the Hückel equation can be used:

$$\frac{u}{E} = \frac{2\epsilon \zeta}{3 \eta} \quad (5.4)$$

Henry (35) has shown that both equations (5.3) and (5.4) are limiting forms of the equation:

$$\frac{u}{E} = \frac{2\epsilon\zeta}{3\eta} f(\kappa a) \quad (5.5)$$

The values of $f(\kappa a)$ are given as a function of κa and this correction allows for the retardation effect but it does not take into account the relaxation effect. The latter was introduced by Overbeek et al (211 - 12) in their studies on the electrophoretic mobility of a colloidal particle. They also calculated the effect of other factors such as shape, Brownian motion, surface conductance of the particle and the viscoelectric effect. All of these corrections make determination of the zeta-potential from mobility data very laborious and in some cases impossible because of the lack of information on the correction terms.

Because of the uncertainties involved in the use of the above equations as well as the lack of data concerning electrolytes such as sodium oleate and sodium silicate, electrophoretic mobilities were used throughout in the present work. Approximate values of the zeta-potential are also given and they were calculated from eq (5.3). In addition no attempt was made to control the ionic strength so that the magnitude of the electrophoretic mobilities and zeta-potential quoted at high electrolyte concentrations are reduced because of the compression of the double-layer.

5.2. Influence of the pH

The influence of pH on the electrophoretic mobility and zeta-potential of calcite, barite and fluorite is shown in Figs. 5.2 to 5.4 inclusive. Calcite was negatively charged at pH values above 9.5 and it became more negative with an increase in pH. An IEP was

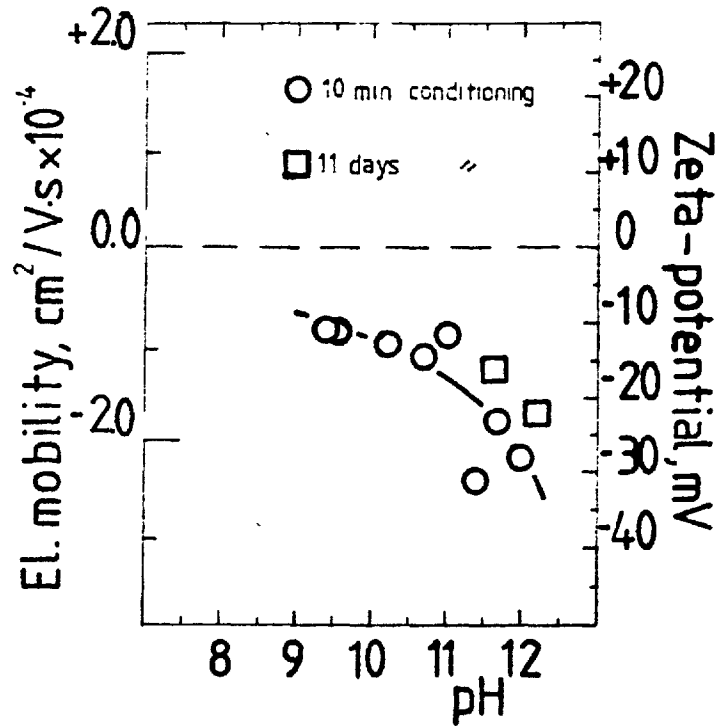


Fig. 5.2. Electrophoretic mobility and zeta-potential of calcite as a function of pH.

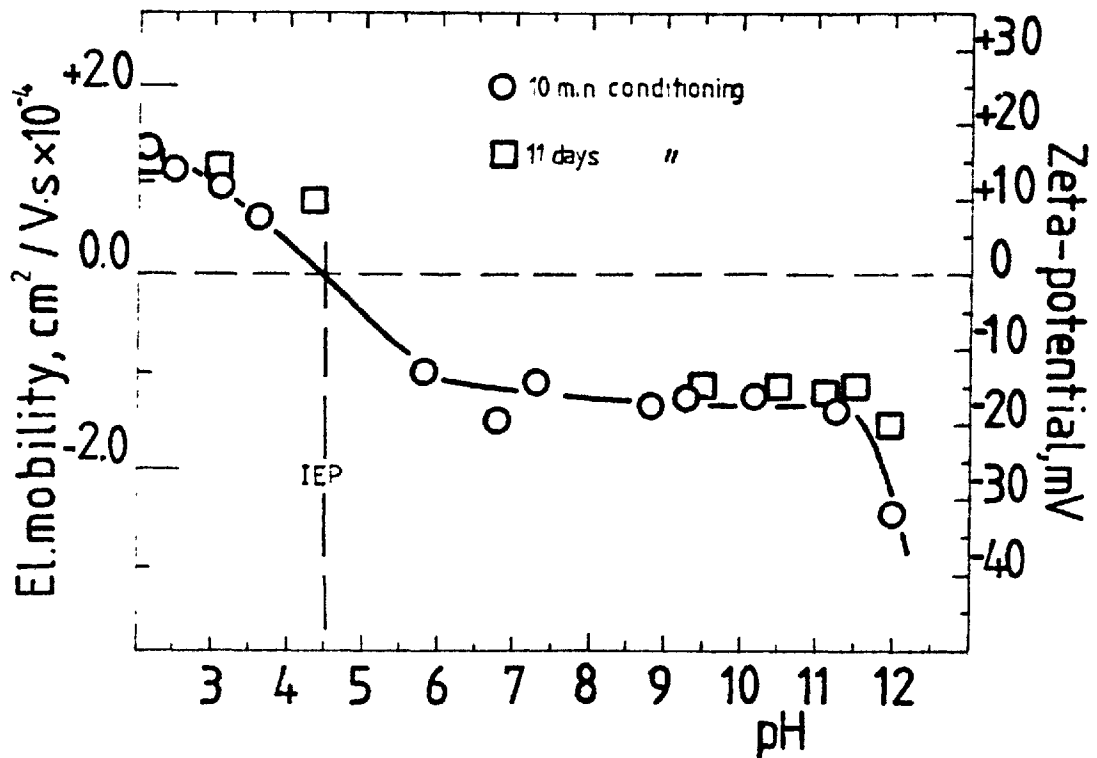


Fig. 5.3. Electrophoretic mobility and zeta-potential of barite as a function of pH.

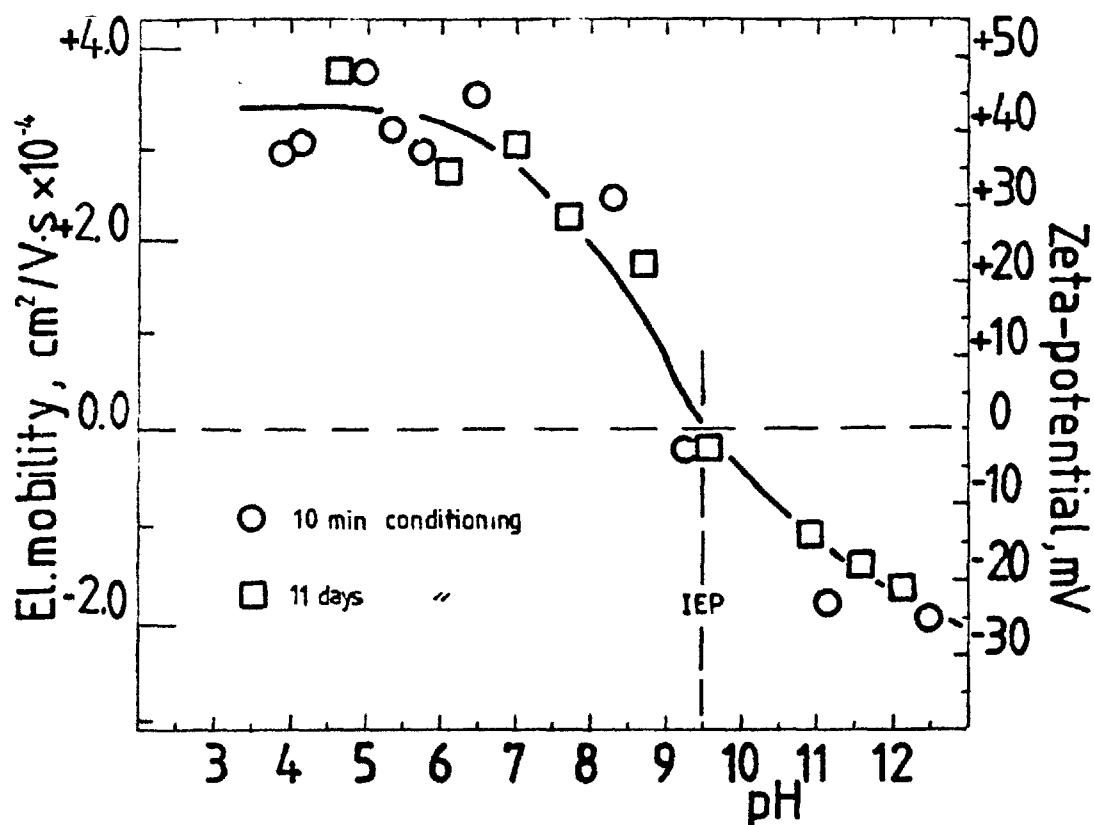


Fig. 5.4. Electrophoretic mobility and zeta-potential of fluorite as a function of pH.

not observed because of dissolution at pH values below 9.5 but extrapolation of the curve obtained suggests that it probably occurs in the range pH 8 - 9. This is consistent with the results of Somasundaran and Agar (37). Ageing the calcite for 11 days did not change the electrophoretic mobilities significantly.

The electrophoretic mobility of barite, Fig. 5.3, was independent of pH in the range 6 to 11 and was negative. At low pH values the mobility decreased to zero at pH 4.5 and then became positive. A similar value for the IEP was obtained by Plitt and Kim (35). At high pH values (>11) the mobility became more negative. Similar to calcite, ageing the barite did not produce a marked change in the mobilities.

The electrokinetic behaviour of fluorite as a function of pH is

shown in Fig. 5.4. At low pH values the mobility values were independent of the pH but at pH 6 they decreased rapidly and reversed sign at pH 9.5. Above this pH the surface of fluorite became progressively more negative up to pH 12.5 which was the highest pH used. The shape of the curve agrees well with those obtained by Miller and Hiskey (21) and Fuerstenau et al (32), although these authors give slightly higher values for the IEP, i.e. at pH 10.2 and pH 10.0, respectively.

5.3. Influence of sodium oleate

The effect of sodium oleate on the electrophoretic mobilities of calcite, fluorite and barite at constant pH is shown in Figs. 5.5 to 5.7. A pH value of 10.0 ± 0.2 was used because in practice an alkaline circuit is used to float salt-type minerals, calcite dissolves at pH values below 9.6, and preliminary Hallimond tube tests showed that sodium silicate influenced the oleate flotation of all three minerals under these conditions. The electrophoretic mobilities of the minerals became more negative with an increase in oleate concentration, but although the same value of approximately $-4 \times 10^{-4} \text{ cm}^2/\text{V}\cdot\text{s}$ was obtained in $1.0 \times 10^{-3} \text{ M}$ oleate, there were some differences in the intermediate concentration region. Thus, whereas the electrophoretic mobility of barite and fluorite decreased continuously with an increase in oleate concentration from $2.5 \times 10^{-6} \text{ M}$, the electrophoretic mobility of calcite only changed markedly above $1.0 \times 10^{-4} \text{ M}$.

A number of authors have shown that the positive zeta-potential of calcite (94, 213), fluorite, barite (39), magnesite and dolomite (214) decreases with an increase in oleate concentration and eventually changes sign, and they have ascribed this behaviour to adsorption by

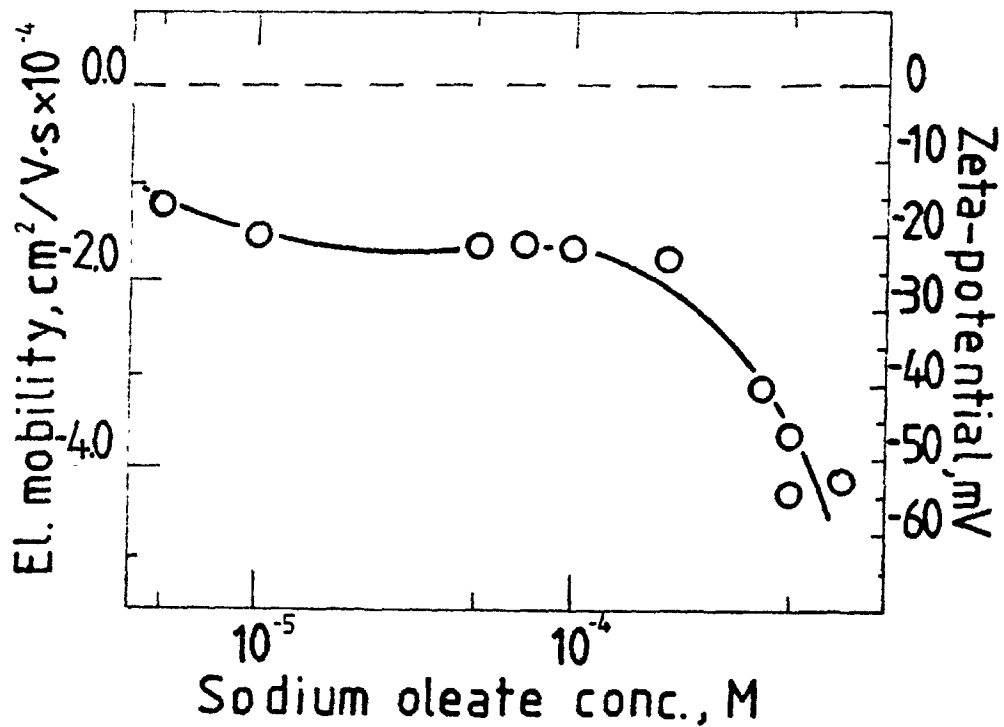


Fig. 5.5. Electrophoretic mobility and zeta-potential of calcite as a function of sodium oleate concentration at $\text{pH } 10.0 \pm 0.1$.

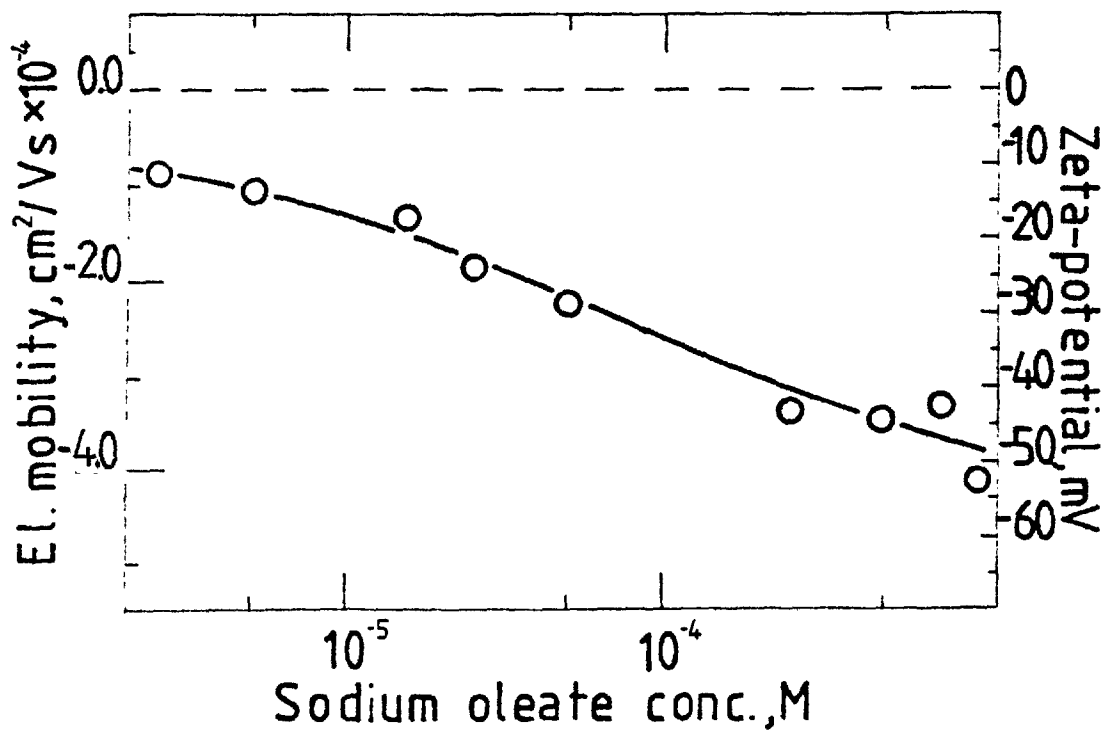


Fig. 5.6. Electrophoretic mobility and zeta-potential of barite as a function of sodium oleate concentration at $\text{pH } 10.0 \pm 0.1$.

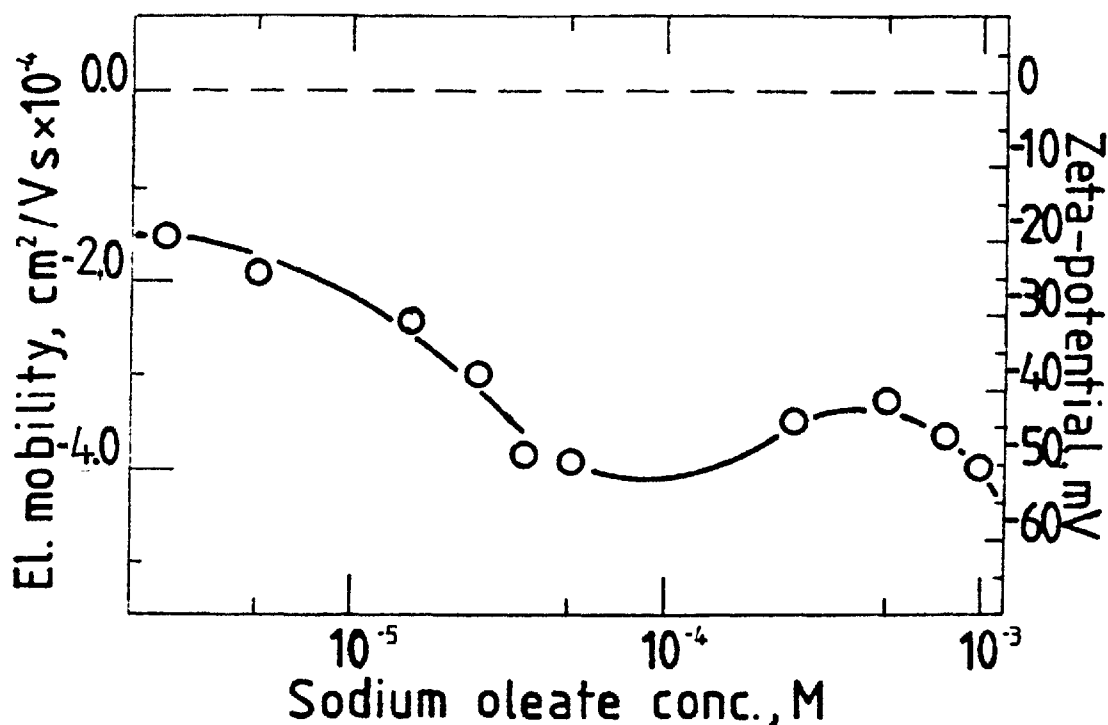


Fig. 5.7. Electrophoretic mobility and zeta-potential of fluorite as a function of sodium oleate concentration at pH 10.0 ± 0.1 .

coulombic attraction and hydrophobic association (215). Such a mechanism is unlikely in the present case, unless, despite the overall negative surface charge, there are some positive sites present. The gradual, rather than marked, increase in the electrophoretic mobility of fluorite and barite with an increase in oleate concentration militates against this. Furthermore, adsorption by hydrophobic bonding to give the polar groups pointing into the aqueous solution is unlikely because flotation (cf Chapter 7) was obtained under these conditions.

The solubility results shown in section 4.3 indicate that oleate reduces the calcium concentration in apparent equilibrium with fluorite and calcite. This behaviour is consistent with the adsorption of oleate or more probably the formation of a precipitated layer of calcium oleate on the mineral surface. If the latter is the case then

the electrophoretic mobilities obtained will be those of the precipitated metal oleate rather than the mineral. Calcium oleate has a high negative electrophoretic mobility value at alkaline pH values (198) and it is to be expected that barium oleate behaves similarly. The electrokinetic results obtained in the present work are, therefore, consistent with the formation of a layer of metal oleate on the mineral surface. Furthermore, if calcium or barium oleate is formed then oleate ions will be potential determining and the electrophoretic mobility should become more negative as the concentration increases. Supportive evidence for the formation of precipitated metal oleate is given in the next chapter.

5.4. Influence of sodium silicate and lattice cations

The effect of sodium silicate with various silica to soda ratios on the electrophoretic mobility of barite, calcite and fluorite is illustrated in Figs. 5.8 , 5.9 and 5.10. Results obtained in the presence of the lattice cations are also included in the same figures. The pH at which all the measurements were made was 10.0 ± 0.2 .

Small additions of the lattice cations reversed the sign of the electrophoretic mobility of all three minerals. Further additions made the electrophoretic mobility values obtained progressively more positive. Barite and calcite were positive even at very low concentrations of the constituent cations in solution and the pCa or pBa value at which the mobility changed sign could not be determined. In contrast fluorite reversed sign at a calcium concentration of $4-7 \times 10^{-5}$ moles/litre, i.e. pCa = 4.1-4.3, which is much higher than the value reported in the literature (41). Calcium and barium ions are considered to be potential determining for calcite/fluorite and barite, respectively and the above

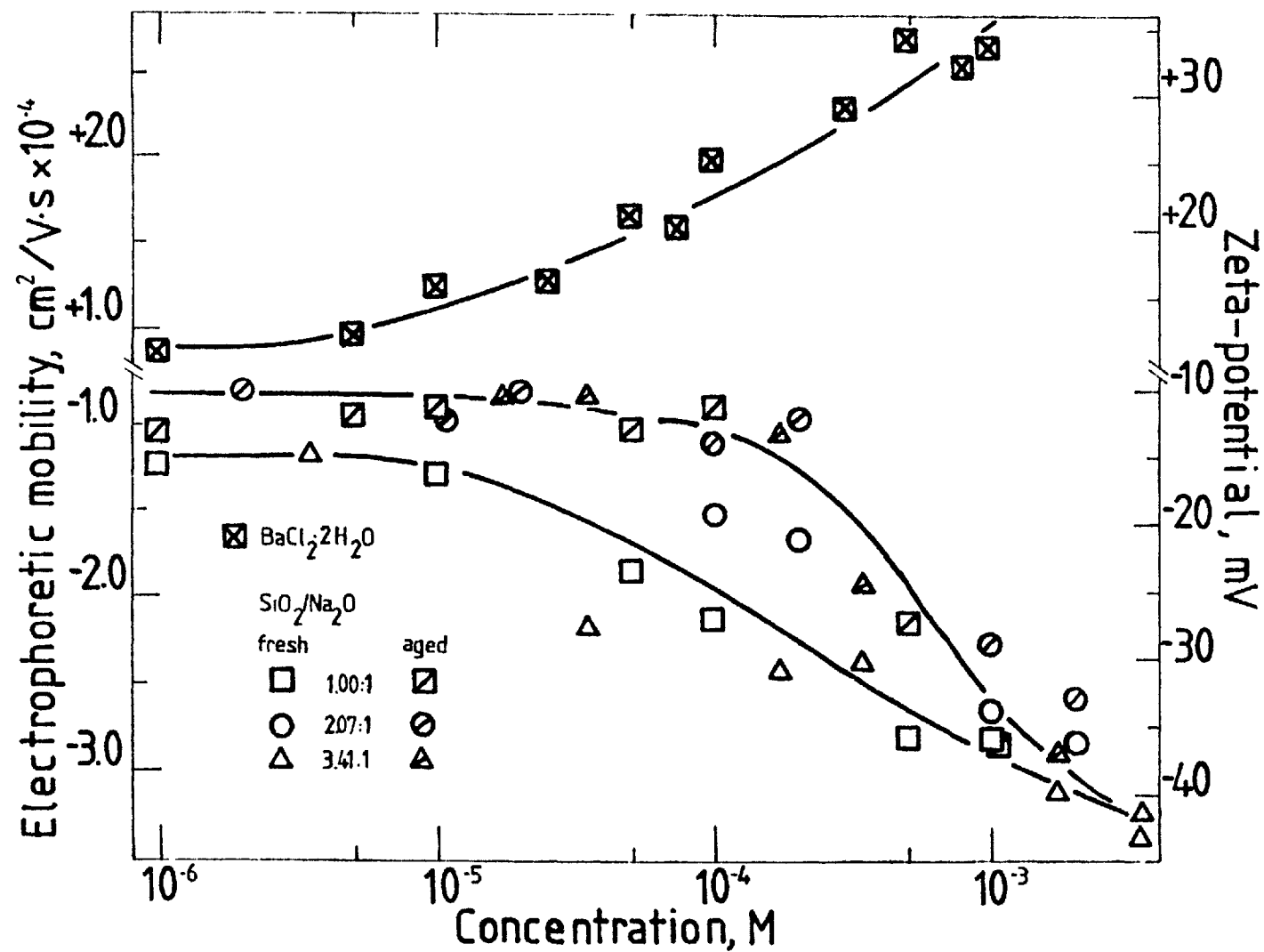


Fig. 5.8. Electrophoretic mobility and zeta-potential of barite at various concentrations of sodium silicate and barium chloride at pH 10.0 ± 0.1 .

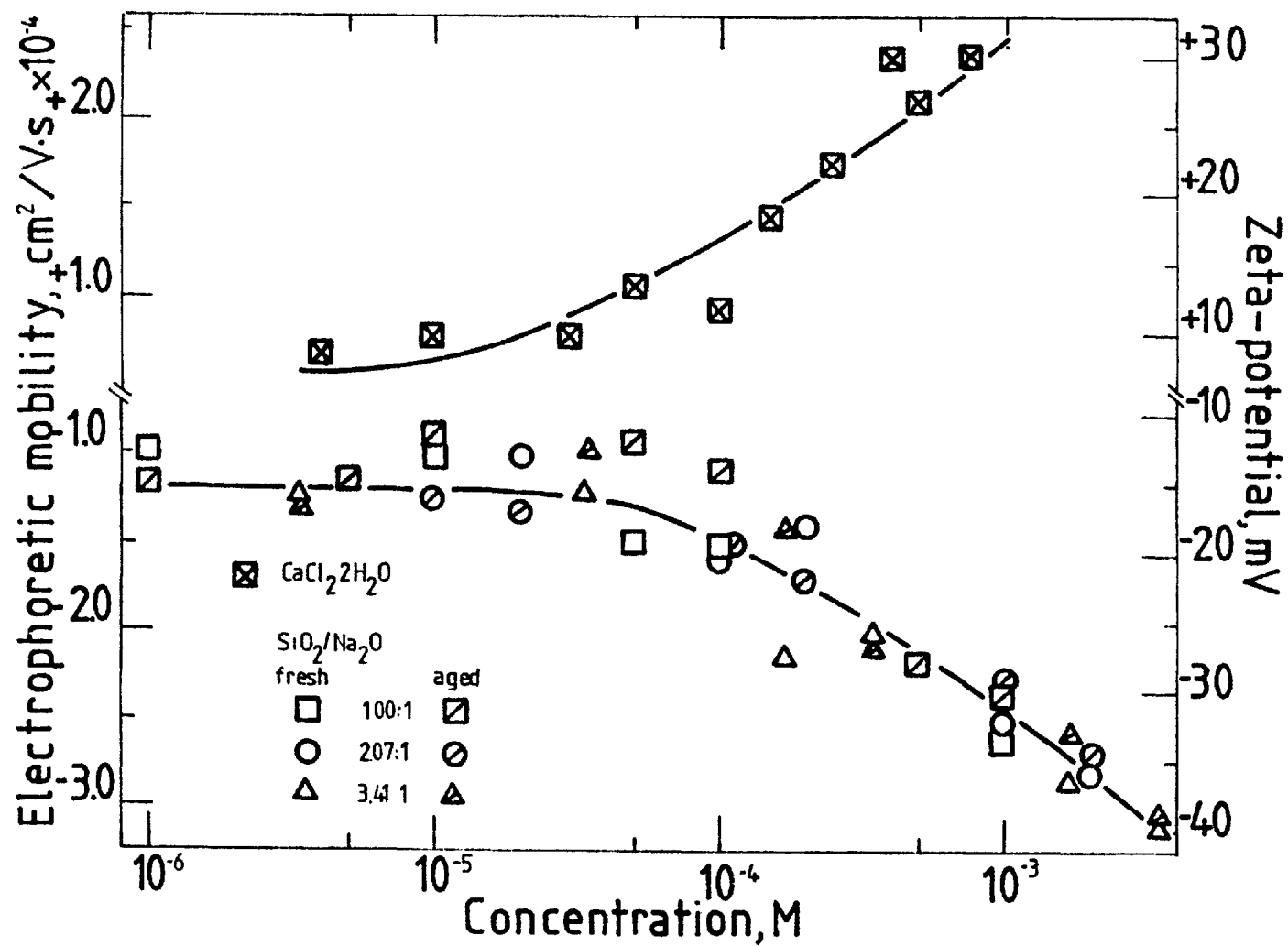


Fig. 5.9. Electrophoretic mobility and zeta-potential of calcite at various concentrations of sodium silicate and calcium chloride at pH 10.0 ± 0.1 .

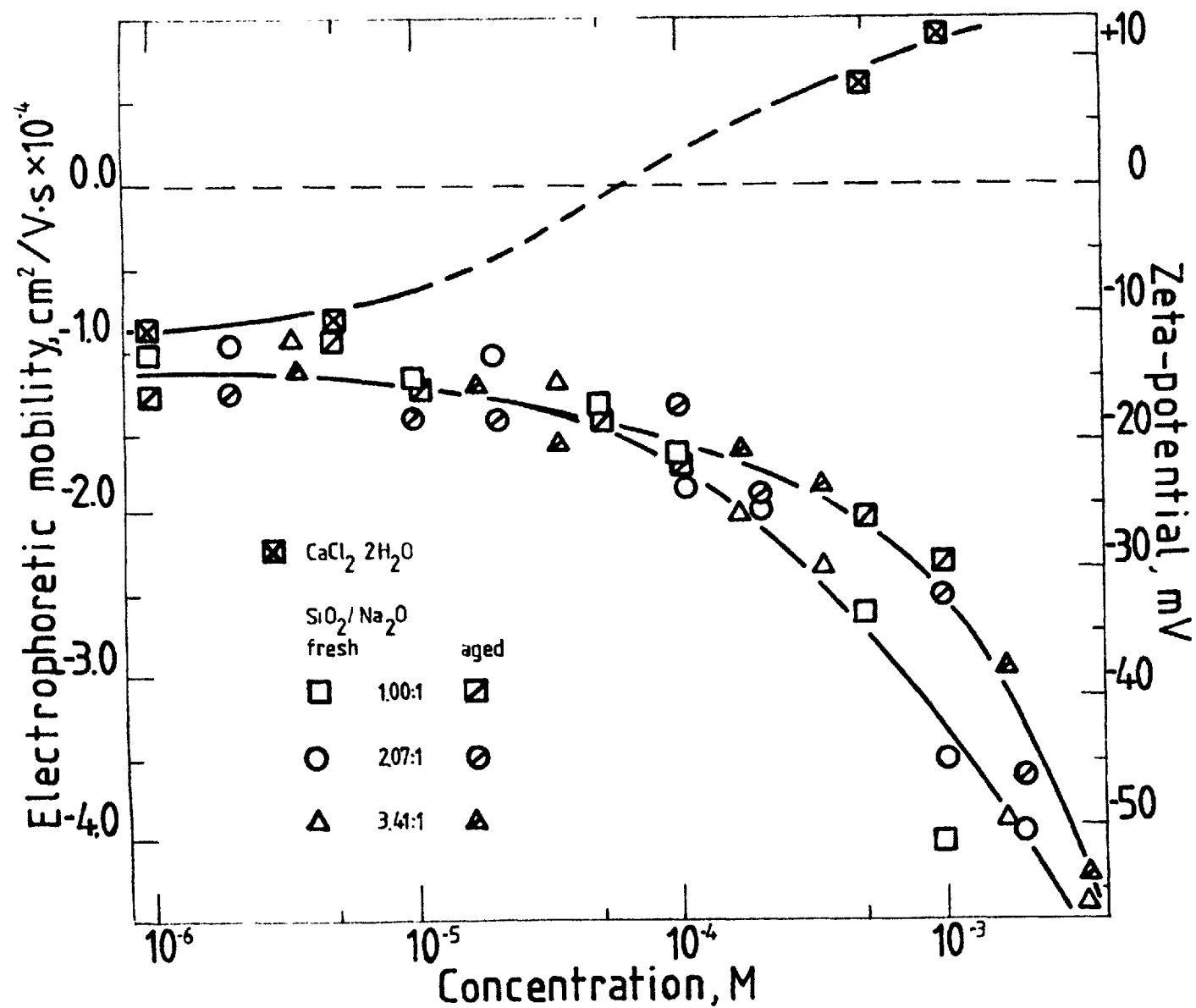


Fig. 5.10.

Electrophoretic mobility and
zeta-potential of fluorite
at various
concentrations of sodium
silicate and calcium chloride
at pH 10.0 ± 0.1 .

results support this view.

Although the constituent anions are also believed to be potential determining for salt-type minerals their influence on the electrophoretic mobility of these minerals is less pronounced. Small additions of SO_4^{2-} , CO_3^{2-} and F^- ions in suspensions containing barite, calcite and fluorite, respectively, caused no changes in the magnitude of the electrophoretic mobility. At higher concentrations (5.0×10^{-5} M), however, the electrophoretic mobility shifted to smaller negative values and measurements were not possible. Although this effect is to be expected at high ionic strengths because of the compression of the double-layer, it is a little surprising that it occurred at relatively low concentrations of potential determining ions. The apparent independence of the mobility of the salt-type minerals on the lattice anion concentration has been observed by other authors (47, 48, 216 - 8). It would, therefore, appear that the exact potential determining role played by the lattice anion requires further elucidation.

The electrophoretic mobilities of the three minerals in the presence of aged sodium silicate solutions were independent of SiO_2 concentration below approximately 5×10^{-4} M. At higher SiO_2 concentrations the electrophoretic mobility values became more negative with an increase in concentration. These results are in qualitative agreement with those of Sun (219) and Steiner (220). Comparison of the electrokinetic data with the solubility results (Figs. 4.7 - 8 and 5.9 - 10) shows that the increase in negative values of electrophoretic mobility corresponds to a decrease in the calcium concentration in apparent equilibrium with fluorite and calcite. Precipitation of a calcium silicate is unlikely as indicated in section 4.4, therefore, the increase in negative electrophoretic mobility must be caused by specific adsorption

of anionic silicate species.

Similar electrokinetic results were obtained with sodium silicates with different silica to soda ratios. This contrasts with the generally accepted view that the depressing properties of sodium silicate vary with this parameter. Atademir et al (45) found that sodium silicates with higher ratios were more effective in reducing the negative value of the electrophoretic mobility of scheelite than silicates with a low ratio. However, they did not control the pH and the concentration used was more than ten times the solubility of silica.

Fresh sodium silicate solutions produced more negative mobility values than aged solutions except in the case of calcite where no significant difference was obtained.

CHAPTER 6. MECHANISM OF ADSORPTION OF OLEIC ACID AND SILICA ON CALCITE, FLUORITE AND BARITE

6.1. Introduction

The mechanism of adsorption of sodium oleate and sodium silicate by the salt-type minerals is unclear. Furthermore, it is not known whether or not the presence of silicate inhibits the adsorption of oleate or vice versa. Tests were, therefore, done to determine the amount of oleate and silicate adsorbed by fluorite, barite, and calcite, and to determine how this adsorption effects the flotation of the minerals.

6.2. Interaction of oleic acid with the salt-type minerals

6.2.1. Mechanism of oleate adsorption

The uptake of oleic acid by barite, calcite and fluorite at pH 10.0 ± 0.2 is presented in Figs. 6.1 - 3 as a function of the equilibrium oleate concentration. Isotherms produced at different solid to liquid ratios were not coincident, thus indicating that the abstraction process was not reversible. The curves shown in Figs. 6.1 to 6.3 are characterised by two well-defined regions. In the first region, at low oleate concentrations, the "adsorption" displayed a marked dependence on the oleate concentration whereas

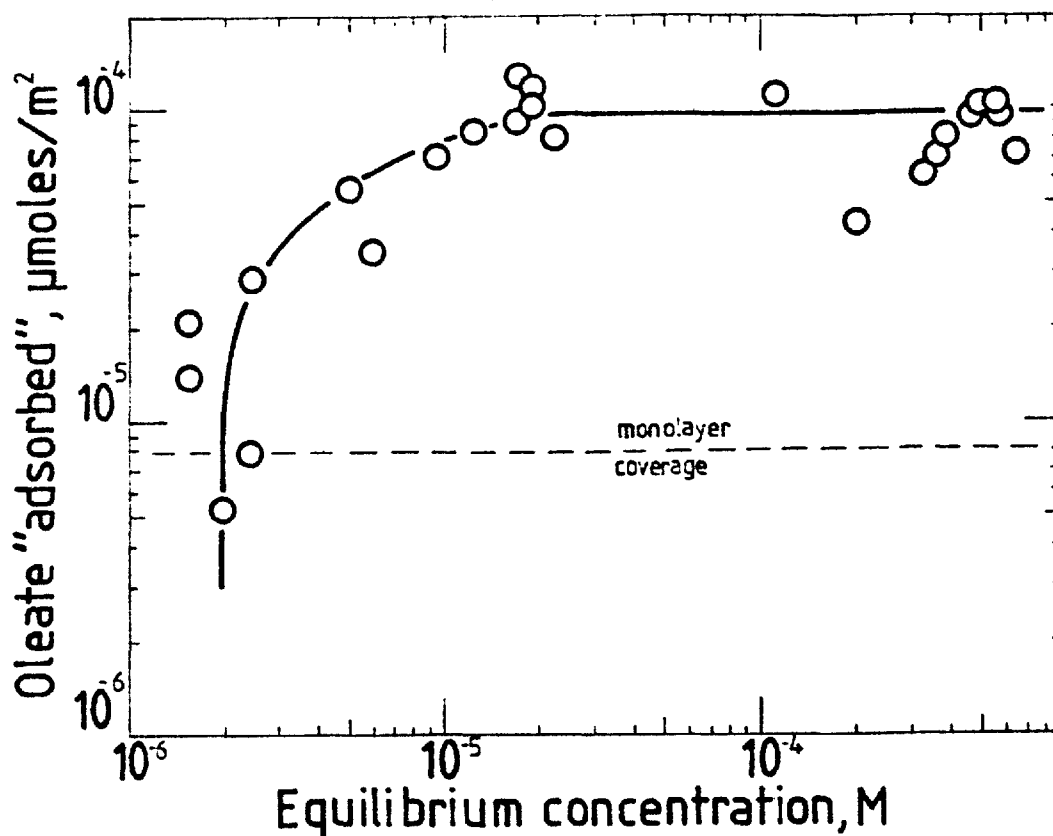


Fig. 6.1. "Adsorption" isotherm of sodium oleate on barite at $\text{pH } 10.0 \pm 0.2$.

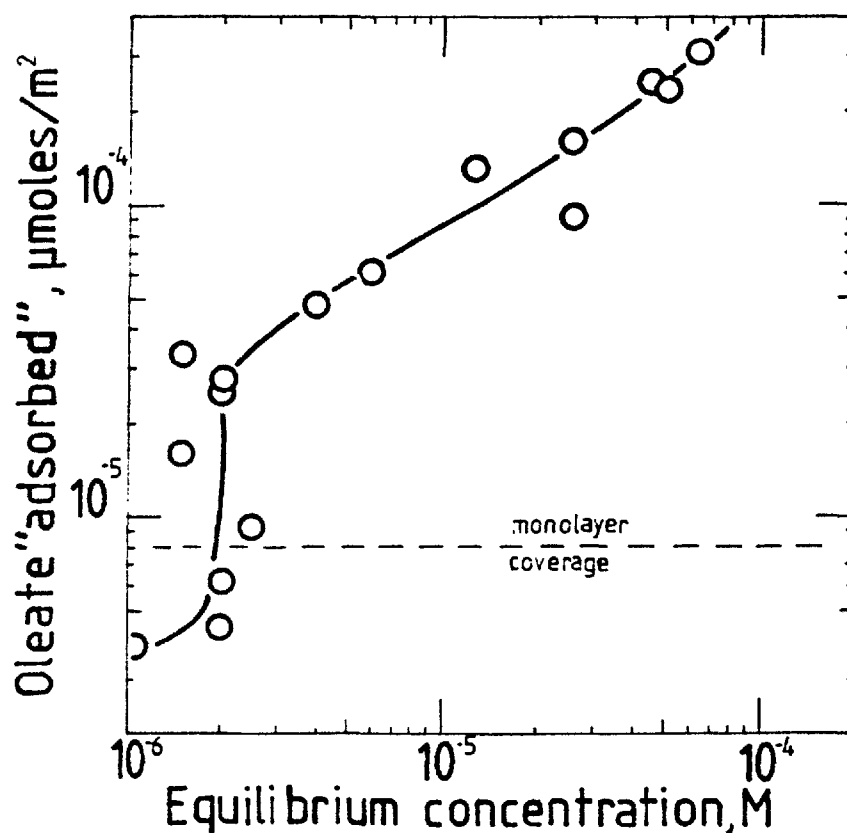


Fig. 6.2. "Adsorption" isotherm of sodium oleate on calcite at $\text{pH } 10.0 \pm 0.2$.

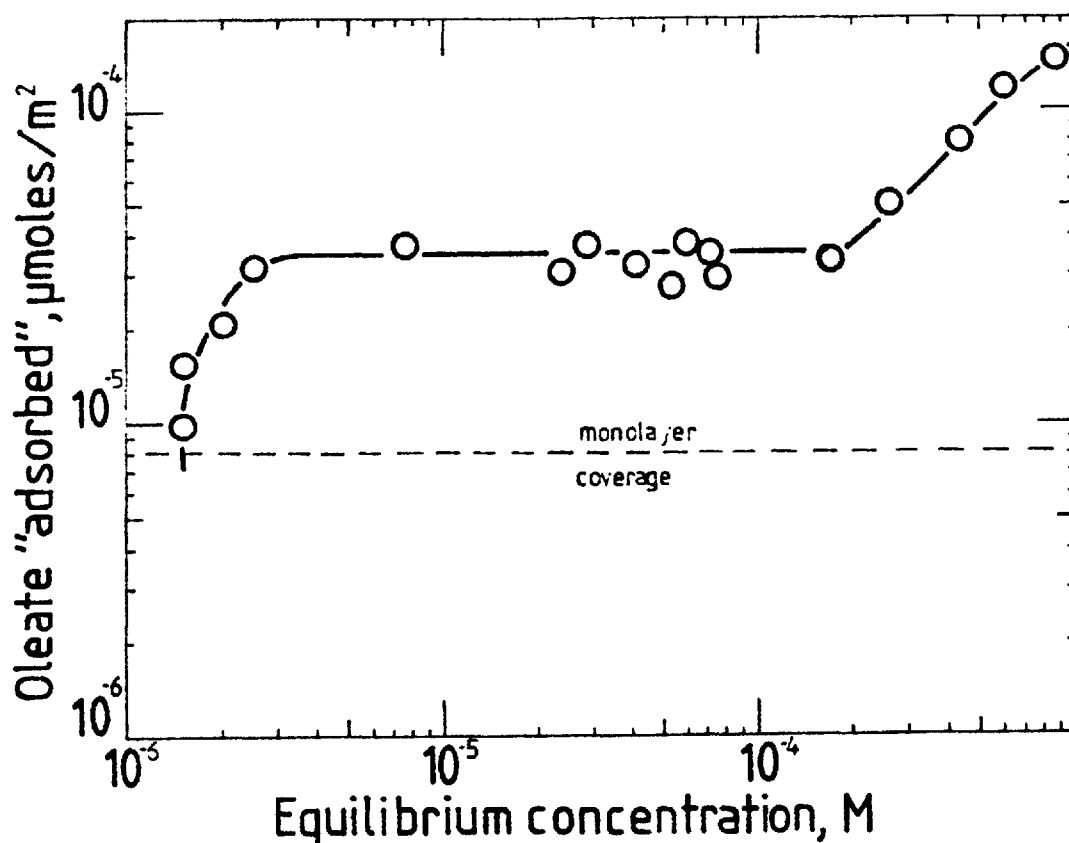
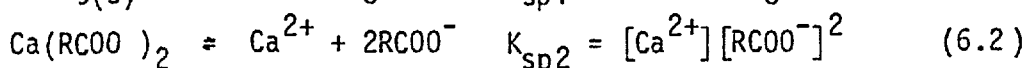
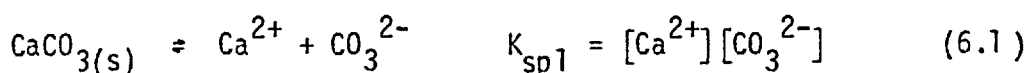


Fig. 6.3. "Adsorption" isotherm of sodium oleate on fluorite at pH 10.0 ± 0.2 .

in the second region the "adsorption" increased slowly with an increase in concentration or it remained constant. In all cases "adsorption" densities in an excess of a close-packed vertically oriented monolayer were obtained.

Irreversible, multilayer adsorption is inconsistent with the adsorption of oleic acid by a chemisorption process followed by physical adsorption. An explanation of the "adsorption" results can be obtained by considering the equilibrium conditions required for the precipitation of calcium oleate:



where RCOO^- represents the oleate ion.

If sodium oleate is added to a solution saturated with calcium carbonate and its concentration exceeds that given by the solubility product of calcium oleate, then calcium oleate will precipitate. At equilibrium, a mass balance on oleate and carbonate ion gives:

$$[\text{RCOO}^-]_a = [\text{RCOO}^-]_i - [\text{RCOO}^-]_e \quad (6.3)$$

and

$$\begin{aligned} [\text{CO}_3^{2-}]_e &= K_{sp1}^{\frac{1}{2}} + \frac{1}{2} [\text{RCOO}^-]_a = K_{sp1}^{\frac{1}{2}} + \frac{1}{2} \{ [\text{RCOO}^-]_i - [\text{RCOO}^-]_e \} \\ &\approx K_{sp1}^{\frac{1}{2}} + \frac{1}{2} [\text{RCOO}^-]_i, \quad [\text{RCOO}^-]_i > 1.0 \times 10^{-5} \text{ M} \end{aligned} \quad (6.4)$$

where the a, i and e indicate abstracted, initial and equilibrium concentrations, respectively. It is assumed in equations (6.3) and (6.4) that atmospheric CO_2 is excluded and that the hydrolysis of the oleate, carbonate and calcium ions is negligible. Dividing eq (6.1) by (6.2) and substituting the concentration of carbonate ions from eq (6.4) results in:

$$[\text{RCOO}^-]_e = \sqrt{\frac{K_{sp2}}{K_{sp1}} (K_{sp1}^{\frac{1}{2}} + \frac{1}{2} C)} \quad (6.5)$$

Substitution of eq (6.5) in (6.3) shows that if precipitation occurs the amount abstracted should display a linear dependence on the initial concentration. Alternatively, when $[\text{RCOO}^-]_e \ll [\text{RCOO}^-]_i$, a logarithmic plot should give a straight line with a slope of unity. The results represented in Figs. 6.4 - 6 show that the experimental points fall on or near the line predicted by eq (6.3). A calcium and barium oleate solubility product of 3.98×10^{-16} and 1.25×10^{-15} moles³/litre³ (82) was used in the construction of the theoretical curves, respectively.

The agreement between the theoretical and experimental curves for calcite is good but with fluorite the amount of oleate abstracted is somewhat lower than expected, at high oleate concentrations. With barite, at initial oleate concentrations below 5.0×10^{-4} M, the

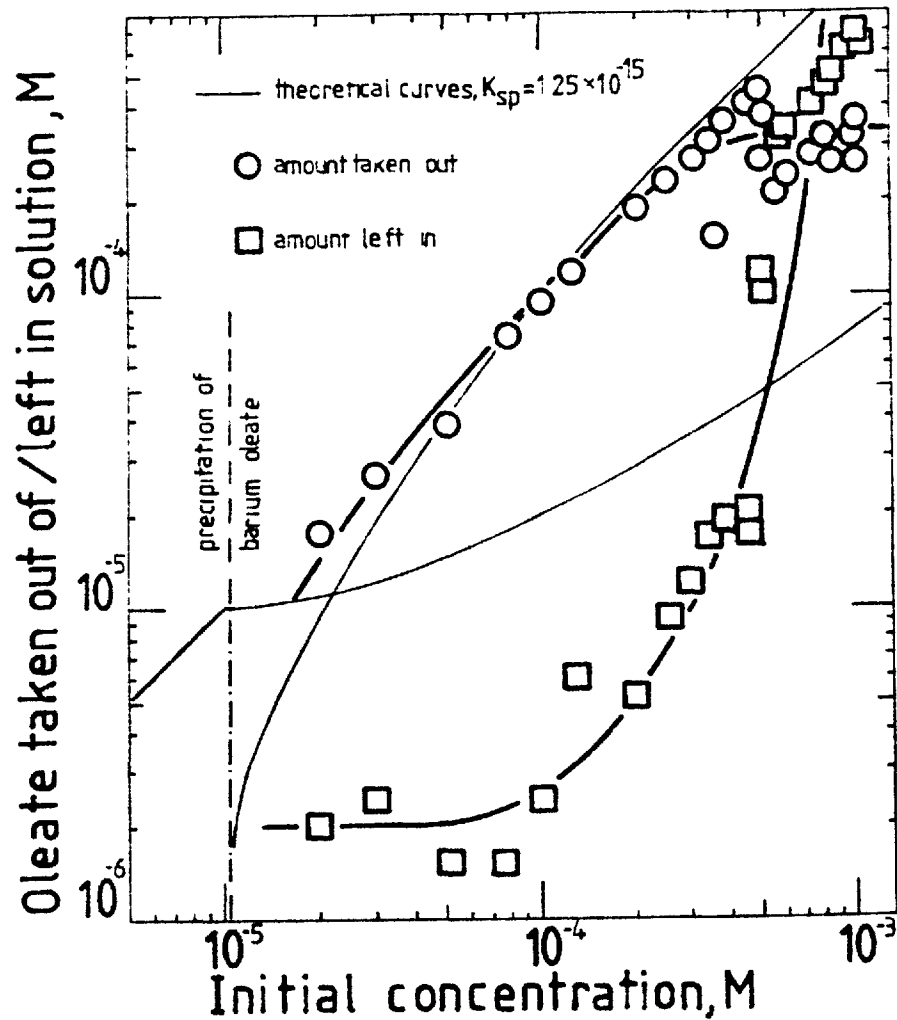


Fig. 6.4. Amount of oleate abstracted from solution in equilibrium with 0.1 g barite at pH 10.0 ± 0.2 .

equilibrium oleate concentration is approximately ten times less than the theoretically predicted value. This discrepancy indicates that the value used for the solubility product of barium oleate might be in error by a factor of 100.

Consideration of the equilibrium oleate concentration as a function of initial oleate concentration curves suggests that the conversion of the mineral to a metal oleate is inhibited by some process. If the reaction goes to completion the equilibrium concentration should be equal to that predicted from eq. (6.5). However, the curves in

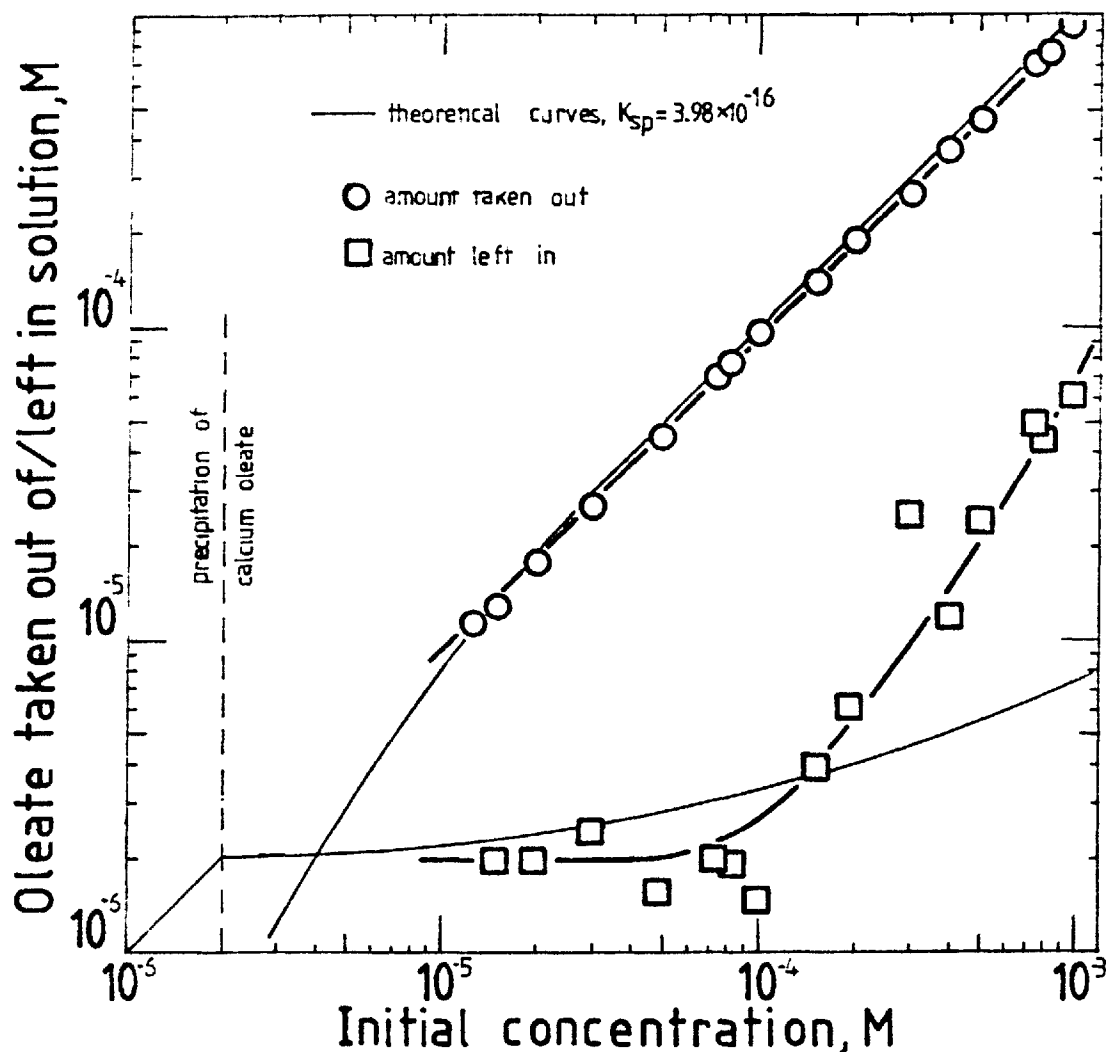


Fig. 6.5. Amount of oleate abstracted from solution in equilibrium with 0.1 g calcite at $\text{pH } 10.0 \pm 0.2$.

Figs. 6.4 - 6 show that this is not the case and that the equilibrium concentration is higher than that calculated from eq (6.5). This is more pronounced at higher initial oleate concentrations. Comparison of Figs. 6.4 - 6 with 6.1 to 6.3 shows that the increase in equilibrium concentration corresponds to the region where the "adsorption" displays a small dependence on the equilibrium concentration. It would, therefore, appear that, under these conditions, the precipitated metal oleate at the surface prevents further reaction between the lattice

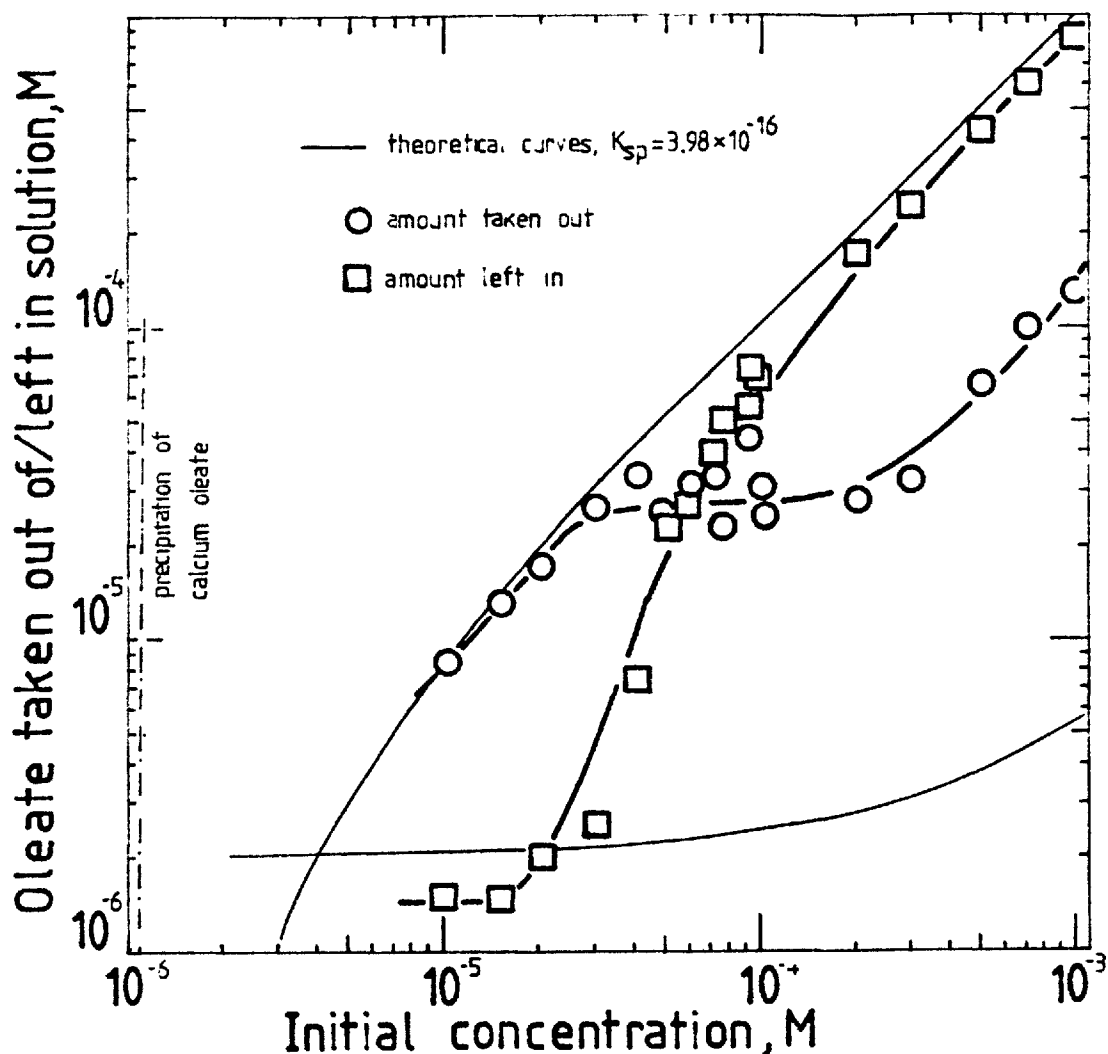


Fig. 6.6. Amount of oleate abstracted from solution in equilibrium with 0.1 g fluorite at pH 10.0 ± 0.2.

cation and the oleate ion. This effect does not affect the linearity of the curves shown in Figs. 6.4 and 6.5 for barite and calcite, respectively because the equilibrium concentration is negligible compared to the initial concentration over most of the range studied. With fluorite, however, the formation of calcium oleate on the surface considerably inhibits further reaction between calcium and oleate ions and as a result the experimental results do not concur with theoretical predictions.

The formation of a layer of metal oleate which inhibits further reaction or dissolution is consistent with the results obtained in the solubility and electrokinetic studies (Chapters 4 and 5). In the solubility studies it was argued that true equilibrium was not obtained and the same must be true for the results shown in Figs. 6.1 to 6.6. The equilibrium concentrations quoted in the preceding paragraphs are therefore not true equilibrium values even though they were reproducible and similar values were obtained after conditioning for 30 min and 24 h. Presumably the surface layers of metal oleate are so compact that the diffusion of lattice cation or oleate through it is very slow.

The structure, texture and strength of adhesion of the soap layers must in some way be controlled by the availability of cations at the mineral surface. This probably explains why the calcium oleate layer on fluorite had a greater inhibiting effect than that on barite and calcite. Of the three minerals fluorite has the highest density of lattice cations on the various crystallographic planes.

6.2.2. Effect of pH on oleate adsorption and flotation recovery

Since oleate precipitates and does not chemisorb on the surface of all three minerals, its effectiveness as a collector will be dependent on the strength of adhesion of the precipitate to the mineral surface and not on the relative amount of oleate abstracted by each mineral. The flotation of these minerals with oleic acid will be influenced by any parameter which affects the formation and stability of the precipitate on the surface. The pH of the solution will be one of these parameters because of its effect on the solubility and rate of dissolution of all three minerals and the hydrolysis of oleate ions

(Fig. 1.7).

The flotation recovery of barite, calcite and fluorite as a function of pH at two different levels of sodium oleate concentration is presented in Figs. 6.7 , 6.8. and 6.9 , respectively. In the same figures, the amount of oleate abstracted by each mineral, at various pH values, is also included. Although the two sets of experiments were not carried out on the same particle size fraction some useful comparisons can be made.

Abstraction of oleate by all three minerals was high at alkaline pH values and it decreased with a decrease in pH. With fluorite low abstractions were obtained at acid pH values but with barite the "adsorption" increased again at pH values below 6.5. Determinations were not made with calcite at low pH values because of its dissolution. The good abstraction of oleate under alkaline conditions is consistent with a chemical reaction between the oleate ion and the lattice cation. At pH values above 8.0 and at a total oleate concentration of 5.0×10^{-5} M, almost all of the oleate is in the form of oleate ions which are available to react with the cations on the surface. Below this pH, the oleate mainly exists in solution as the neutral oleic acid molecules (Fig. 1.7) and as precipitated oleic acid. Several authors (6, 221) have suggested that fatty acid adsorption at low pH values involves some physical process. If this is the case then the process is apparently selective between fluorite and barite. The recovery of barite in 1.0×10^{-4} M sodium oleate solution was constant at pH values above 7.0. Reducing the concentration by a factor of ten had little effect on the recovery at pH 7.0 but at higher pH values a small decrease was obtained. The decrease in recovery at pH values below 7.0 corresponds to a rapid decrease in the oleate abstraction. However,

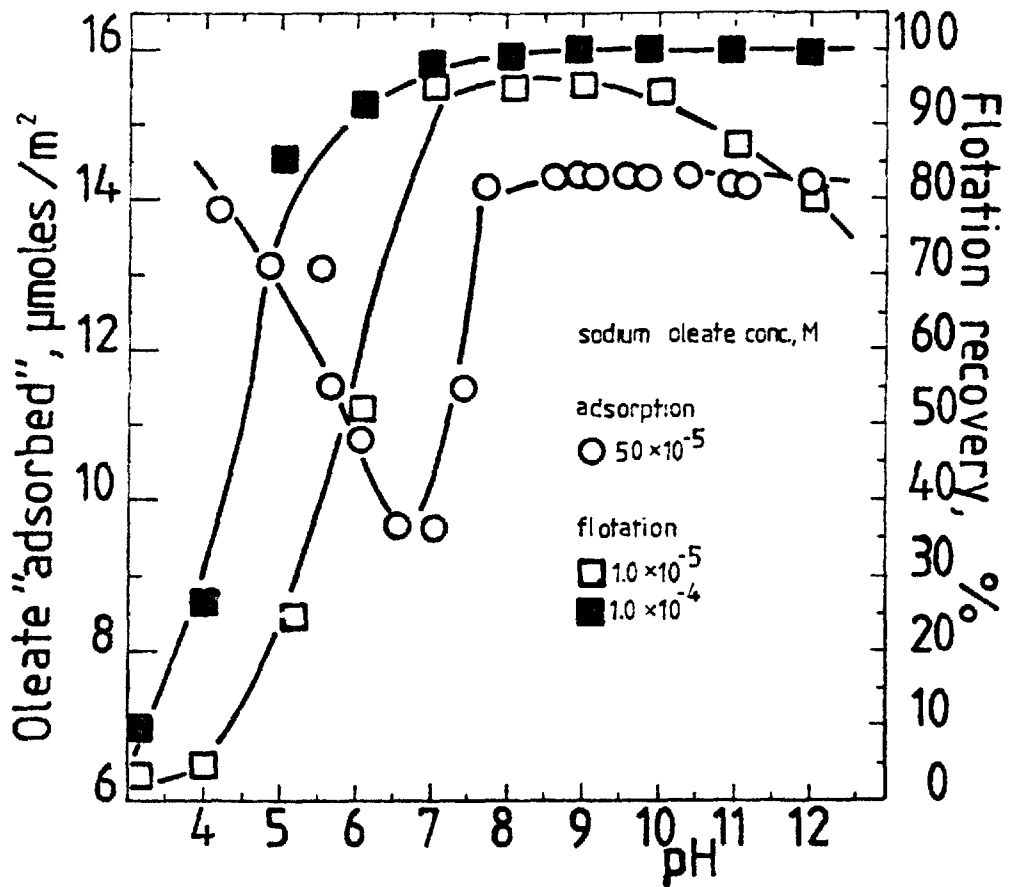


Fig. 6.7. Effect of pH on oleate "adsorption" and flotation recovery of barite.

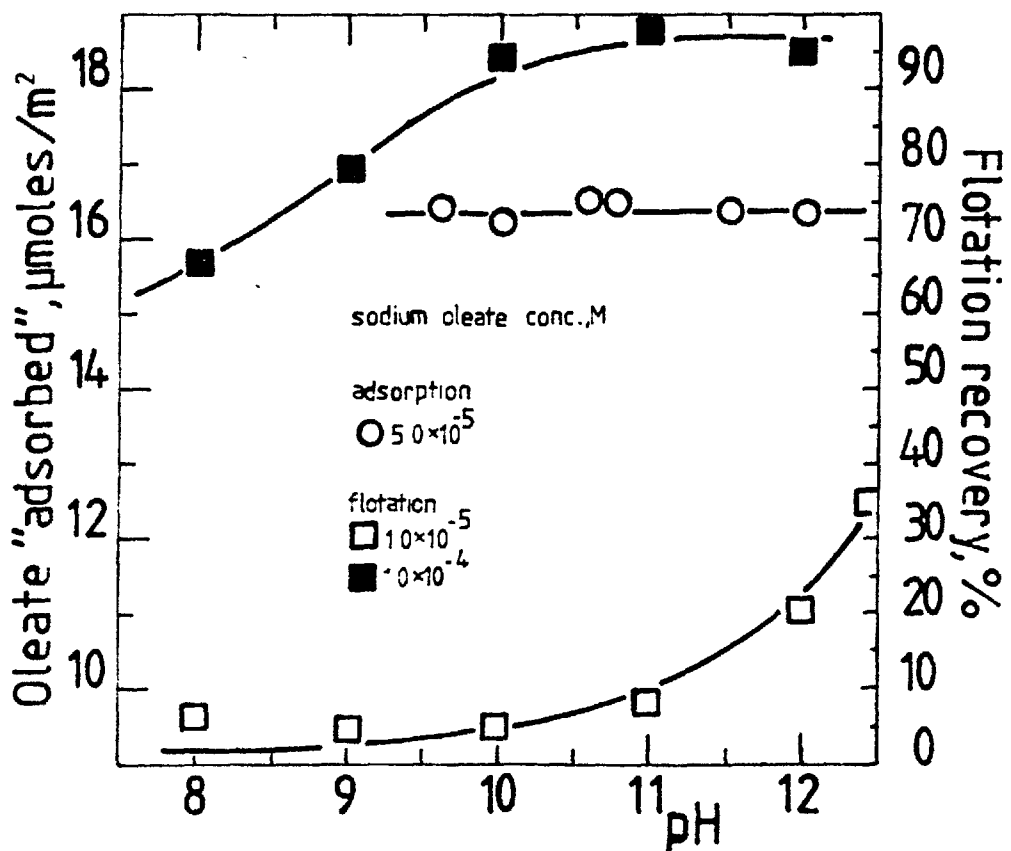


Fig. 6.8. Effect of pH on oleate "adsorption" and flotation recovery of calcite.

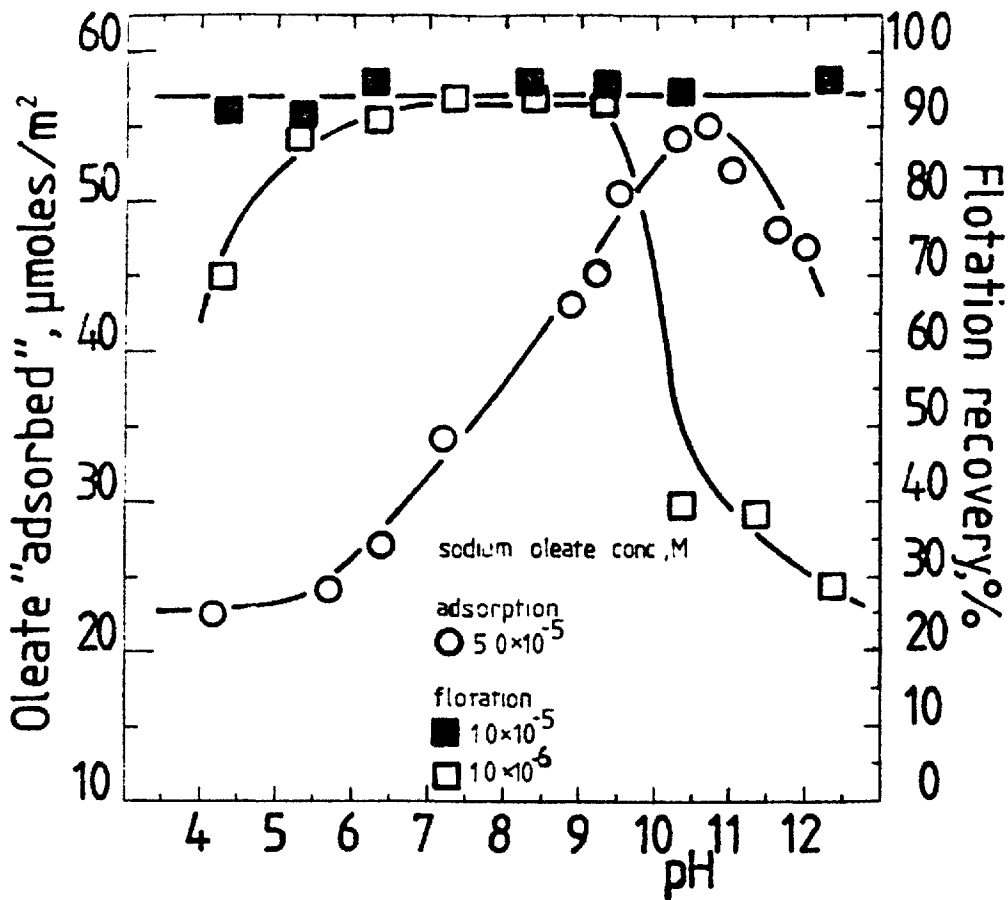


Fig. 6.9. Effect of pH on oleate "adsorption" and flotation recovery of fluorite.

whereas the "adsorption" increased again at pH values below 6.0 the recovery continued to decrease. This shows that although "adsorption" of oleate species, presumably oleic acid molecules or precipitated oleic acid, occurred a hydrophobic surface was not obtained.

The flotation of fluorite in 1.0×10^{-4} M sodium oleate was complete throughout the pH range (results not shown) and reducing the concentration to 1.0×10^{-5} M had little effect. In 1.0×10^{-6} M sodium oleate the recovery decreased at pH values above and below 9.0 and 7.0, respectively. Hence fluorite floats best under similar pH conditions to barite although the latter requires a higher oleate concentration. A similar observation has been made by other authors (6, 222).

Comparison of the fluorite recovery and oleate "adsorption" curves suggests that the flotation is independent of the adsorption. Obviously this cannot be the case and the results must reflect the degree to which the calcium oleate adheres to the fluorite surface. Thus, in the pH range below 9.0 proportionally more of the calcium oleate adheres to the fluorite surface than at higher pH values. It is perhaps significant that the IEP of fluorite occurs at pH 9.5 so that if the calcium oleate is negatively charged (section 4.3) the calcium oleate will coulombically adhere to the surface at pH values below 9.0. At high oleate concentrations some of the calcium oleate will adhere to the mineral surface despite the presence of charges of similar signs on the calcium oleate and mineral surfaces. The favourable coincidence of calcium oleate formation and unlike surface charges could explain why less oleate is required to float fluorite than barite and calcite.

Comparison of the flotation recovery curves for calcite, fluorite and barite shows that selectivity is unlikely to be obtained between these minerals by varying the pH. Fluorite apparently floats less readily than calcite and barite at high pH values, but at the oleate concentrations required to float the latter two minerals, also floats.

6.3. Adsorption of silica

6.3.1. Mechanism of adsorption of silica

The use of a modifying reagent to obtain selectivity in the flotation of salt-type minerals with oleic acid is necessary and this is evident from the results given in the preceding two sections. In this respect, sodium silicate has been widely used for many years, but as yet its mode of action has not been satisfactorily explained. This is not because of the lack of experimental data but mainly due to

difficulties of interpretation. One of the main problems is the complexity of the aqueous sodium silicate solutions, the chemistry of which is not well understood.

Depending on the total silica in solution and the experimental conditions prevailing, colloidal silica may either be present or not. This factor has often been neglected by earlier researchers (42, 102 - 10) and the presence of colloidal silica has been assumed even in very dilute solutions. As a result the data have been wrongly interpreted.

It is well known that polymeric (colloidal) species exist in concentrated sodium silicate solutions and that they are negatively charged (Chapter 3). Because of this they have found extensive use in the coagulation of positively charged particles (alumina, ferric oxide, etc.). In these systems, colloidal silica does not exhibit any selectivity other than to be attracted electrostatically to oppositely charged particles. Monosilicates predominate in dilute sodium silicate (i.e. with a SiO_2 content below the solubility of amorphous silica) and their mechanism of dispersion and depression most likely differs from that of the colloidal silica. In the present studies the concentration of silica in solution, expressed as moles SiO_2 per litre, was at least five times lower than the value given for the solubility of amorphous silica (section 3.2.2). Consequently the composition of these sodium silicate solutions can be adequately described by the distribution diagram shown in Fig. 3.1 plotted for 1.0×10^{-3} M SiO_2 solution. These conditions were thought necessary to avoid any uncertainties arising during the interpretation of the results because of the presence of colloidal silica or even polymeric species.

The adsorption isotherms of sodium silicate on calcite and fluorite are shown in Figs. 6.10 and 6.11. The experimental procedures used to

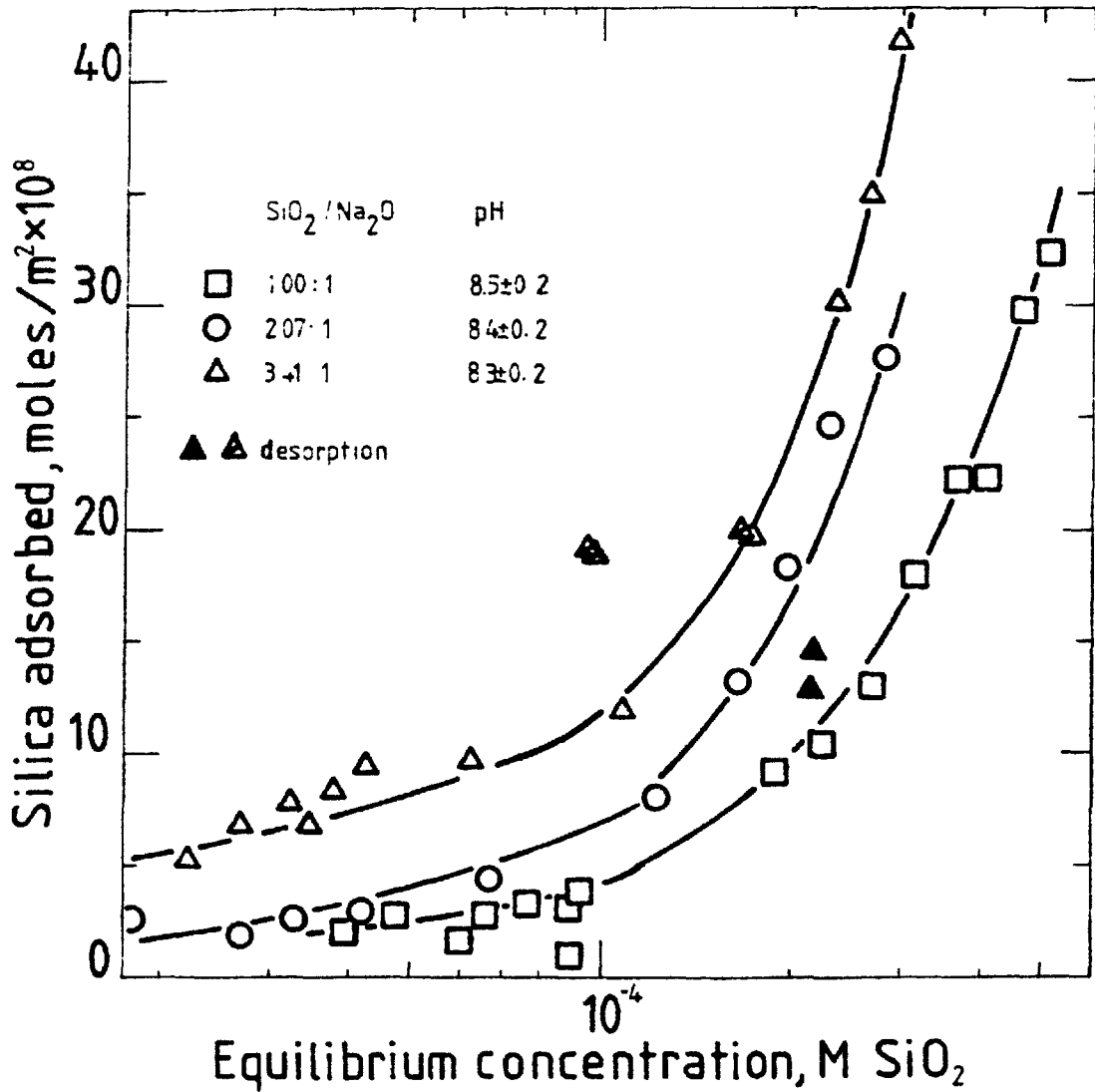


Fig. 6.10. Adsorption isotherms of sodium silicate with different silica to soda ratios on calcite

determine the adsorption of silica on the minerals were discussed in detail in section 2.2.41. Time and temperature effects on the adsorption of silica on the three minerals were studied first. Thus, it was found that the adsorption was a rapid process in the initial stage and that the reaction was almost complete in less than 4 h, though minor increases in the amount of adsorbed silica occurred over a prolonged period of time, i.e. more than 15 h. A constant time of 15 h was used in all experiments mainly to allow the sodium silicate

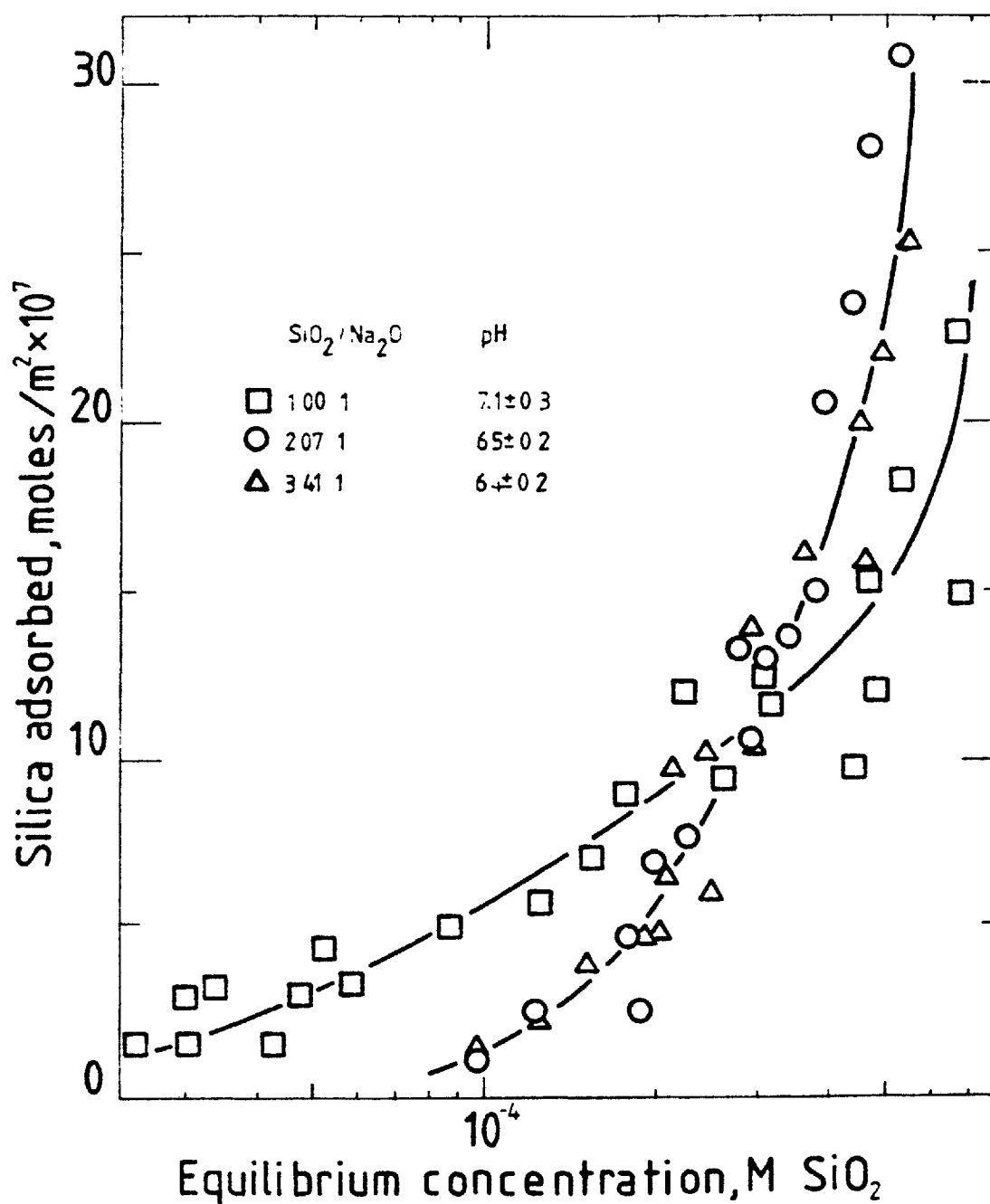


Fig. 6.11. Adsorption isotherms of sodium silicate with different silica to soda ratios on fluorite.

solutions to reach equilibrium (section 2.2.41).

Adsorption measurements carried out at various temperatures showed that the amount of silica adsorbed on calcite and fluorite did not appreciably change with temperature, at least in the range 15-30°C.

Consequently, all the subsequent measurements were conducted at room temperature (15-20°C).

To establish if the adsorption process was reversible or irreversible, the adsorption of silica was measured either from solutions having different solid/solution ratios or by dilution at constant pH. The latter was done by replacing half of the volume of the solution with distilled water adjusted to the same pH value and equilibrating the mineral with this solution for another 15 h. The results obtained are shown in Fig. 6.10, in the case of calcite. Both types of experiments showed that the adsorption of silica was an irreversible process.

Figs. 6.10 and 6.11 show that at sodium silicate concentrations not exceeding 2.0×10^{-4} M SiO_2 the adsorption of silica on both minerals was low and that an abrupt increase in the adsorption occurred at higher silica concentrations. All isotherms are of the S2 type of Giles' classification (223) which indicates a tendency of the adsorbed solute to condense on the surface, at high surface coverages, rather than to remain as isolated units. If the surface area of the silica unit adsorbed on the surface is taken as equal to $12.3 \text{ \AA}^2$ ($12.3 \times 10^{-20} \text{ m}^2/\text{molecule}$) (150) then a close packed monolayer would be obtained at an adsorption density of $1.34 \times 10^{-5} \text{ moles/m}^2$ for both minerals. Although a surface area of $25 \text{ \AA}^2$ ($25 \times 10^{-20} \text{ m}^2/\text{molecule}$) has also been reported (224) for the Si(OH)_4 molecule, this does not change the conclusion that in the concentration range studied (Figs. 6.10 - 11) the adsorption density was far below the value calculated for the completion of a monolayer. This indicates that silica adsorbs on distinct sites on the surface and that lateral interactions among the adsorbed species will be negligible. Although this appears to be true for low silica concentrations, as in the present case, it does not contradict the assumption

that at higher silica concentrations condensation-polymerization of the silica may occur on the surface, especially since such a process takes place in solution under the appropriate conditions of pH and silica concentration. It is also worth mentioning that under these conditions the silica exists in solution, at least partially, in a colloidal or polymeric form and not in the form of Si(OH)_4 molecules and silicate ions the adsorption of which may proceed through a completely different mechanism.

Solubility studies with calcite and fluorite (section 4.4) and measurements of the electrokinetic properties of all three minerals (section 5.4) in the presence of sodium silicate showed that sodium silicate prevents dissolution of the minerals and makes their negative zeta-potential more negative. Comparison of this data with the adsorption results (Figs. 6.10 - 11) shows that the concentration range in which the silicate was most effective ($>1.0 \times 10^{-4}$ M SiO_2) corresponds to that in which appreciable adsorption of SiO_2 occurred. Since electrostatic adsorption of neutral Si(OH)_4 molecules or negatively charged silicate ions cannot account for the results some other mechanism must be operative. Furthermore, in view of the irreversibility of the adsorption it is probable that the mechanism is chemical in origin.

First to be considered is the formation of hydrogen bonds between the adsorbed silicate species and the mineral surface. The irreversibility of the adsorption process does not rule out this possibility, since there is not general agreement on whether hydrogen bond formation is a reversible or an irreversible process. Silanol groups have been reported (126) to be capable of hydrogen bond formation through the hydrogen of the -OH group. Furthermore, the presence of oxygen containing groups on the surface of barite and calcite and fluoride on

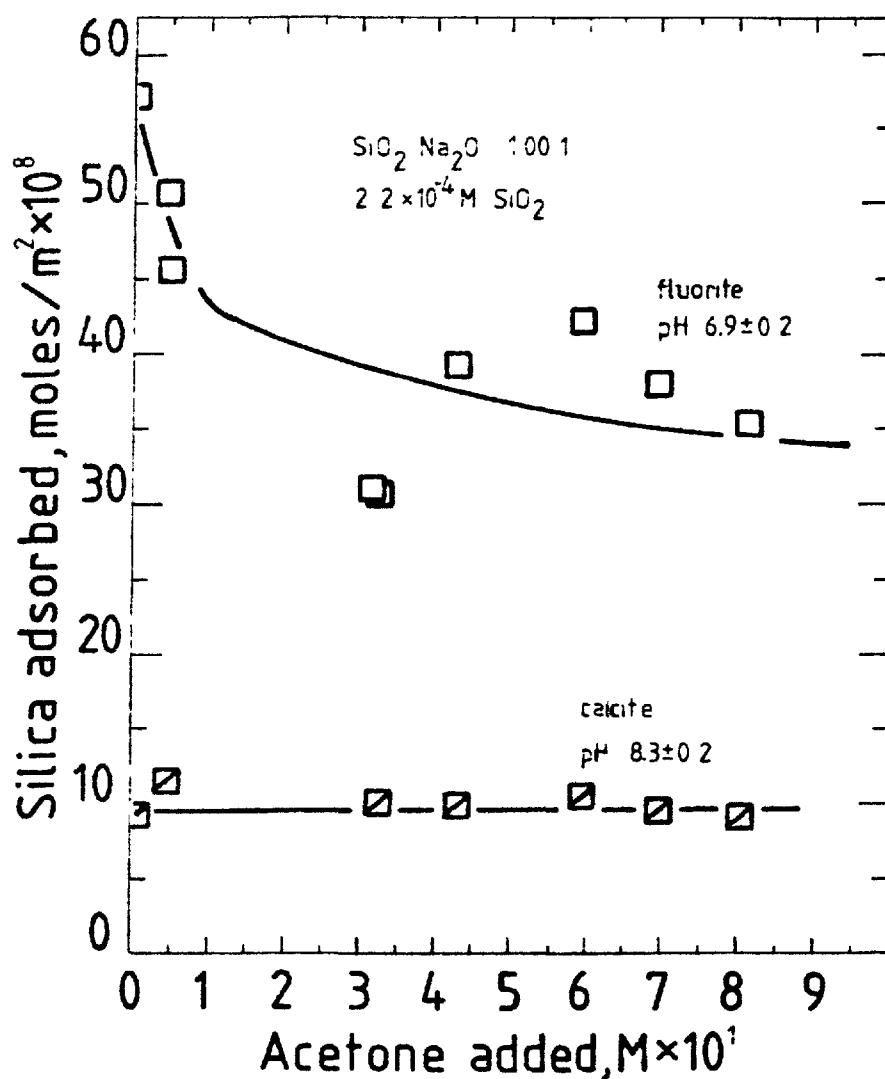


Fig. 6.12. Influence of acetone on the amount of silica adsorbed on calcite and fluorite.

on the surface of fluorite, together with the possible presence of OH^- groups produced by hydrolysis, might favour the formation of such a bond with silicate species. To determine whether or not hydrogen bonding contributed to the adsorption of silica tests were done in the presence of a compound known to be a hydrogen bonding competitor (225). These reagents readily form hydrogen bonds and their presence should reduce the silica adsorption if hydrogen bonding is involved. Although a large number of organic compounds have been used as hydrogen bonding competitors,

acetone was chosen in the present experiments because it was readily available. The results obtained are shown in Fig. 6.12. It is clear that acetone hardly affected the adsorption of silica on calcite even at relatively high concentrations, i.e. 9.0×10^{-1} M. In contrast, the amount of silica adsorbed on fluorite decreased to almost a half of its original value upon addition of acetone ($\approx 3.0 \times 10^{-1}$ M) and then remained constant with further additions.

Silica has been reported (153) to form complexes with some organic compounds and consequently the latter may interfere with the spectrophotometric determination of silica. Because of this, determinations of silica were carried out in the presence of various additions of acetone. The results are presented in Table 6.1 (section 2.3.52).

Table 6.1. Influence of acetone on the spectrophotometric determination of silica (initial silica added 2.0×10^{-4} M SiO_2)

Acetone conc., M	SiO_2 conc. found, M	Number of determinations
5.4×10^{-2}	2.1×10^{-4}	2
3.2×10^{-1}	2.1×10^{-4}	2
4.3×10^{-1}	2.1×10^{-4}	1
5.9×10^{-1}	2.2×10^{-4}	1
7.0×10^{-1}	2.2×10^{-4}	2
8.1×10^{-1}	2.2×10^{-4}	2

It is evident that acetone does not interfere with the silica determination under the conditions used, at least, at concentrations not

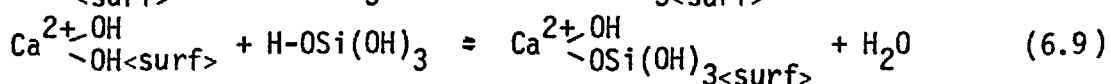
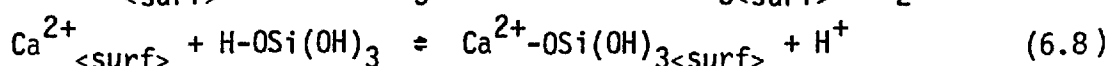
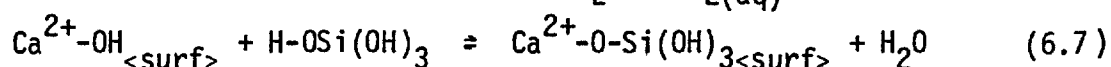
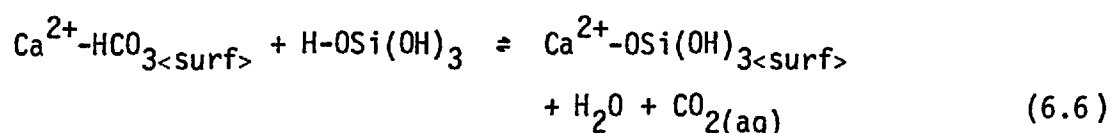
exceeding $8.1 \times 10^{-1} \text{ M}$ acetone. Thus, the decrease observed in the adsorption of silica on fluorite is real and indicates that the silica is partly adsorbed through the formation of hydrogen bonds. The above data does not, however, explain how the rest of the silica is adsorbed or how the silica is adsorbed on calcite. The formation of some hydrogen bonds on the surface of calcite cannot be completely excluded because acetone is a weak hydrogen bonding competitor.

Secondly, the precipitation of silica in the form of a stoichiometric calcium or barium silicate is considered. Although these compounds exist in a crystalline form as minerals (wollastonite, etc.), their formation in solution is rather obscure and definite data on the conditions under which they form and their formulae are not available. It is known, however, that they can form in solution only at moderately high silica concentrations and high pH values. Details of such a reaction have been discussed in section 4.4. It is evident from the data given that precipitation of either calcium or barium silicate is not favourable under the conditions at which the adsorption isotherms were determined.

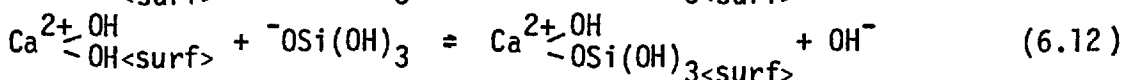
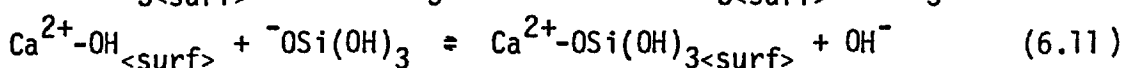
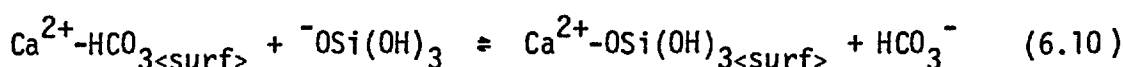
The next possible adsorption mechanism to be considered is that of a chemical reaction between the silicate species present in solution and available sites for adsorption on the surface. Both cationic and anionic sites will be present on the mineral surface but the adsorption of silicate species on the latter is energetically unfavourable. The composition of an aqueous solution saturated with respect to barite, calcite and fluorite was discussed in detail in section 1.2.2, and the equilibria existing between the various species as well as the equilibrium constants are given. It is a reasonable assumption to consider that the various species present in solution are also present on the surface. This may result either by formation of these species in solution with subsequent

adsorption on the surface or by direct formation on the surface. Both mechanisms are equally probable and have been discussed by various authors (27). In addition, although the equilibrium constants for the reactions on the surface are expected to be different to those in solution (probably higher than those in solution) (226), the relative proportions of each species on the surface will probably be similar to those in solution. Under these conditions and taking as an example calcite the following reactions can be written, each of which might describe the mechanism of adsorption of silica on this mineral:

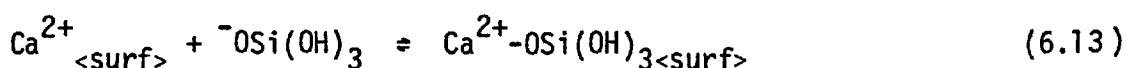
A. Adsorption of orthosilicic acid



B. Anion exchanges



C. Net anion adsorption



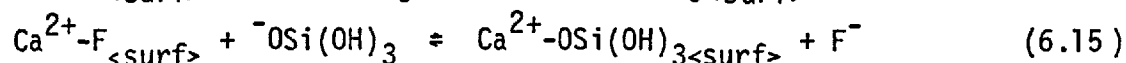
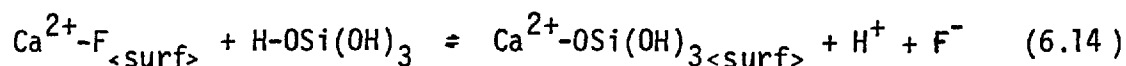
Reactions (6.6) and (6.8) are unfavourable because both reactants are acidic in character. In addition, silicic acid is a weaker acid than carbonic acid and it cannot, therefore, displace carbonate from its

compounds (reaction 6.6). Reactions (6.10), (6.11) and (6.12) are anion exchange reactions but they are not likely to proceed to a great extent. The concentration of $\text{Ca}^{2+}\text{-HCO}_3\text{_{<surf>}}$ will be very low at high pH values (>10.0) where the SiO(OH)_3^- ion predominates and therefore reaction (6.10) is unlikely. The concentration of $\text{Ca}^{2+}\text{-OH}_{\text{<surf>}}$ and $\text{Ca}^{2+}\text{OH}_{\text{<surf>}}$ species on the surface will probably be high at high pH values but the OH^- ions will compete with the SiO(OH)_3^- ions for the same surface sites and this will reduce the adsorption of the latter. For similar reasons reaction (6.9) is unlikely to contribute to the adsorption of silica since the concentration of Si(OH)_4 will be negligible at pH values where the $\text{Ca}^{2+}\text{OH}_{\text{<surf>}}$ species are present in appreciable quantities. Finally, only reactions (6.7) and (6.13) remain. Both of these are chemically possible and it is therefore reasonable to postulate that the adsorption of silica on calcite proceeds mainly through these two reactions. Furthermore, both are reactions between an acid (Si(OH)_4 , $\text{Ca}^{2+}\text{_{<surf>}}$) and a base ($\text{Ca}^{2+}\text{-OH}_{\text{<surf>}}$, SiO(OH)_3^-) according to the definitions of acids and bases given by Brønsted-Lowry (6.7) and Lewis (6.13), i.e. neutralization reactions.

Similar reactions to those written for the SiO(OH)_3^- ion could be written for the $\text{SiO}_2(\text{OH})_2^{2-}$ ion but since the concentration of these species is appreciable only above pH 12.5 (Fig. 3.1) their contribution to the adsorption process is probably minor. In addition, the high concentration of hydroxyl ions as well as the high negative charge of the mineral surface at these pH values would mitigate against the adsorption of these ions.

The adsorption of silica on fluorite is likely to occur by the same mechanism as the one proposed for calcite and similar reactions to those written for this mineral (reactions 6.7 - 9 and 6.11 - 13)

could also apply. The following additional reactions should also be considered:



Both of these reactions show that the concentration of fluoride in solution must increase in the presence of sodium silicate. The results obtained in the solubility measurements (section 4.4) contradict this and indicate that reactions (6.14) and (6.15) may not proceed to a great extent.

It was proposed above that the adsorption of silica on both calcite and fluorite may take place mainly through the reactions (6.7) and (6.13) and that it results in the formation of a surface calcium silicate. Both of these reactions will be very dependent on the pH and it follows therefore that the silica adsorption should be pH-dependent. This is illustrated in Figs. 6.13 and 6.14 where the adsorption of silica on calcite and fluorite has been plotted as a function of pH. The initial concentration of sodium silicate was 2.0×10^{-4} and 5.0×10^{-4} M SiO_2 for calcite and fluorite, respectively. It is evident from Fig. 6.13 that the adsorption of silica on calcite attains a maximum value at a pH around 9.5 and that it decreases abruptly on both sides of this pH. A maximum in the amount of silica adsorbed on fluorite was not observed at any pH. Instead, the adsorption increased considerably at pH values above 6.5 and then remained constant in the pH region 7.5 to 10.5. Above pH 10.5 it increased again. Both the flat part of the adsorption isotherm and the subsequent increase in the adsorption at pH values above 10.5 were more distinguishable when an initial sodium silicate concentration of 2.4×10^{-4} M SiO_2 was used (Fig. 6.14). The increase in the "adsorption" at high pH values was attributed to the

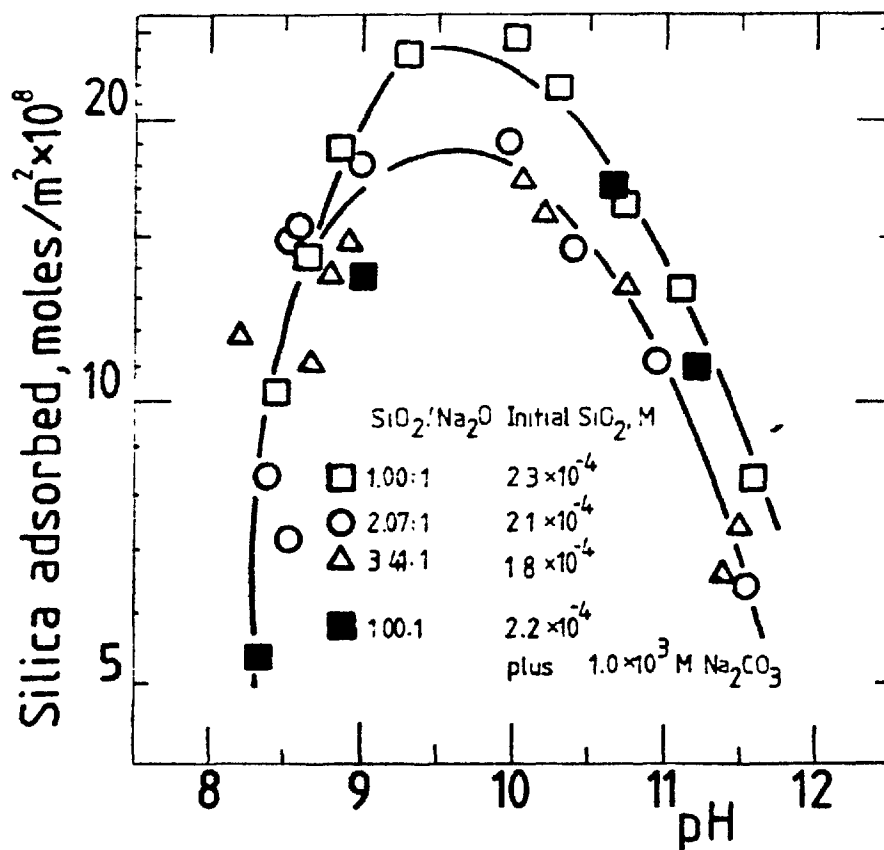


Fig. 6.13. Adsorption of silica on calcite and effect of carbonate.

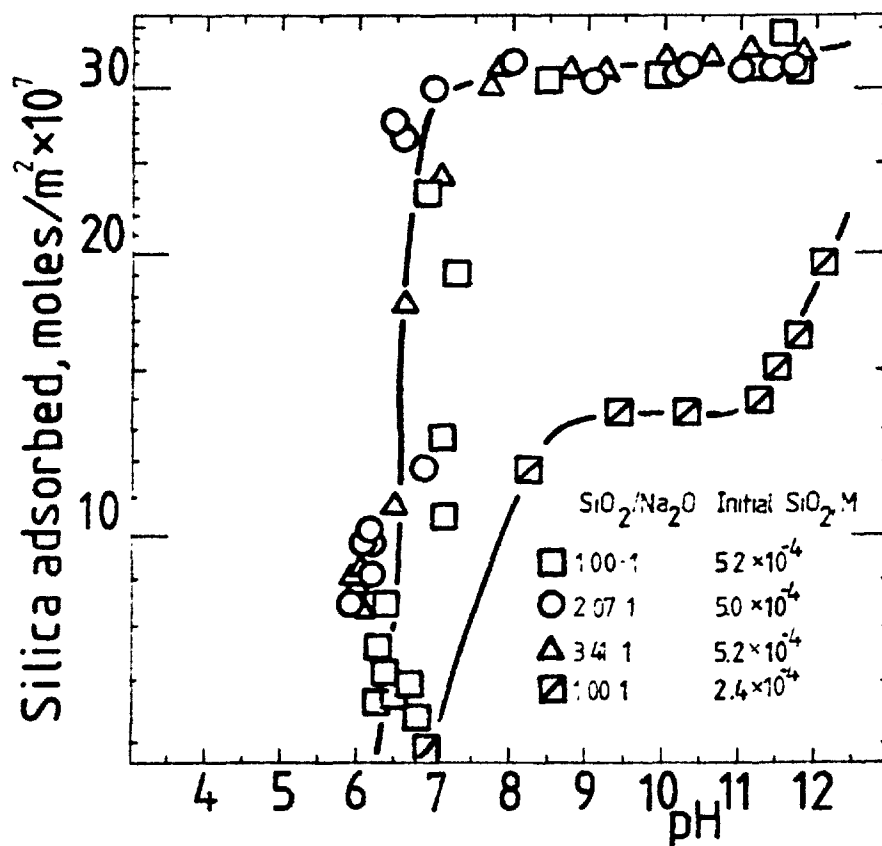


Fig. 6.14. Adsorption of silica on fluorite as a function of pH.

precipitation of silica as calcium silicate and not to adsorption on the mineral. Fig. 1.5 shows that at pH values above 10.5, the concentrations of CaOH^+ and $\text{Ca(OH)}_2(\text{aq})$ increase considerably and results in the precipitation of silica as was pointed out in section 4.4. In this case, the formula of the precipitated compound is not known. Under the same conditions precipitation did not occur in case of calcite since the concentration of CaOH^+ and $\text{Ca(OH)}_2(\text{aq})$ is more than ten times less than in the case of fluorite (Fig. 1.3).

In Fig. 6.15 the distribution diagram for the silicate species present in a sodium silicate solution is given at two sodium silicate concentrations, i.e. 2.0×10^{-4} and 5.0×10^{-4} M SiO_2 . These two concentrations correspond to those used in the adsorption experiments with calcite and fluorite, respectively (Figs. 6.13 and 6.14). In the same figure the concentrations of Ca^{2+} and CaOH^+ species in solutions saturated with calcite and fluorite are also given. If it is assumed that the concentration of surface $\text{Ca}^{2+}\text{-OH}_{\text{<surf>}}$ and $\text{Ca}^{2+}_{\text{<surf>}}$ sites follows the concentration of CaOH^+ and Ca^{2+} in solution then this figure shows that reaction between $\text{Ca}^{2+}_{\text{<surf>}}$ sites and SiO(OH)_3^- ions will be most favoured in the pH range 9.5 to 12 where these sites and the monosilicate ion predominate together. This corresponds approximately to the pH range where the silicate adsorbed on calcite and fluorite although in the latter case precipitation also occurred at high pH values. It would therefore appear that reaction (6.13) is more important than reaction (6.7) and that the silica adsorbs via $\text{Ca}^{2+}_{\text{<surf>}}$ sites rather than $\text{Ca}^{2+}\text{-OH}_{\text{<surf>}}$. Fig. 6.15 shows that the adsorption of silica on calcite will exhibit a maximum in the pH range 9 to 12, at a pH value which will shift to higher pH values with a decrease in silica concentration.

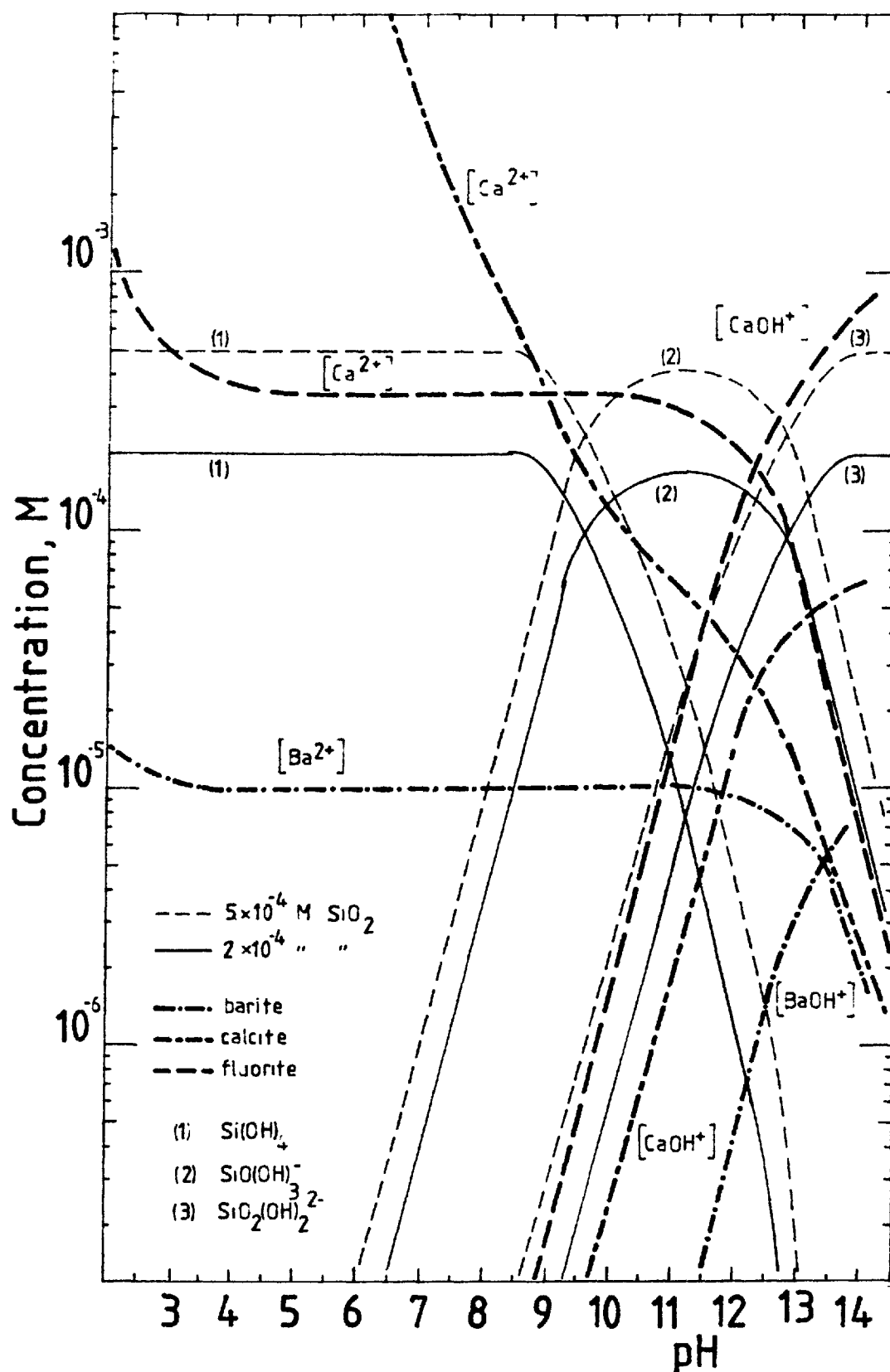
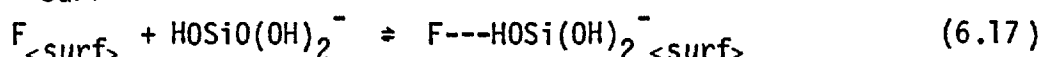
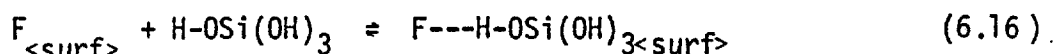


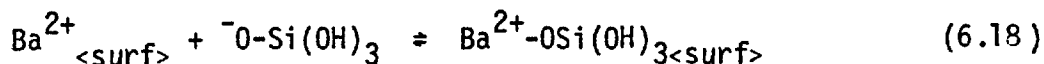
Fig. 6.15. Comparison of the concentration of the silicate species in 2×10^{-4} and 5×10^{-4} M sodium silicate at different pH values with the concentration of calcium or barium species in saturated solutions of calcite, fluorite or barite.

Comparison of the Figs. 6.13 and 6.14 shows that the amount of silica adsorbed (adsorption density) is greater on fluorite than on calcite at all pH values studied. Evidence was provided previously that silica may adsorb on fluorite through hydrogen bonding which may account for the higher adsorption on this mineral. The difference in the behaviour of fluorite compared to that of calcite may be attributed to the presence of fluoride in the former mineral. It is known that fluoride exhibits a tendency to form hydrogen bonds. Hydrogen bonds between fluorite and the silicate species adsorbed might be formed according to the following scheme:



where broken lines represent hydrogen bonds.

Finally, in Fig. 6.16 the adsorption of silica on barite is shown as a function of pH at an initial sodium silicate concentration of 5.0×10^{-4} M SiO_2 . Adsorption isotherms could not be determined in the case of barite because the adsorption of silica was low and the change in silica concentration was smaller than the experimental error. Fig. 6.16 shows that the amount of silica adsorbed on barite at pH values below 9.0 was negligible and that it increased continuously at pH values above 9.0. Because of the low concentration of $\text{Ba}^{2+}\text{-OH}_{<surf>}$ (Fig. 6.15), it is reasonable to assume that the adsorption of silica on barite proceeds mainly through the reaction:



which can only take place, to some extent, at pH values above 9.0, where the $\text{SiO}(\text{OH})_3^-$ ions predominate. Presumably below pH 9.0 the concentration of $\text{Ba}^{2+}\text{-OH}_{<surf>}$ sites is too low for adsorption to take place through the reaction:

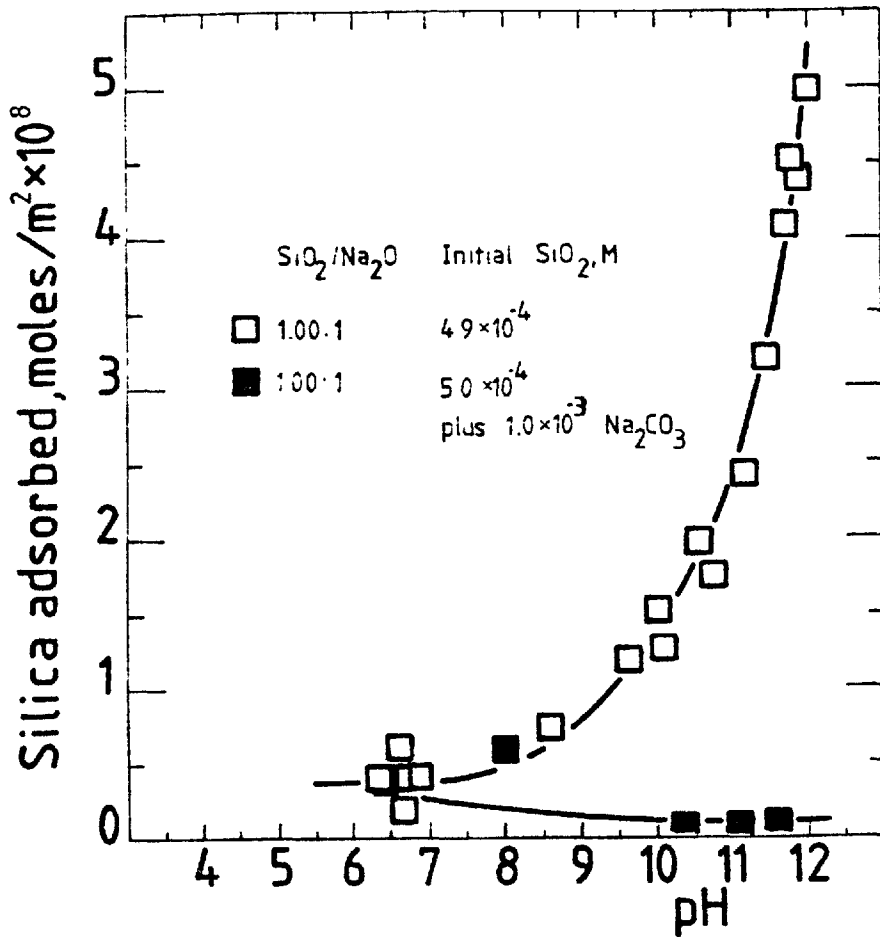
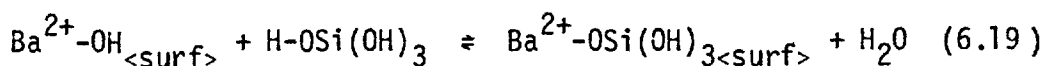


Fig. 6.16. Adsorption of silica on barite as a function of pH and effect of carbonate.



Comparison of the figures 6.13 , 6.14 and 6.15 leads to the conclusion that the amount of silica adsorbed on the three minerals decreases in the order: fluorite > calcite > barite and directly reflects the crystallographic properties of the minerals. Indeed, since the adsorption of silica depends on the availability of cationic sites it will be higher on that mineral with the higher concentration of cationic sites on the surface. If the cleavage plane (111) of fluorite is assumed to be covered by calcium sites only (100%) then 70% of the cleavage plane (10T1) of calcite and 46% of the cleavage plane (001)

of barite will be covered by calcium and barium sites, respectively, per unit surface area.

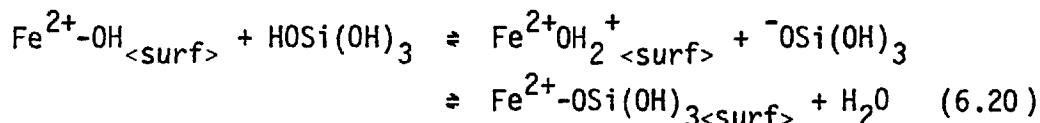
Direct comparison of the results obtained in this work with those obtained by other authors is not possible because the latter have used high concentrations of sodium silicate and in many cases the experimental conditions have not been given. Infrared techniques have been used to identify surface species but adsorption isotherms have not been obtained (102 - 10, 113). Surface polymerization of the silica is generally suggested as the silica adsorption mechanism. Recently, Kononov et al (227) suggested, as a result of studies of the luminescence spectra of fluorite, that the adsorption of silica on fluorite occurs through calcium sites and that additional adsorption occurs by attachment of silicate to the first monomolecular layer. Presumably the second and subsequent layers would only form at high silica concentrations.

More reliable results have been obtained from studies of the adsorption of monosilicates by soils. Thus, Beckwith and Reeve (228) and Mekeague and Cline (229) attributed the adsorption of silica on various soils to the monosilicic acid, $\text{Si}(\text{OH})_4$; but the simultaneous adsorption of $\text{SiO}(\text{OH})_3^-$ ions was not excluded. In addition, maximum adsorption of silica occurred at pH values around 10.0 for all the soils studied. Cho and Wadsworth (230) attributed the adsorption of silica on thoria to a reaction between the silanol groups of $\text{Si}(\text{OH})_4$ and the hydroxyl sites present on the surface of the thoria. The same mechanism is proposed by Furlong et al (231) for the adsorption of silica on titanium dioxide.

Hingston et al (224, 232 - 4) measured the adsorption of a number of anions, including silicates, on goethite and gibbsite at different pH values. From these papers it would appear that the authors are

suggesting that silicate adsorbs by exchange against surface $\text{OH}_2^+_{\text{surf}}$ and/or $\text{OH}^-_{\text{surf}}$ and that this process is induced by proton transfer.

That is for a surface hydroxyl group:



Furthermore, they claim, paradoxically, that the energy for the proton donation is minimum at a pH equal to the pK_{a1} of silicic acid, which in turn explains, according to them, the maximum in the adsorption obtained at that pH. They consider that adsorption of the anion is unlikely to occur on a negatively charged surface and that it may take place only when the surface is oppositely charged. The results obtained in the present study contradict both the above conclusions. Jepson et al (235) attributed the adsorption of silica on gibbsite to the formation of a calcium silicate, followed by the polymerization of the silicic acid on the surface. The concentration of silica used ($\approx 3.2 \times 10^{-3}$ M SiO_2) and the shape of the isotherms obtained, they level off at high silica concentrations ($> 1.6 \times 10^{-3}$ M SiO_2), do not favour such a conclusion. Finally, Breeuwsma and Lyklema (236) have proposed that adsorption of phosphate on hematite takes place through an exchange reaction between phosphate species and $\text{OH}_2^+_{\text{surf}}$ and $\text{OH}^-_{\text{surf}}$ sites.

The adsorption of silica on calcite and fluorite was measured using sodium silicates with three different silica to soda ratios namely 1.00:1, 2.07:1 and 3.41:1 and the results obtained are illustrated in Figs. 6.10 - 11 and 6.13 - 14. Small differences were observed in the adsorption isotherms obtained at different silica to soda ratios but this might be attributed to a small variation in the equilibrium pH. In the pH region where the isotherms were obtained the adsorption was very dependent on the pH and this is demonstrated in Figs. 6.13 - 14.

Since the adsorption of silica on all three minerals results in the formation of a surface calcium or barium silicate, it was thought that the presence of this compound might be detected by determining its infrared spectrum. The infrared spectra of barite, calcite and fluorite were recorded in the region $4000 - 200 \text{ cm}^{-1}$ with a Perkin-Elmer 599B double beam infrared spectrophotometer. KBr discs containing the mineral samples which had been exposed to sodium silicate (section 2.2.42) and then dried for 24 h under vacuum were used. Due to the strong adsorption of carbonates and sulphates in the infrared region discs containing more than 0.2% calcite and 0.6% barite could not be used. Taking into account the amount of silica adsorbed on these two minerals it was calculated that under the most favourable conditions the concentration of silica in the discs would not exceed 2.0×10^{-8} moles SiO_2 , which is far too low to be detected by this method. Indeed, the infrared spectra of calcite and barite samples prior to and after adsorption of silica were identical.

In Fig. 6.17 the infrared spectra of (1) untreated fluorite and (2), (3) fluorite after adsorption of silica are given in the region $1600 - 600 \text{ cm}^{-1}$. It is clear that the presence of new bands is hardly evident but some speculations can be made relative to the position and shape of the band at 1080 cm^{-1} . Although this band is present in all the recorded fluorite spectra (67, 80, 87) an explanation of its presence has not been given. It is likely that it is due to an impurity in the fluorite samples used. In the same region the band due to the Si-O bond also occurs (100) and its exact position depends on the cation bound to the oxygen. This might explain the origin of the band in the fluorite sample used in the present study. The presence of such a band makes it difficult to determine whether or not the formation of a

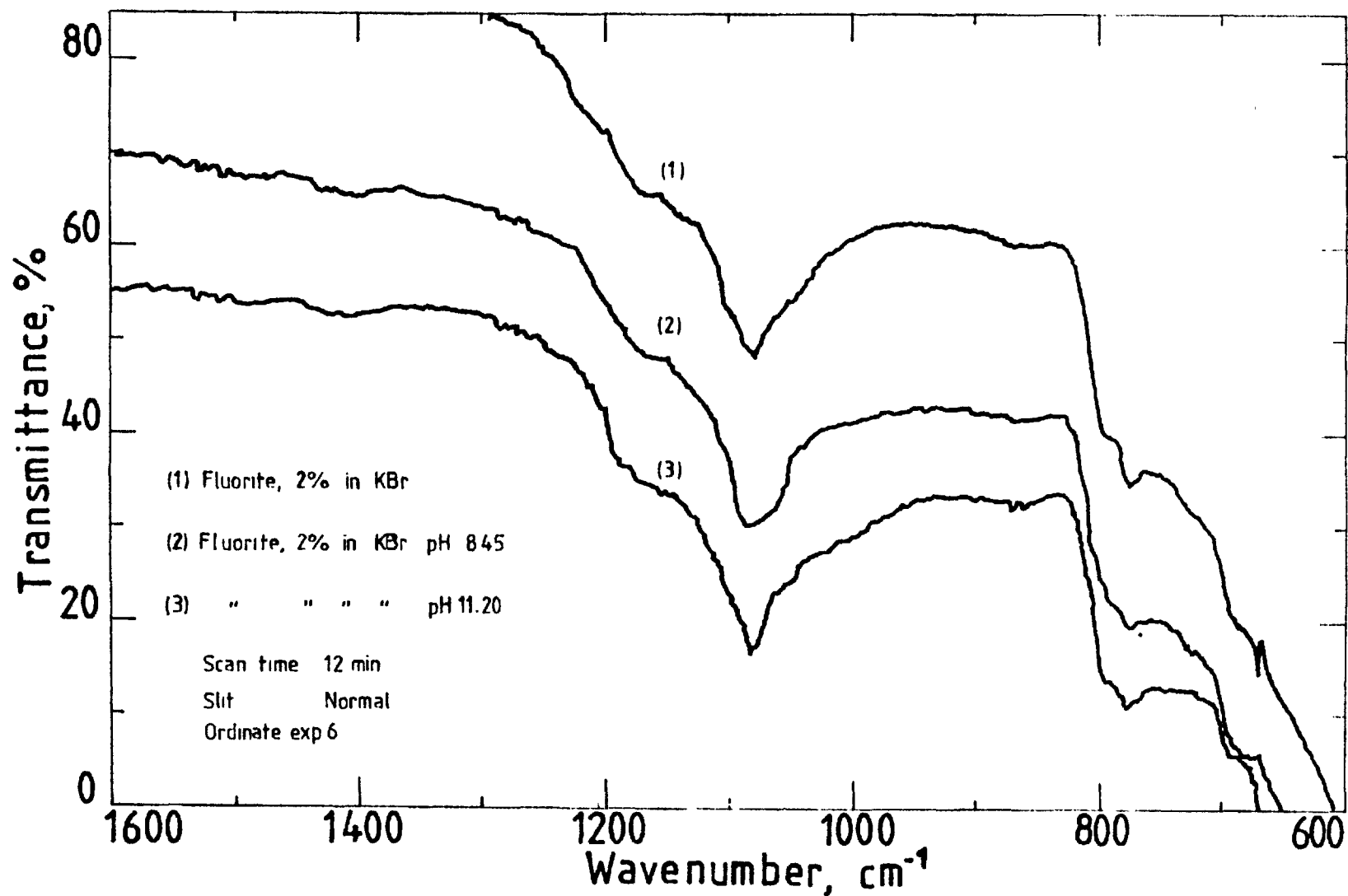


Fig. 6.17. Infrared spectra of (1) untreated fluorite and (2), (3) fluorite after adsorption of silica in the region 1600-600 cm^{-1} .

surface calcium silicate occurs with an absorption band at a wavenumber of 1065 cm^{-1} (237). Although there is a small indication that an additional band tends to be formed at this wavenumber, the evidence is not conclusive. The low silica content of the discs does not permit definite identification of such a compound. The fluorite sample used in these experiments had a surface area of $0.8238\text{ m}^2/\text{g}$. A sample with higher surface area could not be obtained even after prolonged grinding due to the agglomeration of the sample.

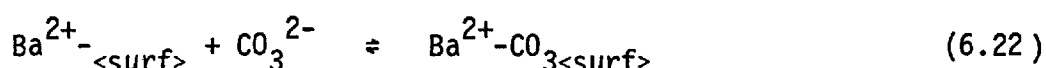
6.3.2. Influence of carbonate species on the adsorption of silica

The adsorption of sodium silicate on all three minerals was measured in the presence of carbonate, added as $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, at various pH values. The results obtained with barite, calcite and fluorite are shown in Figs. 6.16 , 6.13 and 6.18 respectively. In this series of experiments the sodium silicate with a silica to soda ratio 1.00:1 was used.

Sodium carbonate additions up to $1.0 \times 10^{-3}\text{ M}$ did not have an effect on the adsorption of silica on calcite in the pH range 8.5 to 12.0. Carbonate is one of the constituent ions of the crystal lattice of calcite, it should, therefore, affect the surface properties in two ways. Firstly, as a potential determining ion it should adsorb and increase the negative surface charge and thereby, partially, prevent the adsorption of silicate, and secondly, it should decrease the solubility of the mineral due to the common ion effect. It was found, however, that carbonate did not appreciably change the electrophoretic mobility of calcite which indicates that it is not strongly adsorbed under these conditions. Furthermore, the decreased solubility would not affect

the availability of the adsorption (cationic) sites and hence the adsorption of silica should not be influenced by the presence of carbonate.

In contrast, the addition of 1.0×10^{-3} M sodium carbonate results in the complete depression of silica adsorption on barite at all pH values studied. Since carbonate ions are not potential determining for barite, they appear to adsorb specifically on this mineral and to prevent the adsorption of silica. This indicates that the two ions are competitors for the same surface sites, i.e. $\text{Ba}^{2+}_{\text{<surf>}}$ sites. The adsorption of carbonate ion on barite can be described by the following reaction:

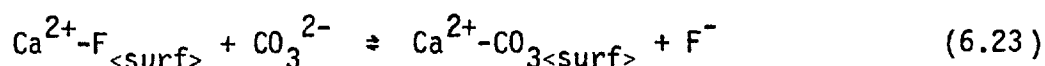


and it results in the formation of surface barium carbonate and the decrease of silica adsorption. The formation of barium carbonate is thermodynamically favourable under the above conditions as discussed in more detail in section 4.2.1.

The influence of sodium carbonate on the adsorption of silica on fluorite is shown in Fig. 6.18 as a function of pH at a carbonate concentration of 6.0×10^{-3} M. It is clear that the presence of carbonate resulted in a decrease of the adsorption of silica on fluorite at all pH values and that the effect was more pronounced at pH values below 11.0.

The depressing effect of carbonates on the adsorption of silica on fluorite has been noticed by various workers (98, 76, 103) and it has been attributed either to an anion exchange reaction between carbonate and silicate ions or to the changes in the properties of sodium silicate resulting from the increase in the pH produced by the addition of sodium carbonate. In the present study the effect of carbonate species on fluorite was studied at various pH values and at constant carbonate

concentration (Fig. 4.4). The results obtained are indicative of a carbonation reaction which may take place on the surface of fluorite and result in the partial conversion of the surface of this mineral to calcium carbonate. If such a reaction occurs then it may proceed according to the following scheme:



and/or



The net result will be a decrease in the availability of $\text{Ca}^{2+}\text{-F}_{\text{<surf>}}$ and $\text{Ca}^{2+}_{\text{<surf>}}$ sites with subsequent decrease in the silica adsorption.

If carbonation is really the mechanism of action of carbonate on fluorite, then prolonged conditioning of a fluorite suspension with a carbonate solution prior to the addition of the sodium silicate solution would result in a further decrease in the amount of silicate adsorbed. The results obtained are illustrated in Fig. 6.18 and show that this was the case. In these experiments 10 g of fluorite was conditioned in a 1.2×10^{-2} M sodium carbonate solution for 16 h, prior to the addition of the sodium silicate solution. This was followed by another 16 h conditioning in the presence of both (Fig. 6.18), curve 3).

In the electrokinetic measurements small differences were found between the results obtained with barite and fluorite in the presence of fresh and aged sodium silicate solutions. The presence of carbonate species in the aged sodium silicate solutions from the dissolution of atmospheric CO_2 is not unlikely. The decrease in the pH of these solutions upon ageing (section 2.2.3) may also be attributed to CO_2 adsorption. Since carbonate decreases the adsorption of silica on barite and fluorite but not on calcite, the silica adsorption will be

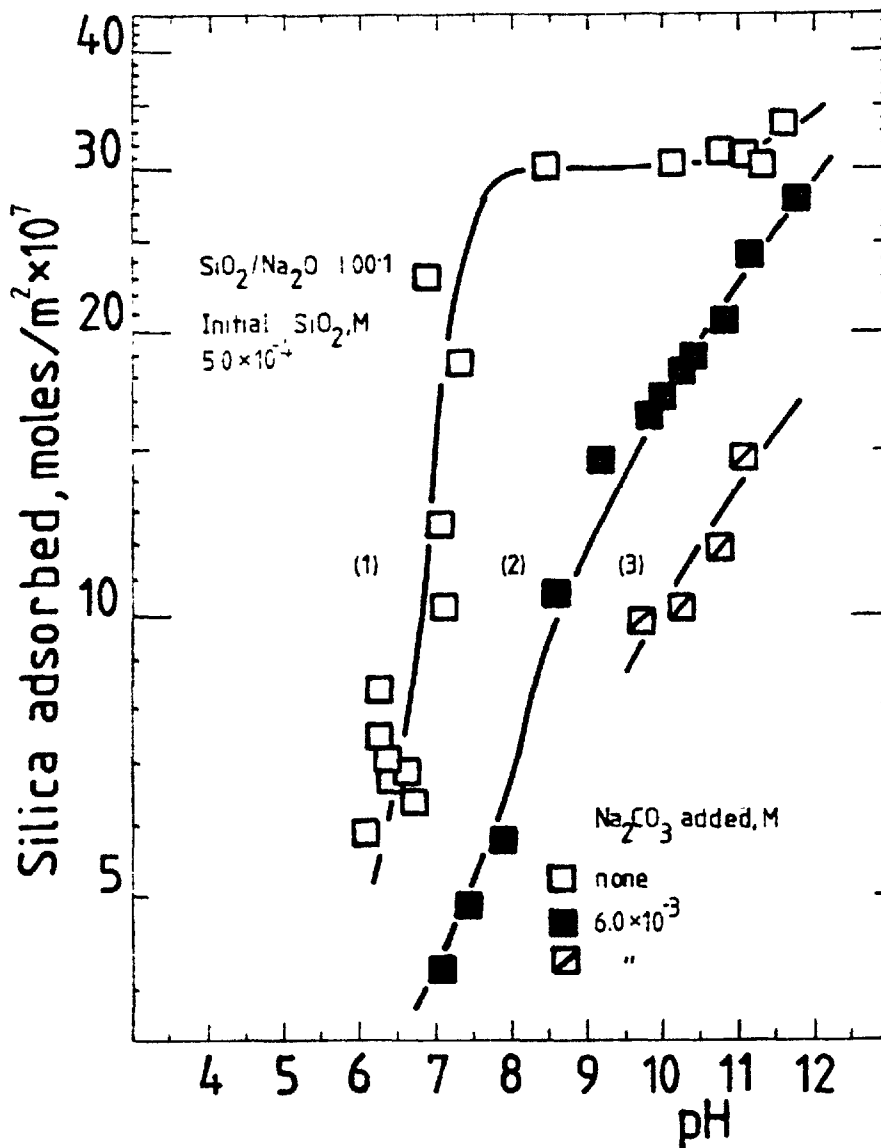


Fig. 6.18. Adsorption of silica on fluorite as a function of pH in the presence of 6.0×10^{-3} M Na₂CO₃·10H₂O.

less from the aged sodium silicate solutions in the case of the former two minerals. As a result the electrophoretic mobility of barite and fluorite should be more negative in the presence of fresh sodium silicate solutions which was the case.

CHAPTER 7. FLOTATION OF FLUORITE, CALCITE AND BARITE IN THE PRESENCE OF SODIUM SILICATE

7.1. Introduction

The mechanism of adsorption of oleic acid and sodium silicate on barite, calcite and fluorite was discussed in detail in the preceding chapter. It was shown that silica adsorbs (chemisorbs) on all three minerals and that the extent of the adsorption depends on the state of the silica in solution and the mineral and its surface properties. In contrast, oleic acid does not exhibit any selectivity for an individual mineral other than to precipitate on the surface as metal oleate whenever the oleate concentration in bulk solution exceeds that given by the solubility product of the corresponding metal oleate. Precipitation of some of the oleate in solution must also occur but the amount has not been determined.

In this chapter the flotation response of all three minerals in the presence of sodium silicate, oleic acid and at various pH values is considered. The results are correlated with the amount of oleic acid "adsorbed" under similar conditions. Although the influence of oleic acid on the adsorption of silica is of interest such measurements could not be made because of the low adsorption of silica and the large amount of mineral sample needed for its determination. Fresh and aged sodium

silicate solutions with various silica to soda ratios were used.

7.2. Effect of silica on flotation

7.2.1. Fluorite

The flotation of fluorite in the presence of sodium silicate is shown in Figs. 7.1 - 2 as a function of pH and at an oleate concentration of 1.0×10^{-5} M. The results in Fig. 7.1 were obtained with fresh sodium silicate solutions whereas those in Fig. 7.2 were obtained with aged solutions. The sodium silicates used had silica to soda ratios of 1.00:1, 1.65:1, 2.56:1, 2.94:1 and 3.41:1 and SiO_2 concentrations between 1.0×10^{-3} and 3.41×10^{-3} M.

With the exception of the sodium silicates with ratios of 1.00:1 and 1.65:1 which did not depress the flotation of fluorite in the acidic region, all the other sodium silicates used produced depression at pH values below 7.0 and above 9.0. Ageing of the sodium silicate solutions reduced the depression slightly and this effect was more pronounced at high pH values. Since the stronger depression effect of sodium silicates with ratios above 2.56:1 might be attributed to the presence of polysilicate species, flotation tests were carried out with these sodium silicate solutions at lower concentrations. The results given in Fig. 7.3 show that depression was obtained under similar pH conditions, although not so strong, which indicates that the different results obtained with various silicates can be attributed to different SiO_2 contents rather than the presence of polysilicates.

The flotation response of fluorite in the presence of oleic acid and sodium silicate is reflected in the oleate "adsorption" results and this is demonstrated in Figs. 7.4a, b and 7.5. In the absence of silicate maximum abstraction of oleate was obtained at pH 10.5 but in

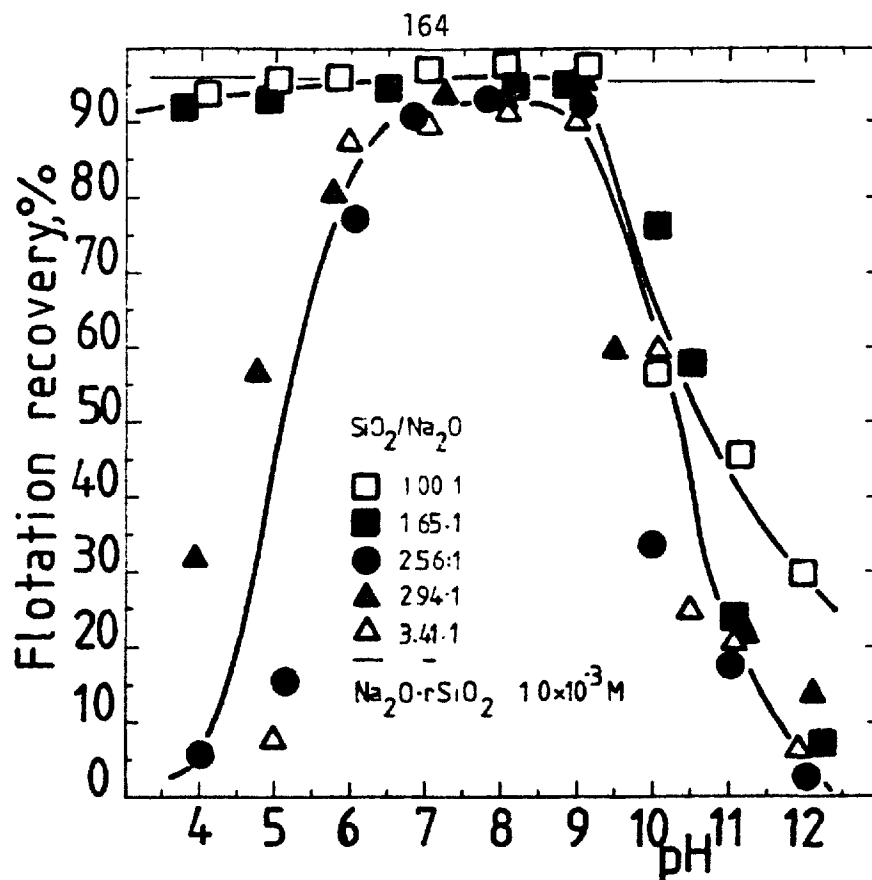


Fig. 7.1. Flotation recovery of fluorite as a function of pH in the presence of fresh sodium silicates (sodium oleate conc. $1.0 \times 10^{-5} \text{ M}$).

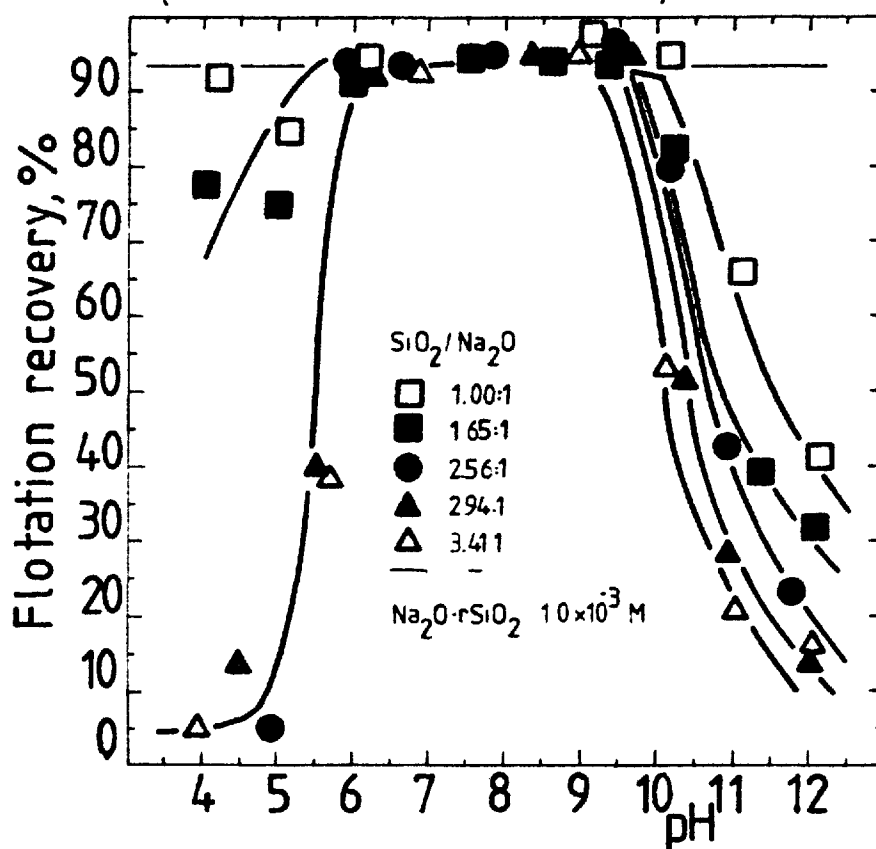


Fig. 7.2. Flotation recovery of fluorite as a function of pH in the presence of aged sodium silicates (sodium oleate conc. $1.0 \times 10^{-5} \text{ M}$).

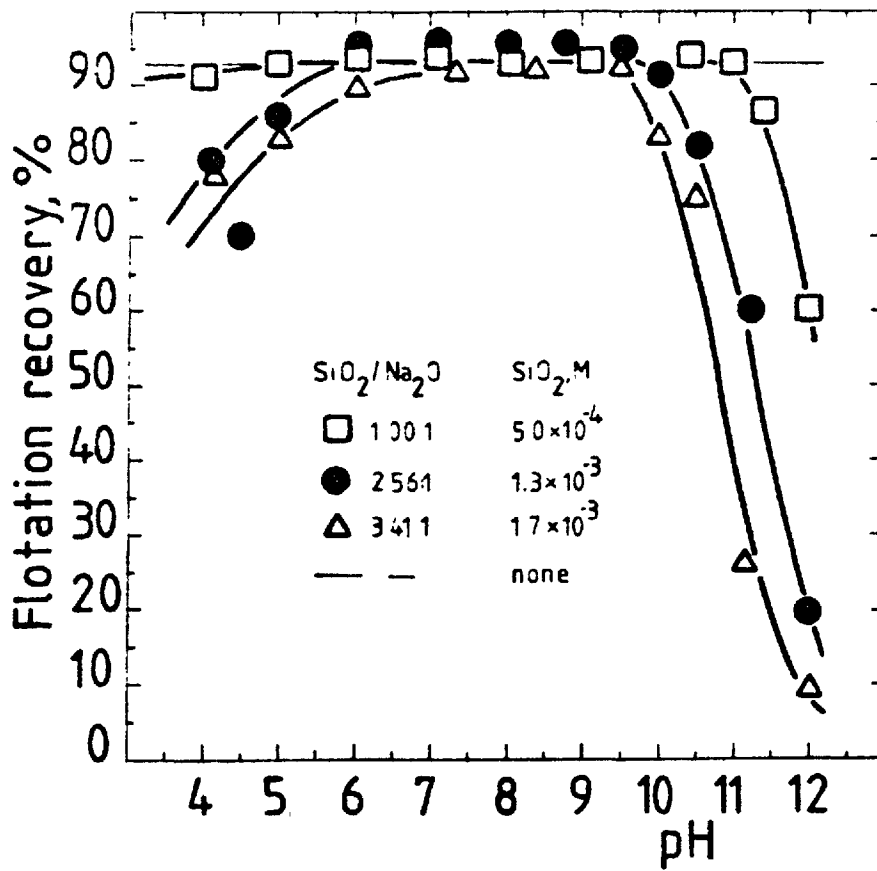


Fig. 7.3. Flotation recovery of fluorite as a function of pH in the presence of fresh sodium silicates (sodium oleate conc. 1.0×10^{-5} M).

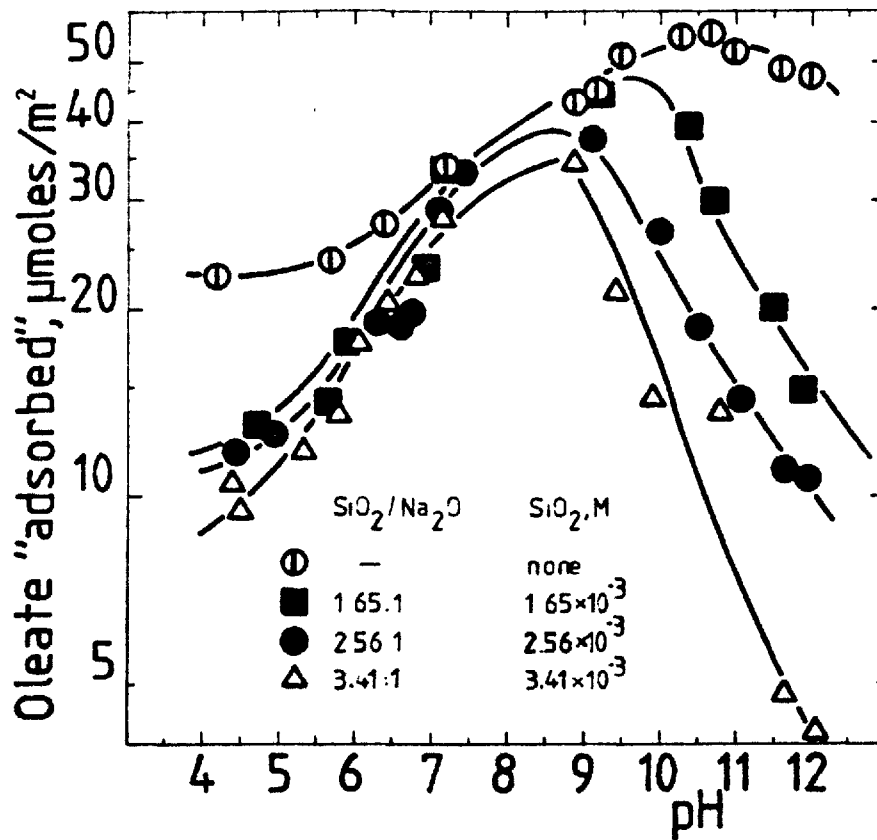


Fig. 7.4a. Abstraction of oleate by fluorite as a function of pH in the presence of fresh sodium silicates with silica to soda ratios of 1.65:1, 2.56:1 and 3.41:1 (initial sodium oleate conc. $5.0 \times 10^{-5} \text{ M}$).

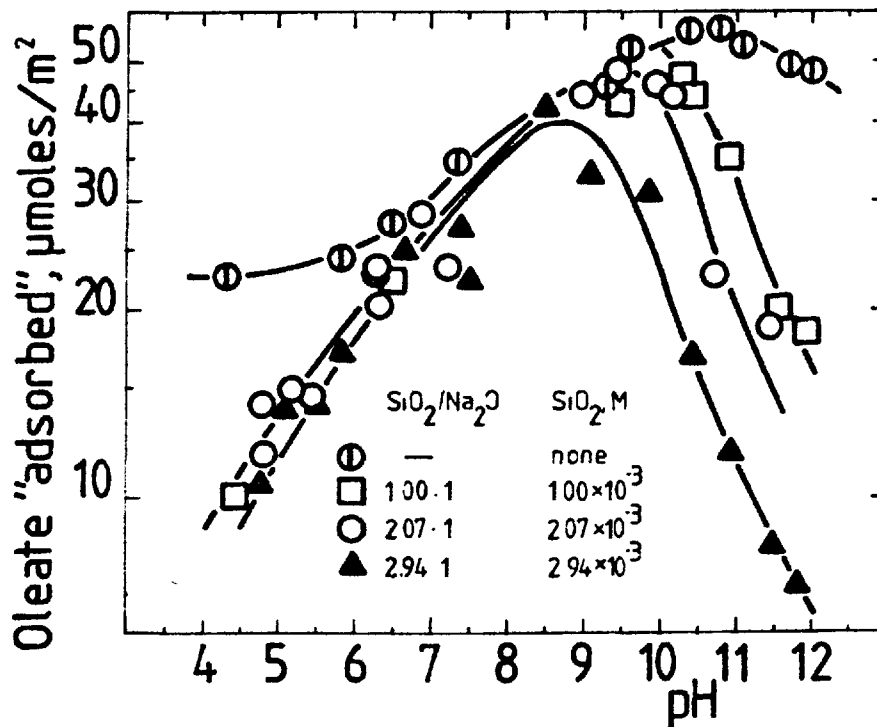


Fig. 7.4b. Abstraction of oleate by fluorite as a function of pH in the presence of fresh sodium silicates with silica to soda ratios of 1.00:1, 2.07:1 and 2.94:1 (initial sodium oleate conc. $5.0 \times 10^{-5} \text{ M}$).

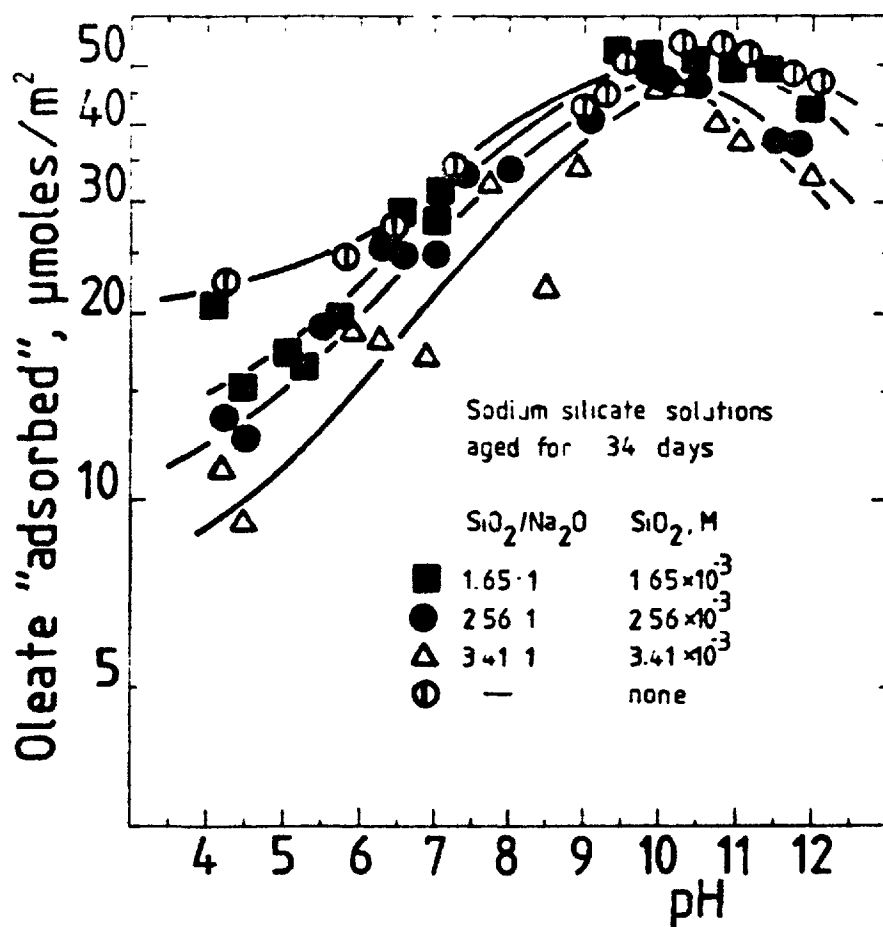


Fig. 7.5. Abstraction of oleate by fluorite as a function of pH in the presence of aged sodium silicates with different silica to soda ratios (initial sodium oleate conc. 5.0×10^{-5} M).

the presence of silica it occurred at lower pH values. Increasing the silica to soda ratio (or alternatively increasing the SiO_2 concentration) reduced the pH corresponding to maximum oleate abstraction. The decrease in oleate abstraction at pH values above and below the abstraction maximum corresponds to the pH conditions where depression of the fluorite flotation was obtained.

Replotting the data shown in Fig. 7.4 to show the oleate abstraction as a function of the ratio of sodium silicate at pH 11.0 gives a straight line with a slope of approximately -1. The linearity of the curve implies that the oleate and silica interact with the same surface sites on the fluorite surface, however, the exact meaning of the slope is not known because the relationship between silica adsorption and silica concentration under these conditions is not known.

Ageing the sodium silicate solutions produced only a small decrease in the oleate adsorption at high pH values but at lower pH values the effect was similar to that obtained with fresh solutions (compare Fig. 7.5 with 7.4a, b). Aged sodium silicate solutions also produced less flotation depression of the fluorite at high pH values.

The difference in the oleate "adsorption" results obtained with fresh and aged sodium silicate solutions can be explained in a number of different ways. In Chapter 3 it was stated that the sodium silicate solutions were prepared by dilution of concentrated solutions with compositions in the stable polymeric domain (Fig. 3.8). Since fresh sodium silicate solutions are not at equilibrium the relative concentration of $\text{Si}(\text{OH})_4$ to $\text{SiO}(\text{OH})_3^-$ will be higher than in aged solutions. Silica adsorption should therefore be greater from unaged solutions if the reactive species is $\text{Si}(\text{OH})_4$. Assuming that similar $\text{Ca}^{2+}\text{-OH}_{\text{<surf>}}$ sites are involved in the silica and oleate adsorption then an increase

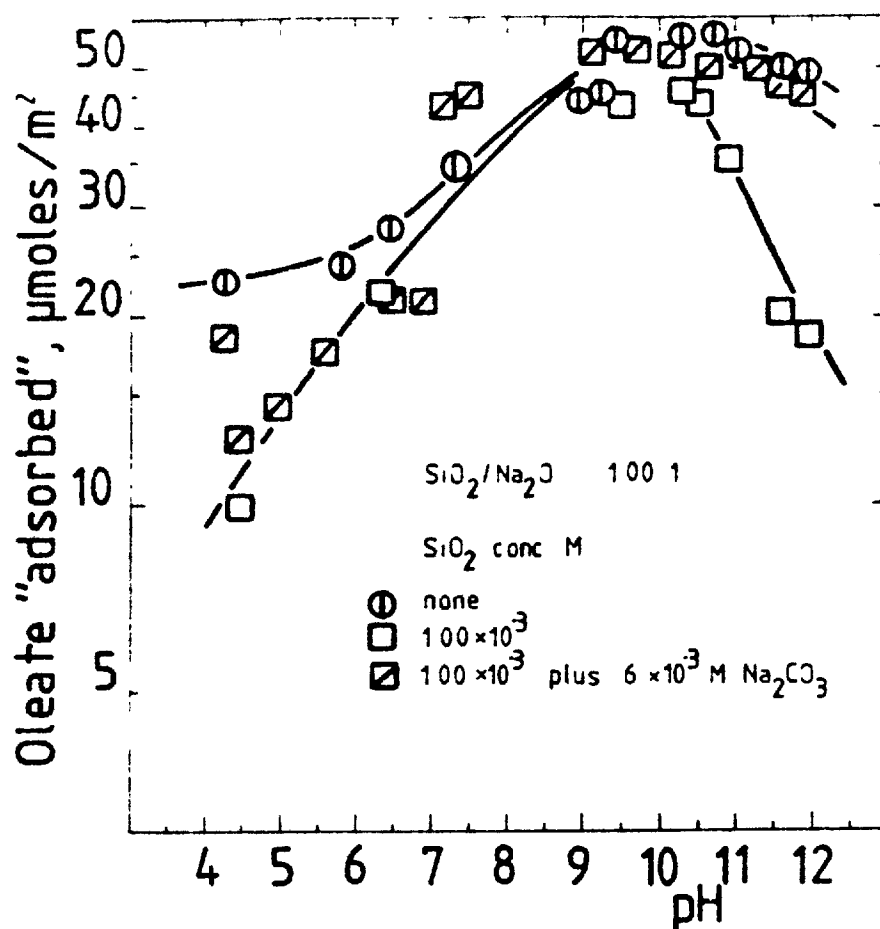


Fig. 7.6. Abstraction of oleate by fluorite as a function of pH in the presence of sodium silicate and sodium carbonate (initial sodium oleate conc. 5.0×10^{-5} M).

in the former should decrease the latter. In other words, oleate "adsorption" from aged sodium silicate solutions at high pH values should be greater than that from fresh solutions; this was the observed effect.

A further reason for the difference observed at high pH values could be that since the aged solutions contain predominantly silicate ions the silicate will be precipitated as calcium silicate and will not interact with the fluorite surface. The effect of aged silicate on oleate "adsorption" will therefore be small.

Another possible reason for the difference obtained with aged and unaged sodium silicate solutions is related to the possible effect of carbon dioxide. It was shown in Chapter 6 (Fig. 6.1) that the addition of sodium carbonate considerably reduced the adsorption of silica. Although precautions were taken to exclude CO_2 from the ageing sodium silicate solutions it is possible that some contamination occurred. To determine what the effect of absorbed CO_2 would be on the abstraction of oleate in the presence of silica, tests were done with fresh sodium silicate solutions containing sodium carbonate. The results obtained with the sodium silicate with a ratio of 1.00:1 are presented in Fig. 7.6. Clearly in the presence of carbonate the adsorption of oleate is reduced so that the oleate adsorption curve resembles that obtained in aged sodium silicate solutions. It is, however, unlikely, that the carbonate level in the aged sodium silicate solutions was as high as 6×10^{-3} M, so that the presence of CO_2 can only be a partial cause, if at all, of the difference between aged and unaged solutions.

Both silicate and oleate species adsorb on the same surface sites and they are therefore competitors, i.e. the adsorption of one species will prevent the adsorption of the other. The result obtained showed

that the adsorption of silica decreased the amount of oleate adsorbed but whether or not the converse is true is not known. Even if the adsorption of silica remained unchanged in the presence of oleate, there would still be some surface sites available for interaction with the latter. In this case, the effect of the adsorbed silica would be to increase the negative charge on the surface and thus prevent, to some extent, the negative oleate ions from approaching and reacting with cationic sites.

7.2.2. Calcite

The flotation response of calcite in the presence of fresh and aged sodium silicate solutions is shown in Figs. 7.7 and 7.8 as a function of pH. The collector concentration was 1.0×10^{-4} M sodium oleate while the sodium silicate concentration varied between $1.0 - 3.41 \times 10^{-3}$ M SiO_2 according to the silica to soda ratio of the sodium silicate used. It is evident that under these conditions all the sodium silicates studied depressed the flotation of calcite at all pH values and that, in general, the results are in agreement with those reported in the literature (42). The depression action of fresh sodium silicate solutions was greater than that of aged solutions at pH values above 10.0 but it was almost the same at lower values of pH.

In Figs. 7.9a and 7.9b the influence of fresh sodium silicate solutions on the amount of sodium oleate abstracted by calcite is given. The results obtained with aged sodium silicate solutions are shown in Fig. 7.10. With the exception of the sodium silicate with a ratio of 1.00:1 all fresh sodium silicate solutions decreased the amount of oleate abstracted by calcite in the pH range 9 to 12 but not to the same extent.

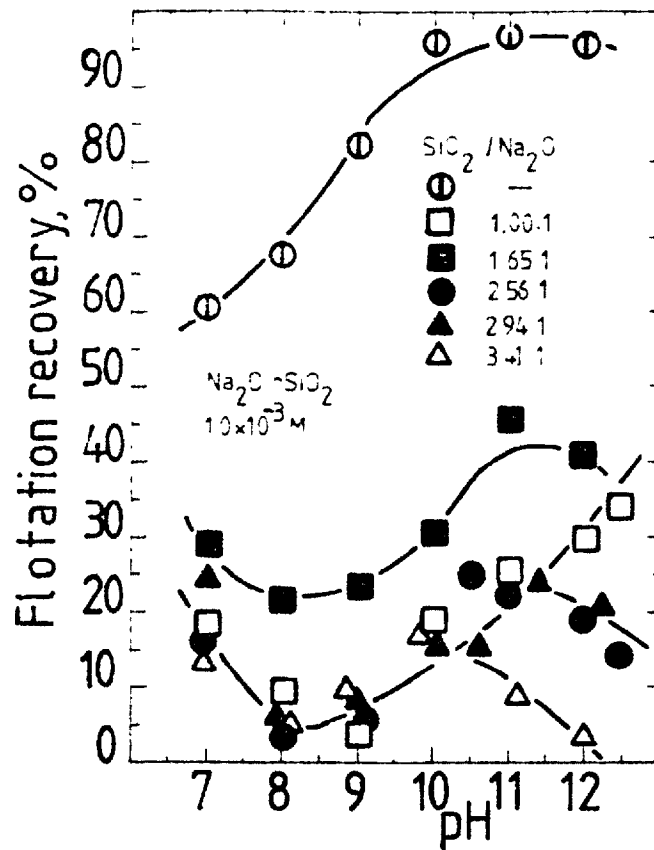


Fig. 7.7. Flotation recovery of calcite as a function of pH in the presence of fresh sodium silicates (sodium oleate conc. $1.0 \times 10^{-4} \text{ M}$).

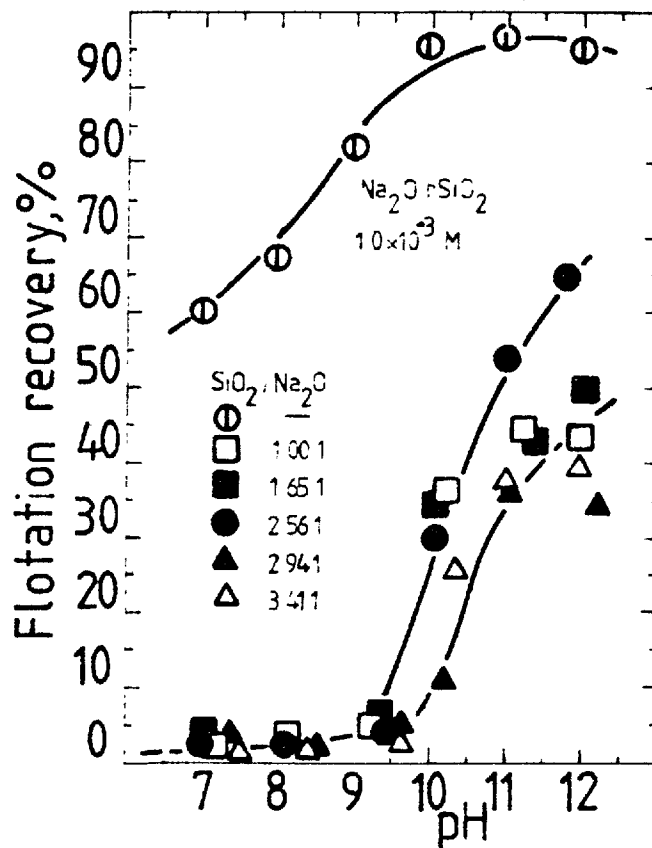


Fig. 7.8. Flotation recovery of calcite as a function of pH in the presence of aged sodium silicates (sodium oleate conc. $1.0 \times 10^{-4} \text{ M}$).

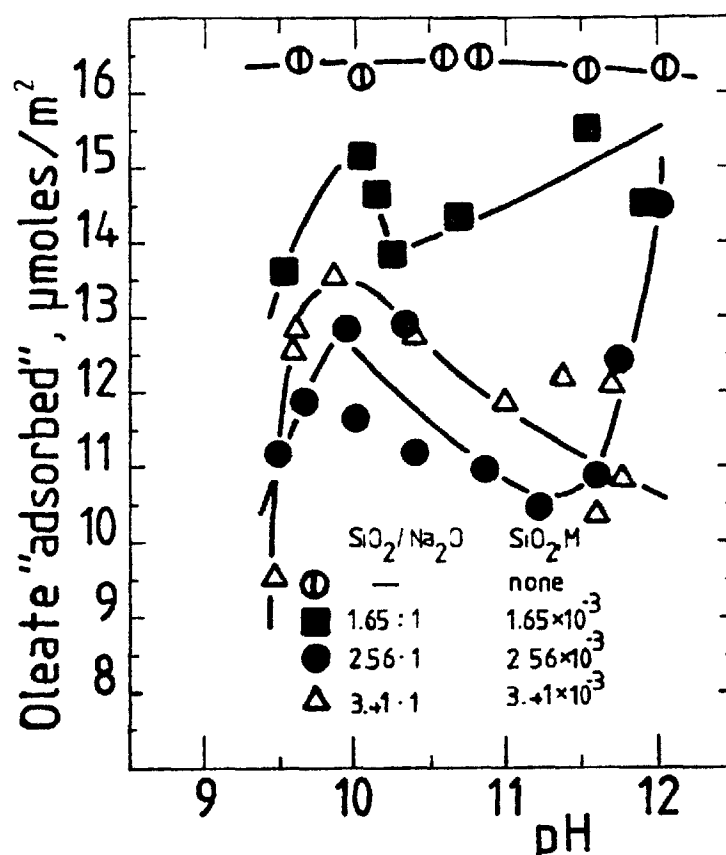


Fig. 7.9a. Abstraction of oleate by calcite as a function of pH in the presence of fresh sodium silicates with silica to soda ratios of 1.65:1, 2.56:1 and 3.41:1 (initial sodium oleate conc. $5.0 \times 10^{-5} \text{M}$).

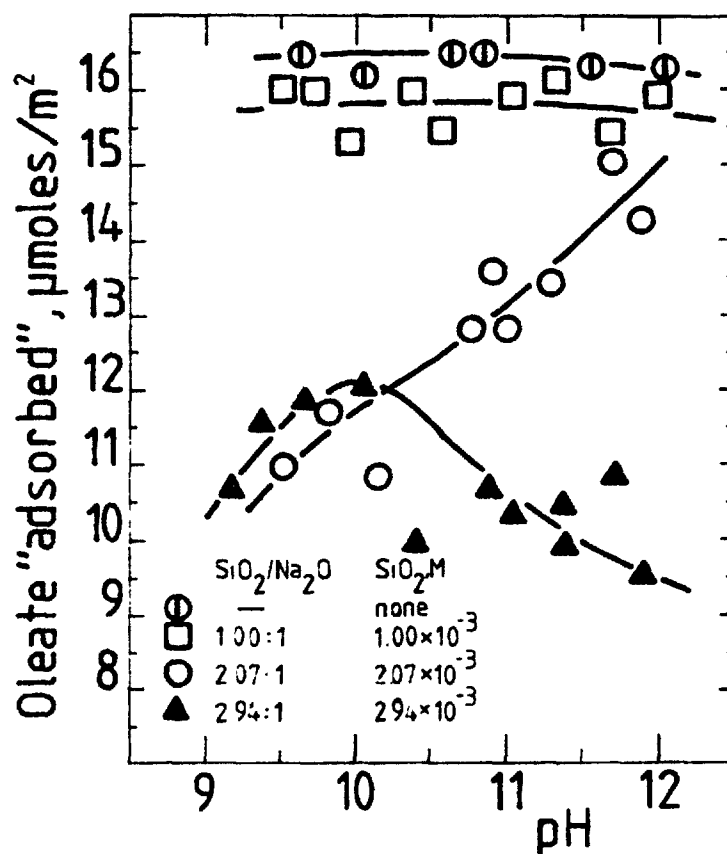


Fig. 7.9b. Abstraction of oleate by calcite as a function of pH in the presence of fresh sodium silicates with silica to soda ratios of 1.00:1, 2.07:1 and 2.94:1 (initial sodium oleate conc. $5.0 \times 10^{-5} \text{M}$).

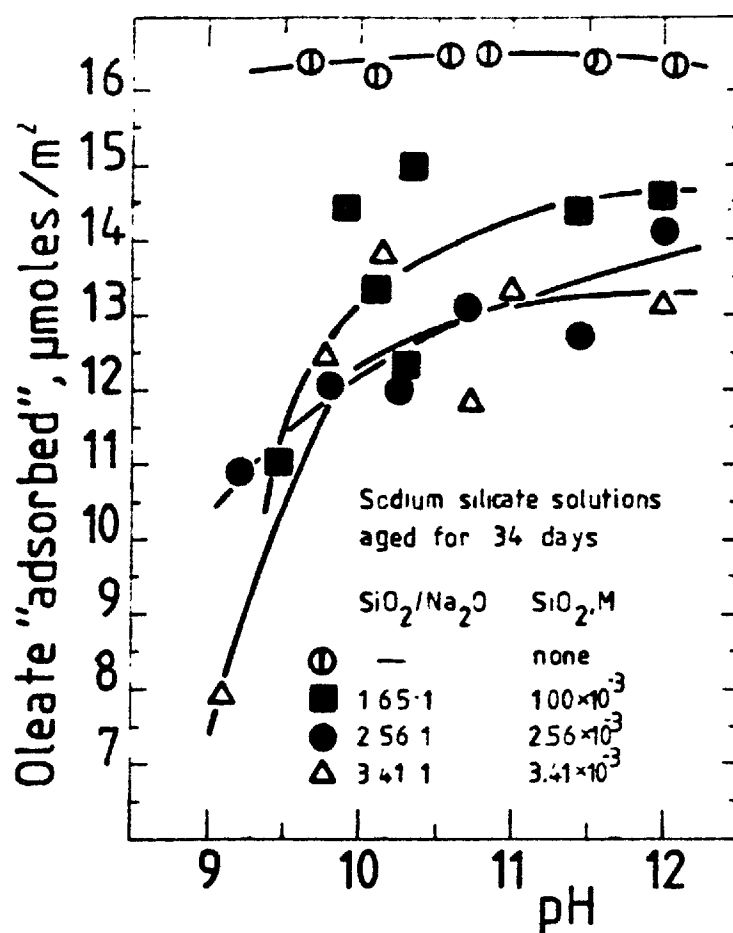


Fig. 7.10. Abstraction of oleate by calcite as a function of pH in the presence of aged sodium silicates with different silica to soda ratios (initial sodium oleate conc. 5.0×10^{-5} M).

In the presence of sodium silicates with ratios of 1.65:1, 2.56:1, 2.94:1 and 3.41:1, maximum oleate abstraction was obtained at pH 10.0. This pH also corresponds to where maximum adsorption of silica occurred in the absence of oleate. It follows therefore that the formation of precipitated calcium oleate is not completely prevented by the presence of silica on the calcite surface. At pH values below 10.0 the abstraction of oleate decreased markedly but the reason is not well understood. Presumably at these pH values adsorption of silica might prevent the dissolution of calcite and consequently the precipitation of calcium oleate. Above pH 10 the abstraction also decreased but an additional reason here could be that the adsorption of silicate ions increases the negative surface charge so that the oleate ions are less likely to reach the surface sites. The reduction in oleate abstraction obtained with an increase in the ratio, i.e. with an increase in SiO_2 concentration, of the sodium silicate is consistent with both these models.

The abstraction of oleate from fresh sodium silicate solutions with ratios greater than 2.56:1 decreased continuously at pH values above 10. Contrarily, at pH values above 10 an increase in the amount of oleate abstracted was obtained in the presence of sodium silicates with ratios of 1.65:1, 2.07 and 2.56:1. These observations cannot be attributed to the different silica contents because the difference in SiO_2 concentration was not large. A possible reason is that the Si(OH)_4 to SiO(OH)_3^- ratio of the various (fresh) sodium silicate solutions differed due to the non-equilibrium conditions, and that it was a function of total silica concentration, pH and time. Longer equilibration times are needed for the sodium silicate solutions with ratios above 2.56:1 and this was demonstrated by the fact that a low

concentration of polysilicate species was detected in these solutions soon after their preparation (section 3.4.3). Because of this the adsorption of silica will be higher from the sodium silicate solutions with ratios above 2.56:1, since the Si(OH)_4 to SiO(OH)_3^- will be higher. This, in turn, explains the lower "adsorption" of oleate under these conditions.

The oleate abstraction results obtained in the presence of aged sodium silicate solutions (Fig. 7.10) reflected the flotation results. At pH values below 10 both the flotation recovery and oleate abstraction decreased markedly. In general increasing the silica to soda ratio decreased the flotation recovery and oleate abstraction. Comparison of Fig. 7.10 and 7.9a and 7.9b shows that the oleate abstraction in the presence of aged sodium silicate solutions was greater than that from unaged solutions. Indeed, the adsorption of silica from unaged solutions is expected to be higher because of the higher ratio of Si(OH)_4 to SiO(OH)_3^- in these solutions.

A number of authors (6, 42) have ascribed the depression of the oleic acid flotation of calcite to the presence of colloidal silica especially when sodium silicates with a ratio greater than 2:1 are used. To ensure that this was not the case, additional flotation tests were done at various silica concentrations and sodium silicate ratios. The results showed that the calcite recovery was independent of the ratio of the sodium silicate but dependent on the total SiO_2 content. This is demonstrated in Figs. 7.11 - 12. Increasing the SiO_2 concentration decreased the recovery and the recovery against pH curves were all of a similar shape. These results indicate that there is not a critical ratio of sodium silicate above which some special interaction occurs. It is concluded that colloidal silica is not responsible for

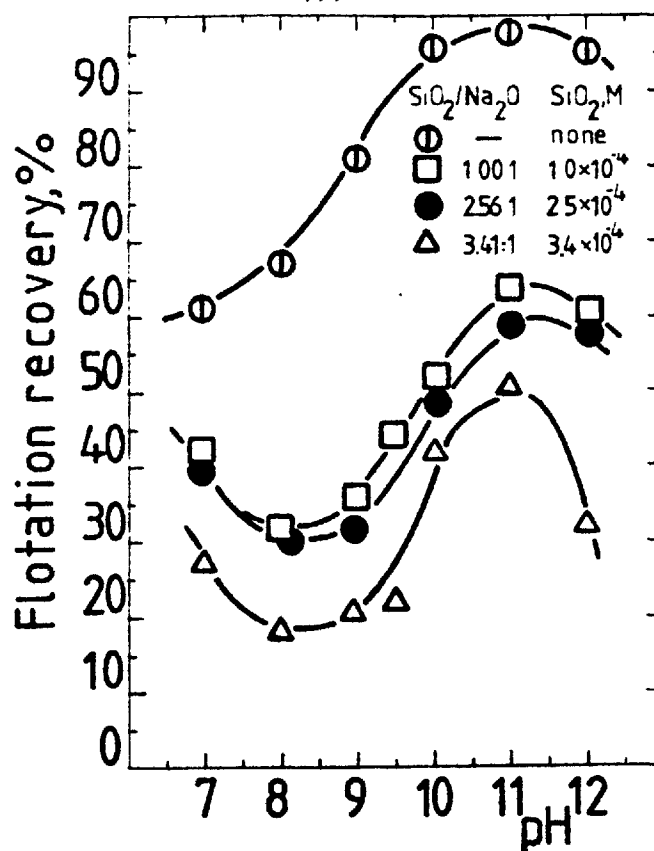


Fig. 7.11. Flotation recovery of calcite as a function of pH in the presence of fresh sodium silicates (sodium oleate conc. 1.0×10^{-4} M).

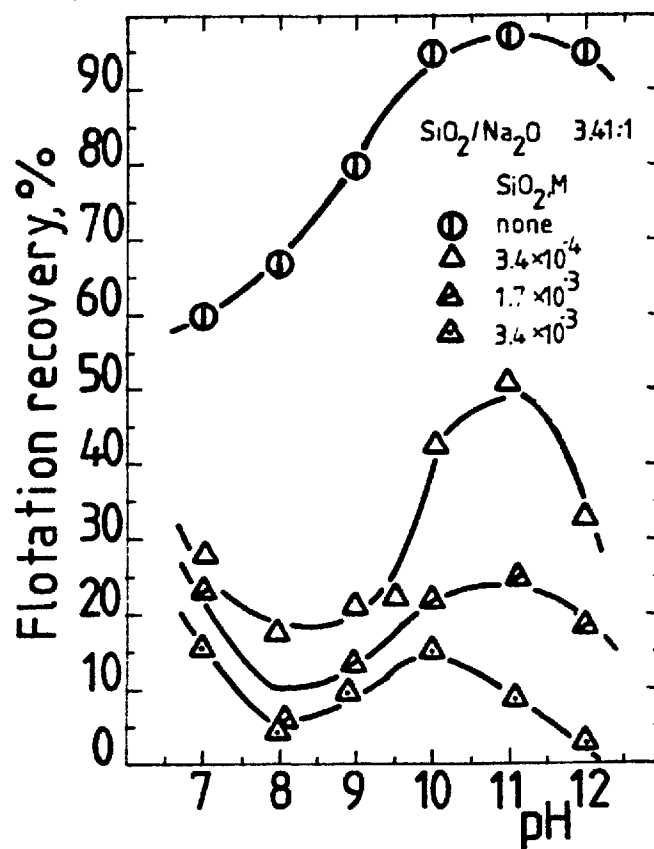


Fig. 7.12. Flotation recovery of calcite as a function of pH in the presence of different concentrations of SiO_2 (sodium oleate conc. 1.0×10^{-4} M).

the depression obtained in the presence of sodium silicate.

7.2.3. Barite

The influence of sodium silicate on the flotation of barite with 1×10^{-5} M sodium oleate is illustrated in Figs. 7.13 and 7.14 for fresh and aged sodium silicate solutions, respectively. All the sodium silicates tested depressed the flotation of barite at pH values above 8.0 but the aged solutions produced slightly less depression than the fresh solutions. Furthermore, whereas fresh silicate solutions produced complete depression at pH values above 10.0, the aged solutions did not and the recovery increased again above pH 11.0. The effect of sodium silicates, both aged and non-aged, in the acid region ($\text{pH} < 7.0$) was not marked, however, the recovery decreased sharply even in the absence of sodium silicate and this could have obscured the effect of silica in this pH region.

The amount of oleate abstracted by barite in the presence of fresh sodium silicate solutions exhibited a maximum at a pH around 8 (Figs. 7.15a and 7.15b) which correlates well with the maximum in flotation recovery obtained at the same pH. Below this pH, and especially in the pH range 7 to 4, the amount of oleate abstracted decreased but the reason is not known. The adsorption of silica at these pH values is negligible and because of this it cannot account for the results obtained. At pH values above 8 the "adsorption" of oleate initially decreased, then increased sharply and at pH 12 attained almost the same value as in the absence of sodium silicate, i.e. all the oleate was abstracted from the solution. The initial decrease in oleate "adsorption" was in agreement with the adsorption of silica on barite, which increased between 9 to 12 (Fig. 6.16) and the flotation results

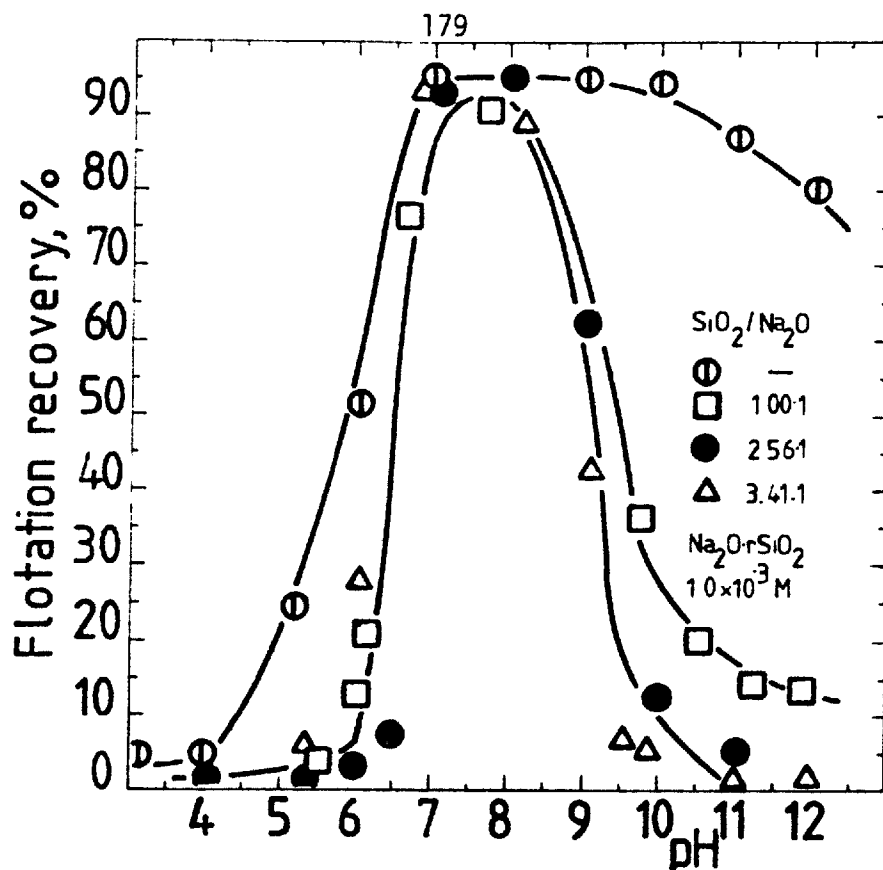


Fig. 7.13. Flotation recovery of barite as a function of pH in the presence of fresh sodium silicates (sodium oleate conc. $1.0 \times 10^{-5} \text{ M}$).

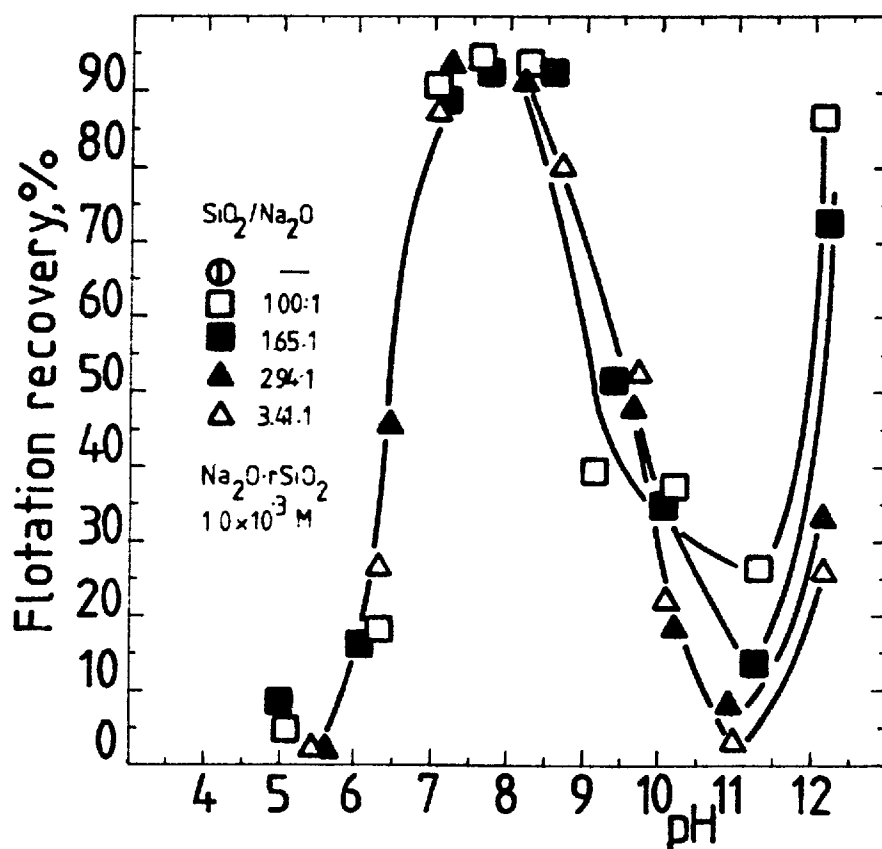


Fig. 7.14. Flotation recovery of barite as a function of pH in the presence of aged sodium silicates (sodium oleate conc. $1.0 \times 10^{-5} \text{ M}$).

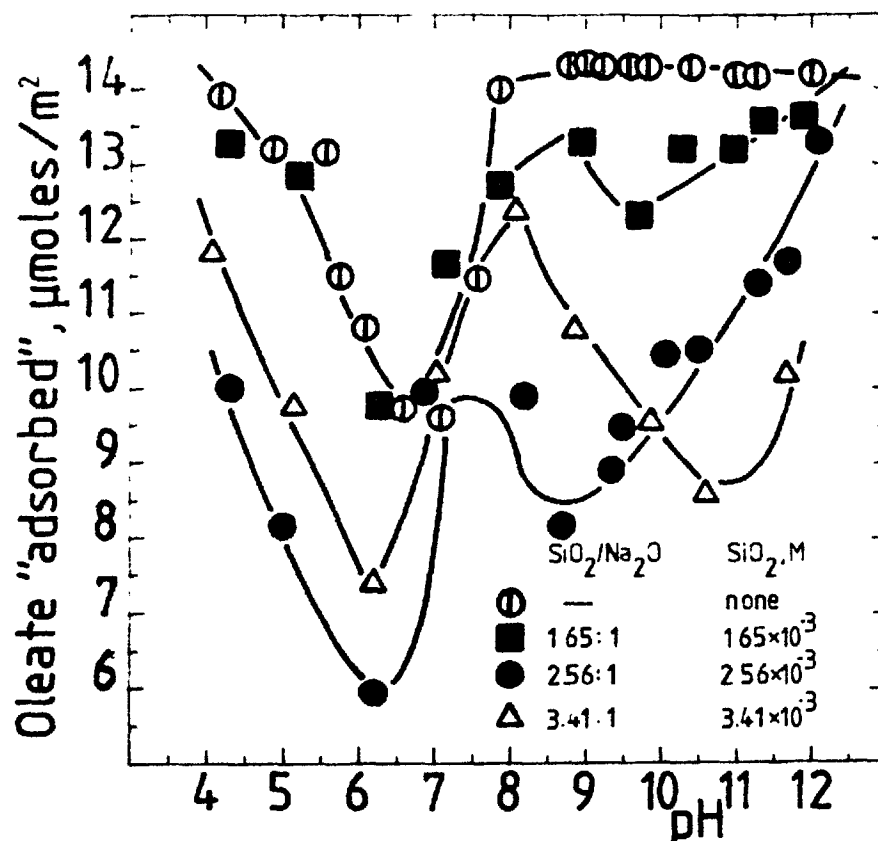


Fig. 7.15a. Abstraction of oleate by barite as a function of pH in the presence of fresh sodium silicates with silica to soda ratios of 1.65:1, 2.56:1 and 3.41:1 (initial sodium oleate conc. $5.0 \times 10^{-5} \text{ M}$).

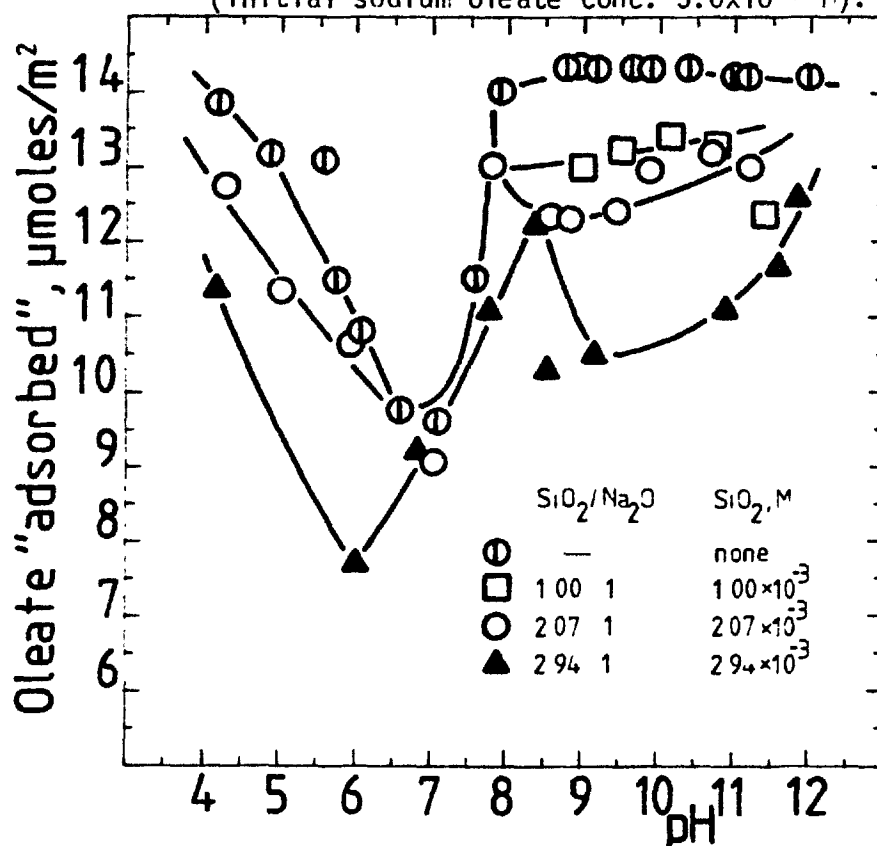


Fig. 7.15b. Abstraction of oleate by barite as a function of pH in the presence of fresh sodium silicates with silica to soda ratios of 1.00:1, 2.07:1 and 2.94:1 (initial sodium oleate conc. $5.0 \times 10^{-5} \text{ M}$).

(Fig. 7.13) but no definite explanation can be given for the subsequent increase observed at high pH values; perhaps the solubility of barium oleate is lower at high pH values so that precipitation of oleate in solution occurs. Precipitation of barium oleate in solution could account for the decrease in recovery obtained under the same conditions. A small decrease in the flotation recovery of barite was noticed even in the absence of sodium silicate at pH values above 10.0.

The adsorption of silica on barite from aged sodium silicate solutions should be lower than that from fresh solutions, if it is dependent on the concentration of Si(OH)_4 . The results presented in Fig. 7.16 show that this was the case and that at pH values above 7 the effect of the sodium silicate on the oleate "adsorption" was not marked. Very little difference could be found between the various sodium silicate solutions under these conditions because the oleate concentration was at its limit of detection by the analytical technique used so that large experimental errors were incurred.

A comparison of Figs. 7.15a and 7.15b with Fig. 7.16 shows that aged and non-aged sodium silicate solutions hardly affected the amount of oleate abstracted by barite at $\text{pH} > 11.0$, while flotation recovery increased in this region only when aged sodium silicate solutions were used (Figs. 7.13 and 7.14). It is possible that the presence of carbonates in the aged solutions might account for these results. Carbonate inhibits the adsorption of silica on barite (Fig. 6.16) and consequently favours the precipitation of oleate on the surface rather than in solution as is the case with fresh sodium silicate solutions.

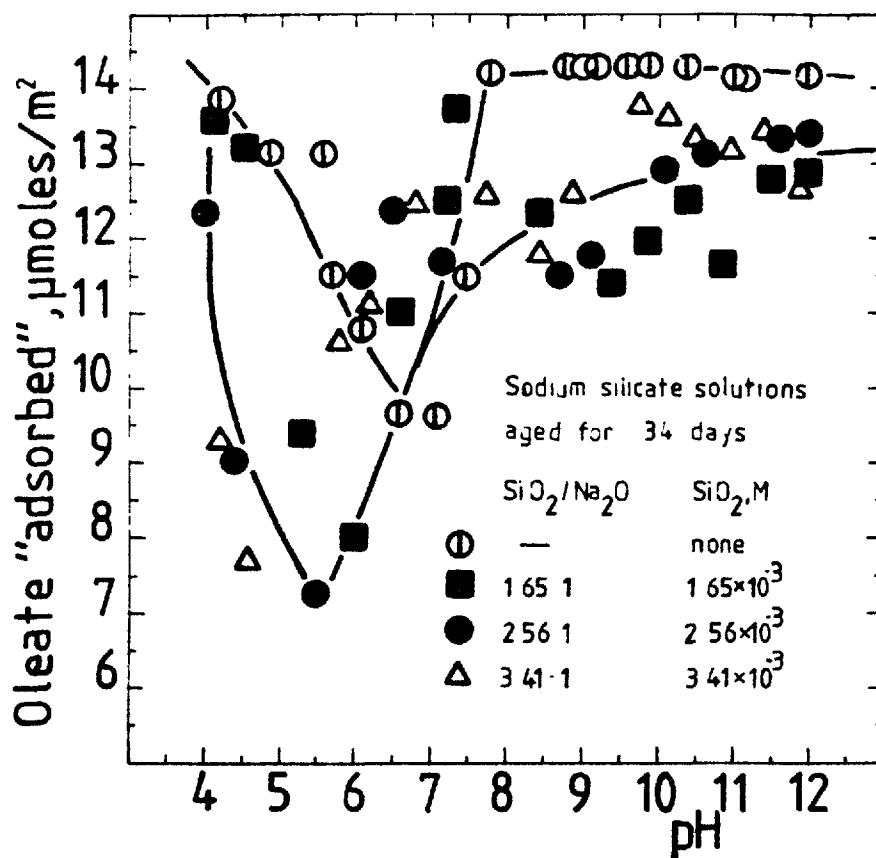


Fig. 7.16. Abstraction of oleate by barite as a function of pH in the presence of aged sodium silicates with different silica to soda ratios (initial oleate conc. $5.0 \times 10^{-5} \text{ M}$).

7.2.4. Mechanism of action of sodium silicate on the
flotation of salt-type minerals with oleic acid.

It has been claimed that "... the almost total lack of correlation between collector adsorption and flotation response is widely recognised" (238). Although this is apparently true in some cases, it need not be generally so because other phenomena can occur which obscure the relationship between flotation and collector adsorption. This is demonstrated to some extent by the results presented in the preceding section. Although flotation tests showed a marked decrease in the flotation recovery of all three minerals with the addition of sodium silicate, the influence of the latter on the amount of collector abstracted was relatively small. In general, however, depression of flotation was accompanied by a decrease in oleate adsorption.

One of the problems of trying to correlate the flotation and abstraction data, in the present work, is that some of the abstracted oleate is accounted for by the precipitation in bulk solution of the metal oleate and the extent of this process is not known. In addition, more oleate will probably be precipitated in solution in the adsorption tests than in the flotation tests because of the smaller particle sizes and the longer conditioning times used. In view of this, the amount of collector, which actually adsorbs on the minerals, is probably more accurately reflected by the flotation results rather than by the abstraction data (83). Of course, in the former case the presence of the gas/water interface and its influence on the behaviour of the system should also be considered.

Silica adsorbs on all three minerals forming a chemical (covalent) bond with the surface sites, and the extent of such an adsorption is dependent on the surface properties of the individual mineral.

Adsorption of silica results in the neutralization of positive sites on the surface which then becomes more negative. The increase in the negative charge of the surface inhibits the approach of oleate anions to the available cationic sites. Since oleate anions are the collector species which react with the surface and they predominate at pH values above 8.0, the effect of the silica will be more pronounced under these conditions. In addition, the adsorption of silica prevents the dissolution of the mineral which, in turn, decreases the amount of oleate precipitated in solution.

It was stated in section 6.2.1 that the calcium oleate layer formed on the surface of fluorite would be more ordered than that on calcite and barite because of the higher crystal symmetry of fluorite. Furthermore, at pH values below 9.5, where fluorite is positive, calcium oleate will also be held on the surface of fluorite electrostatically but not on calcite and barite. The strong adhesion and ordering of the oleate layer on fluorite could explain why fluorite floats better than calcite and barite even though it adsorbs more silica. A similar suggestion has been made by Hanna (239) to explain why fluorite floats with oleic acid after the adsorption of a large amount of starch.

It is not known from the present work whether silica co-adsorbs with oleate or whether the "adsorption" of the oleate inhibits the adsorption of the silica. Whatever is the case the results show that if the formation of the metal oleate layer on the surface cannot be prevented then the result is a hydrophobic surface and the mineral responds to flotation.

In the present study an attempt was made to determine both the adsorption of silica and the effect of silica on the amount of oleate abstracted by all three minerals. To achieve this the concentration of

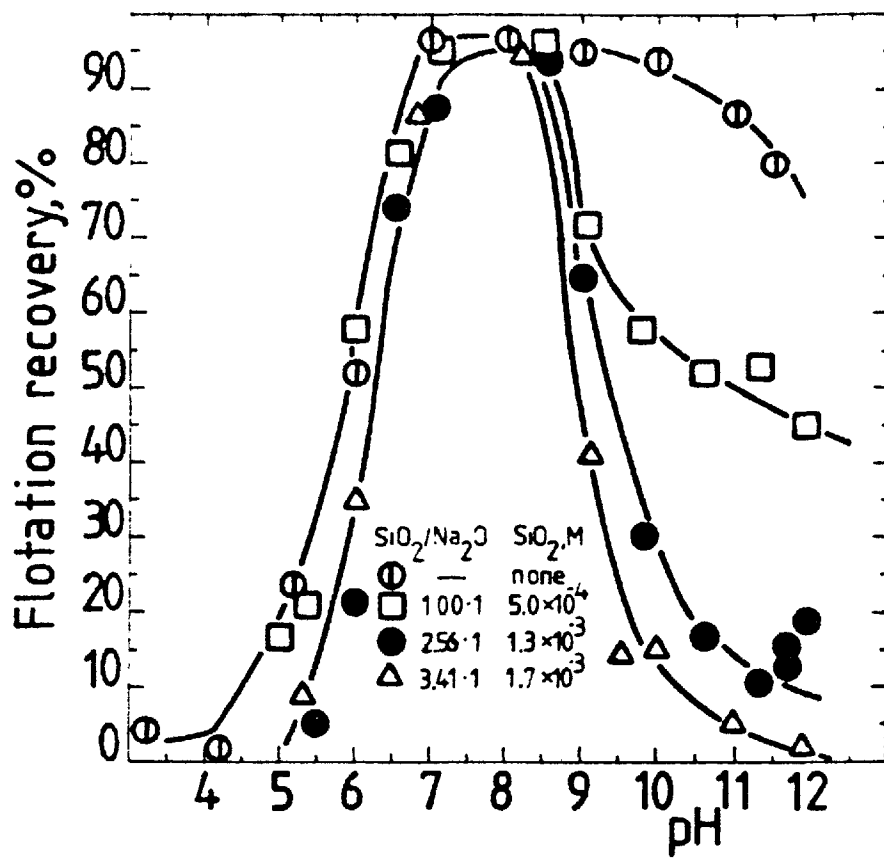


Fig. 7.17. Flotation recovery of barite as a function of pH in the presence of fresh sodium silicates (sodium oleate conc. 1.0×10^{-5} M).

silica in the former experiments did not exceed 5.0×10^{-4} SiO_2 , while in the latter case higher sodium silicate concentrations were necessary to obtain detectable differences ($\approx 1.0 \times 10^{-3}$ M SiO_2). To determine whether or not the mechanism of silica adsorption changed with concentration flotation tests were also carried out using lower silica concentrations. The results given in Figs. 7.3, 7.11 - 12 for fluorite and calcite and in Fig. 7.17 for barite, respectively, show that low concentrations of silica depress the minerals in a similar way to high concentrations but the effect is less pronounced. It is therefore concluded that the mechanism of silica adsorption does not change in the concentration range 1.0×10^{-5} to 3.41×10^{-3} M SiO_2 .

7.3. Influence of polyvalent metal ions - Aluminium

7.3.1. Adsorption of silica and/or aluminium on barite and calcite.

It was shown in the preceding sections that sodium silicate can effectively depress the flotation of calcite with oleic acid at all pH values but its depressing effect on barite and fluorite is rather limited. Although the effect of sodium silicate on barite was slightly stronger than on fluorite in the alkaline region both minerals floated quite well in the pH range 7 to 9 even with relatively high additions of sodium silicate. The latter indicates that the separation of these two minerals from each other is unlikely to be possible using sodium silicate alone. Since the adsorption of silica on barite was almost negligible below pH 9.0, while that on fluorite was quite high, it seems reasonable to assume that selectivity might be improved if the adsorption of silica on the former mineral is enhanced.

In practice, salts of polyvalent metals, added with sodium silicate,

have been found to improve the selectivity and, in some cases, separations of the salt-type minerals have been achieved. Although polyvalent metals have been extensively used for a long time their mode of action is still not well understood. In the present study the effect of aluminium on the flotation of barite, calcite and fluorite was investigated and an attempt was made to explain its mechanism of action. Aluminium was chosen for many reasons but mainly because of its reported negligible effect on the flotation of fluorite and its depression of calcite (117, 95). No data are available in the literature concerning the effect of aluminium on barite flotation.

The adsorption of aluminium from a solution containing 1.0×10^{-4} g-atoms Al/l was determined in the absence of silicate and oleate species. The results obtained are shown in Figs. 7.18 and 7.19 (open circles) for barite and calcite, respectively. Tests were not conducted in the case of fluorite because an appropriate analytical method of determining aluminium in the presence of fluoride ions was not available.

The adsorption of aluminium on barite increased considerably at pH values below 10.0 and maximum adsorption was obtained at pH 7.0, which was the lowest pH at which measurements were carried out. Tests were not conducted in the pH region 5 - 7 because the flotation of barite with oleic acid at these pH values is very low. The adsorption of aluminium on calcite decreased continuously in the pH region 8.5 - 10.0 and it was nearly zero at high pH values (>11.5).

In the same figures the adsorption of silica and aluminium on barite and calcite from solutions containing both reagents is given. It is evident that the presence of both aluminium and silica results in the mutual enhancement of the adsorption. Thus, in the case of barite maximum adsorption of silica and aluminium occurred at pH 9.5 while at

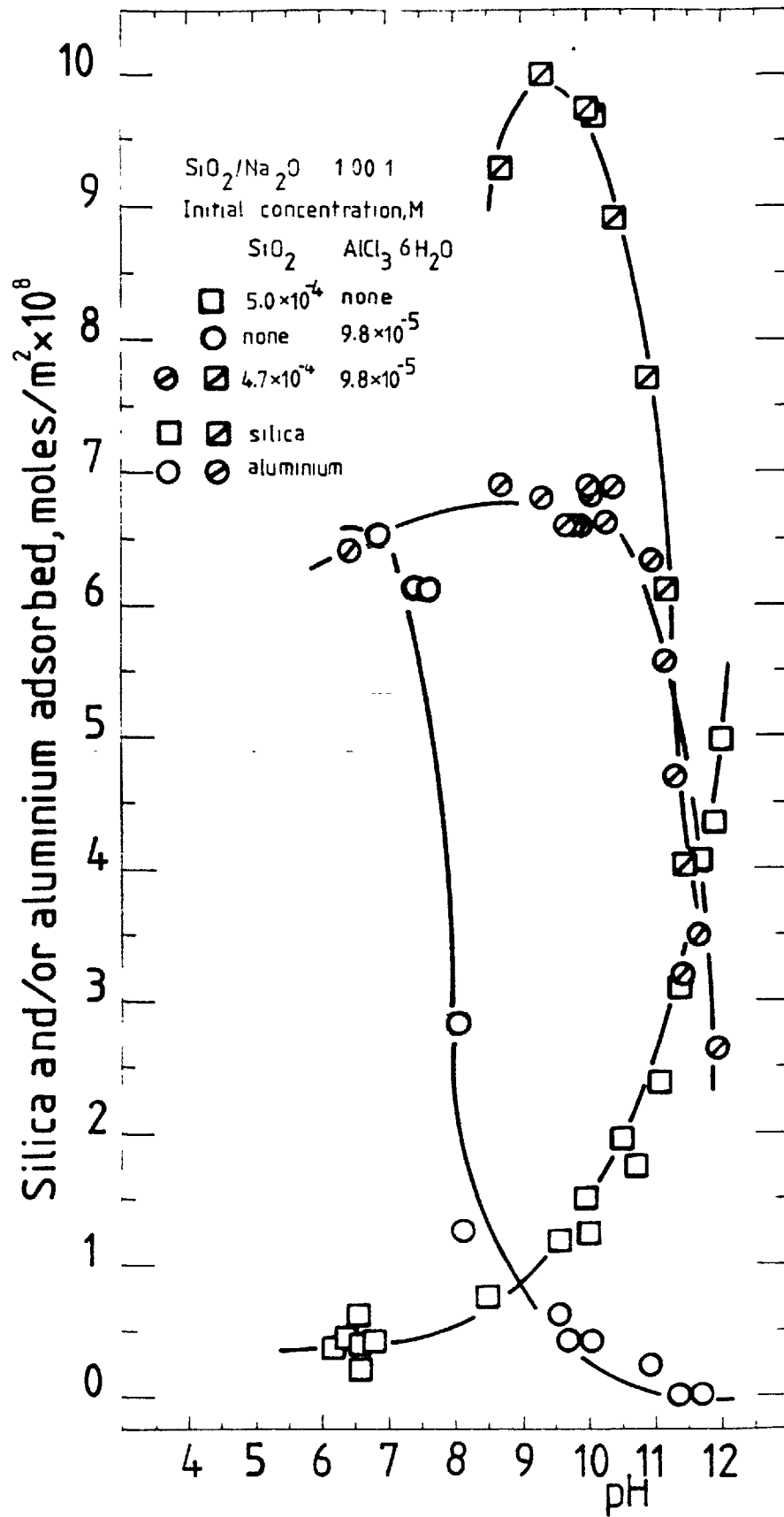


Fig. 7.18. Adsorption of silica and/or aluminium on barite as a function of pH.

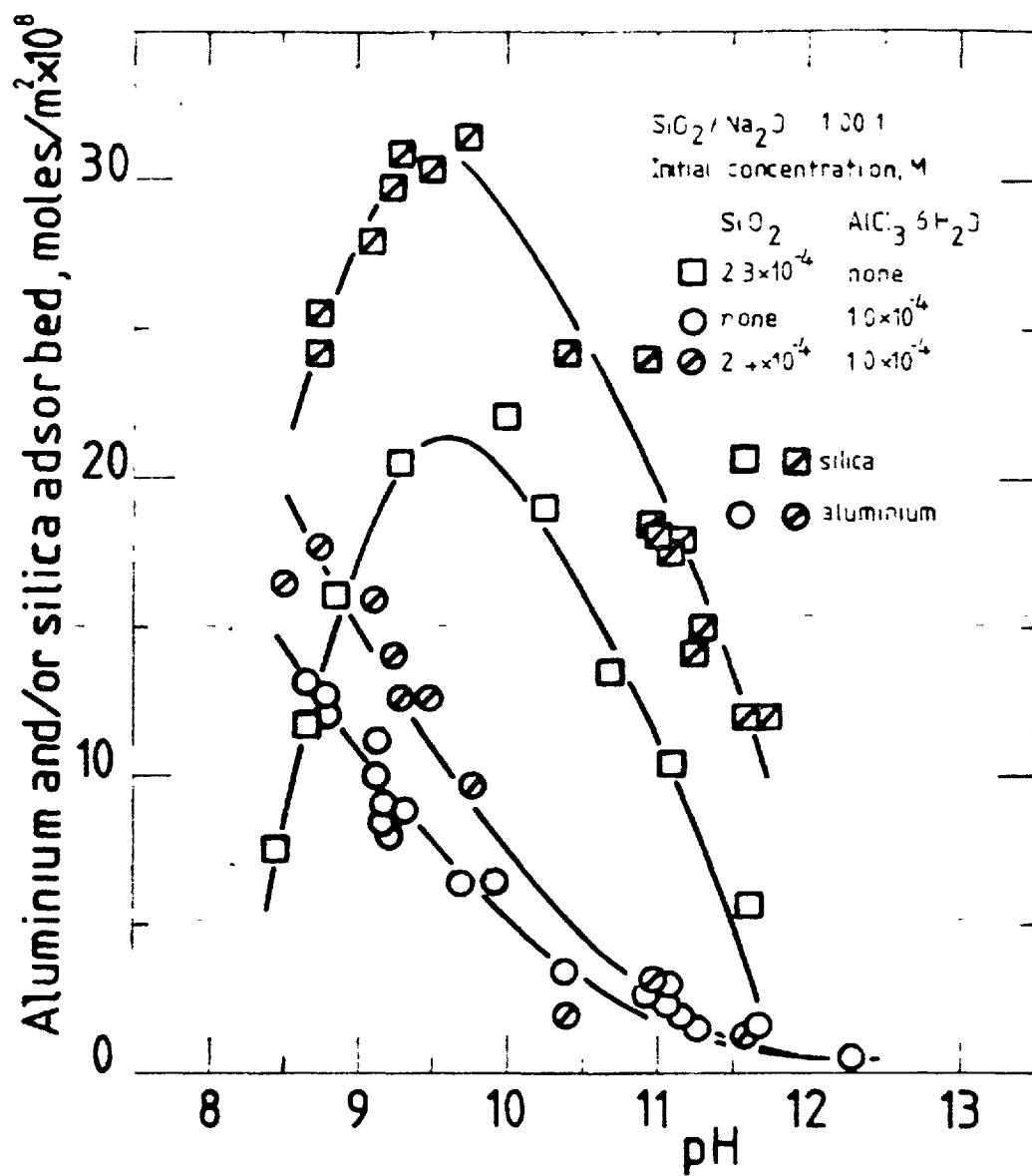


Fig. 7.19. Adsorption of silica and/or aluminium on calcite as a function of pH.

the same pH the adsorption of either of these two species on its own was quite low. Above this pH value the adsorption of both species decreased rapidly and at high pH values (≈ 12.0) the effect of aluminium on the adsorption of silica was negligible. At pH 12.0 the same amount of silica adsorbed as in the absence of aluminium. In the case of calcite the amount of aluminium adsorbed did not reach a maximum but it increased continuously, and it was higher at low values of pH. The curve giving the amount of silica adsorbed on calcite in the presence of aluminium resembles that obtained in the absence of aluminium but it has been shifted to higher values. The influence of aluminium on the silica adsorption was greater at pH values below 10.0 and this is in agreement with the higher adsorption of aluminium found in the same region.

7.3.2. Aqueous chemistry of aluminium.

In the preceding section the term "aluminium" was used to describe the total aluminium concentration in solution or that adsorbed on the mineral surface rather than to indicate any particular species. In an aqueous aluminium salt solution the aluminium cation, Al^{3+} or $\text{Al}(\text{H}_2\text{O})_6^{3+}$, hydrolyses to give a number of different products depending on the equilibrium pH. It would appear that both monomeric and polymeric species are possible but there is considerable controversy over the exact nature of some of the polynuclear species. One of the problems in studying aqueous aluminium solutions is that equilibrium is only slowly obtained. As a result the hydrolysis products, which are formed reversibly according to stability data predictions, are referred to as stable hydrolysis products to distinguish them from the metastable large polymeric or colloidal particles (240).

A review of the hydrolysis of aluminium has been made recently by Baes and Mesmer (240) and their data have been used to construct Fig. 7.20. The calculations were made using the following equilibria:

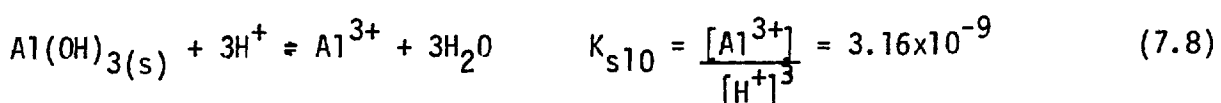
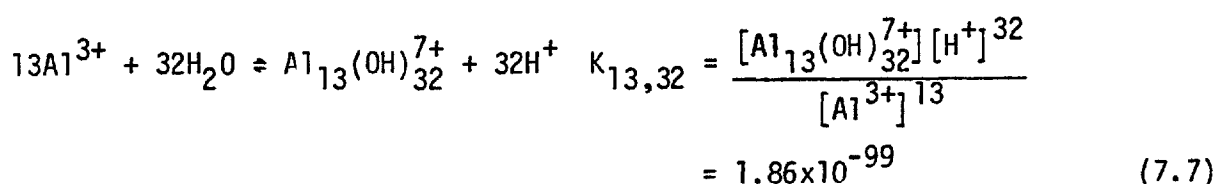
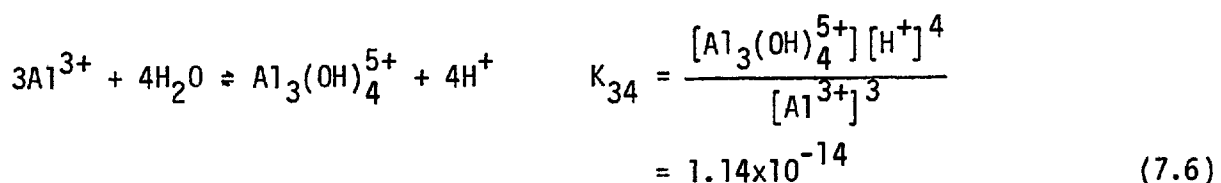
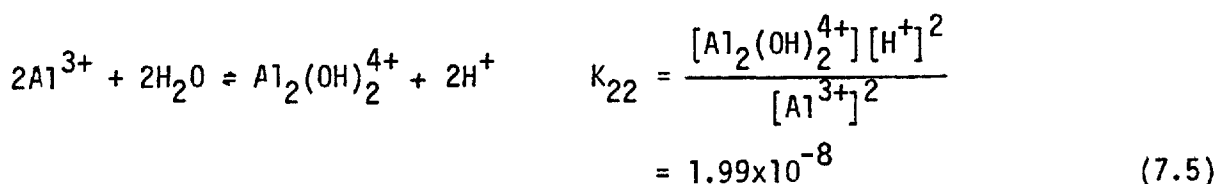
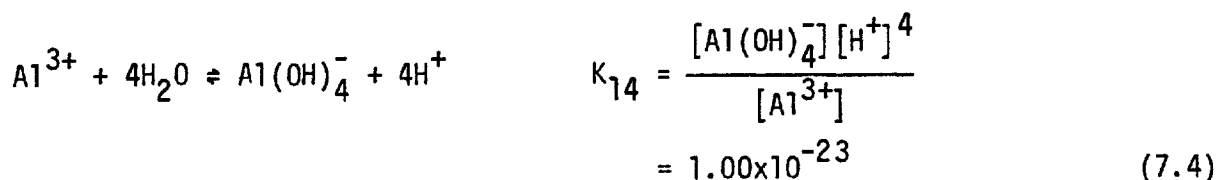
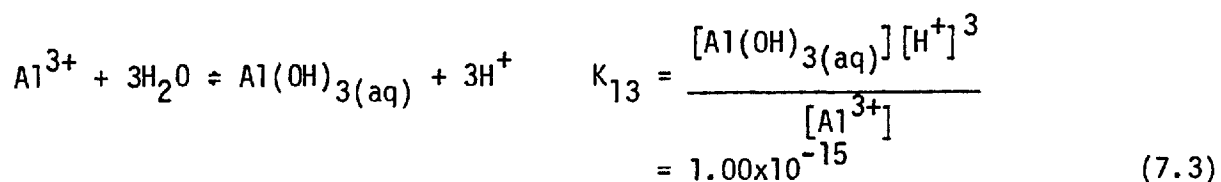
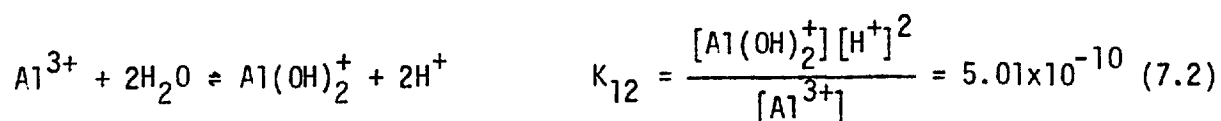
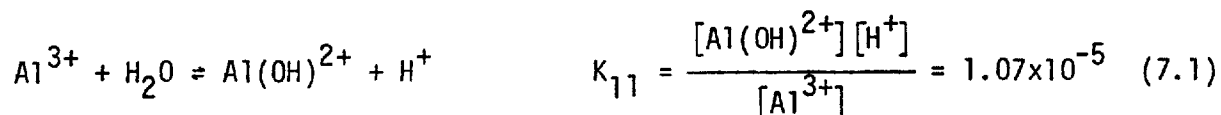


Fig. 7.20 shows the concentration of the various aluminium species in a solution saturated with respect to $\alpha\text{-Al}_2\text{O}_3$ (gibbsite). To construct this diagram the polynuclear species $\text{Al}_2(\text{OH})_2^{4+}$, $\text{Al}_3(\text{OH})_4^{5+}$ and $\text{Al}_{13}(\text{OH})_{32}^{7+}$ were assumed to be present together with the mononuclear species Al^{3+} ,

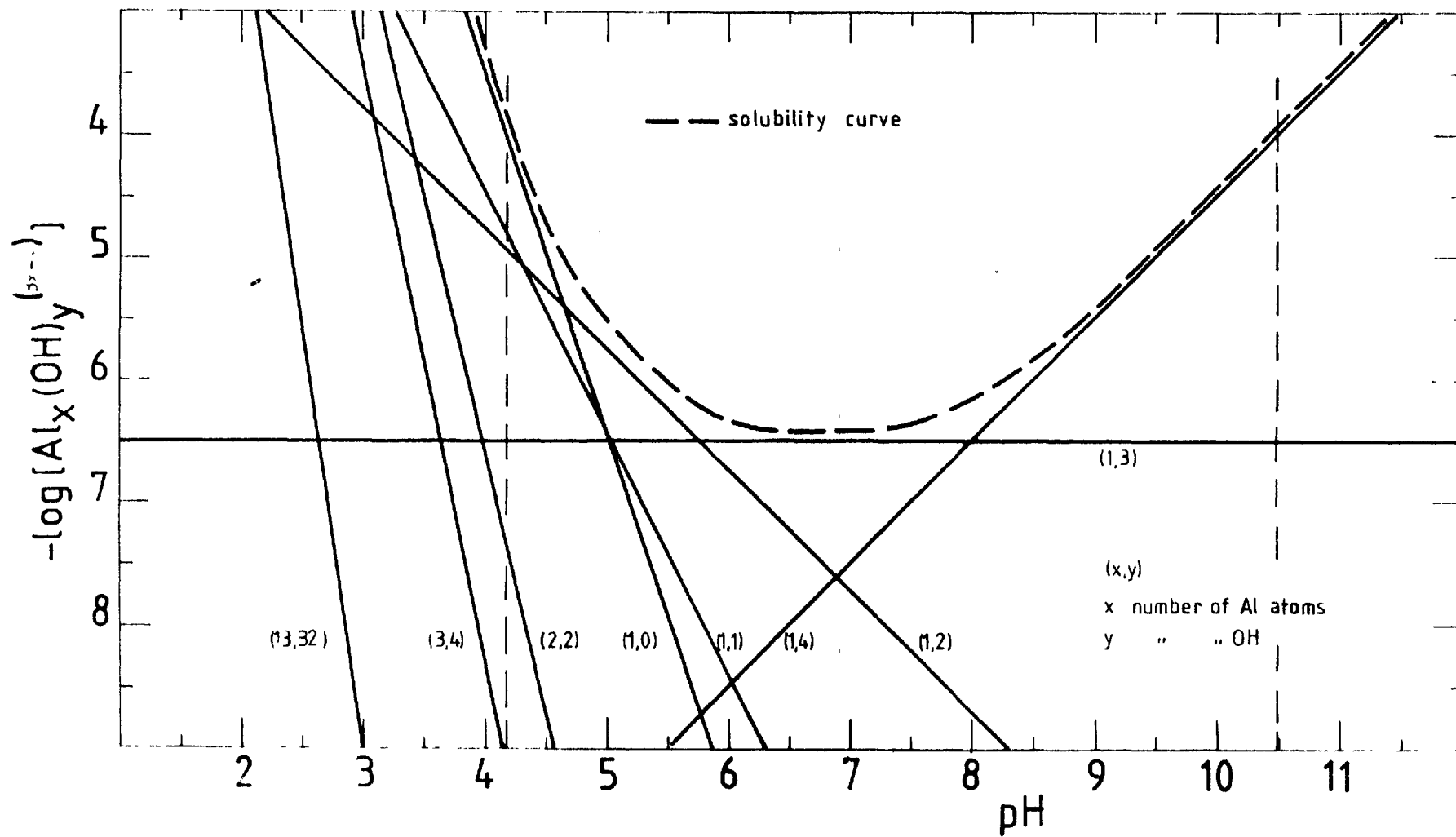


Fig. 7.20. Concentration of hydrolysis products of aluminium in a solution saturated with respect to gibbsite ($\alpha\text{-Al}_2\text{O}_3$) (constants taken from ref. 240).

$\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_3(\text{aq})$ and $\text{Al}(\text{OH})_4^-$. Of the monomeric hydrolysis products the existence of the $\text{Al}(\text{OH})^{2+}$ and $\text{Al}(\text{OH})_4^-$ has been well established. The formation constants of the species $\text{Al}(\text{OH})_2^+$ and $\text{Al}(\text{OH})_3(\text{aq})$ are relatively uncertain and the values used are probably too high (240). Dimeric and trimeric species, of minor importance at 25°C, are based largely on measurements at higher temperatures. The presence of the large polynuclear species, $\text{Al}_{13}(\text{OH})_{32}^{7+}$, although present in aged solutions, has been in doubt for fresh solutions and other species such as $\text{Al}_8(\text{OH})_{20}^{4+}$ have been proposed instead (241 - 3). The concentration of the polynuclear species will be appreciable only at low pH values, whereas their contribution to the total aluminium concentration will be a function of the concentration of the latter in solution and over a narrow pH range; this is a typical property of a polynuclear system. The concentration of all these species decreases with an increase in pH and solid aluminium hydroxide starts to form (244 - 5). At this point the only aluminium species present in appreciable amounts is the $\text{Al}_{13}(\text{OH})_{32}^{7+}$. The concentration of total aluminium in solution, i.e. the solubility of the aluminium hydroxide, is at a minimum at around pH 7.0. Above this pH value the solubility increases again due to the formation of the aluminate ion, $\text{Al}(\text{OH})_4^-$, which is the only aluminium species present at pH values above 9.0. Although quite a large number of aluminium species exist in concentrated solutions, dilute solutions ($<1.0 \times 10^{-3}$ M) can be satisfactorily described assuming that only the mononuclear species are present (246).

Dashed lines in Fig. 7.20 indicate the pH region in which precipitation of aluminium hydroxide is thermodynamically possible and consequently it may occur at the concentration level used in the adsorption tests, i.e. 1.0×10^{-4} g-atoms Al/l. The precipitation pH range, 4.1 - 10.5,

under these conditions is a little wider than that given by Hayden and Rubin (247) which is 4.8 - 10.0, and indicates how dependent the distribution diagram is on the values of the constants assumed in the calculations. Hydrolysis reactions are slow to reach equilibrium, especially when polynuclear species or precipitates are initially present, and because of this the following procedure was used in the present work to prepare the aluminium solutions. A stock solution of 1.0×10^{-3} g-atoms Al/l was prepared using $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, prior to each series of measurements. This salt was chosen since aluminium has not been reported to form any stable complexes with chlorine. Indeed the available data are only indicative (248) and stability constants have not been given except in the case of concentrated AlCl_3 solutions in organic solvents (249). Under the present conditions (aqueous solutions, low concentrations of AlCl_3 and high pH values) the formation of such complexes was considered unlikely. The pH of the 1.0×10^{-3} M $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ solution was kept at approximately pH 3.5 which is the pH at which Al^{3+} ions predominate (>90%). The final solutions, with a concentration of 1.0×10^{-4} M $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, were obtained by diluting the predetermined amount of stock solution at pH values above 9.0 and in the presence of vigorous stirring. This procedure avoided the initial precipitation of aluminium as aluminium hydroxide. When both aluminium chloride and sodium silicate solutions were mixed the former solution was always added to the latter. The addition of the aluminium chloride solution did not produce a precipitate and all the final solutions were optically clear. This is in agreement with what has been reported in the literature (250).

7.3.3. Mechanism of adsorption of aluminium

The adsorption data obtained with calcite and aluminium have been

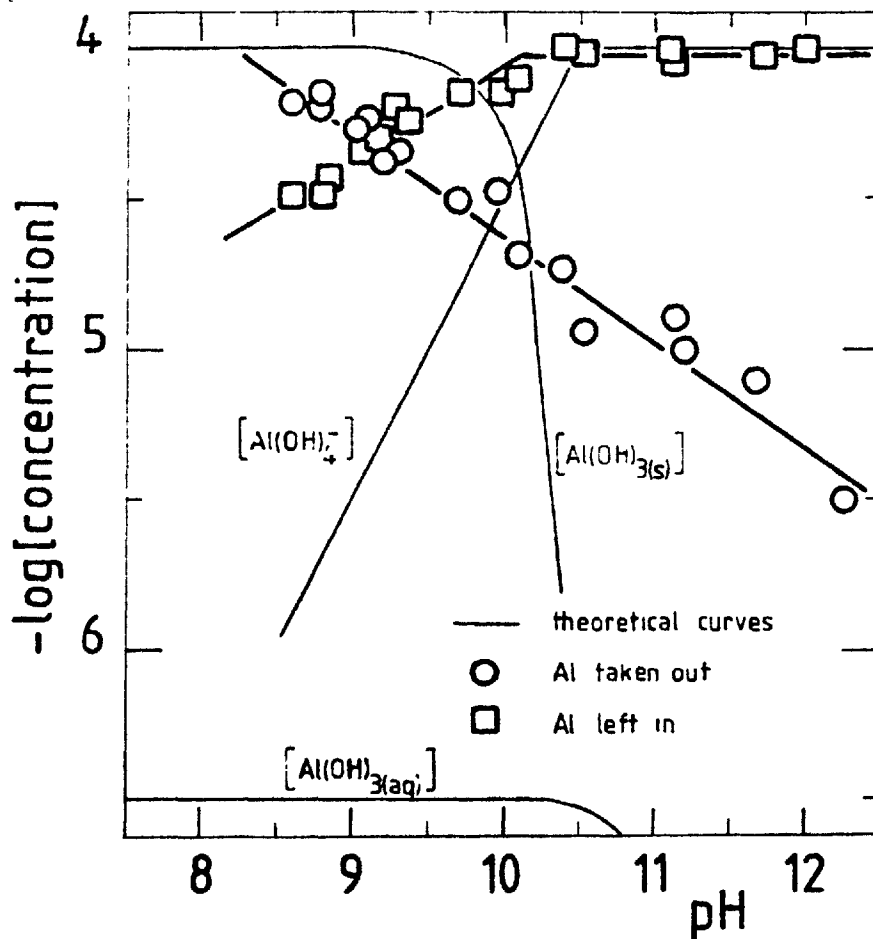


Fig. 7.21. Distribution of aluminium species in a 1.0×10^{-4} M $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ solution and amount of aluminium taken out of and left in solution from solutions saturated with calcite.

replotted in Fig. 7.21 to show the total amounts of aluminium taken out (open circles) and left in solution as a function of pH. In the same figure continuous lines indicate the calculated concentration of the various forms of aluminium species present in solution under the conditions of the adsorption experiments. Similar curves are obtained if the adsorption data obtained with barite is plotted in the same way. It is evident that adsorption of aluminium was quite high at pH values below 10. In this pH region most of the aluminium should be precipitated as aluminium hydroxide. Under the same pH conditions the amount of

aluminium left in solution closely follows the theoretical concentration of $\text{Al}(\text{OH})_4^-$ which indicates that $\text{Al}(\text{OH})_4^-$ ions are unlikely to be involved in the adsorption process. It follows, therefore, that the adsorption of aluminium is closely related to the precipitation of aluminium hydroxide.

The precipitation of aluminium hydroxide was not observed in any of the aluminium solutions after their preparation but this does not rule out its formation at some later stage (during the conditioning time). Although the formation of the precipitate is thermodynamically favourable precipitation proceeds very slowly at low concentrations and its detection is difficult unless instruments with high sensitivity are used (247).

Aluminium hydroxide may either precipitate on the surface of the mineral or in solution followed by adsorption on the surface. Both mechanisms are equally likely. In the first case the particles of the mineral would be the nucleus for the precipitation process. The coagulation of silica sols by aluminium under conditions where the formation of aluminium hydroxide is favourable has been ascribed to this reason (250 - 2). In the second case, the aluminium hydroxide initially precipitated in solution would adsorb on the minerals by electrostatic interaction.

Aluminium hydroxide hydrosols are positively charged in weakly alkaline and acidic media and they have an IEP around pH 9.0 (253 - 5, 27). Both calcite and barite were negatively charged at these pH values and if aluminium hydroxide is adsorbed by coulombic attraction it should do so at pH values below the IEP of the aluminium hydroxide. Figures 7.18 and 7.19 show that this was indeed the case. At pH values above 10.0, where all the aluminium is present as $\text{Al}(\text{OH})_4^-$, the adsorption was almost zero. The coulombic adsorption of $\text{Al}(\text{OH})_4^-$ ion is unlikely under these

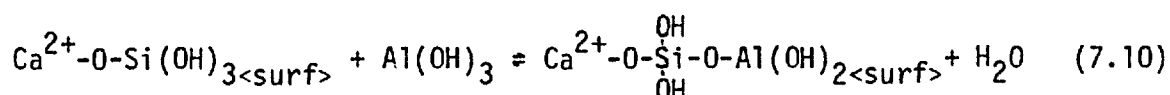
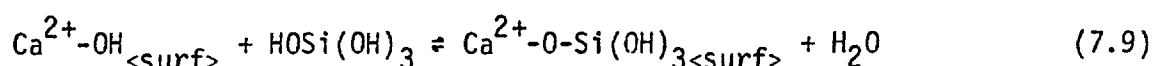
conditions.

The presence of aluminium hydroxide on the mineral surface will increase the concentration of hydroxyl sites. Since at pH values below 10.0 the adsorption of silica on barite and calcite proceeds through reactions (6.7) and (6.19), respectively, the increased aluminium adsorption at these pH values will favour the enhanced adsorption of silica on both minerals. At pH values above 10.0 both the decrease in the adsorption of aluminium and concentration of Si(OH)_4 species results in the abrupt decrease in the adsorption of silica.

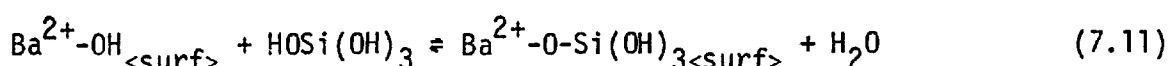
It is worth mentioning that the presence of silica also enhanced the adsorption of aluminium on both minerals but this effect was more pronounced in the case of barite, where measurements were made at lower pH values than those for calcite. Thus, although the adsorption of aluminium in the pH range 8.0 - 10.5 was low in the absence of silica (Fig. 7.18) it was considerably higher in its presence. Almost all the aluminium initially added was abstracted from solution under these conditions. Aluminium has been found to decrease the concentration of silica in solution through the formation and precipitation of aluminosilicate compounds, but at lower pH values and higher concentrations of both reactants than those used in the present work (155, 256). It has also been reported that at silica concentrations lower than $2 \times 10^{-3} \text{ M SiO}_2$ the precipitation boundaries for an aluminium solution are typical of those reported for alumina (257) without any silica present. Although precipitation of aluminium as aluminosilicate cannot therefore account for the results obtained the formation of soluble aluminosilicate complex anions in solution is highly probable. The chemistry of aluminosilicates is rather involved and whilst the properties of their crystalline forms are well understood, the reactions preceding their formation are not fully explained,

and the formula and equilibrium constants for the formation of these species are not available.

Complex aluminosilicate species may even form on the surface of the minerals. In this case the adsorption of silica would precede the adsorption of aluminium and the following reactions could be written.



Reaction (7.10) seems reasonable in the case of calcite but it cannot explain the adsorption of aluminium on barite because at these pH values the adsorption of silica through reaction:



is negligible. In the latter case the adsorption of aluminium either takes place first followed by the adsorption of silica or the aluminosilicate anions are formed in solution and then adsorb on the surface according to the reactions:

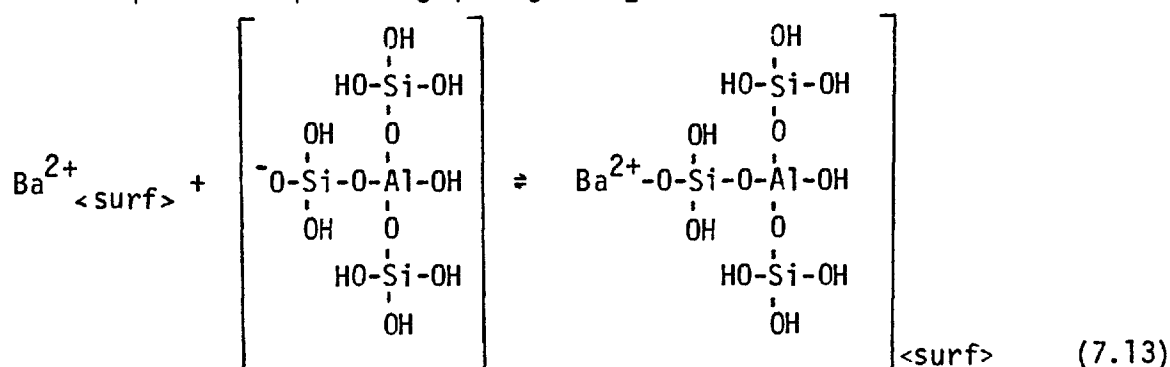
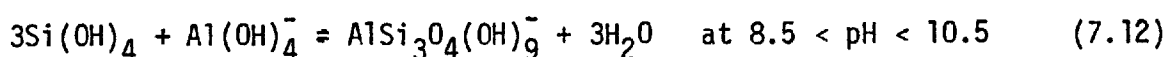
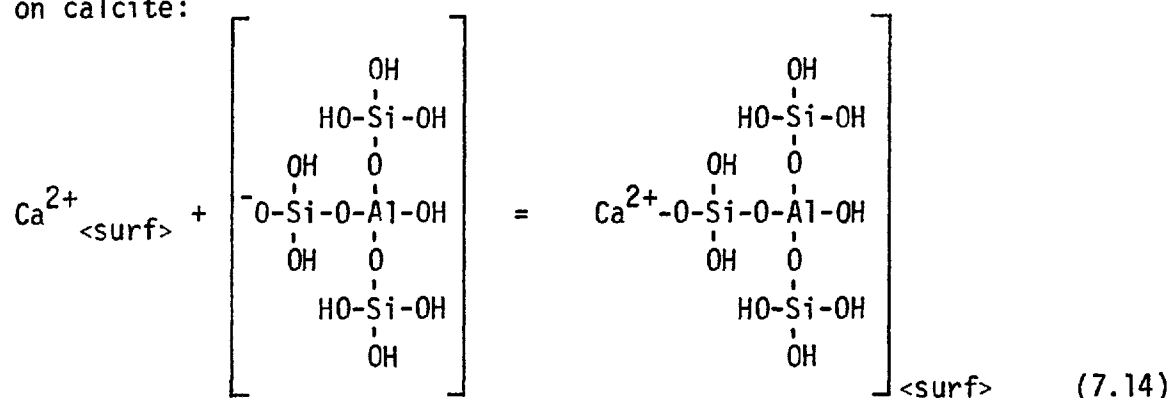


Figure 7.18 (open circles) shows that the adsorption of aluminium on barite at pH values below 8.5 was quite high even in the absence of

silica which indicates that the adsorption of silica in the presence of aluminium can be ascribed to the precipitation of aluminium hydroxide on the surface followed by the adsorption of silica.

At pH values above 8.5, however, the concentration of $\text{Al}(\text{OH})_4^-$ increases and reaction (7.12) may take place, which results in the formation of the $\text{AlSi}_3\text{O}_4(\text{OH})_9^-$ anion. The presence of such an anion at these pH values, $8.5 < \text{pH} < 10.5$, where $\text{Ba}^{2+}_{\text{<surf>}}$ sites predominate favours the adsorption of silica which now is at a maximum. In the absence of aluminium adsorption of silica was negligible at the same pH values since the concentration of $\text{SiO}(\text{OH})_3^-$ was too low. It is evident that a similar reaction to (7.13) could also be written for the adsorption of silica and aluminium on calcite:



A similar reaction to (7.14) has also been proposed by Abeidu (117) for calcite. It is well known that a large number of aluminosilicate anions exist in the solid state and their structure has been adequately described (2). In the present study the $\text{AlSi}_3\text{O}_4(\text{OH})_9^-$ anion is assumed to be the adsorbing species. This assumption is mainly based on the fact that the amount of silica adsorbed on both minerals in the presence of aluminium was always twice or slightly more, but less than 3 times, the amount of aluminium adsorbed under the same conditions. Of course, another anion with silicon to aluminium ratio in the same range, i.e. 2 to 3, would be equally acceptable.

At even higher pH values (>10.5) reaction (7.12) does not take place

because of the decrease in the Si(OH)_4 concentration. Adsorption of silica cannot therefore be improved by the presence of aluminium, by either of the two mechanisms proposed above. Because of this the adsorption decreases continuously and finally it attains the same value as that obtained in the absence of aluminium.

7.3.4. Flotation of barite, calcite and fluorite in the presence of aluminium.

In Figs. 7.22, 7.23 and 7.24 the flotation recovery of barite, calcite and fluorite is given as a function of pH, and in the presence of aluminium. In all but one series of tests (Fig. 7.24) the concentration of silica was 5.0×10^{-4} M SiO_2 . The sodium oleate concentration was 1.0×10^{-4} M for calcite and 1.0×10^{-5} M for barite and fluorite. The concentration of sodium silicate for the latter mineral was 1.0×10^{-3} M SiO_2 . In all three cases 1.0×10^{-4} M $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ was added which is the same as that used in the adsorption measurements. The sodium silicate with silica to soda ratio 1.00:1 was used.

It is evident that the flotation of barite and calcite was completely depressed at pH values below 10.0 when both aluminium and silica were present. At pH values above 10.0 the flotation recovery gradually increased and was similar to that obtained in the absence of aluminium at pH values above 11.5. The flotation results were in excellent agreement with the previously reported adsorption data and indicate that the higher adsorption of silica was responsible for the depression obtained.

The adsorption of the aluminosilicate species could prevent the adsorption of oleate anions by blocking out the active cationic sites. They are more effective in this respect than the simple silicate species, not only because of their higher density on the surface, but also because

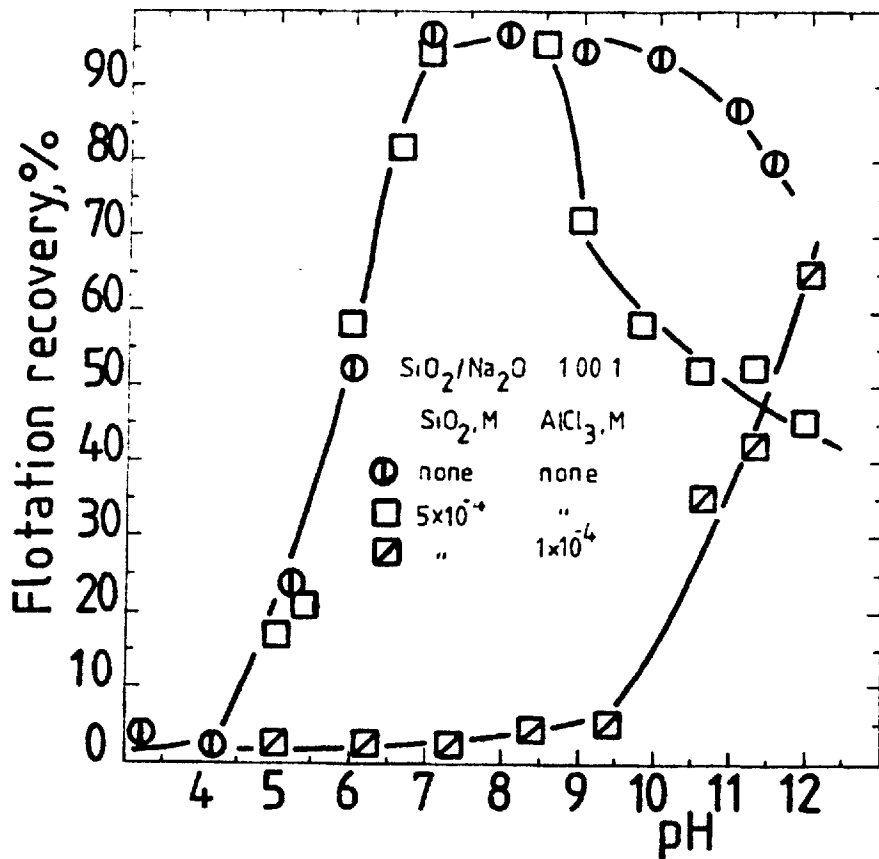


Fig. 7.22. Flotation recovery of barite as a function of pH in the presence of aluminium and silica (sodium oleate conc. 1.0×10^{-5} M).

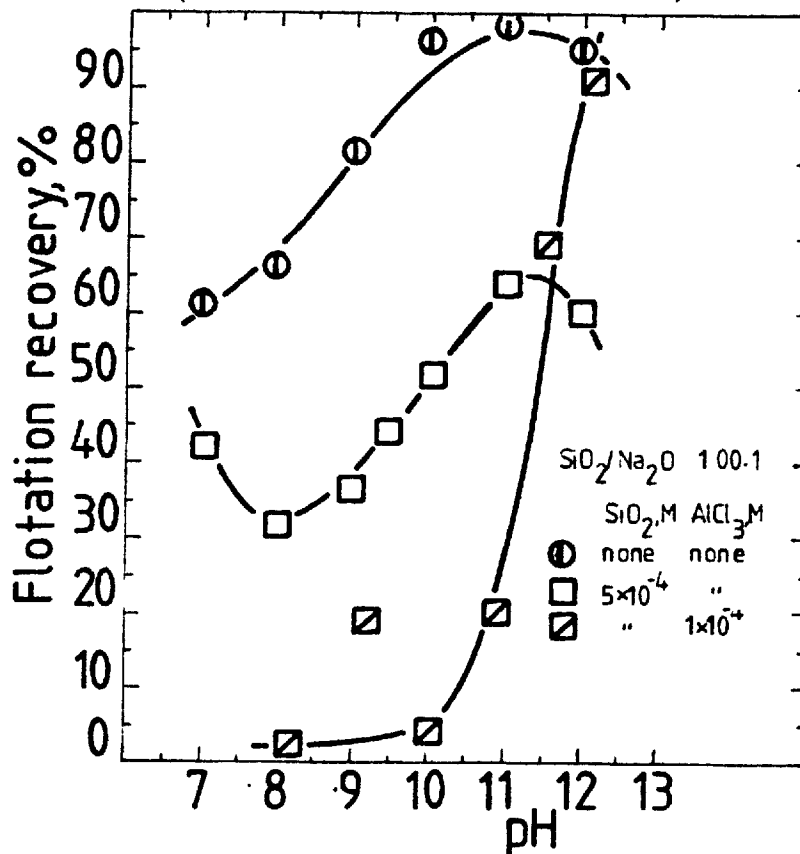


Fig. 7.23. Flotation recovery of calcite as a function of pH in the presence of aluminium and silica (sodium oleate conc. 1.0×10^{-4} M).

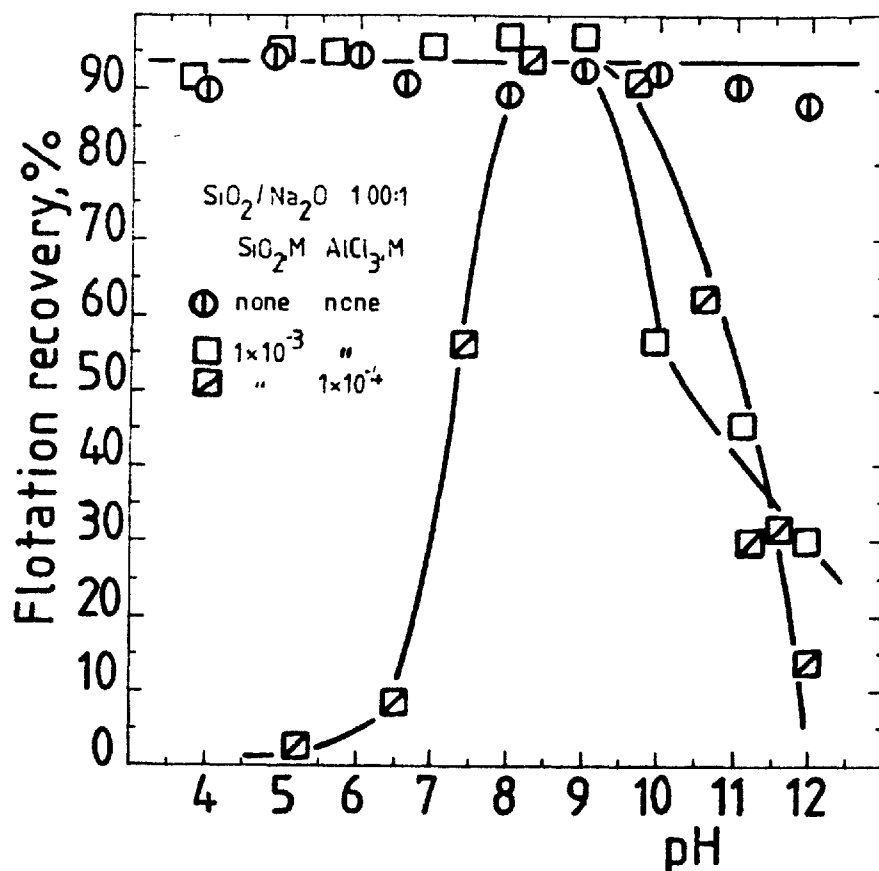


Fig. 7.24. Flotation recovery of fluorite as a function of pH in the presence of aluminium and silica (sodium oleate conc. 1.0×10^{-5} M).

of their configuration and size. Thus, the adsorption of the $\text{AlSi}_3\text{O}_4(\text{OH})_9^-$ ion on a $\text{Ca}^{2+}_{\text{surf}}$ or $\text{Ba}^{2+}_{\text{surf}}$ site not only prevents the oleate from adsorbing on the same site but also on other available sites in the vicinity.

Fig. 7.24 shows that aluminium had no effect on the flotation of fluorite in the alkaline pH range but it depressed the flotation at pH values below 8.0. It is well known that aluminium forms very strong complexes with fluoride with the general formula AlF_n^{3-n} . From the available thermodynamic data (243, 258) it can be concluded that n increases with pH and in alkaline pH values the complexes are: AlF_3 , AlF_4^- , AlF_5^{2-} etc. Calculations carried out at total fluoride and aluminium concentra-

tions of 1.0×10^{-4} M showed that most of the aluminium would be present as the fluoride complexes. The concentration of fluoride in a fluorite suspension was found to be 4.8×10^{-4} M in the pH range 5 - 12. This indicates that under the conditions of the flotation experiments aluminium was not available to react with silica to form the aluminosilicate ions which are assumed to be the main species responsible for the depression of the flotation of barite and calcite at pH values in the range 8.5 to 10.5. Contrary to the results given by other investigators (117), the addition of aluminium along with sodium silicate strongly depressed the flotation of fluorite at pH values lower than 8.0. Since adsorption measurements with this mineral were not carried out for reasons explained in section 7.3.1, it is not known whether this was due to the increase in the amount of silica adsorbed or to some other reason. In this pH region aluminium will be present in solution either as hydroxy or fluoride complexes. All these species will be positively charged and electrostatic adsorption cannot take place on the surface of fluorite since the latter also possesses a positive charge. It was thought that the decrease in flotation recovery might be due to the precipitation of the collector in solution. The solubility product of aluminium oleate is 1.0×10^{-30} moles⁴/litre⁴ (82). At an oleate concentration of 1.0×10^{-5} M aluminium oleate precipitates when the concentration of Al^{3+} ion is greater than 1.0×10^{-15} g-atoms/l.

CHAPTER 8. CONCLUSIONS

An investigation has been made of the effect of sodium silicate on the flotation of barite, calcite and fluorite with oleic acid. The action of sodium silicate in this system has been critically discussed and published data has been compared with those obtained in the present study. A mechanism of adsorption of silica on all three minerals is proposed. The investigation included both flotation and adsorption studies conducted in the absence and presence of sodium silicate, supplemented by solubility and electrokinetic measurements.

Experiments involving sodium silicate solutions were conducted at total silica concentrations below the solubility of amorphous silica in water at 25°C. Under these conditions the sodium silicate solutions were free of colloidal silica but some polysilicate species were present. The polysilicate concentration was, however, low and dependent on the total concentration of silica in solution, the pH and ageing time.

As a result of this investigation the following conclusions can be made:

1. (a) The variation in solubility of barite, fluorite and calcite with pH is adequately described by existing solution equilibria data. The solubility of barite is constant in the pH range 2 - 12, that of fluorite in the range 5 - 12 and that of calcite at pH values

above 11.

(b) In the presence of carbonate the fluorite surface is partially converted to calcium carbonate. The carbonation reaction occurs at pH values above 8.6 and this is consistent with the thermodynamic predictions.

(c) Sodium oleate inhibits the dissolution of calcite and fluorite due to the formation of a layer of calcium oleate on the surface.

(d) Sodium silicate decreases the solubility of calcite and fluorite because of the formation of an adsorbed silicate layer.

2. (a) Barite and fluorite exhibit an IEP at pH values 4.5 and 9.5, respectively, while calcite is negatively charged in the pH range studied, i.e. 9.5 - 12.0.

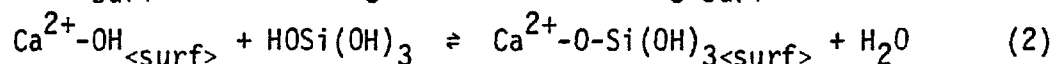
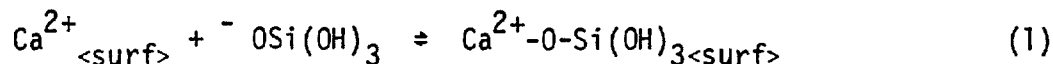
(b) At pH 10 and in the presence of sodium oleate the electrophoretic mobility of all three minerals becomes more negative at oleate concentrations above 1×10^{-5} M.

(c) At pH 10 and in the presence of sodium silicate the electrophoretic mobility of all three minerals becomes more negative at relatively high sodium silicate concentrations ($> 5.0 \times 10^{-5}$ M SiO_2). This is attributed to the adsorption of silicate ions. In this respect sodium silicate solutions aged for 34 days are less effective than the solutions prepared prior to each measurement.

3. (a) The mechanism of "adsorption" of oleic acid on barite, calcite and fluorite is the precipitation of the barium or calcium oleate on the surface. The collecting ability of this reagent therefore depends on the strength of adhesion, structure and textures of the precipitate on the surface.

4. (a) Silica adsorbs on calcite through a chemical reaction of

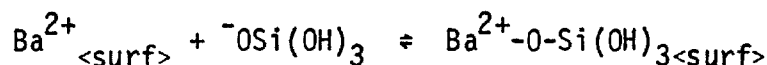
the Si(OH)_4 and SiO(OH)_3^- species with the $\text{Ca}^{2+}\text{-OH}_{\text{<surf>}}$ and $\text{Ca}^{2+}_{\text{<surf>}}$ sites, respectively. The suggested reactions are of the acid/base type and result in the formation of a surface calcium silicate:



Of the above two reactions, reaction (1) is more important and contributes more to the silica adsorption.

(b) The mechanism of silica on fluorite is similar to that on calcite but some silica is also adsorbed through hydrogen bonding with the fluoride sites on the surface.

(c) The adsorption of silica on barite is appreciable only above pH 9, where SiO(OH)_3^- ions predominate. It is suggested that the adsorption is based on the reaction:



(d) The amount of silica adsorbed on all three minerals decreases in the order: fluorite > calcite > barite.

(e) The amount of silica adsorbed on barite, calcite and fluorite is independent of the ratio of sodium silicate used, as long as the sodium silicate solutions are at equilibrium.

(f) Carbonation of the barite and fluorite results in a decrease of the silica adsorption. It appears, therefore, that silicate and carbonate ions are competitors for the same surface sites. Carbonate concentration does not affect the adsorption of silica on calcite.

5. (a) The adsorption of silica reduces the abstraction of oleate but does not prevent it occurring. The increase of the negative charge and the decrease in solubility induced by the adsorption of silica accounts for the lower oleate abstraction in the presence of silica.

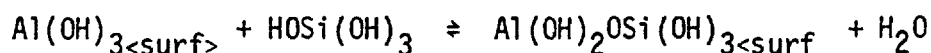
(b) Sodium silicate depresses the flotation of calcite with

oleic acid in the pH region 8 to 12. The flotation of barite and fluorite is depressed at pH values above 9 and below 7 but it remains unchanged in the pH region 7 to 9.

(c) Aged sodium silicate solutions produce slightly less depression than fresh ones in the alkaline region, but their effect in the acidic and neutral pH region is almost the same.

6. (a) The adsorption of aluminium species on calcite and barite is negligible at pH values above 9, where the $\text{Al}(\text{OH})_4^-$ anion predominates. It increases, however, below this pH value, where aluminium hydroxide precipitates. Precipitation of aluminium hydroxide occurs either on the surface or in solution followed by electrostatic adsorption on the surface.

(b) Aluminium and silica mutually enhance the adsorption of each other on barite and calcite. In the presence of aluminium and at pH values below 9 it is suggested that the adsorption of silica takes place on the aluminium hydroxy sites according to the scheme:



At pH values 9 - 11, adsorption of aluminium and silica proceeds through the formation of an aluminosilicate ion in solution which, subsequently, is adsorbed on the surface.

(c) The flotation of calcite and barite with oleic acid in the presence of both silica and aluminium is completely depressed at pH values below 10 but it increases considerably above this pH value. Aluminium has no effect on the flotation of fluorite.

(d) Flotation of fluorite or barite from calcite with oleic acid can be achieved at pH values 7 - 9 by the addition of sodium silicate alone. The presence of aluminium will further improve the separation of fluorite from calcite. Selectivity in the flotation of fluorite from a fluorite/barite mixture is feasible in the pH range 7 - 9 and in the presence

of both silica and aluminium. These conclusions, however, are based on tests conducted with each mineral separately. The presence of carbonate and fluoride species resulting from the dissolution of calcite and fluorite, respectively, and the effect of carbonation of the fluorite surface (carbonate) and complexing of aluminium in solution (fluoride) must be taken into account when a mixture of the minerals is considered.

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