THE SURFACE CHEMISTRY OF DIAMOND

A thesis submitted for the
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by

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"ANY SUFFICIENTLY ADVANCED TECHNOLOGY
IS INDISTINGUISHABLE FROM MAGIC"

Arthur C. Clarke

ABSTRACT

The physical properties, occurrence and recovery of diamond have been reviewed. The surface chemistry of carbons, and the methods available to determine surface groups have been discussed. A study has been made of the physical chemistry of the diamond/water interface, with respect to the possible recovery of diamond by froth flotation. The techniques used include contact angle measurement with air and heptane, zeta-potential determination, adsorption of hydroxyl ions, acid/base titrations of the surface, and infrared spectroscopy.

Two types of diamond samples were used in the contact angle studies, 'hydrophobic' and 'hydrophilic' natural diamond crystals. Diamond powder with a specific surface area of 8.0 m^2 g^{-1} was used in the zeta-potential and adsorption studies.

The air contact angle for 'hydrophobic' diamond was $25^{\circ} \pm 3^{\circ}$, and for 'hydrophilic' diamond $12^{\circ} \pm 2^{\circ}$. These values decreased to zero, after storing the diamond in water for several weeks. Drying the aged diamond at $120^{\circ}C$ did not increase the contact angle.

The zeta-potential of fresh diamond was dependent on pH, with an i.p. at pH 3.5. For aged diamond, the zeta-potential was markedly more negative, less dependent on pH, and there was no i.p. in the pH range 3 - 10.

Acid groups of various basicities were detected on diamond by titration with various bases; about 33% were carboxylic acid type. There was a net abstraction of hydroxyl ions over the pH range 3 - 10, by diamond, which was not affected by ageing.

Carbonyl groups were removed from the diamond surface, by reduction with sodium borohydride, which caused a marked

reduction in the adsorption of hydroxyl ions. Ionizable hydrogen was removed by methylation with diazomethane, which also caused a marked reduction in the adsorption of hydroxyl ions.

A cross-linking oxygen group was detected on the diamond surface by infrared spectroscopy. This group was removed by washing the diamond with 20% HF.

The adsorption of sodium dodecyl sulphate (SDS), dodecylamine (DDA), butylamine (BuA), benzylamine (BeA), oleic acid and dithiophosphates at the diamond/water interface was studied. SDS, DDA, BuA and BeA increased the contact angle of diamond, and caused a reversal of the zeta-potential, from negative to positive in the case of DDA and BuA, and from positive to negative for SDS. Oleic acid caused an increased negative zeta-potential, but reduced the contact angle slightly. Diethyldithiophosphate had no effect on the surface properties, but cresyl dithiophosphate increased the contact angle. The result for SDS and DDA are consistent with coulombic adsorption of surfactant ions, followed by further adsorption due to hydrophobic bonding between the hydrocarbon chains.

Metal ions (Cu^{2+} and Al^{3+}) caused a reversal of the zeta-potential from negative to positive on both fresh and aged diamond. The results are consistent with the adsorption of hydroxy complexes of the metal ions by diamond.

The possible application of froth flotation to the recovery of diamond has been discussed. The recovery of diamond directly from kimberlite by froth flotation is unlikely to be possible. However, diamond recovery from the heavy mineral concentrate may be feasible by froth flotation.

A model of the diamond surface has been developed. There are many features of the diamond/water system that are similar to the oxide/water system.

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CHAPTER 1. INTRODUCTION

1. INTRODUCTION

Diamond is the most sought after gemstone in the world, however very few natural diamonds are suitable for cutting into jewels. Less than one in ten diamonds recovered from kimberlite rocks are potential gems, and less than one in a million are of the "first water". Many diamonds find their way into humbler uses in industry, particularly as abrasives. The extraordinary properties of this material often make it the only viable substance for many important purposes. In recent years much research has been done on the interesting and sometimes, surprising, properties of diamond.

One major topic of research has been the growth of artificial diamonds. It is now possible to convert black carbon into diamond crystals, using very high pressures and temperatures, thus simulating the conditions for the creation of diamond in the earth's interior. Many diamonds less than 0.5 mm in size are now produced artificially. It is uneconomic to produce large diamonds artificially, as they can be recovered from the diamond deposits at sizes greater than 0.5 mm.

Coarse diamonds continue to be mined in a few areas of the world; southern Africa and the USSR are the two major producers. The first deposits that could be mined on a large industrial scale were found at Kimberley, in South Africa, about 100 years ago. Many more deposits have been subsequently found, including the alluvial deposits on the 'Diamond Coast' in South West Africa.

Diamonds from kimberlite rocks are generally hydrophobic, whereas alluvial diamonds tend to be hydrophilic. The reason for this difference is not known. In the last twenty years a great deal of research has been carried out on diamond processing, particularly the possible application of froth flotation to diamond recovery. It was hoped to recover diamond from kimberlite in one operation, at much finer sizes than are presently recovered.

Froth flotation is one of the most widely used mineral separation processes, due to the ease with which many mineral mixtures can be separated, by making one mineral hydrophobic, and thus floatable. In recent years very large flotation machines have been developed, which makes the process very attractive for handling the large tonnages of diamond bearing rock mined in the various operations throughout the world.

The majority of the testwork to date on the recovery of diamond by froth flotation, has consisted of batch flotation tests, using artificially seeded kimberlite suspensions. These have encountered many problems, particularly the sliming of the clay minerals that make up the kimberlite rock. The flotation response of diamond in the presence of various collectors was similar to that of kimberlite minerals, and so little selectivity has been obtained. Many reagents have been used in these studies, ranging from long chain cationic surfactants to short chain xanthates.

This research project is an investigation of the physical chemistry of the diamond/water interface. The information obtained should enable an accurate prediction of the viability of applying froth flotation to diamond recovery.

CHAPTER 2. PROPERTIES OF DIAMOND

2. PROPERTIES OF DIAMOND

2.1 Physical Properties

2.1.1 Crystal structure

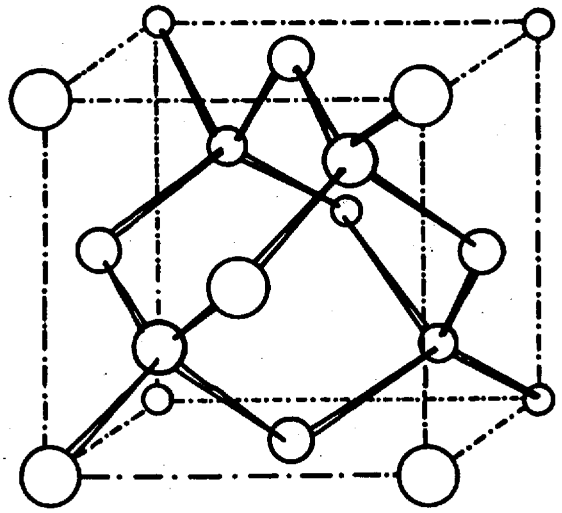
Diamond is one of the three naturally occuring crystalline forms of carbon, the other two being graphite and chaoite. The three crystal structures are shown in Figure 2.1.

Diamond has a cubic crystal system, in which the unit cell has a side length of 0.3567 nm. The covalent bond length between neighbouring carbon atoms is 0.1544 nm.

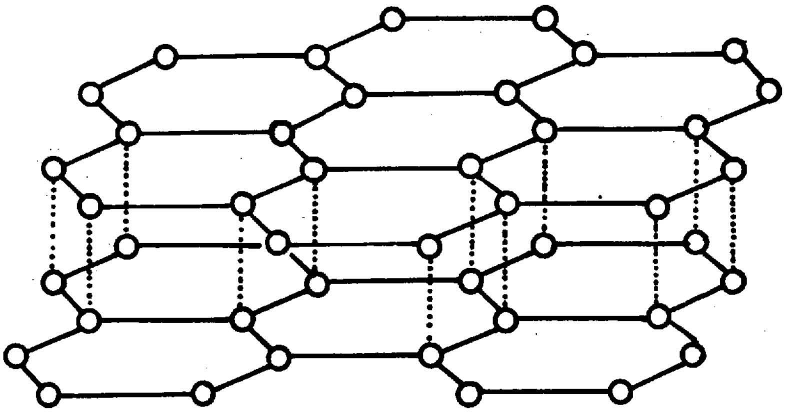
Graphite consists of plates, made up of six-membered carbon rings, held together by Van der Waal's forces. Chaoite has only been found in small quantities, always in association with graphite. This allotrope of carbon is thought to be formed by the action of pressure on graphite. The π-bonds in the graphite sheets are broken and carbon-carbon bonds are formed between adjacent sheets(1).

Natural diamonds generally occur as irregular fragments with curved faces. The most common regular crystal form is an octahedron, consisting of (111) faces; a twinned octahedron also occurs and forms a flat triangular crystal known as a macle. Dodecahedra with (110) and (111) faces, and cubes are also found. Carbonado is black diamond, which contains traces of graphite, and boart is an aggregate of small diamond fragments.

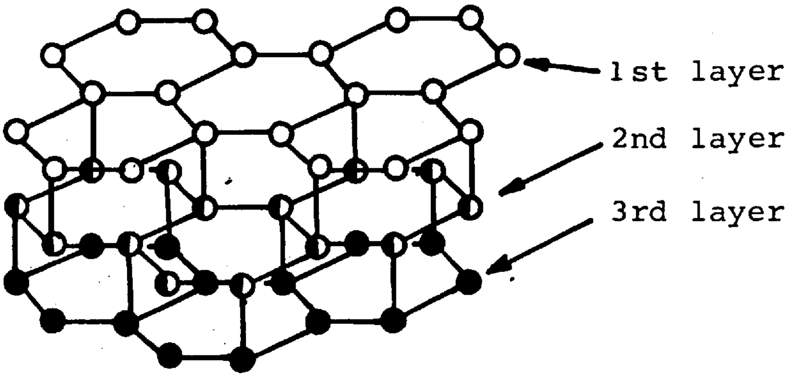
Large, well formed diamond crystals can now be grown artificially, by two methods. Non-diamond carbon can be converted into diamond crystals by applying very high pressures and temperatures(2). A vapour deposition process has also been developed employing low pressures and high temperatures. In this latter method, diamond carbon is grown on boron doped



Diamond



Graphite



Chaoite

Figure 2.1: Crystal structures of the three allotropes of carbon: Diamond, Graphite and Chaoite

natural diamond seed crystals, in an atmosphere consisting mainly of methane(3). Synthetic diamonds are very impure, containing up to 10% transition metal elements.

All diamonds contain small quantities of impurities, although these rarely exceed a few hundred parts per million; inclusions, however, are common in diamond.

2.1.2 Hardness

The strong covalently bonded crystal structure makes diamond the hardest naturally occurring substance. The hardnesses of all other materials are measured relative to that of diamond, which has a value of 10 on the Moh scale. Actual values of hardness show a large variation, depending on the method of measurement employed. Unlike silicon and germanium, which have similar isotropic crystal structures, diamond shows great anisotropy of hardness.

An idealized explanation of this surprising property has been proposed(4). The diamond surface is considered to consist of octahedral and tetrahedral blocks, thus octahedron faces would be smooth, whereas cube and dodecahedron faces would be jagged. It has also been suggested that surface defects and cleavage directions may be responsible for the anisotropy of hardness. This latter theory can be illustrated by consideration of the dodecahedron plane, as shown in Figure 2.2. Projected on this plane are the first four layers of atoms adjacent to an octahedron plane, with the broken lines indicating one set of cleavage planes running through the surface. The hardness will change depending on whether the determinative technique moves from left to right, or vice versa. If an attempt is made to remove a piece of material bounded by the cleavage planes in the direction ab, the block will tend to jam in, whereas in the opposite direction, it will tend to slide out.

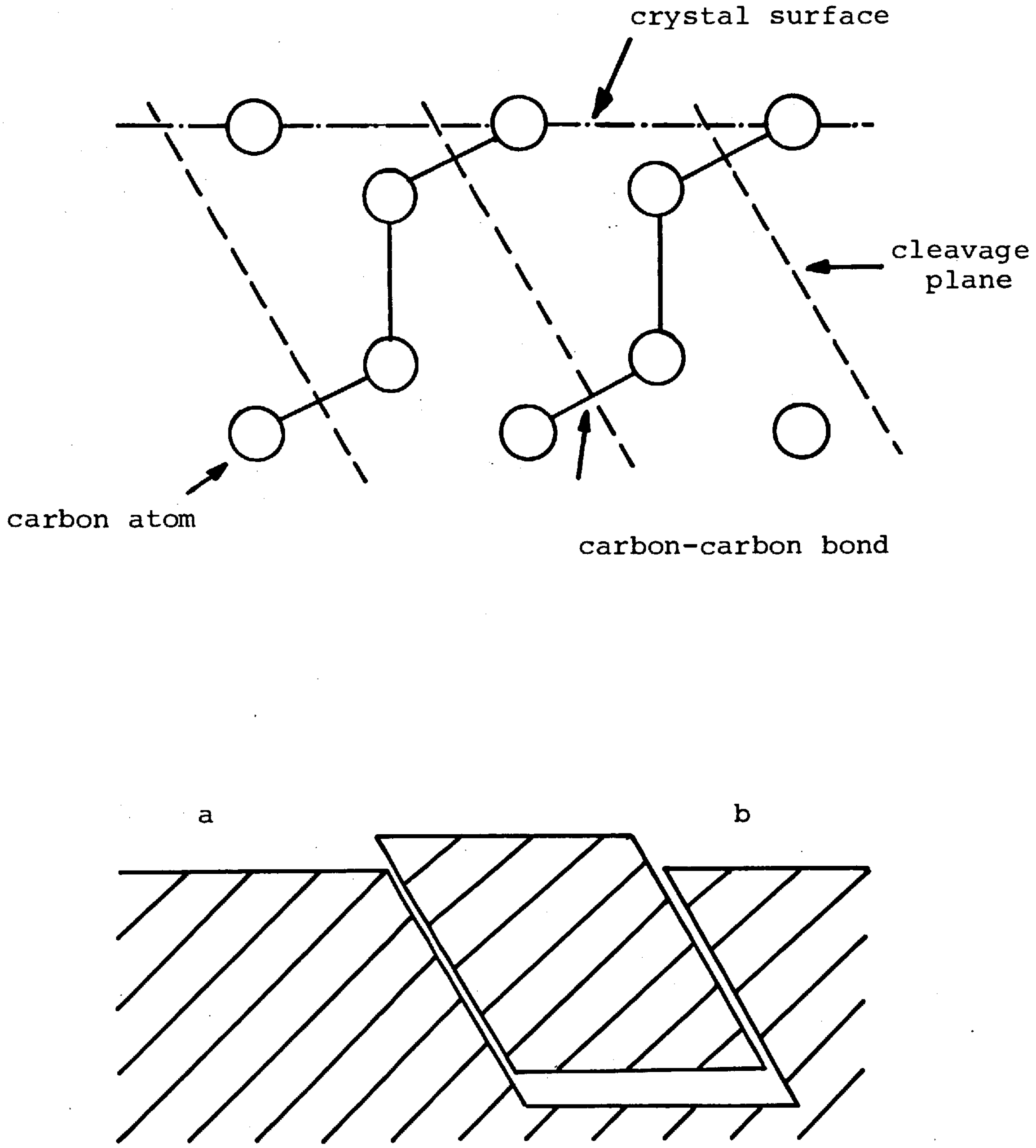


Figure 2.2: Cleavage of an octahedral (111) face of diamond

Diamond hardness can be measured most accurately by an indentation technique. The value obtained on various faces is of the order of 10^{10} Nm^{-2} (5). Although diamond is very hard, it is also very brittle, and diamonds are easily fractured.

2.1.3 Optical properties

Diamond is very attractive as a gem stone due to two optical properties, which give properly cut crystals a 'fire'(6). The high refractive index (2.417 at 589 nm) implies a low angle of total internal reflection, and the high dispersion causes colour changes in the reflected light when the crystal is moved by small amounts. Certain diamonds show colouration due to low intensity absorption bands in the visible region (400 - 700 nm).

Diamonds can be divided into two types on the basis of their light absorption properties (7). By this broad classification, 96% of natural diamonds are type I, showing continuous absorption to radiation of wavelengths shorter than 330 nm, with an absorption peak at 7.8 µm in the infrared region of the electromagnetic spectrum. The rarer type II diamonds have the continuous absorption edge at 220 nm, and they have no marked absorption peaks in the infrared. Diamonds with intermediate properties are not uncommon, thus emphasising that this classification system is somewhat imprecise.

Type I diamonds can be further subdivided by absorption in the infrared, and type II by conduction properties(8)(9). The spectral data for type I diamonds are presented in Table 2.1.

These absorption phenomena are not present in type II diamonds. A relationship has been found between nitrogen content and the intensity of the 7.8 µm peak(10), but none of the other peaks have been adequately explained.

Table 2.1 Spectral data of type I diamonds

	I_a	I_b
Infrared peaks (μm)	7.8, 8.3, 9.1, 20.8	7.0, 7.3, 7.5, 8.5, 10.0, 12.9, 30.5
u.v. absorption edge (nm)	306.5	415

The adsorption edge in type II diamonds at 220 nm, is equivalent to the fundamental absorption edge for electronic transistions from the valence band to the conduction band(9); thus it is thought that type II diamonds are the most chemically pure, and have a near-perfect crystal structure. The shift of the edge to 330 nm in type I diamonds, has been attributed to defects in the lattice, allowing energy levels within the energy gap. Further evidence of defects in type I diamonds can be obtained from consideration of the 7.8 μm line. Single photon absorption corresponding to this line is forbidden by the symmetry of the ideal diamond lattice(11). Imperfections in the lattice are thought to provide a local coupling between the fundamental frequency and the radiation field. Type IIb diamonds often have a blue colouration due to the tail of the infrared absorption spectrum associated with boron present in the lattice(12).

As diamond has a cubic crystal system, it should be isotropic, but this is only true when the lattice is unstrained. Many natural diamonds show strain bands, which generally have no effect on the quality of the stones, but they can make shaping difficult. Diamond can be annealed by heating to 1600°C under pressure.

Fluorescence of diamonds has been widely studied particularly spectra excited by 365 nm radiation(13). The spectra suggest that the principal lines are due to electronic transitions, and that the ancillary lines arise out of an interaction between the electronic states and lattice vibrations. The spectra are very sensitive to temperature changes, especially with respect to the half-width of the component lines. There is, however, a marked difference in temperature sensitivity between types I and II diamonds. The fluorescence intensity increases by up to 150% when type II diamonds are cooled from 290°K to 80°K, but the same cooling causes only a 30% increase in the fluorescence of type I diamonds. This difference is thought to be due to the different forms of emission centre present in each diamond type.

Diamonds frequently exhibit a yellow phosphorescence after a blue or green fluorescence, This spectrum is usually similar to the fluorescence spectrum. Type I diamonds show a general emission spectrum (2 - 3 eV), whereas type II diamonds have only one strong peak (2eV).

X-rays excite fluorescence from diamonds, but there are no features of these spectra which are unique to diamond.

2.1.4 Conduction properties

Type IIb diamonds are p-type semiconductors with a resistivity of 100 ohm-cm, and exceptionally even lower. All other types of diamond are, however, insulators with resistivity values of 5×10^{14} ohm-cm.

All diamonds are good conductors of heat, for example, a type IIa diamond will conduct heat five times better than copper at room temperature. This property, combined with its hardness makes diamond unique as an abrasive. The high thermal conductivity prevents decomposition and fracture at the cutting point of a diamond tool.

Table 2.2 Variation of thermal conductivity of diamond with temperature(14)

20°C	Type I	9 watt degC cm^{-1}
	Type IIa	26 watt degC cm^{-1}
	Cu	4 watt degC cm^{-1}
	SiC	4 watt degC cm^{-1}
-190°C	Type I	24 watt degC cm^{-1}
	Type IIa	120 watt degC cm^{-1}
	SiC	50 watt degC cm^{-1}

2.1.5 Surface defects

Natural diamond surfaces show many imperfections but the two most common ones are trigons and ring cracks. Trigons only occur on (111) crystal faces, whereas ring cracks can be found on all faces, but especially on alluvial diamonds.

Trigons are triangular indentations, orientated in the opposite direction to the triangular face on which they occur. This is termed a negative orientation. They are pyramidal or flat-bottomed, with either steep or shallow sloping sides. Their depth can vary from a few nm to a few μm, whilst their sides are 10 - 150 μm long. There are two theories for their origin, Tolansky suggested that they were growth defects(15), whereas Evans implied that they were etch pits(16). Tolansky has shown that etching, by various methods, produced positively orientated triangular pits with rounded corners. Evans, however showed that oxidation with wet oxygen above 1000°C gave negatively orientated etch pits. Neither theory has been conclusively proved, although the evidence obtained by Tolansky outweighs that obtained by Evans(17)(18).

Ring cracks, the other naturally occurring surface defect, are known to be caused by the impact of sharp objects on diamond surfaces(5). They are found in the greatest abundance on the surfaces of diamonds from coastal deposits, and they can take the form of half-moons or complete circles.

A number of phenomena have been observed on the surfaces of variously etched diamonds. Dodecahedral faces etched with fused KNO_3 at 450°C, showed two different forms of network. In one case a network aligned in the directions of the rhomb of the dodecahedral face was formed, which consisted of ridges bounding shallow cups about 10 nm deep. The other form was an irregular group of ruts, which were thought to be etch effects. The orientated networks were considered to be growth defects.

2.2 Chemical Properties

2.2.1 Chemical composition

Almost all the stable elements in the periodic table have been found in diamond, but the most common are nitrogen, aluminium, boron and silicon(19).

Nitrogen has been found in concentrations of up to 0.23%, either spread randomly through the lattice, or as aggregates or platelets(20). As nitrogen has one more electron than carbon, it must act as an electron donor, when it substitutes for carbon in the diamond lattice. The donation, however, cannot occur simply in diamond, and in general, the electron is shared between the nitrogen atom and only one of the neighbouring carbon atoms. Quantitative paramagnetic studies have shown that only a small fraction of the nitrogen, present in diamond, exists as singly bound atoms(21). X-ray diffraction patterns have shown anomalous spikes, which, coupled with other evidence, have shown that some nitrogen is present as plates parallel to the (100) plane. In this latter configuration, the electron donated by nitrogen can resonate between many bonds.

Aluminium and boron, both group III elements, are able to substitute for carbon by using sp^3 orbital hybrids, to form tetrahedral bonds with neighbouring carbon atoms. There is one electron too few to fill the lattice requirements, but the hole created can stay localized on the substitution centre, as the ionization potentials of aluminium and boron are several eV lower than that of carbon. One of the bonds takes on a different length, and the hole is shared between the heteroatom and the preferred carbon.

Silicon is a group IV element, and therefore can substitute isoelectronically into the diamond lattice, but because of its larger size, the crystal structure becomes mechanically strained.

2.2.2 Chemical reactivity

Diamond is very inert, but, if heated in air, oxidation occurs at temperatures above 650°C, with an activation energy of 40 kcal $mole^{-1}$ (22). Above 400°C chemisorption of both oxygen and hydrogen has been observed(23). Graphite is formed if diamond is heated in a vacuum above 1700°C, and at tempertures between 800 and 1700°C surface graphitization occurs by an oxidation mechanism.

$$\underset{\text{DIAMOND}}{2C} + O_2 \rightleftharpoons \underset{\text{(surface complex)}}{2(CO)} \qquad (1)$$

$$(CO) + CO \longrightarrow CO_2 + \underset{\text{GRAPHITE}}{C} \qquad (2)$$

Carbon is soluble in many transition metals. Wetting studies with melts of these metals have shown that strong chemical bonds are formed at the metal/diamond interface, due to the formation of either a binary alloy (e.g. Fe, Co, Mn, Cr), or a carbide (e.g. W, Ta, Ti)(24).

Diamond is not attacked by any known acid, but it can be etched by certain fused salts.

2.2.3 Surface chemistry

Cleavage of diamond results in the fracture of covalent bonds, leaving the new surface covered with unsaturated, or 'dangling' bonds(25). Electron spin resonance measurements on diamonds crushed in inert atmospheres of nitrogen and argon have shown, however, that only 1 in 1000 of the surface atoms possesses a dangling bond(26). Similar results have been obtained on fine diamond powders, outgassed at 950°C in a vacuum of 10^{-6} torr(27).

Three low energy electron diffraction studies (LEED) have been carried out on diamond(28)(29)(30), but no agreement has been reached about the mechanisms or conditions required for surface reconstruction. Electron spectroscopy for chemical analysis (ESCA) has also been used to study diamond surfaces(31). As both these techniques involve approximately the same penetration into the surface (10 Å), it is therefore useful to compare the results of the studies.

The cleaning techniques employed have varied widely from study to study. The latest LEED study(30) used mineral acid washes, followed by outgassing at high temperatures, whereas other more violent techniques were used by the earlier workers(28)(29). Lurie and Wilson(30) are critical of surface cleaning by ion-bombardment, as extensive annealing is required to reconstruct the surface. All authors, however, did observe some surface reconstruction during their experiments. The structure of this reconstructed surface has not been determined but a benzene-ring type structure seems the most appropriate.

There is considerable disagreement about the temperature at which surface graphitization occurs. Marsh and Farnsworth(28) reported graphitization at 450°C, but the other authors heated their samples to temperatures in excess of 1000°C without any graphitization occurring. Lurie and Wilson(30) suggest that the low temperature of graphitization obtained by Marsh and Farnsworth was due to impurities present in the system. Oxygen catalyses the conversion of diamond to graphite, by the formation of surface oxide complexes.

Gaseous adsorption was found to occur very slowly, unless some excited species was used, for example microwave discharge oxygen, which contains both atomic and molecular forms of oxygen(31). These results are contradictory to those obtained by less sensitive techniques(27)(32)(33). Boehm(32), in particular, reported that surface oxides were always formed when outgassed diamond samples were brought into contact with oxygen. Hydrogen is adsorbed by diamond at temperatures above 400°C (23). LEED studies have shown that after outgassing hydrogenated diamond, a diffraction pattern equivalent to the bulk compound was obtained, indicating that the surface carbon atoms had been removed(30).

There is also disagreement about the effect that mineral acids have on diamond surfaces. LEED showed that some chemisorbed chlorine could be found after cleaning a diamond with hydrochloric acid(30), whereas ESCA showed an increased oxygen content, but no anion from the acids used(31). This difference may be due to the different initial cleaning techniques, as the ESCA diamond was argon-ion bombarded, whereas the LEED diamond was polished with diamond paste on a selvyt cloth.

The discrepancies between these studies show that a reproducible diamond surface is very difficult to obtain.

CHAPTER 3. THE RECOVERY OF DIAMOND FROM KIMBERLITE

3. THE RECOVERY OF DIAMOND FROM KIMBERLITE

3.1 Geology of Diamonds

Natural diamonds occur in two types of deposit, volcanic pipes and alluvial deposits. The volcanic pipes are composed of kimberlite a primary igneous ultrabasic rock. There is considerable controversy as to whether kimberlite was the point of origin of the diamonds, or whether it was purely a transporting medium from the magma(34). Diamonds are not only found dispersed throughout the pipe, but also as inclusions in xenoliths, which are pieces of the lower crust and upper mantle. These latter diamonds are nearly always sharp edged octahedra, showing that they were formed at great depth. Until recently, there was some controvery about the existence of a kimberlite magma. The wall rocks of most South African pipes show no thermal alteration, and the kimberlite is undoubtedly a fragmental rock. These pipes are thought to have arisen as a cold fluidized mass from a depth in excess of 150 km. Kimberlite dykes and sills, found elsewhere, have given rise to thermal alteration of wall rocks, and some autoliths have been found in these rocks, thus conclusively proving the existence of a kimberlite magma.

There are two anomalies concerning kimberlite pipes which need some explanation. Namely, how were large, heavy mineral xenoliths transported upwards, and how did the diamonds survive in the molten magma? The first point can be explained by assuming a very fast rate of ascent of the magma, but the second question can only be answered by consideration of the initial magma composition. Isotopic analysis has shown that the water present in kimberlites is high level ground water, thus the diamond could not be etched by the kimberlite. This coupled with the high rate of ascent, would allow for diamond occurrence, although well outside its region of stability.

The major minerals occurring in kimberlites are olivine, serpentine, mica, diopside, garnet ilmenite and zircon.

The second type of deposit, the alluvial deposit, is the result of the weathering of pipes. Most diamond bearing pipes appear to have been formed in the Late Cretaceous period, some 70 million years ago. There are many types of alluvial deposit, including rewashed gravels derived from the exposed surface of the pipe, and deposited close to the pipe, and the secondary deposits, in which the diamonds have been transported, probably by water, many hundreds of miles before being deposited along river beds or marine terraces.

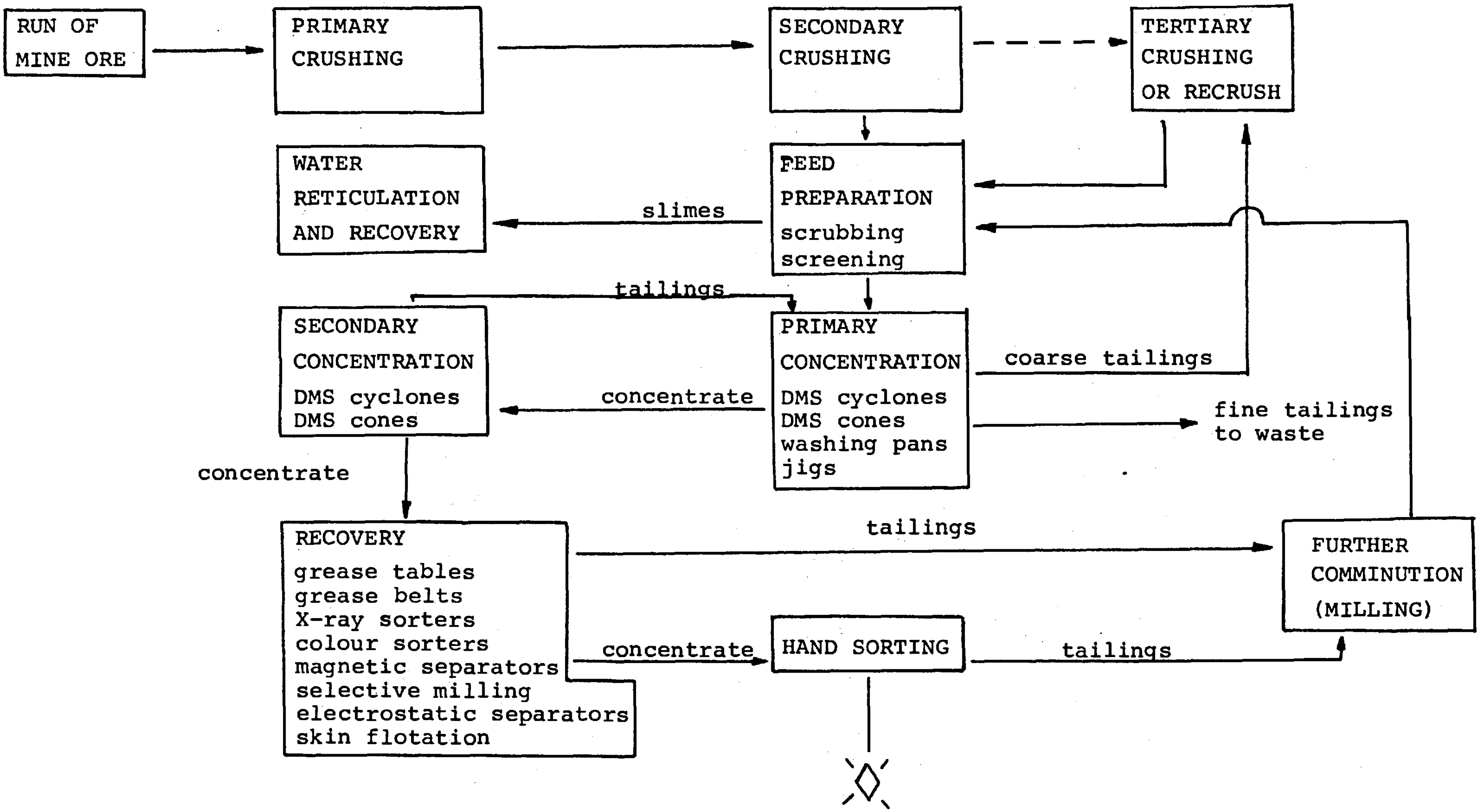
3.2 Concentration of Diamonds

A rich diamond deposit may contain 0.2 ppm diamond, whereas poorer deposits may have concentrations of diamond an order of magnitude lower. Even though the value of individual stones may be high, the overall value of the run of mine ore is extremely low. Thus, the concentration process must be as cheap as possible. A generalized flowsheet for diamond recovery is presented in Figure 3.1(35).

The run of mine ore is crushed down to -40 mm in two stages. The choice of the top size is controlled by the possibility of finding very large diamonds. Recently, plant has been installed at one mine to screen the run of mine ore for diamonds up to 75 mm in size. Liberation of small diamonds from the kimberlite matrix is a great problem. On many mines, this is achieved simply by allowing the soft kimberlite to break up in the primary concentration process.

The crushed ore is then sieved into various size fractions, which are fed into the primary concentration process. As diamond has a higher specific gravity than most of the minerals in kimberlite, a gravity separation process is

Fig. 3.1: GENERALISED FLOWSHEET FOR DIAMOND RECOVERY



invariably the first concentration stage. Many techniques are used, the most modern plants employ dense media separation, whereas the older plants use jigs and washing pans. The heavy mineral concentrate from these processes, is fed to a second gravity concentration process, whilst the coarse tailings are recrushed and reseparated, and the fine tailings are dumped.

The second gravity concentration process is always a dense medium separation process. The concentrate from this is fed into the final diamond recovery plant, and the tailings are recirculated to the primary separation process.

The final recovery methods in common use today are X-ray sorting and grease belt recovery. Diamond fluoresces from X-ray excitation, whereas the other commonly occurring heavy minerals do not, and this provides, therefore, a good method for recovering diamonds. The grease belts collect the hydrophobic diamonds, by trapping them on the sticky surface and the hydrophilic minerals are washed over the surface with water.

Final sorting of diamond into various classes is done by hand in one of the big diamond trading centres.

3.3 Flotation of Diamond

During the last 20 years, a great number of laboratory batch flotation tests of diamond have been performed by research organisations in South Africa and the U.S.S.R. Many of the results have been contradictory, and little knowledge of the flotation response of diamond has been acquired. A review of a great deal of work was published internally for De Beers Diamond Research Laboratory(36).

Many tests showed that diamonds less than 1 mm in size could be floated, but with little selectivity. A variety of reagents have been used by various workers, and the most successful results have been obtained with cationic, amine type, reagents. These reagents, however, also floated many of the minerals in the kimberlite rocks. Successful diamond flotation has also been obtained with aryl dithiophosphates, a group of oily liquids, but again no selectivity was obtained, as, presumably, this reagent was indiscriminately smeared over all the minerals.

The Russians are reported to have used a form of electro-flotation to concentrate fine diamonds during the assay of ore bodies(37). The costs of this process are prohibitive, and it has never been tried in the West. They have also reported some success in separating diamond from kimberlite, by using froth separation, in which a dewatered mineral mixture is dropped through a froth bed.

Thus, although diamond has been recovered by a surface sensitive technique, the grease table, for over a century, and there has been twenty years of research on the flotation of diamond, the reason why some diamonds are hydrophobic, and the others hydrophilic is still not known. Furthermore, knowledge of how the wettability of diamond can be controlled is sparse. According to the classification system of Gaudin, Miaw and Spedden(25), a fractured diamond surface should be hydrophilic due to the presence of numerous dangling bonds. LEED, however has shown that some surface rearrangement can occur(30), and only about 1 in 1000 of the surface atoms has a dangling bond(26). Alluvial diamonds are hydrophilic, as is an anomalous proportion of diamonds from the Finsch mine. No attempts have been made, however, to explain these anomalies.

The objectives of this work were to study the surface chemistry of the diamond/water interface, and to determine how the wettability of diamond could be controlled. The studies involved measurement of acid-base properties, electrical double-layer characteristics and wettability of diamond, after various surface treatments. Attempts were made to relate the changes in these properties with the proportions of different groups of the diamond surface. The wettability of diamond in the presence and absence of surfactants was compared to that of silica and silicates, and the viability of a flotation process for the recovery of diamond from kimberlite was considered.

CHAPTER 4. THE SURFACE CHEMISTRY OF CARBON

4. THE SURFACE CHEMISTRY OF CARBON

The adsorption of many substances onto pure carbons has been studies in great detail. In the 1930's Barrer(23) studied the kinetics of chemisorption of oxygen on carbons, including diamond. More recently Walker and his co-workers have extended these studies(33). Above 0°C the adsorption of oxygen was found to be purely chemical, whereas below -75°C it was predominantly physical. The activation energy for chemisorption of oxygen was found to increase linearly with temperature, with increasing oxygen coverage. The adsorption of gases other than oxygen is controlled by the proportions of various oxygen groups on the diamond surface.

A great amount of research has been done on the adsorptive properties of outgassed carbons(27)(38)(39), but very little is known about natural surfaces. The adsorption properties of the various carbons are related to the carbon-carbon spacing on the surface. Adsorption of gases on graphitic carbons has been found to occur in two distinct phases(38)(39). At low pressures (<0.01 torr), adsorption occurs onto an array of high energy sites, which are carbon atoms located in the prism faces; and at higher pressures, further adsorption takes place on lower energy sites, composed of carbon atoms in the basal planes. Diamond, however, shows no such discontinuity in the adsorption of gases, and simple Langmuir adsorption isotherms have always been observed(22)(33)(38).

Carbons are good adsorbents of many organic compounds, and consequently they are widely used to extract impurities from aqueous solution. An outgassed carbon surface is hydrophobic(27), and it has been shown that the adsorption of surfactants from aqueous solution increases with increasing outgassing temperature(40). The mechanism of adsorption is one of hydrophobic bonding of the hydrocarbon chains to the carbon surface, displacing the water molecules. Oxidised carbons do not adsorb as much surfactant as purer carbon surfaces, and they are hydrophilic. The surface oxygen groups interact with the polar water molecules, and probably become partially ionized.

4.1 Surface Groups on Carbon

There are many different types of groups present on a carbon surface, and they have been reviewed by Puri(41). The most important types of these groups are the carbon-oxygen complexes, which give rise to most of the surface properties of the various carbons. The structures of many of the carbon-oxygen complexes have not been determined, and they are frequently referred to as carbon monoxide or dioxide surface complexes. Examples of simple functional groups that have been identified on carbon surfaces are: carbonyl, cross-linking oxygen (ether-like), carboxylic acid, alcohol, phenol, quinone, lactone, chromene and hydroquinone groups. There have been many attempts to determine one or more of these groups on various carbons(27)(42-48).

The effect of the various groups on the surface properties of carbon has also been widely studied, by removing or complexing certain groups with specific reagents.

4.1.1 Techniques for the determination of surface groups on diamond.

A wide variety of techniques have been used to study surface groups on different carbons. In this project the wettability, electrical and adsorption properties of diamond were studied before and after certain reactions which are known to remove or complex oxide groups on carbon surfaces. In addition, infrared spectroscopy was used to attempt to monitor the change in proportion of the different oxide complexes, on the diamond surface, caused by these reactions.

4.1.1.1 Infrared spectroscopy

Infrared spectroscopy is useful for a qualitative determination of some specific functional groups on carbon surfaces. The background absorbance of a carbon substrate is, in general, too high, however, to allow detailed spectra to be obtained.

It is generally agreed that any spectral lines obtained from a carbon powder are attributable to surface groups only, and that no bulk absorbance effects are seen(49). Two methods for measuring the infrared spectra of solids have been used with equal success. The powders can be finely ground, then mixed with an inert ionic solid, such as KBr, and formed into a disc; or dispersed in a mull. The former technique was chosen for the study of the diamond surface.

The most commonly reported group by this technique is the cross-linking oxygen, which has a very strong absorbance band at 9.18 μm(49), alcohol and carbonyl groups have also been detected(27). Evidence of fluorine and chlorine has been obtained in infrared spectra(27), but ESCA is a much more sensitive technique for the determination of heteroelements on surfaces(31).

4.1.1.2 Acid/base titrations

Carbons are said to be either acidic or basic, depending on whether they consume alkali or acid. This property depends on the temperature used to 'activate' the particular carbon. Generally those carbons activated below 700°C are acidic, and those activated above 900°C basic. There is no definite temperature range, however, within which activation results in the exclusive development of one characteristic.

The degree of alkalinity or acidity of a carbon can be determined by a titration method. Two techniques have been used to determine these values, and they involve either a direct titration of acid or alkali against a strong base, followed by a repeat titration in the presence of the carbon solid. Both these techniques were used in this work to study the acidity of diamond.

Acids and bases of different strengths have been used to determine the proportion of various groups on carbon surfaces. However, identification of functional groups by this method is difficult, because it is unlikely that a functional group on a carbon surface will have the same ionization characteristics as the equivalent bulk compound.

A more useful technique is that of reacting the carbon with a complexing reagent prior to a titration. A comparison of the titration results from treated and untreated carbon allows conclusions to be made about the functional groups responsible for the various degrees of acidity of carbons(42)(43)(45)(47). The presence of carboxylic acid, phenolic and hydroquinone groups has been shown by this latter method.

4.1.1.3 Methylation of carbon surfaces

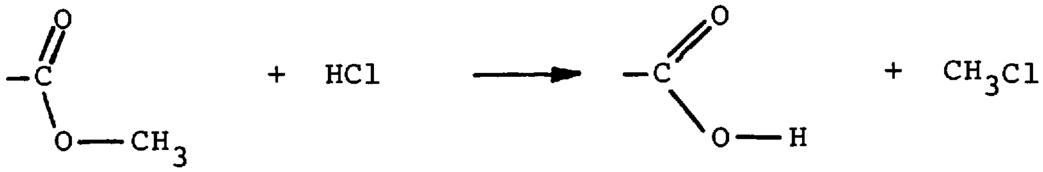
One of the most useful complexing reactions for a study of carbon surface is the methylation of hydroxyl groups. Diazomethane (CH_2N_2) is a very powerful methylating agent, and it will react with any ionizable hydrogen on a carbon surface(41). The general reaction for methylation by diazomethane is shown below(50).

$$\Vert\!-\mathrm{H}^* \quad + \quad \mathrm{CH_2N_2} \longrightarrow \Vert\!-\mathrm{CH_3} \quad + \quad \mathrm{N_2} \qquad (1)$$

A hydrogen atom which can ionize from a carbon surface is known as 'active hydrogen' and can originate in many groups. The major groups containing active hydrogen, that have been identified on carbon surfaces, are phenol, carboxylic acid, lactone, chromene and hydroquinone groups. Apart from the methylation of active hydrogen, there are other possible reactions between carbon surfaces and diazomethene, which result in the uptake of nitrogen, but these do not interfere with the methylation of hydroxyl and other groups(4).

Two types of methyl group, referred to as hydrolysable and non-hydrolysable, are formed by this reaction. Hydrolysable, in this context, refers to the breaking of the methyl-surface link by reaction with hot dilute hydrochloric acid. The hydrolysable groups generally arise from methylated hydroxyl groups with are adjacent to a carbonyl group.

(2)



(3)

Equations (2) and (3) show the methylation and hydrolysis of a carboxylic acid group.

Diazomethane has not been used as a reagent for the quantitative determination of active hydrogen,but by performing an acid/base titration on a carbon powder, before and after methylation, the role of active hydrogen in the acid/base properties of carbons has been determined(42)(45). Furthermore, by hydrolysing the carbon sample and retitrating, an indication of the active hydrogen present as strongly acidic groups has been obtained.

These techniques have not been used widely on diamond, and so the effect of methylation on the surface properties of diamond was studied in this project.

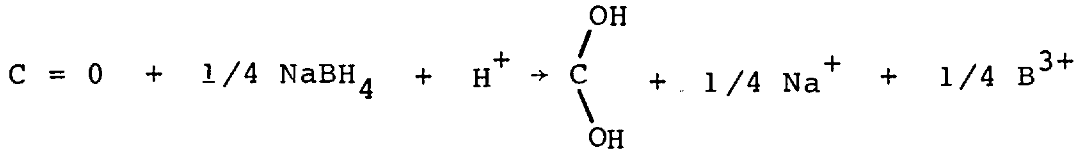
4.1.1.4 Oxidation and reduction of carbon surface groups

Oxidation of natural carbons occurs readily, because most functional groups on carbon surfaces are unstable$^{(41)}$. Reaction with aqueous solutions of reagents such as potassium permanganate, potassium dichromate and concentrated nitric acid, produces a hydrophilic acidic carbon, partially covered with carboxylic acid and phenolic groups, with the evolution of carbon dioxide. However, little information about carbon surface groups has been obtained from the oxidation of carbons, because the reactions are not selective. Treatment of diamond surfaces with microwave discharge oxygen and concentrated solutions of halogen acids increases the surface coverage by oxygen$^{(31)}$.

A study of the effect of oxidizing agents on the wettability of diamond was included in this work, as it had been demonstrated previously that oxidation affects the wettability of carbons$^{(27)(51)}$. The reduction of diamond surfaces was thought to be much more useful as some groups can be selectively removed.

The acid/base properties of carbons are thought to be mainly due to the influence of carbonyl groups, present as part of quinone, lactone and chromene functional groups on the surface$^{(41)(45)}$. Carbonyl groups are strongly polar, and by weakening the oxygen-hydrogen bond in neighbouring alcohol groups, they can lead to the formation of active hydrogen.

The reduction of carbonyl groups, in organic compounds, by reduction with lithium aluminium hydride ($LiAlH_4$) or sodium borohydride ($NaBH_4$) is well known, and these reagents have also been used in the study of carbon surfaces$^{(41)(43)(46)}$. Sodium borohydride, the weaker of the two reagents, has an affinity for carbonyl groups, reducing them to secondary alcohol groups, as shown in equation (4) below,



$$C = 0 + 1/4\ NaBH_4 + H^+ \rightarrow \overset{OH}{\underset{OH}{C}} + 1/4\ Na^+ + 1/4\ B^{3+}$$

(4)

There is, however, some evidence to suggest that the carbonyl groups are partially quinoid in character, as the following reaction has been observed with carbons(41)(43).

$$C = 0 + 1/4\ NaBH_4 + 1/2H_2O \rightarrow C - OH + 1/4\ NaBO_2 + 1/2\ H_2$$

(5)

Consideration of these reactions indicates that, by conducting acid/base titrations on diamond powder, before and after reduction with sodium borohydride, the effect of carbonyl groups on the acid/base properties of diamonds can be determined.

4.2 The Diamond/Water Interface

4.2.1 Wettability

Many diamonds are recovered on grease belts or tables. Hydrophobic diamonds adhere to the grease, whereas hydrophilic diamonds and minerals are carried over the surface by water. To prevent losses of hydrophilic diamonds, it is necessary to make them selectively hydrophobic, while keeping the other minerals hydrophilic.

The degree of hydrophobicity of a substance can be conveniently represented by the contact angle at the three phase line, solid/water/gas. This phenomenon has been described by Young(52), and it is illustrated in Figure 4.1.

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \qquad (1)$$

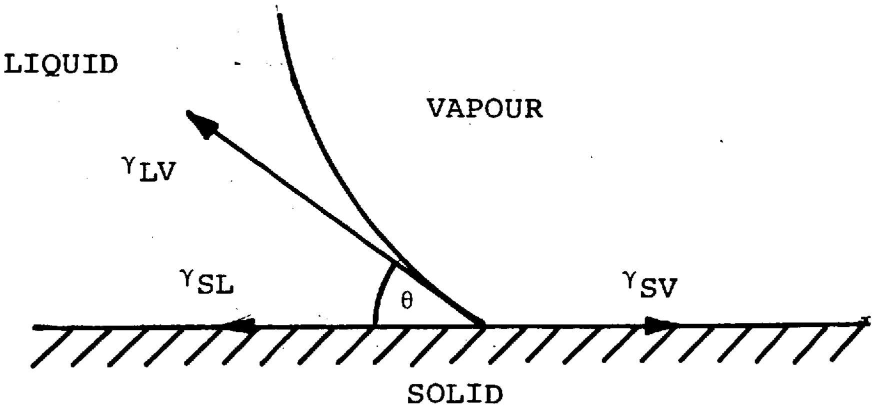


Figure 4.1: Contact angle at the three phase-line solid/liquid/vapour.

where: γ_{SV}, γ_{SL} and γ_{LV} are the interfacial tensions of the solid/vapour, solid/liquid and liquid/vapour interfaces,
and θ is the contact angle, measured through the liquid phase.

By replacing γ_{SV} and γ_{SL}, which are immeasurable, with the work of adhesion at the solid/liquid interface (W_{ad}), a practical relationship can be obtained.

Thus,

$$W_{ad} = \gamma_{LV} + \gamma_{SV} - \gamma_{SL} \qquad (2)$$

by simple substitution in equation (1)

$$W_{ad} = (1 + \cos\theta)\gamma_{LV} \qquad (3)$$

Therefore, if $\theta = 180^{\circ}$, i.e. the solid is not wetted, then $W_{ad} = 0$, conversely if the work of adhesion is to be maximized, then for a given γ_{LV} value, θ must be as small as possible. This approach is purely qualitative, but it is useful to obtain an approximation of wettability in a particular system.

The thermodynamics of the Young equation is very complicated, and it has never been verified experimentally, satisfactorily(53). The vertical component of γ_{LV} is ignored for treatments of solid systems. However, on soft substances raised ridges have been observed(54), and surface stresses must be present in rigid solids. If the three phase line is of molecular dimension, then the vertical component of γ_{LV} could induce stresses approaching the yield point of the most rigid solids. The contact angle, in that case, would be determined by the balance of surface stresses, rather than free energies.

Another approach to the theory of wettability has been discussed, involving the consideration of the spreading coefficient of liquid on solid, $S_{L/S}$. Thus,

$$S_{L/S} = \gamma_{SV} - \gamma_{LV} - \gamma_{SL} \qquad (4)$$

when there is a finite contact angle.

For spreading to occur $S_{L/S}$ should be positive, thus, γ_{SV} must be maximised, while γ_{LV} and γ_{SL} are minimised. There are many substances that change one of the interfacial tensions suitably, but very few reagents alter the overall value of the spreading coefficient for a particular system.

Hysteresis between advancing and receding contact angles has been observed frequently during contact angle studies. Three contributory factors have been suggested to explain this phenomenon.

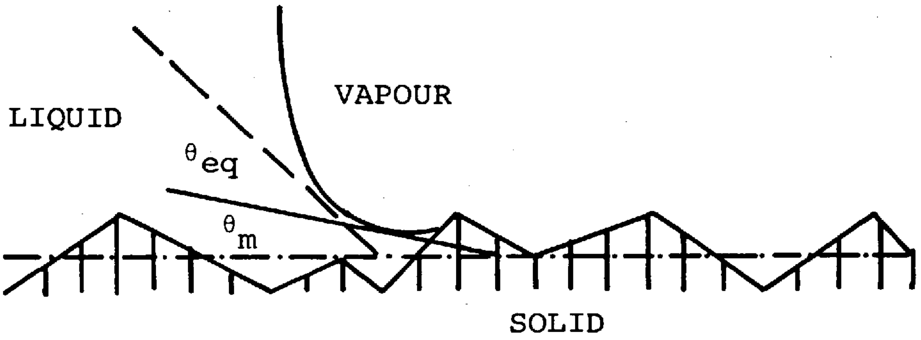
Firstly, contamination of either the solid surface or the liquid could cause a difference between the advancing and receding contact angles. Surfactant contamination in the water would concentrate at the air/water interface, and, as the bubble was advanced over the solid surface, a film might be deposited on the solid. When the bubble was retracted, the contamination might not be removed, and the receding contact angle would be different from the advancing contact angle.

A second cause of hysteresis is surface roughness. Although the contact angle at the three phase line of contact may be at its equilibrium value, sufficient spreading of the bubble across the surface might not occur, to allow the measurable contact angle to be the equilibrium value. Thus, the advancing contact angle on a rough surface will generally be lower than the equilibrium value, and the receding contact angle will be higher than the equilibrium value. This is shown in an exagerated form in Figure 4.2.

Surface immobility is thought to be the third reason for

θ_{eq} = equilibrium value for the contact angle

θ_m = measured value for the contact angle



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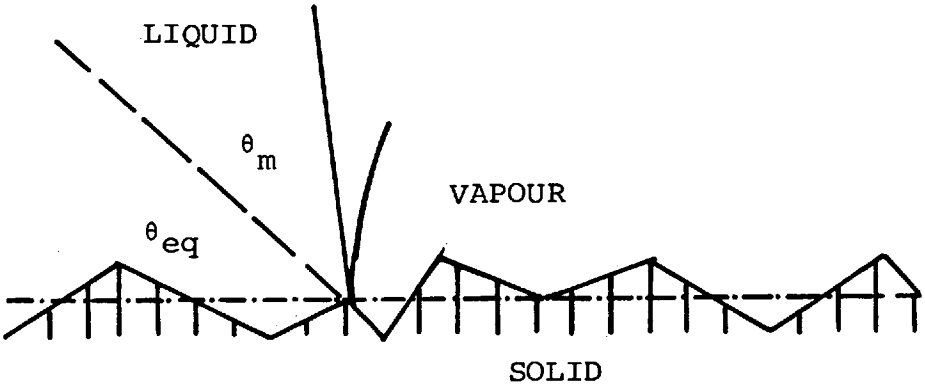


RECEDING

Figure 4.2: Effect of surface roughness on contact angle

hysteresis, but this idea cannot be generally applied to rigid solid systems. The motion of the three phase line of contact across a solid surface could possibly be stopped by substrate drag. The only possible adaptation of this theory to rigid solids, would be a system in which the vapour film on the solid surface was not mobile.

In this study, the wettability of diamond has been represented by measuring the contact angle between air, water and diamond, and also heptane, water and diamond. The contact angles were all measured through the aqueous phase.

4.2.2 Electrical phenomena at the diamond/water interface

When a solid is immersed in water the surface acquires a charge due to either the dissociation of surface groups, or the preferential adsorption of ions. Carbon surfaces are at least partially covered with oxygen groups, and the more polar of these will either dissociate, or adsorb ions. As the system must be electrically neutral an equal and opposite charge must be present in the liquid surrounding the solid. This gives rise to the electrical double layer.

The ions responsible for the surface potnetial (ψ_o) are referred to as 'potential determining ions' (P.D.I.'s), and they are unique for a particular solid. For salt-type minerals, such as barite and fluorite, they are those ions that make up the lattice, and for oxides and silicates, they are H^+ and OH^- ions. In the latter case, therefore, the surface potential is dependent on pH. The reactions controlling the potential on an oxide can be represented by:

$$-OH_2^+ \overset{H^+}{\rightleftharpoons} -OH \overset{OH^-}{\rightleftharpoons} -O^- \qquad (5)$$

At a particular pH value, the net adsorption of P.D.I.'s will be zero, this is termed the zero point of charge (z.p.c.).

The total surface charge at this value may not be zero, however, as there may be some specific adsorption of ions. The net charge is zero at the isoelectric point (i.p.), but provided that there is no specific adsorption of ions, the i.p. and z.p.c. will have the same pH value.

Some of the oxide groups on diamond will exhibit either acidic or basic properties. It is, therefore, reasonable to assume that H^+ and OH^- will affect the surface potential of diamond, and that the diamond surface will be similar in some respects to that of metal oxides. The extent of this similarity, and whether or not H^+ and OH^- ions are the only P.D.I.'s is not known.

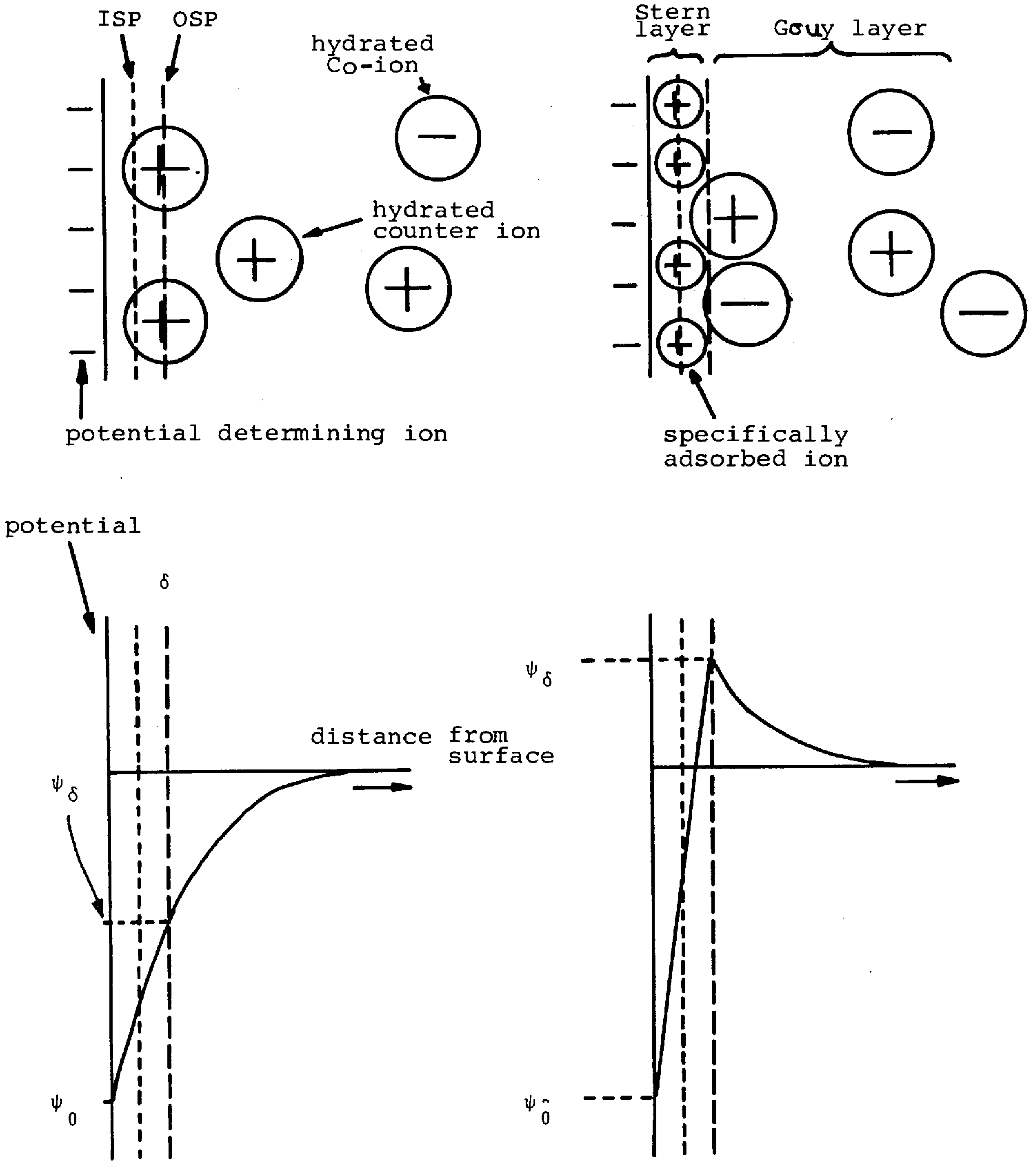
The relationship between surface potential (ψ_o) and the composition of an aqueous solution is given by the Nernstian expression:

$$\psi_o = \frac{kT}{ze} \ln \frac{a}{a_o} \qquad (5)$$

where k = Boltzmann constant
T = absolute temperature
z = valence of P.D.I.
e = electronic charge
a = activity of P.D.I.
a_o = activity of P.D.I. at the z.p.c.

The electrical double layer at the mineral/water interface is illustrated in Figure 4.3, after Grahame(55). This concept was investigated initially by Helmholtz(56), and it was modified by Gouy(57) and Chapman(58). The distribution of ions in solution, in a direction perpendicular to the surface, was considered to follow a Boltzmann relationship,

$$n_i = n_o e^{-\frac{z_i e \psi}{kT}} \qquad (6)$$



(a) (b)

Figure 4.4: Stern-Grahame model of the solid/water interface, in (a) the absence and (b) the presence of specific adsorption.

where n_i is the concentration of ions at a point where the potential is ψ

and

n_o is the bulk concentration of ions.

The net charge density (ρ) at any point is given by,

$$\rho \quad = \quad ze(n^+ - n^-) \quad = \quad -2n_o ze \sinh\left(\frac{2e\psi}{kT}\right) \qquad (7)$$

and the overall surface charge (σ) is given by,

$$\sigma = - \int \rho \; dx \qquad (8)$$

Various solutions to this equation have been developed (see Ref. 59 for a comprehensive summary). The Gouy-Chapman solution using the Poisson equation relating electrical potential and the space charge density gives the equation below,

$$\sigma = \sqrt{\frac{2n\varepsilon kT}{\pi}} \sinh \frac{ze\psi_o}{2kT} \qquad (9)$$

where n = total concentration of symmetrical indifferent electrolyte

ε = dielectric constant

ψ_o = total double layer potential

When the potential is very small (<< 25 mV), the hyperbolic function may be expanded to give the expression below,

$$\sigma \quad = \quad \frac{\varepsilon \; \kappa}{4\pi} \psi_o \qquad (10)$$

where κ = Debye - Huckel function, which is a measure of double layer thickness

$$\kappa = \sqrt{\frac{8\pi n z^2 e^2}{\varepsilon kT}} \qquad (11)$$

For small values of ψ_o, the potential, at a distance x from the surface is given by,

$$\psi_x = \psi_o e^{-\kappa x} \qquad (12)$$

Therefore, as distance form the solid surface increases, the potential falls exponentially to zero.

In a case where the surface potential is high, and therefore,

$$\frac{ze\psi_o}{kT} >> 1 \qquad \text{and} \qquad \frac{ze\psi_x}{kT} << 1$$

then,

$$\psi_x = \frac{4kT}{ze} \beta e^{-\kappa x} \qquad (13)$$

where:

$$\beta = \frac{\exp(\frac{ze\psi_o}{2kT} - 1)}{\exp(\frac{ze\psi_o}{2kT} + 1)}$$

The Gouy-Chapman treatment of the double layer is not valid at high κx values, when there is a high surface potential. This is because it assumes that ions are point charges, thus predicting impossibly high local ion concentrations near the surface. There are also two more incorrect assumptions in this treatment. Firstly, the dielectric constant of the medium is assumed to be independent of distance from the solid surface. The dielectric constant of water, however, is known to vary with electric field strength$^{(60)}$, and its value increases with increasing distance from the surface, until the value for bulk water is reached. The second incorrect assumption is that the surface charge would be spread uniformly over the surface, whereas in reality it exists as discrete ions.

The Gouy-Chapman treatment of the double layer has been extended by Stern$^{(61)}$ and Grahame$^{(55)}$. Stern modified the theory by suggesting that the region near the surface can be considered as two separate layers. The layer nearest to the surface is represented by a compact double layer, and the second layer is a diffuse Gouy layer. The plane where the change occurs, is the closest point that a hydrated counter ion can approach to the surface and it is called the Stern plane. A second modification by Stern is an allowance for a specific chemical interaction between the ions and the surface, within the Stern layer. Therefore by including work terms other than those arising from the electrical potential difference, equation (6) becomes,

$$n_i = 2rn_o e^{\frac{-ze\psi_\delta - \phi}{kT}} \qquad (14)$$

where r = the radius of the ion

ψ_δ = potential at the Stern plane, calculated from the Gouy-Chapman theory

ϕ = term allowing for specific chemical forces, which exist between the adsorbed species and the surface.

n_i = concentration of ions at the Stern Plane moles/cm^2.

Grahame further divided the Stern layer to take into account the two types of ion present. The specifically adsorbed ions are assumed to be without a hydration shell, and thus much closer to the surface than the hydrated counter ions. Stern's concept of a complete layer of immobile ions is replaced by two parallel planes assocated with each ion. These are referred to as the inner and outer Stern planes (i.s.p. and o.s.p.)

4.3 The Adsorption Characteristics of Diamond

An atom or molecule can be adsorbed on a surface in one of two ways, either by physisorbtion or chemisorption. Physisorption is the term applied to systems in which the molecule is held on the surface by purely long range forces, e.g. van der Waals forces. This type of interaction occurs in detergent systems, but it is comparatively rare in mineral/water systems, except in cases where naturally floatable minerals are involved.

THe chemisorption processes by which surfactants adsorb at the mineral/water interface can be broadly divided into three groups(62). The first group involves a specific chemical reaction between the polar group of the surfactant, and a surface site, for example, the interaction of xanthates with heavy metal cations in sulphides. The second group involves an ion-exchange type reaction because of the presence of the electrical double layer, e.g., the interaction of long-chain electrolytes and silicates. A characteristic of this group is that further adsorption occurs at high adsorption densities due to intermolecular hydrophobic bonding. The third group is an intermediate between the first two, involving a semi-specific chemical reaction and hydrophobic bonding, e.g. the adsorption of fatty acids by salt-type minerals, such as calcite.

The change in free energy, when a surfactant is adsorbed at the mineral/water interface can be represented by,

$$\Delta G^o_{ads} = \Delta G^o_{chem} + \Delta G^o_{HM} + \Delta G^o_{coul} + \Delta G^o_{CH_2} \quad (16)$$

where ΔG^o_{chem} = free energy change associated with the formation of a surface compound, between the adsorbing species and the surface

ΔG^o_{HM} = free energy change from the formation of hydrophobic bonds between the hydrocarbon chains of the adsorbing species

ΔG^o_{coul} = $F\psi_\delta$, free energy change associated with the adsorption of ions by coulombic attraction

$\Delta G^o_{CH_2}$ = free energy change from hydrophobic bonding between the species and the surface.

For adsorption processes in the first group ΔG^o_{chem} is the only significant term in equation (16).

Ion-exchange type adsorption, the second of the three types, occurs in two phases. Initially the surfactant ions are adsorbed by electrostatic attraction at the Stern plane, taking the place of the counter ions. As the adsorption density of the surfactant increases, there is often a sudden sharp rise in the adsorption isotherm, due to the interaction of the hydrocarbon chains of the surfactant. This second phase of adsorption is often referred to as hemi-micellization. The zeta-potential of the mineral at high adsorption densities becomes reversed as the surfactant molecules become adsorbed into the Stern plane. The predominant terms in the free energy equation, for this type of adsorption, are ΔG^o_{coul} and ΔG^o_{HM}.

There are many other free energy terms that could be included in equation (16), to account for the effects of solvation of any polar groups in the adsorbing species, hydrogen bonding between the surface and the adsorbing species and so on. In general, the values of these terms are very small compared to the values of those given in the three types of adsorption.

It has also been suggested that adsorption occurs by a condensation reaction, that is, a water molecule is released from the surface on adsorption of a particular species(63)(64). Thus, for a homogeneous surface the adsorption isotherm would be sigmoidal, and for a heterogeneous surface it would be stepped. This approach has been criticized, as the release of a water molecule would markedly increase the entropy of the system. As water structuring at the interface is very important in adsorption mechanisms, it is unlikely that this model can be generally applied to solid/water systems. The assumptions made for the derivation of the theoretical adsorption isotherms are open to doubt, particularly, that the entropic effects are similar in solid/liquid systems to those in gas/solid systems(65). Although it is likely that the breaking down of the hydration layers at the solid/water interface acts to give rise to the hydrophobic properties of surfactants, rather than the effect of dispersion forces between the hydrocarbon chains in the adsorbed layer doing so.

4.3.1 Adsorption of surfactants at the diamond/water interface.

The work on graphitized carbons has shown that anionic, cationic and non-ionic surfactants are adsorbed at the carbon/water interface(66,67). The suggested adsorption mechanism is one of hydrophobic bonding between the surfactant hydrocarbon chains and hydrophobic sites on the carbon surface.

It would appear that the double layer properties of these carbons have little influence on adsorption(68), and that the adsorption of ionic surfactant gives rise to a more hydrophilic surface, because of the reverse orientation of the adsorbed ions. Most of the work on carbons has been done on samples degassed at high temperatures. It is, therefore, unlikely that the results obtained with a natural diamond surface will be similar to those for carbon. A diamond surface is partially covered in oxide groups, and it may be expected to show some adsorption characteristics similar to those of oxides. The effect of the adsorption of surfactants on the electrokinetic properties and the wettability of diamond was determined in this project.

4.3.2 Adsorption of metal ions at the diamond/water interface.

One of the theories put forward to account for the hydrophilic properties of alluvial diamonds was that metal ions had been adsorbed onto their surfaces. Detail studies of the adsorption of metal ions at the diamond/water interface have not been made, but a preliminary investigation at Imperial College(69) revealed that the wettability of diamond was unaffected by the adsorption of such ions as Pb^{2+} and Ca^{2+}. Further studies were made in this work.

The adsorption of gold complexes on activated carbons has been studied(70), and the results indicate that the oxidic groups present on the surface adsorbed the gold species. There has been no positive identification, however, of the particular group responsible for this property, but oxidation of the carbon improved the adsorption of gold, whereas outgassing decreased the adsorption.

CHAPTER 5. MATERIALS AND EXPERIMENTAL TECHNIQUES

5. MATERIALS AND EXPERIMENTAL TECHNIQUES

5.1 Diamond Samples

The diamond samples used in this study were supplied by De Beers, Industrial Diamond Division. Two batches of 5 mm natural diamond crystals were obtained. The first batch of 26 crystals varied in colour from transparent to black, and had been collected by a variety of processes. There were six special diamonds in this batch, three 'macles', which are flat triangular crystals about 2 mm thick, and three 'natural flats', which have large flat crystal faces. A second batch of ten 'hydrophilic' diamonds was obtained from the Finsch mine, where there is an unusually high proportion of these diamonds in the deposit. Two samples of diamond powder, nominally less than one micron in size, totalling 150 g were received.

5.1.1 Analysis of diamond crystals

A recent study has shown that there are numerous impurities in diamond crystals(19). As bulk impurities are unlikely to affect the surface properties, bulk analysis of the diamond was not attempted. Many surface groups are found on diamond, and so a surface analysis by ESCA was undertaken. An untreated macle was analysed on a Vacuum Generators VG ESCA III Mk.I machine. The spectra obtained are presented in Figure 5.1. The two strongest signals were $C1_s$ and $O1_s$, from carbon and oxygen respectively. An expansion of the oxygen peak, shown in the inset in Figure 5.1, showed that there was more than one oxidation state of oxygen present, but insufficient time was available to obtain quantitative results. It was possible, however to determine the maximum limits of the other impurities present on the surface. Silicon, sodium, chlorine and zirconium were present at a concentration very much less than 5% of a monolayer.

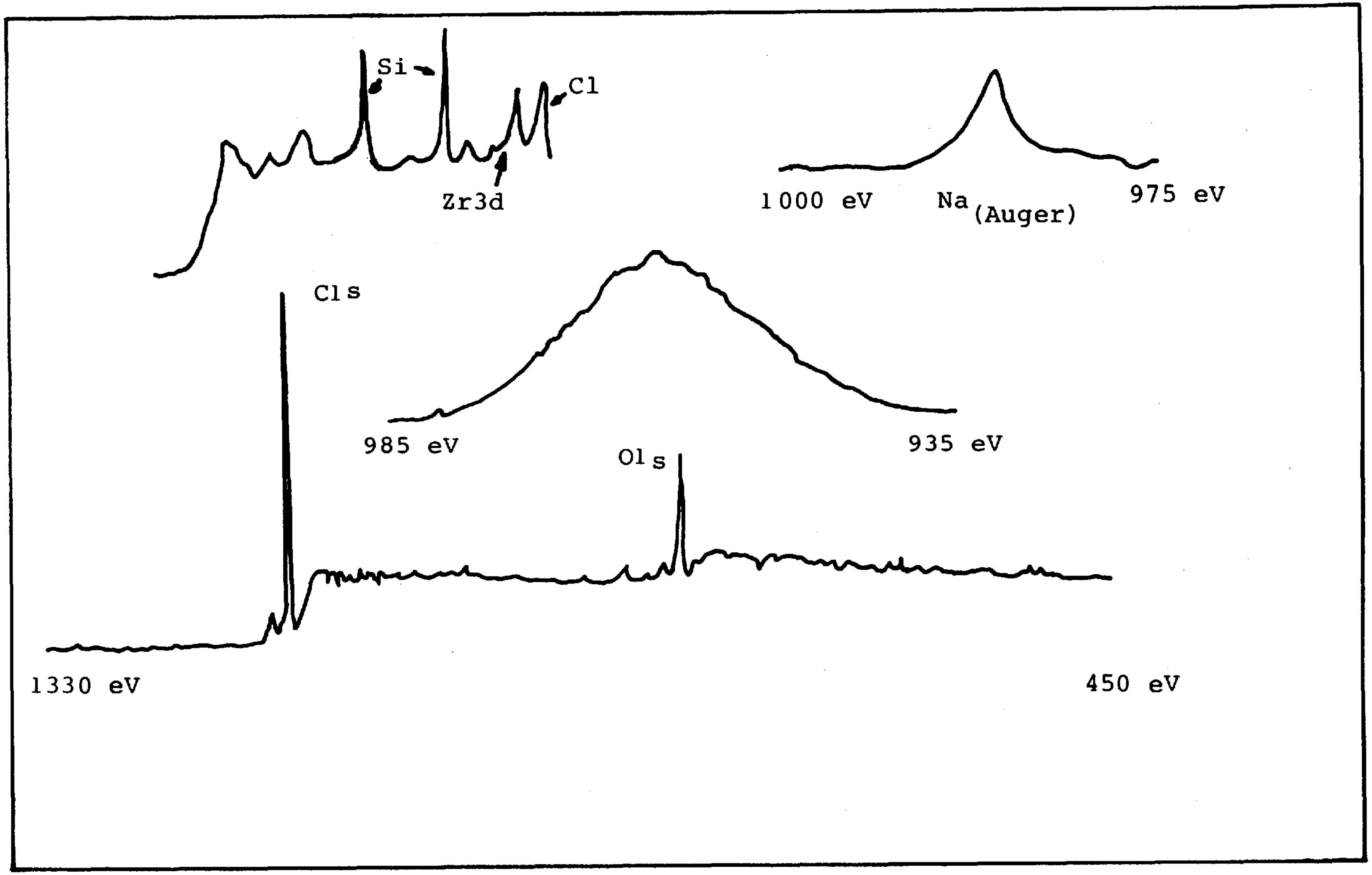


Figure 5.1: ESCA spectrum of diamond

5.1.2 Analysis of diamond powder samples

Diamond powders are produced by a process involving grinding in steel mills, dispersion with sodium silicate and washing with nitric/sulphuric acid mixtures. A careful analysis of the powder samples was undertaken to check the purity of the powder. Bulk analysis was done by X-ray fluorescence (XRF), neutron activation analysis (NAA), and X-ray diffraction (XRD), while infrared spectroscopy was used for surface analysis. The results of the analyses are presented in Table 5.1.

Table 5.1 : XRF and NAA Analyses of a Diamond Powder Sample

XRF

Major > 5%	Intermediate 5% - 0.5%	Minor 0.5% - 0.05%	Trace <0.05%
		Al Si Zr	Mg Fe S Cl K Ca Ti

NAA

Al 0.05%, Fe 2 ppm, W 50 ppm, Mn 4 ppm, Zr and Si <<1%

The XRD analysis was done by a Debye-Scherrer photographic technique. The major mineral phase present was diamond, but there were trace quantities of two other minerals, chaoite and silicon carbide, present(71)(72)(73). There was no graphite present in this sample of diamond powder(74).

The chaoite may have been formed by the comminution processes used in the production of diamond powder, as this mineral phase has reported to be present on dimaonds removed from drill bits$^{(75)}$.

Infrared spectroscopy was used to analyse the effect of various cleaning techniques on surface groups. The presence of certain groups could be inferred from the alteration in intensity of certain absorption peaks, after reacting the diamond powder with reagents known to destroy or complex these groups. A typical infrared spectrum for a diamond powder is presented in Figure 5.2.

The surface area of the diamond powder was determined by a BET krypton adsorption technique, which gave a surface area of $8.0\ m^2 g^{-1}$. The five points determined in this measurement showed excellent linearity. Surface areas were determined regularly throughout the experimental work by a single point technique, using Quantachrome 'Monosorb' apparatus. The surface areas determined by this latter technique, using nitrogen adsorption, were in excellent agreement with those determined by the multi point technique.

5.2 Water Preparation

Water of the highest purity is a necessity for any study of the mineral/water interface. The water must have as little surface active impurity as possible.For this project, a special still was constructed to purify further the conductivity water available in the laboratory.

The still was made entirely of glass using PTFE sleeved butt joints. The whole system had an atmosphere of oxygen free nitrogen, which had been passed through a bed of activated carbon. The pressure of the gas in the system was maintained at a value slightly greater than atmospheric pressure.

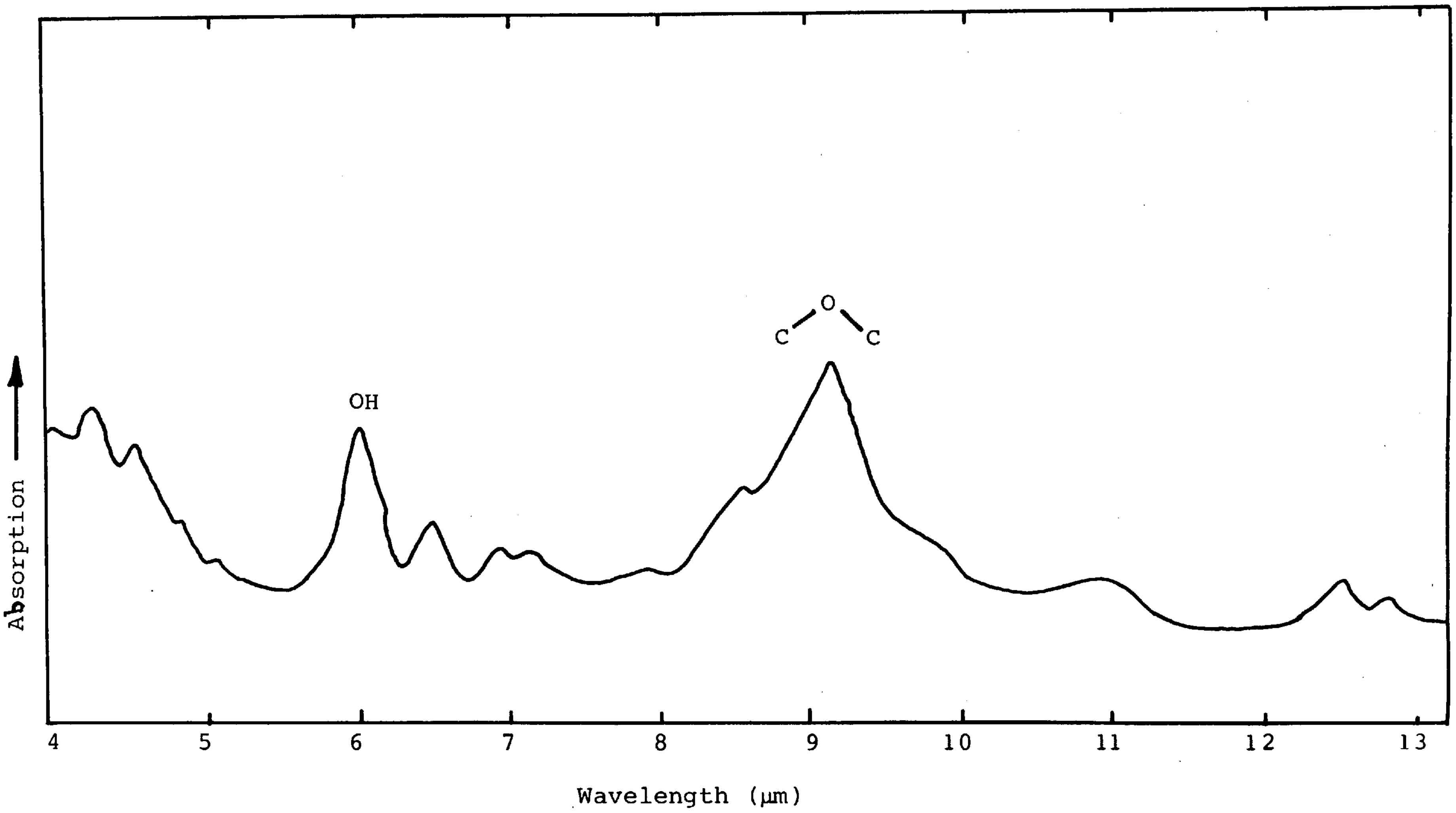


Figure 5.2: Infrared spectrum of diamond

The conductivity water was passed through a bed of activated carbon, and then it was distilled into the final reservoir.

The whole still was cleaned with freshly prepared chromic acid every six months. The activated carbon was replaced every twelve months. The determination of the surfactant concentration at very low levels is almost impossible. One qualitative, but sensitive, technique is the bubble persistence test(76). A sample of the water is shaken in a clean vessel, if the bubbles do not break instantly on reaching the surface, then a surfactant impurity is present. Less than 1 ppm of impurity can cause the bubbles to be stable for more than 2 seconds. Water prepared by this still had very short bubble persistence times, and so it was assumed to be essentially surfactant free.

The bubble rise technique is a very accurate, but complicated method for determining the purity of water(77)(78). Previous work in this department has shown that the bubble rise velocity of similarly treated water was close to the theoretical value for pure water(79)(80). This further suggests that the water was of a high quality.

5.3 Chemicals

The suppliers and grades of the chemicals used in this study are presented in Table 5.2. The organic liquids were purified by passing them through a bed of activated alumina (Camag) to remove polar compounds. The ethanol was dried by leaving the sample in contact with calcium oxide for not less than 14 days.

Chromic acid for cleaning glassware was prepared by dissolving 6 g of sodium dichromate (AnalR) in a small amount of water, then adding 100 cm^3 of sulphuric acid (AristaR).

Table 5.2 Chemicals used in the Project

Inorganic	Grade	Supplier
Hydrochloric acid	AristaR	BDH
Sulphuric acid	AristaR	BDH
Hydrofluoric acid	AnalaR	BDH
Nitric acid	AristaR	BDH
Perchloric acid	AnalaR	BDH
Sodium hydroxide	AristaR	BDH
Sodium chloride	AristaR	BDH
Sodium perchlorate	low in Br	BDH
Sodium carbonate	AnalaR	BDH
Sodium bicarbonate	AnalaR	BDH
Sodium thiosulphate	AnalaR	BDH
Sodium borohydride	Pure	Cambrian
Potassium dichromate	AnalaR	BDH
Potassium bromide	i.r. spec. pure	BDH
Hydrogen peroxide (100 volumes)	AnalaR	BDH
Aluminium foil	AnalaR	BDH
Ammonia	AnalaR	BDH
Copper Sulphate	AnalaR	BDH
Hydrazine hydrate	AnalaR	BDH
Organic		
Heptane	Puriss	Koch-Light
Trichloroethylene	GPR	BDH
Chloroform	Puriss	Koch-Light
Ethanol	Spec. pure	J.Burrough
Acetone	Puriss	Koch-Light
Diethyl ether	Pure	BDH
Sodium ethoxide	Pure	Cambrian
N-Methyl n-nitroso N'nitroguanidine	Pure	Koch-Light
Benzene	Puriss	Koch-Light
Surfactants		
Sodium dodecyl sulphate (SDS)	Pure	B.Newton-Maine
Dodecylamine (DDA)	Pure	Koch-Light
Butylamine (BuA)	Pure	Koch-Light
Benzylamine (BeA)	Pure	Koch-Light
Cis-9,10-ene-octadecanoic acid (oleic acid)	Purum	Fluka
Sodium diethyldithiophosphate	Sodium Aerofloat	Cyanamid
Cresyldithiophosphate	Aerofloat 242	Cyanamid

5.4 Experimental Techniques

5.4.1 Contact angle measurement

An apparatus for the measurement of contact angles on small specimens was constructed. A Beck 6000 microscope and a tungsten lamp were mounted uniaxially, in the horizontal plane. The standard 25 mm objective lens was retained, but the eyepiece was removed, and the microscope was modified to accept a Vickers 'Dick-Wright Slotted Occular', with a magnification of 10x. The eyepiece could be rotated independently of the rest of the instrument to align the cross-wires with any surface. Angles could be read to $\pm 0.1^{\circ}$ on a vernier scale attached to the eyepiece.

The stage of the microscope was modified to accept a 1 cm silica spectrophotometer cell. The specimens were mounted on PTFE rods within the cell.

Air bubbles or heptane droplets were formed on the tip of an 'Agla' micrometer syringe, which was mounted vertically on an extension to the microscope. The position of the syringe was controlled by two 'Research Instruments' micromanipulators. A double-axis positioner, mounted in the horizontal plane, enabled the bubble to be moved over the specimen surface, and a single-axis positioner, mounted in the vertical plane, enabled the bubble to be moved in a vertical direction.

Great care was taken when transferring diamond crystals from one solution to another, during the contact angle measurements. Diamonds were removed through overflowing surfaces and then speedily placed in the next solution. When surfactant solutions were used, the cell, sample and heptane phase were equilibrated with the solution before measurement of the contact angle.

An air bubble or heptane droplet of constant volume was formed on the tip of the syringe in the aqueous phase. After an equilibration time of 5 min, the bubble was brought gently into contact with the diamond surface. After a further 5 min the 'initial advancing' contact angle was measured, then the bubble was increase by a fixed amount. The 'final advancing' contact angle was measured after a further 5 minutes, and the bubble was retracted to its original volume. The 'receding' contact angle was measured after a final 5 min equilibration time. Angles were measured through the aqueous phase.

5.4.2 Electrokinetic measurements

The electrical double layer and the associated surface charge are of great importance in the determination of the surface properties of a solid, particularly the adsorption properties. The most convenient representation of the electrical phenomena at the solid/water interface is the zeta-potential (ζ) which can be regarded as the potential difference between a point some distance from the surface in a practically uniform medium and a point on the plane of shear. Although the shear plane is not exactly identical to the Stern plane, the zeta potential is usually substituted for ψ_δ in equation 4.14.

The zeta potential of a mineral powder can be determined indirectly by microelectrophoresis. The Helmholtz-Smoluchowski equation$^{(81)}$ incorporating Henry's correction for retardation, relates the electrophoretic mobility (u) to the zeta-potential.

$$u = \frac{\xi \zeta}{6 \pi \eta} f(\kappa_a) \qquad (1)$$

where: ξ = permittivity of the medium

η = viscosity of the medium

a = particle radius

The function $f(\kappa)$ can vary in value between 1 and 1.5 depending on the size, shape and orientation of the particles(82).

Correction for the effects of surface conductivity and relaxation have been suggested(83)(84)(85), but it is thought that the approximations necessary lead to an over-estimation of the effects(86).

The electrophoretic mobility of diamond particles was determined using a Rank Bros. microelectrophoresis apparatus (Mk.II). A standard suspension was prepared by dispersing 0.1 g of diamond powder in 100 cm^3 of water. Aliquots of 1 cm^3 of the standard suspension were added to 100 cm^3 electrolyte solution at the required pH. After an equilibration time of 10 minutes the suspension was placed in the flat electrophoresis cell, and the palladium electrodes were inserted carefully. The cell was mounted in a water bath, maintained at a constant temperature of 25°C.

The electrophoretic mobility of the particles was determined by timing the passage of ten particles in one direction across a grid, and then another ten in the reverse direction. The mobility (u) was calculated from the equation ,

$$u = \frac{v\kappa A}{I} \qquad (2)$$

where v = particle velocity

κ = specific conductivity of the suspension

A = cross-sectional area of the cell

I = current

This equation may be expressed more usefully in the form,

$$u = \frac{vL}{V} \qquad (3)$$

where $L = R\kappa A$ = effective interelectrode distance (R = resistance across the cell)

V = applied voltage

The value of L for the cell used in this study was 7.51 cm.

The zeta-potential was calculated from the electrophoretic mobility by equation (1), which reduced to the equation given below at 25°C.

$$\zeta = 12.83\ u\ f(\kappa a) \qquad (4)$$

where u is in μm sec^{-1}/volt cm^{-1}

ζ is in mV

The $f(\kappa a)$ value for the diamond powder used in this study at an ionic strength of 10^{-3} was 1.0(82).

5.4.3 Potentio metric titrations

Titrations of sodium hydroxide against diamond powder suspensions in hydrochloric acid were conducted in a 'Quickfit' 50 cm³ reaction vessel. A miniature combined pH electrode supplied by Pye-Unicam connected to a Pye-Unicam model PW9418 pH meter was used to measure pH. The vessel was purged with oxygen-free nitrogen prior to the measurements, and a constant flow of nitrogen was maintained throughout the titrations.

In nearly all the tests 10^{-2} M NaOH was titrated into 25 cm³ of the 10^{-3} M HCl with a supporting electrolyte of NaCl. The difference between a blank titration and that obtained in the presence of 1 g of diamond powder was taken as the net uptake of H^+ and OH^- ions.

Direct surface titrations were performed by titrating 10^{-4}M aqueous solutions of sodium bicarbonate, carbonate and 10^{-3} M sodium hydroxide in to 1 g of diamond powder dispersed in 25 cm³ of water. Sodium ethoxide dissolved in dry ethanol was titrated similarly against 1 g of diamond powder dispersed in dry ethanol. The end point of these reactions gave an indication of the groups of different basicities on the diamond surface.

5.4.4 Extraction tests

The wettability of the diamond powder was studied by determining the amount of diamond powder concentrated at the heptane/water interface. Contact angle and small scale flotation tests are not possible on material as fine as that present in the diamond powder samples.

An initial series of tests at different ratios of heptane to water volumes , showed that, if the volume of heptane was less than 10% of the total, the recovery of diamond decreased.

0.5 g of diamond powder was agitated for 5 min by a glass stirrer in a baffled glass vessel, containing 40 cm³ of water and 10 cm³ of heptane. The mixture was then allowed to settle for 20 min., and during that time the heptane drops coated with hydrophobic diamonds rose to form a separate layer. After separation of the layers, the samples were dried. The amount of diamond concentrated at the oil/water interface was then calculated.

5.4.5 Measurement of the adsorption of amine on diamond

A preliminary series of adsorption tests showed that the adsorption of DDA at the diamond/water interface was a rapid process. In further tests, therefore, 0.1 g of diamond powder was shaken with 25 cm³ of the DDA solution at the required pH for 20 min. in a sealed 100 cm³ flask. After agitation the solids were separated from the DDA solution by centrifugation, and the pH and the equilibrium concentration of the surfactant solution were determined. The adsorption density of DDA was determined form the difference between the initial and final concentrations of surfactant.

The DDA concentration was determined by a method using a sulphnapthalein indicator, bromocresol green, which forms a coloured complex that can be determined spectrophotometrically(87). The indicator solution was prepared by dissolving 0.1 g bromocresol green in 50 cm³ ethanol, acidifying with 0.1 cm³ conc. H_2SO_4 and diluting to 100 cm³ with water. To determine DDA, 5 cm³ of the surfactant solution was added to 1 cm³ of indicator solution, and the mixture was diluted to 10 cm³. 5 cm³ of chloroform was added, and the mixture was inverted rapidly 100 times. The complex formed between the indicator and DDA has a much higher solubility in chloroform than in water and it was preferentially partitioned in the organic phase. The concentration of the complex in the chloroform phase was determined spectrophotometrically at 416 nm. A Perkin-Elmer model 124 u.v./visible double-beam spectrophotometer was used in the determination . A blank sample was prepared using water instead of DDA solution by exactly the same method detailed above. The calibration curve is presented in Figure 5.3.

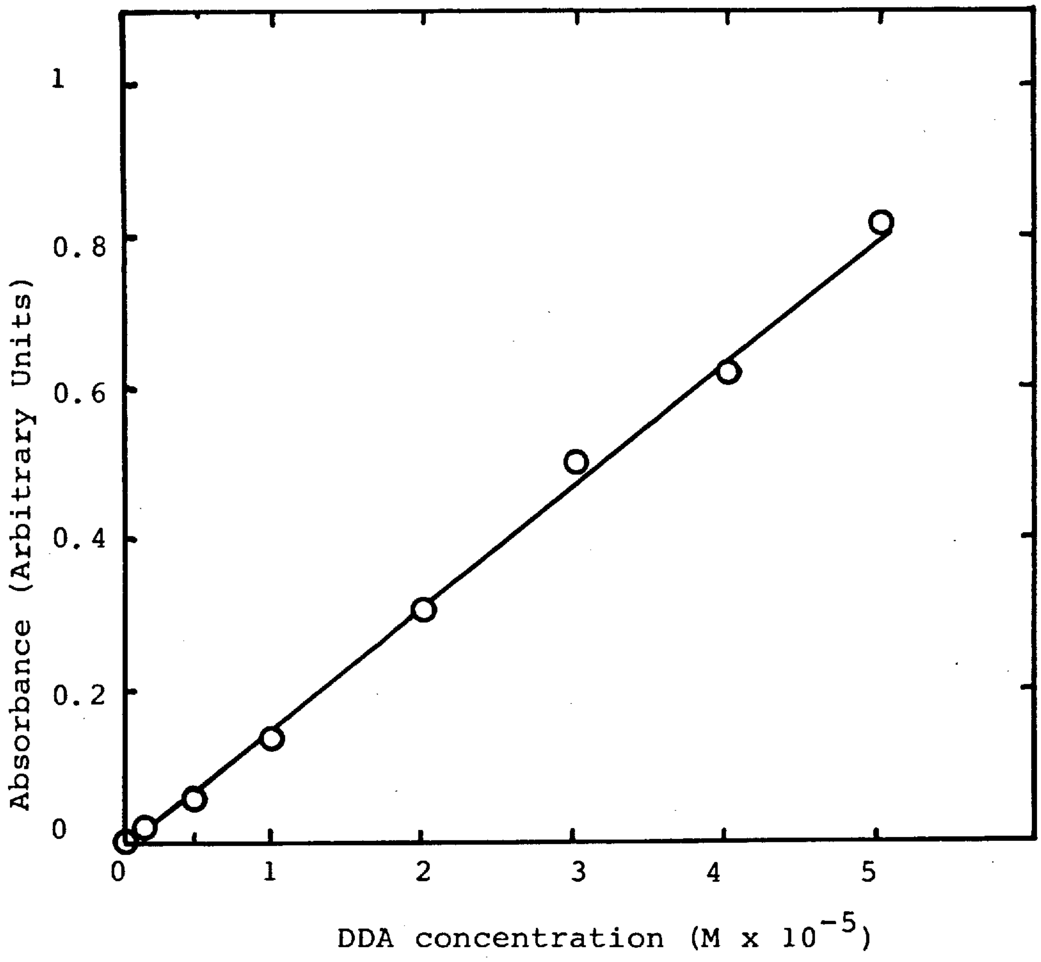


Figure 5.3: Calibration curve for the spectrophotometric determination of DDA.

The reversibility of adsorption was established by two methods. Firstly, different diamond sample weights were used in the adsorption tests, and secondly, after centrifuging the suspension a sample of the supernatant DDA solution was removed and replaced by the same volume of water. This latter suspension was reagitated and re-centrifuged prior to determination of the surfactant concentration.

5.4.6 Infrared spectroscopy

Discs of variously treated diamond powders were accurately made up with KBr to be 0.1 % diamond (by weight), to enable comparisons of the various spectra. The diamond powder was weighed out and mixed with spectroscopically pure KBr, after drying both materials at 150°C for 24 hours. The mixture was ground in a steel vibratory mill for one minute. A 200 mg sample was accurately weighed out and placed in a steel die. The die was evacuated for 5 minutes, after which a pressure of 10 t cm^{-2} was applied for a further 5 minutes. The pressure was carefully released, and the disc was placed in a desiccator prior to analysis. A blank disc for use as a reference was prepared from KBr alone, by exactly the same technique. It was not necessary to provide extra blanking of the reference beam, as was necessary in one study of carbon blacks(88).

The spectra were obtained with a Grubb-Parsons Spectromaster Mk. I. A Nernst filament was used as the source of infrared radiation.

Each batch of spectra contained one standard diamond disc to enable comparison of the intensities of certain absorbance peaks of the variously treated diamond powders.

5.4.7 Preparation of diazomethane

A clean method for methylating carbon surfaces is reaction with diazomethane(41). This chemical is very toxic and explosive, and so great care must be taken during the preparation of a diazomethane solution. The classical method for the preparation of an ethereal solution of diazomethane is to co-distill the diazomethane and ether(89). The reaction of N methyl n-nitrosotoluene 4-sulphonamide with alkali is used to generate the diazomethane. Recently a much simpler technique has been developed(90), and a diazomethane generator has become available from Pierce and Warriner (UK) Ltd., as shown in Figure 5.4, in which minute quantities of diazomethane can be generated from the reaction of N methyl n-nitroso N'nitroguanidine with alkali. This latter reaction was used in the present work.

The diamond powder to be methylated was placed in the outer tube with 3 cm^3 of diethyl ether, which had been dried by sodium. 0.5 cm^3 of water and 0.1 g of N methyl n-nitroso N'nitroguanidine were placed in the central tube. The whole apparatus was sealed and placed in an ice bath, in a fume cupboard behind a blast shield. 0.6 cm^3 of 5 M NaOH solution was injected through the septum by a glass syringe fitted with a hypodermic needle. The mixture was allowed to react for two hours, after which the ethereal suspension was poured carefully into a flask, and sealed with a calcium chloride filled U-tube. The flask was placed in a refrigerator for 48 hours at 4^{o}C. After this period. a yellow colour was always observed in the ethereal solution, indicating the persence of unreacted diazomethane. The diazomethane and ether were evaporated by applying a vacuum from a water pump for one hour. The dry diamond powder was kept in a desiccator until required.

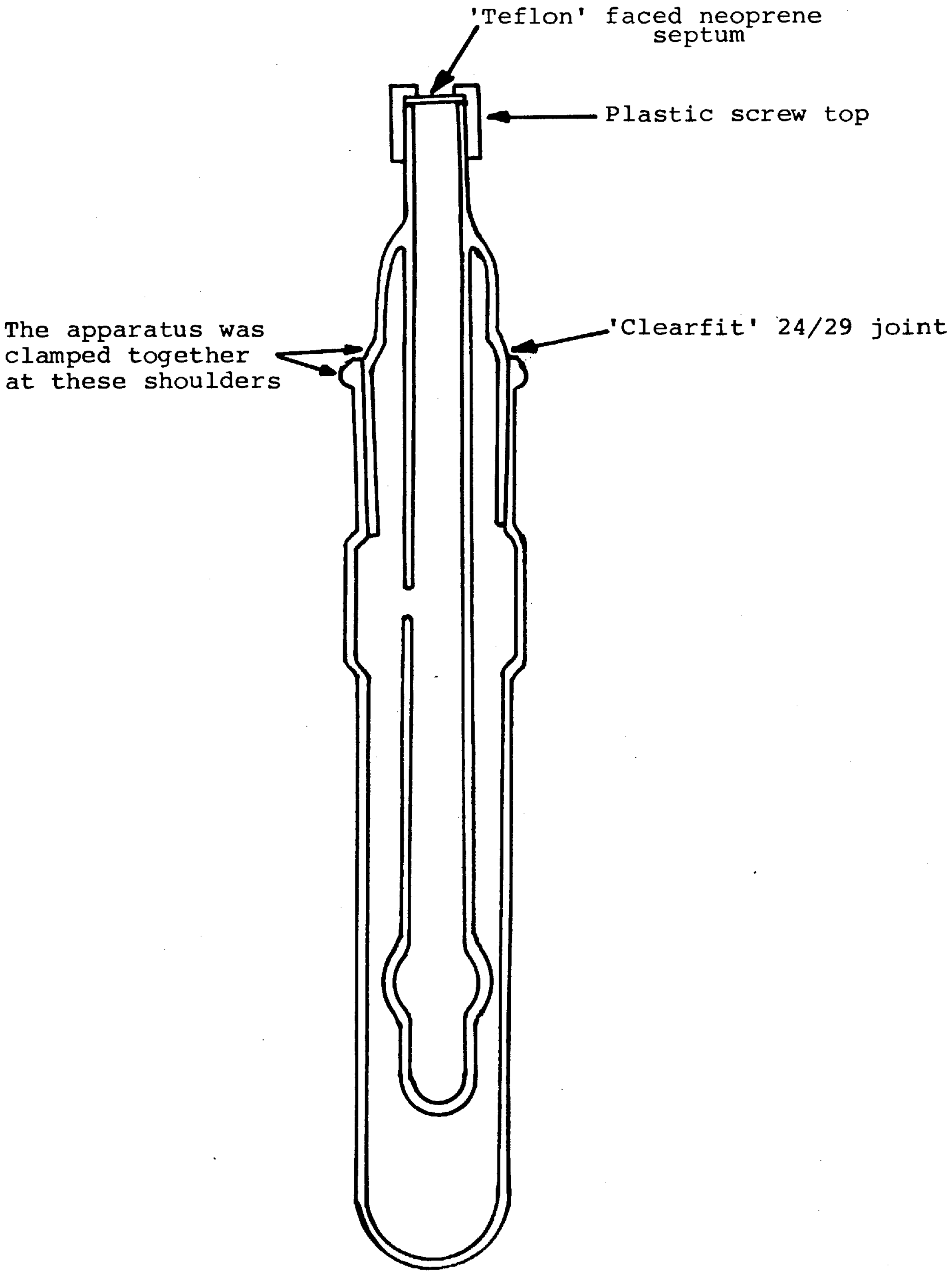


Figure 5.4: Wheaton Scientific Inc. Diazomethane Generator

5.4.8 Sample preparation

The recovery and shipment of diamonds involves many processes which bring them into contact with oily substances. It was therefore likely that the consignment of 26 coarse diamonds, which were received dry, were contaminated by various oily substances. The criterion chosen to represent a clean surface was reproducibility of contact angle, both on the same diamond, and from diamond to diamond. To achieve this equality a variety of washing processes were used.

Initially the diamonds were washed with cold trichloroethylene, but this produced a very variable contact angle, both on the same diamond and between different diamonds. The results of contact angle measurements after various cleaning techniques are presented in Table 5.3 . To check that there was no contamination of the diamond surface by an airborne impurity, the bubble was formed from air passed through a bed of activated charcoal placed in the base of the syringe, and also from nitrogen, drawn off from just above the surface of liquid nitrogen. No change in contact angle was obtained, and it was concluded that the measured angles were not the result of airborne contamination. The diamonds were next washed in a Soxhlet apparatus with trichloroethylene, and again there was little reproducibility of contact angle. As trichloroethylene is a polar compound, it is possible that it did not remove non-polar contaminants, or it may have been adsorbed. Benzene was substituted for trichloroethylene and this produced a very reproducible contact angle. Further washing with benzene, trichloroethylene, acetone or water did not significantly affect the contact angle, with was $25^{\circ} \pm 3^{\circ}$.

There was a large hysteresis in the contact angle measurements, with a difference of 20° between advancing and receding contact angles. Surface roughness was the most likely reason for this difference, because in attempting to maintain a 'natural' diamond surface no polishing of the crystals was done.

Table 5.3 Contact angles of variously cleaned diamonds

Diamond Treatment		Macle 2	Macle 3	Natural flat 4	Natural flat 5	Octahedron 7	Rounded cube 8	Yellow angular 12	Brown angular 18	White angular 19	White angular 21	Brown angular 22	Brown angular 23
As received	A R	28.8 44.6	38.8 46.4	26.1 46.1	18.9 32.8	24.7 49.4	12.8 26.5	25.8 40.3	16.8 37.2	27.4 42.4	32.8 54.5	29.6 32.1	24.5 48.5
6 hours soxhlet trichloroethylene	A R		0.0 9.9	17.5 25.4		0.0 12.7	2.0 10.3		7.4 22.2		0.0 13.3		0.0 0.0
6 hours soxhlet benzene	A R	0.0 29.1	0.0 23.7	25.9 33.4	4.3 27.9	0.0 20.4		0.0 27.2		0.0 27.1	6.8 27.7	0.0 25.2	2.3 26.8
6 hours soxhlet trichloroethylene	A R		0.0 26.5		3.6 27.8						4.8 28.0		
6 hours soxhlet cleaned benzene	A R	4.5 29.8	0.0 25.1	22.5 32.1	0.0 25.1	0.0 20.7		0.0 24.1	0.0 22.7	0.0 29.0	8.3 25.2	4.3 26.5	0.0 26.3

A :Initial Advancing Angle

R : Receding Angle

The Finsch 'hydrophilic' diamonds were not washed initially, and their contact angle was $12^{\circ} \pm 2^{\circ}$. Washing with benzene in a Soxhlet apparatus did not affect this value, indicating that benzene was not adsorbed on diamond during the washing process. All 36 diamonds were stored under water in air-tight glass vessels.

It had been suggested that diamond may become coated with silicates from kimberlite(91), some of the diamonds were washed, therefore, with 40 % HF. This treatment did not affect the contact angle, thus the diamonds could not have been coated with a silicate impurity.

The coarse diamonds were used only for the contact angle studies, whereas all the other data were obtained from measurements on the diamond powder. Normally, with minerals, this presents no problems, as coarse pieces of mineral from one particular location can be ground down. Diamond powder can be obtained only by grinding individual diamonds, and each one is different. Consequently, studies on diamond powders might not produce results comparable with those obtained from studies on one or two coarse diamonds.

Diamond powder is produced by grinding in steel mills, sizing by sedimentation using sodium silicate as a dispersant, and washing with sulphuric/nitric acid mixture. The cleaning procedure chosen for the powder was analogous to that used for coarse diamonds. Initially the powder was washed with 15% HCl, followed by repeated centrifuging and rewashing with water. The final residue was washed four times in acetone, centrifuging between washes, and finally it was washed in a Soxhlet apparatus with benzene. The powder was stored under benzene in an air-tight glass vessel.

The only property of the diamond surface that could be measured for both coarse and fine diamonds was the wettability. After an extraction test, 30% of the powder was retained at the heptane/water interface. The contact angle for heptane on a diamond surface was 60°.

5.4.9 Preparation of fresh surfaces

Two techniques were used to attempt to produce a fresh surface on a diamond crystal, but neither method was easily applicable to produce fresh surfaces for the diamond powder. A diamond crystal was crushed in liquid nitrogen, and another crystal was bombarded with argon ions to strip off surface layers.

A diamond was crushed in a stainless steel die that was submerged under liquid nitrogen contained in a stainless steel beaker. The equipment was initially cleaned by adding ammonia to hydrogen peroxide boiling in the beaker, as this technique is reported to produce the cleanest surfaces(92). The apparatus was washed with water and blown dry. The beaker was placed in a foam-polystyrene jacket, and liquid nitrogen was poured over the die in the beaker. A diamond was inserted when the apparatus had cooled down. The diamond was crushed by gently applying a load to the plunger of the die. A 'crack' was heard on cleavage, and the load gauge of the press showed a sudden decrease. Water was poured into the beaker and the diamond fragments were removed when the ice had melted.

Argon ion bombardment was carried out on a diamond in a glass vessel. The sample was placed between two electrodes in the vessel which was then swept for one hour with argon. The vessel was sealed and pumped down, after which a high electrical potential was applied. A purple Tesla discharge was seen, and an appreciable roughening of the diamond surface occurred. The diamond was placed in water without it coming into contact with the air.

CHAPTERS 6 - 8. RESULTS AND DISCUSSION

6. RESULTS

6.1 Wettability of Diamond

The contact angle measured through the aqueous phase, as an air bubble or oil drop was receded from a diamond surface was taken as a measure of the wettability of the diamond. In the case of the diamond powder, however, an assessment of the wettability was obtained by measuring the amount of powder concentrated at the heptane/water interface.

The contact angle of both the 'hydrophobic' and 'hydrophilic' diamonds was unaffected by variation of pH value from 2 to 12, as shown in Figure 6.1. The constancy of the contact angle at different pH values also indicates that the wettability is independent of ionic strength. This was confirmed by measuring contact angles at different concentrations of sodium chloride up to 10^{-2} M.

Oxidation of diamond is known to produce a more hydrophilic surface(27)(51). Contact angles on a 'hydrophobic' diamond were measured, therefore, in the presence of different concentrations of potassium dichromate, nitric acid and sodium perchlorate; the results are presented in Figure 6.2 . The contact angle was reduced by all three oxidizing agents, with $NaClO_4$ being the most effective, reducing it to zero. This effect was irreversible, with the contact angle remaining at the oxidized value after soaking the diamond for many days in water. Tests on the diamond powder showed a similar trend; the amount of diamond concentrated at the heptane/water interface decreased in the presence of oxidizing agents, as shown in Table 6.1.

In the presence of sodium thiosulphate, there was little change to either the concentration at the interface or the contact angle (Figure 6.3). Sodium borohydride, however, reduced

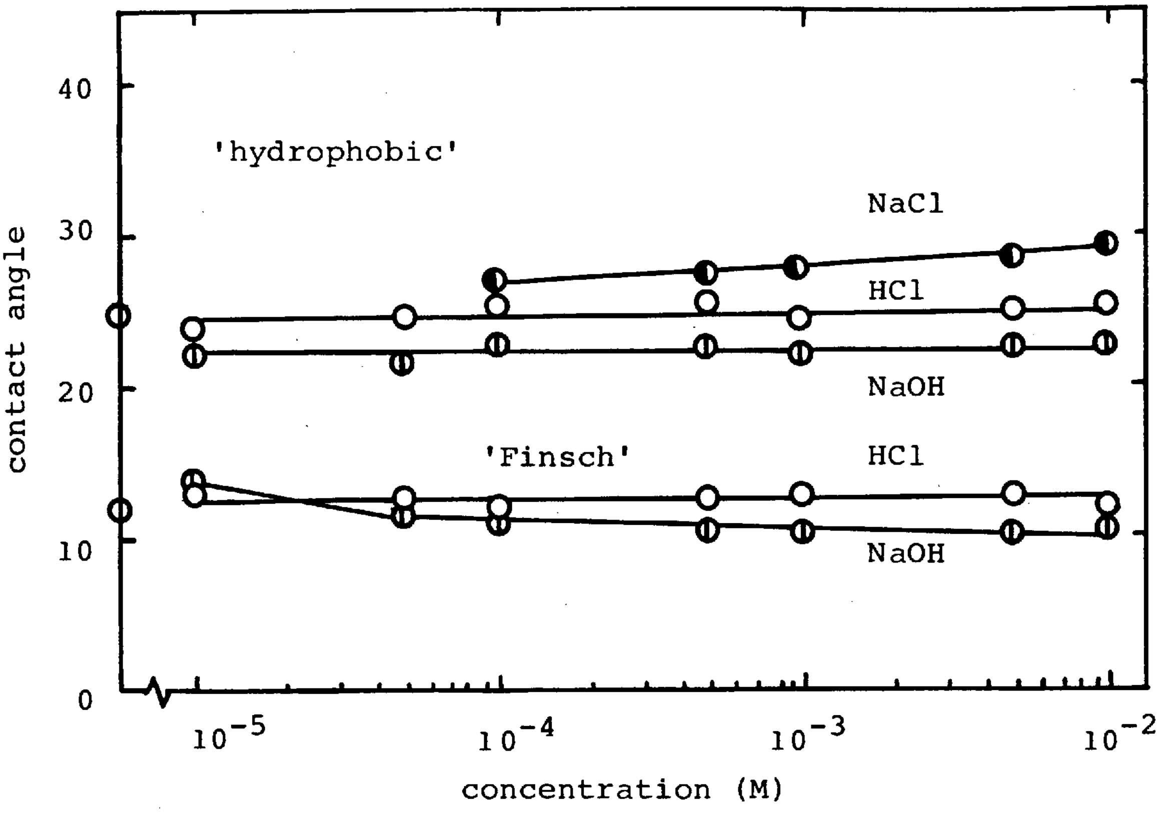


Figure 6.1: Effect of pH and ionic strength on the contact angle of fresh diamond.

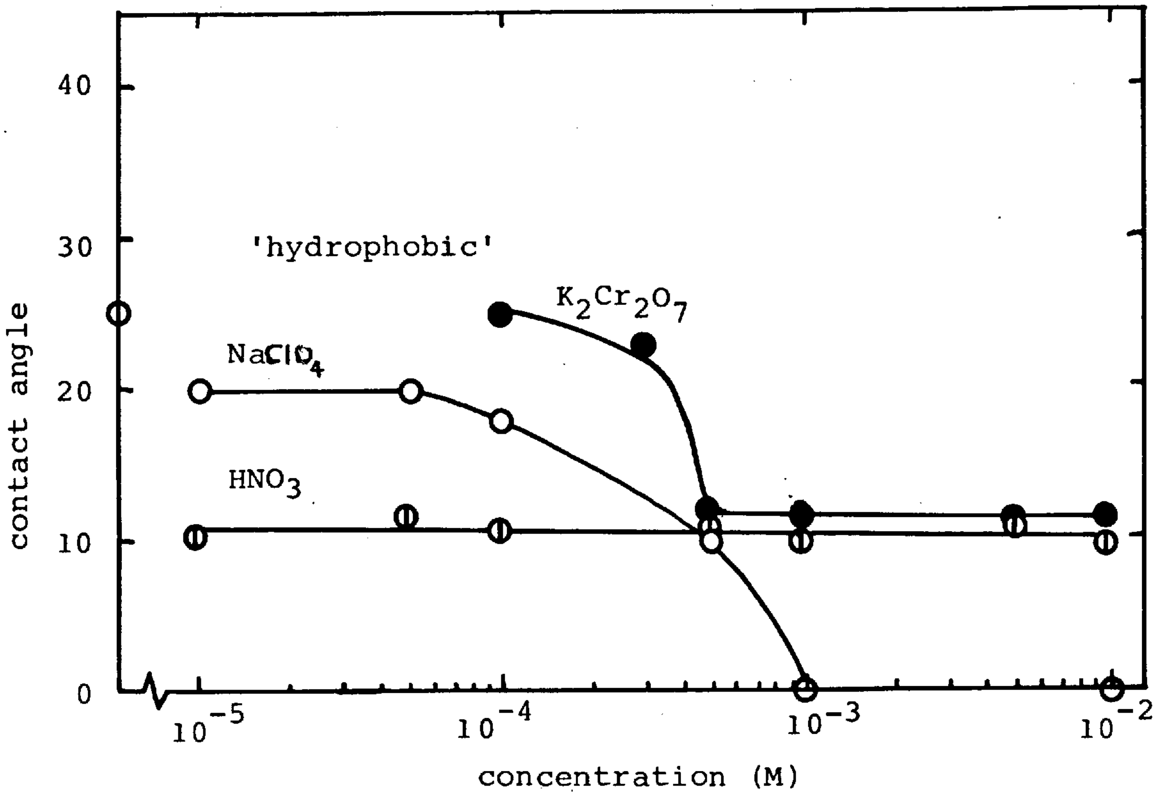


Figure 6.2: Contact angle of fresh diamond in the presence of oxidizing agents.

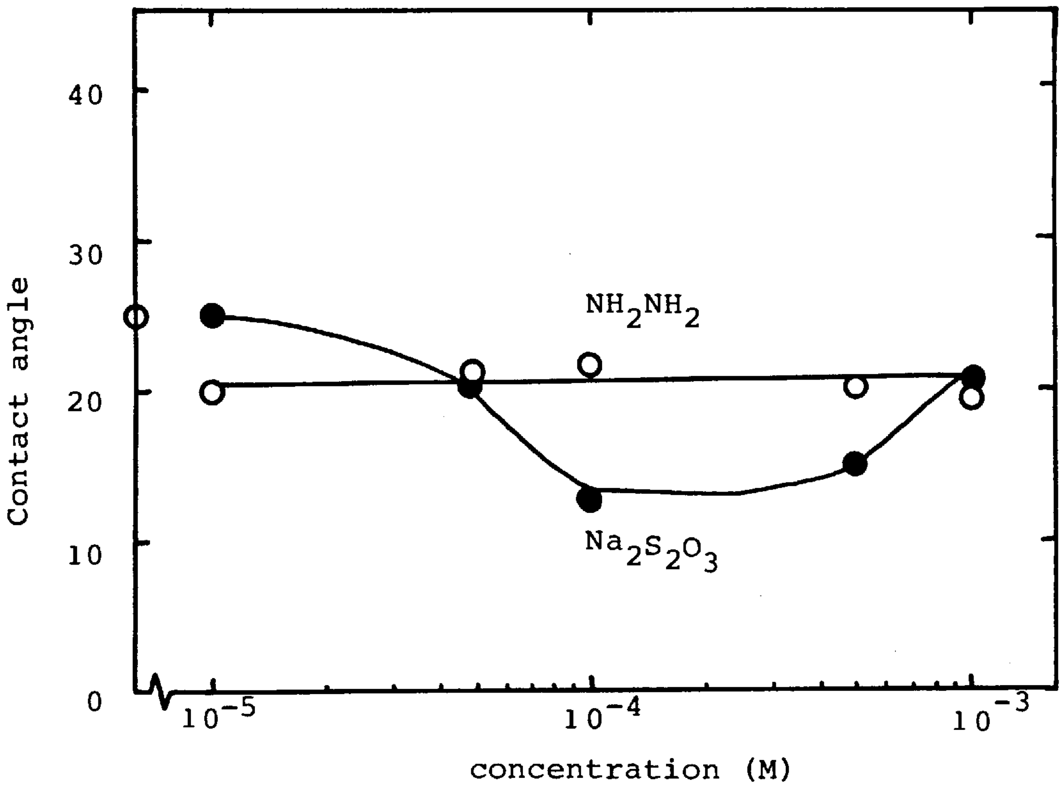


Figure 6.3: Contact angle of fresh diamond in the presence of reducing agents.

the concentration of diamond at the heptane/water interface to 2%, and the contact angle at the air/water/diamond three phase line to zero. Sodium borohydride reacts specifically with carbonyl groups, reducing them to hydroxyl groups, which is a similar effect to oxidation of carbons(31). Hydrogenated diamond surfaces have been shown to be hydrophobic(27). but, a reduced natural diamond surface would be covered in hydroxyl groups rather than hydrogen atoms, so some hydrophilicity would be expected due to the ionization of some of the groups. The effect, therefore, of strong reducing agents and oxidizing agents on the contact angle of diamond was similar, whereas weak reducing agents have little effect. This was demonstrated, further , by treating the oxidized diamonds with sodium thiosulphate solution, which had no effect on the contact angle or the degree of concentration at the heptane/water interface of the oxidized diamond.

Table 6.1 The effect of oxidizing and reducing agents on the concentration of diamond at the heptane/water interface

Reagent	15% HCl	0.1M HNO_3	0.1M $K_2Cr_2O_7$	0.1M $NaClO_4$	0.1M $Na_2S_2O_3$
%Concentrated	38	16	20	12	32

The contact angle of a methylated diamond increased from 25° to 48°, and similarly the concentration of diamond powder at the heptane/water interface increased from 38% to 55%. The contact angle of a surface of methyl groups is 110°(93), and this implies ,therefore, that the diamond surface was only partially covered with methyl groups, after methylation by reaction with diazomethane.

A number of diamonds stored in water contained in air-tight glass containers became completely hydrophilic after several weeks. The previous history of the diamond crystals did not affect, either the rate of ageing, or the final value (0°) of the contact angle. The ageing process could not be easily reversed, as drying an aged diamond at 120°C did not affect the contact angle. Washing an aged diamond with 40% HF did not alter the contact angle, indicating that the ageing process was not an adsorption of silicate material, leached from the glass container, onto diamond. The concentration of diamond powder at the heptane/water interface decreased to 5%, after 28 days ageing in water.

Fresh diamonds were stored in vessels made of polystyrene, polyethylene and tin, that had been soaked in water for 48 hours at 70°C. The contact angles of these diamonds were similar to those stored in the glass vessels for three weeks.

Two aged diamonds were crushed under liquid nitrogen, to produce fresh, clean diamond surfaces. There was no possible method of marking the original crystal faces, without contaminating the system, so the most jagged crystal faces were assumed to be the fresh ones. Their contact angles varied from 25° to 60°, whereas the contact angles of the original faces remained at zero. Another aged diamond was placed in an argon ion discharge, which is reported to strip off the surface layers of diamond crystals(30). A much rougher surface was obtained than that of the natural crystal, but the contact angle remained as zero. These two methods produced, therefore, quite different surfaces. As argon ion bombardment is known to produce a great deal of surface damage, it may be that the new surface became hydroxylated on contact with water, whereas some nitrogen may have been adsorbed by the crushed diamond. It is also possible that the surface atoms became rearranged after cleavage, but a LEED study would be necessary to examine these possibilities. None of the LEED studies to date have used a cleaved surface in their work(28)(29)(30).

6.2 The Zeta-Potential of Diamond

The dependence of the zeta-potential of unaged diamond on pH is shown in Figure 6.4. The isoelectric point (i.p.) of diamond was at pH 3.5, above which the zeta-potential became more negative with increasing pH, up to pH 9. Above pH 7.5 the zeta-potential was independent of pH.

After washing unaged diamond with 30% HCl and 20% HF, the dependence of the zeta-potential on pH changed to that shown in Figure 6.5. Both washes gave rise to similar curves, there was no i.p. in the pH range used, but extrapolation of the curve indicates that the i.p. would be less than pH 2. Above the i.p., the zeta-potential became markedly negative up to pH 5, and then became independent of pH, at a slightly more negative value than that of diamond powder washed with 15% HCl above pH 7.5.

The effect of washing the unaged powder with oxidising and reducing agents on the zeta-potential of diamond is presented in Figure 6.6. Potassium dichromate had very little effect on the zeta-potential, making it a little more negative than that obtained from diamond powder washed with 15% HCl. Washing with perchloric acid and nitric acid, however, produced a diamond surface with a much more negative zeta-potential, which was not very pH dependent. Diamond powder washed with sodium borohydride, had a similar zeta-potential to that of diamond washed with 15% HCl, up to pH 7, above which the zeta potential became less negative.

Methylation of unaged diamond gave rise to a slightly more negative zeta-potential over the pH range, than that of diamond washed with 15% HCl. The i.p. of methylated diamond was less than pH 3. These results are similar to those obtained for methylated silica(93), which had an identical zeta-potential/pH relationship to clean silica, although

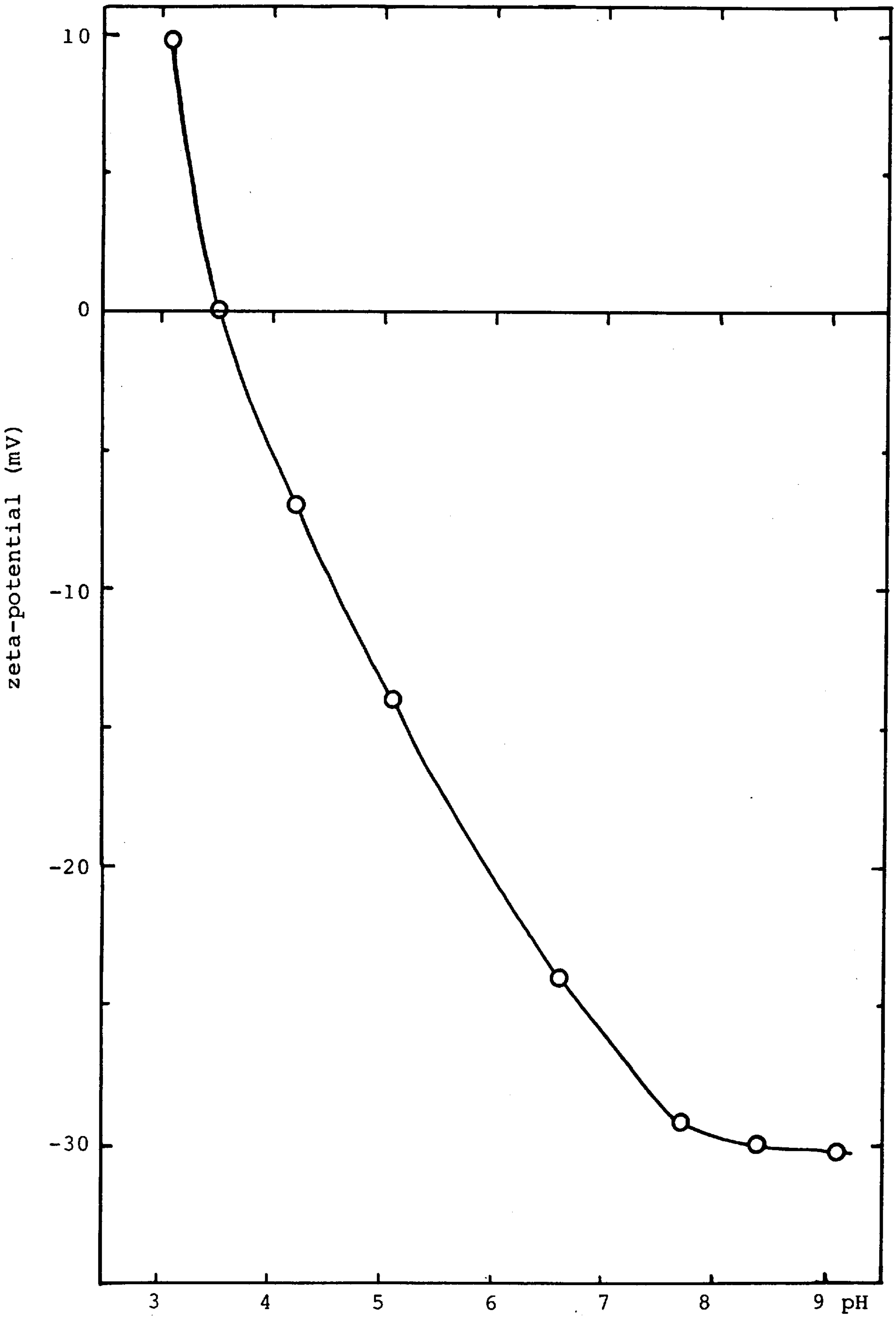


Figure 6.4: Zeta-potential of fresh diamond as a function of pH.

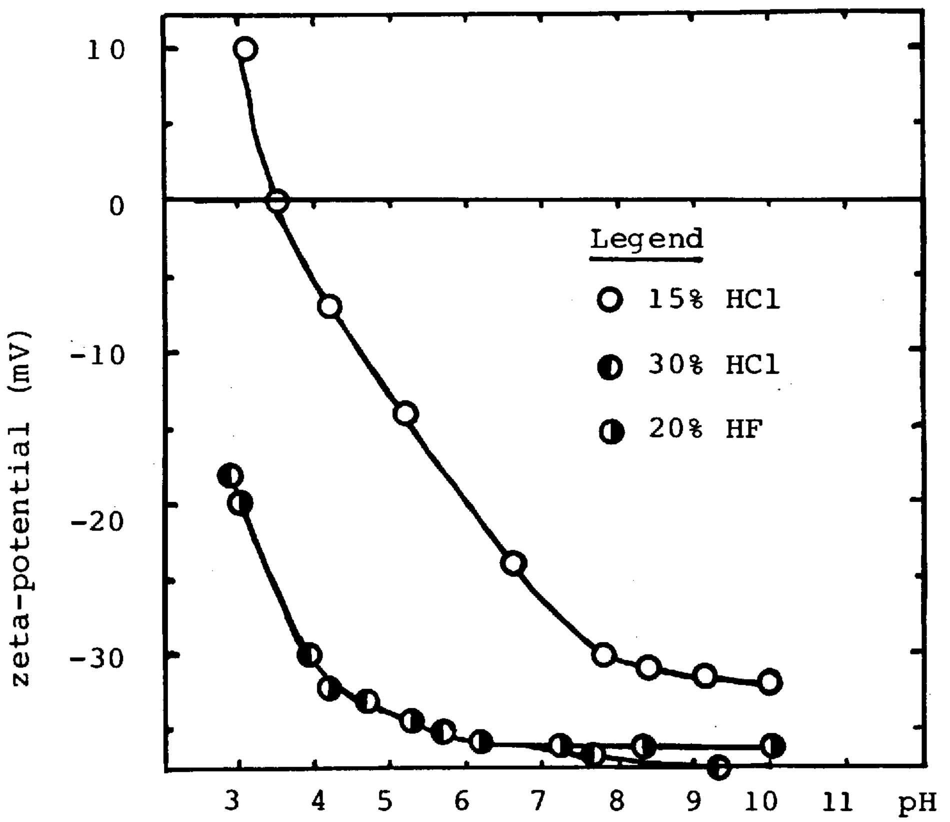


Figure 6.5: Zeta-potential of fresh diamond washed with halogen acids as a function of pH.

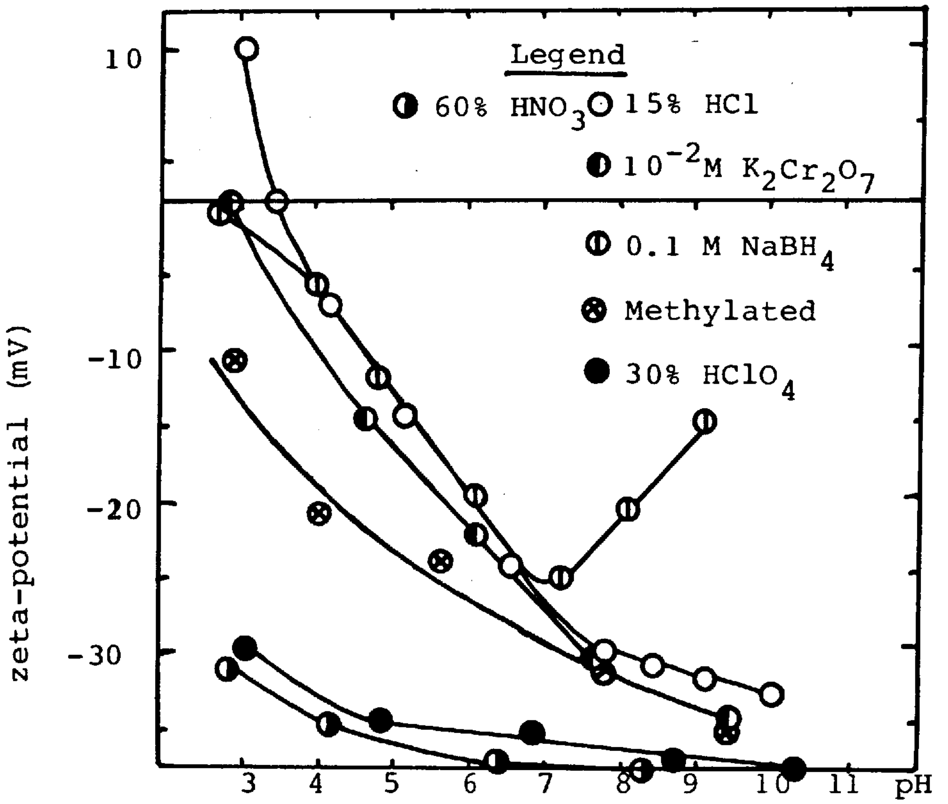


Figure 6.6: Zeta-potential of fresh diamond treated with oxidizing and reducing agents as a function of pH.

it was much more hydrophobic than clean silica. It was postulated that cross-linking siloxane groups could cause a zeta-potential, due to the interaction of water with the lone pairs of electrons on the oxygen atoms. Diamond is known to have ether-like oxygen on the surface, and thus a similar interaction may be occurring.

Ageing the diamond powder in water gave rise to a much more negative zeta-potential with much less dependence on pH, than that obtained after washing fresh diamond powder with 15% HCl. This is shown in Figure 6.7. The ageing effect was most rapid during the first two days, thereafter the rate of increasing negativity of the zeta-potential decreased. After 14 days of ageing the zeta-potential attained a constant value. The zeta-potentials of diamond powders aged in aqueous solutions of NaOH, NaCl and HCl, at concentrations from 10^{-3}M to 10^{-1}M, were the same as those obtained on powders aged in water. The ageing process was, therefore, independent of pH and ionic strength.

The reversal of the ageing process was attempted by drying the aged diamond powder in vacuum, and by heating at 120°C. The zeta-potentials of these samples are presented in Figure 6.8. Both drying processes caused the zeta-potential to become less negative by approximately the same amount. The zeta-potential was almost independent of pH, and there was no i.p. in the pH range 3 - 10. Treatment of an aged diamond powder with sodium borohydride did not significantly affect the zeta-potential. Methylation of an aged diamond powder, however, caused the zeta potential to become markedly more dependent on pH, and much less negative below pH 7.5. The i.p. of this sample, by extrapolation, was approximately pH 2.5. Ageing of oxides and silicates in water has been studied(94)(95), and the changes in the surface properties observed for oxides were similar to those seen with diamond.

Ageing diamond powders initially washed with concentrated halogen acids also produced more negative zeta-potentials.

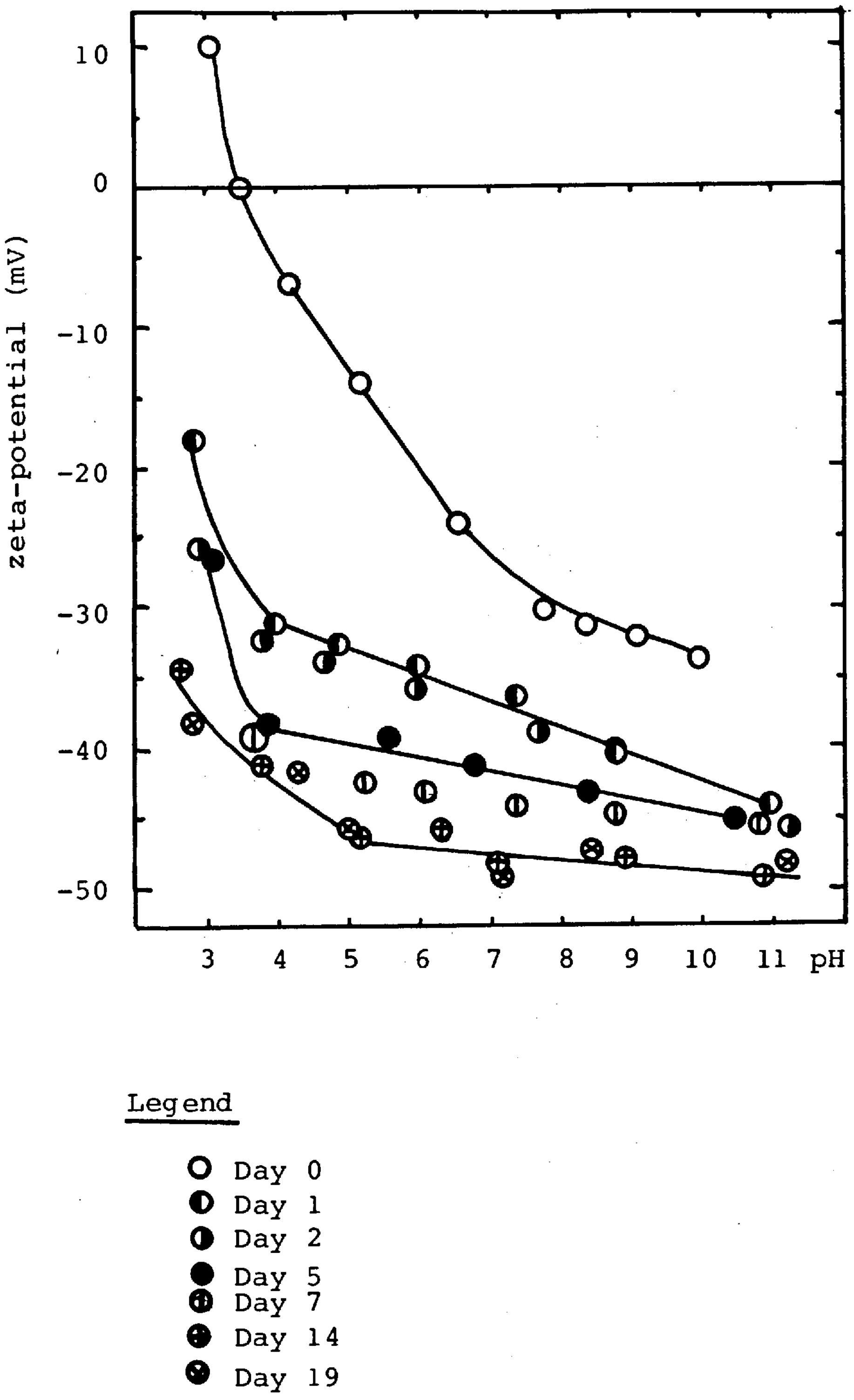


Figure 6.7: Zeta-potential of diamond as a function of pH, after various times of ageing in water.

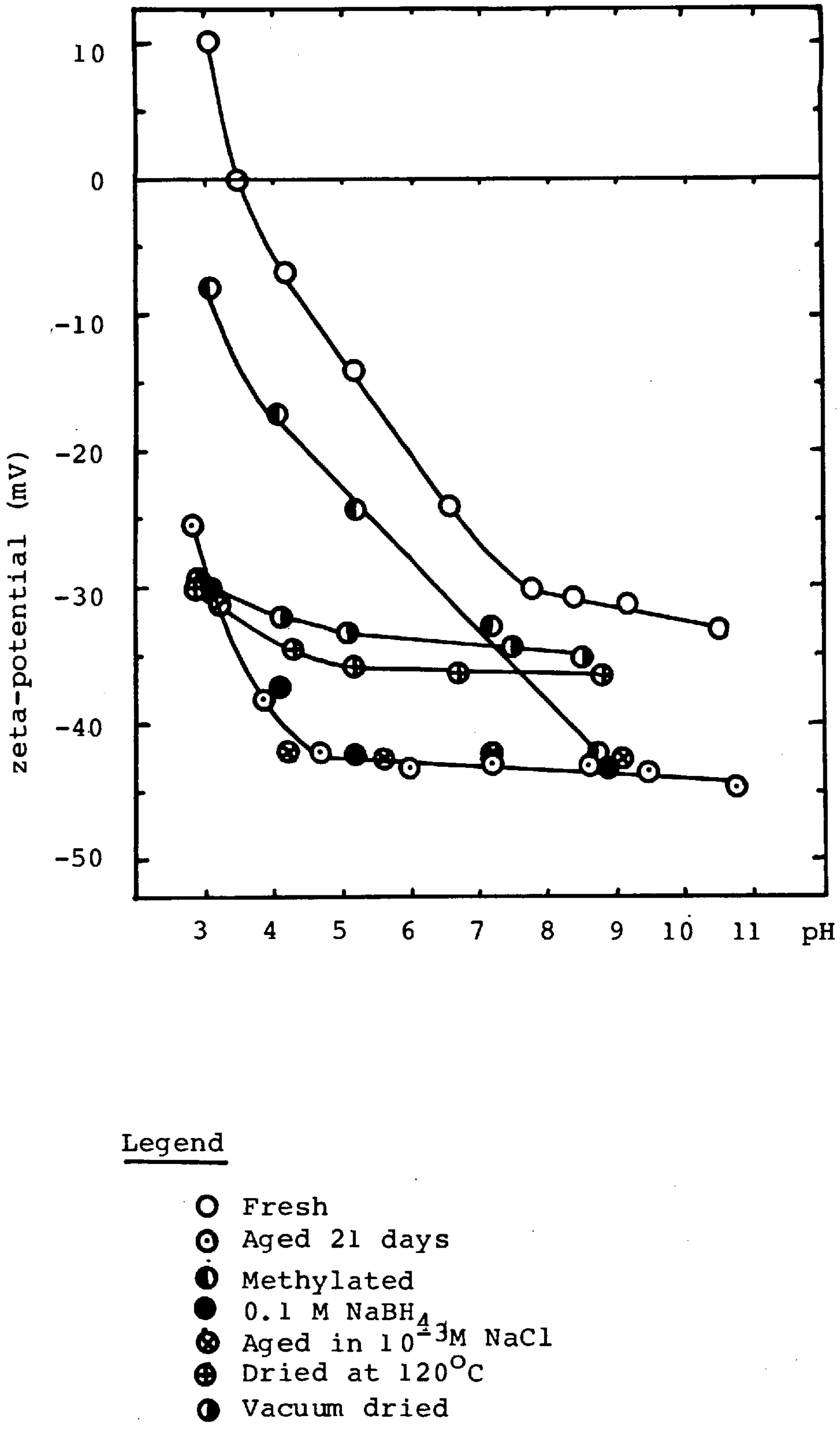


Figure 6.8: Zeta-potential of diamond aged in water for 21 days as a function of pH after various treatments.

The equilibrium zeta-potential/pH curves (Figure 6.9) obtained after 14 days ageing of powder washed with 30% HCl and 20% HF were coincident, and about 15 mV more negative than those obtained with unaged powder. The zeta-potential/pH relationships of these aged powders were identical to that for powder washed with 15% HCl and aged for 14 days.

Hydrolysis of the methylated diamond powders, fresh and aged, did not affect the zeta-potential, the values remained equal to those of the non-hydrolysed methylated powders.

The results for the zeta-potential/pH dependence of diamond, show that, although washing with concentrated acids gives a more negative zeta potential initially, than that of diamond powder washed with 15% HCl, the equilibrium value for a daiaond aged in water is not affected by the conditions of ageing, or the previous treatment of the diamond powder.

6.3 Acid/Base Properties

Two methods of measurement of the acid/base properties were used in this research project. One method was a determination of the proportion of groups of certain strengths on the diamond surface, whereas the other method was a determination of the net consumption of hydroxyl ions by a diamond powder.

The curves for the titration of unaged diamond samples with four bases are shown in Figures 6.10 and 6.11, and Table 6.2 shows the consumption of the bases to achieve neutralization of the surface groups on diamond.

The results show that groupsof different acidities were present on the diamond surface. The bicarbonate end point has been attributed to carboxylic acid type groups(27), and that of sodium carbonate to carboxylic and lactone groups. Sodium hydroxide is considered to neutralize the latter

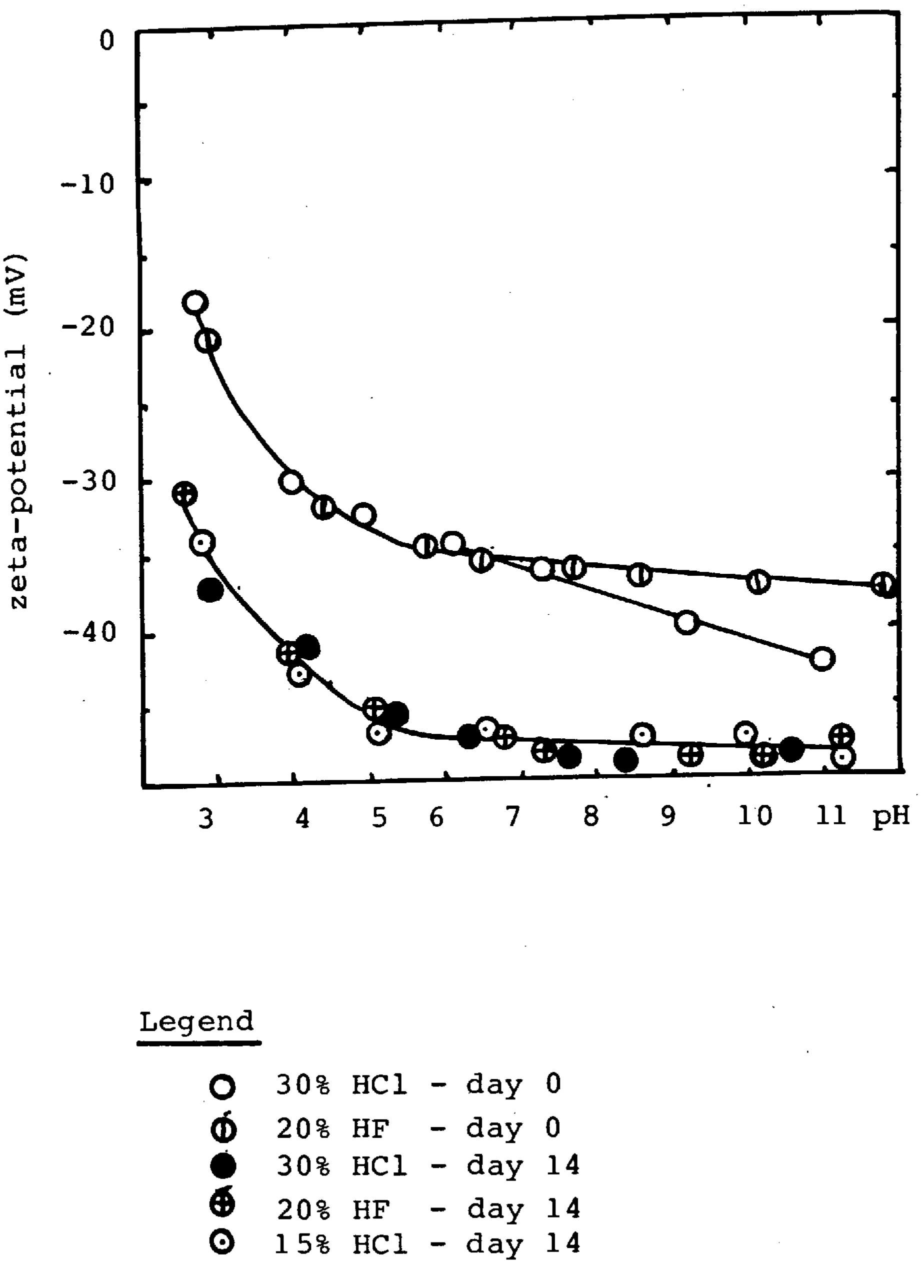


Figure 6.9: Zeta-potential of diamond washed with halogen acids as a function of pH, after ageing in water.

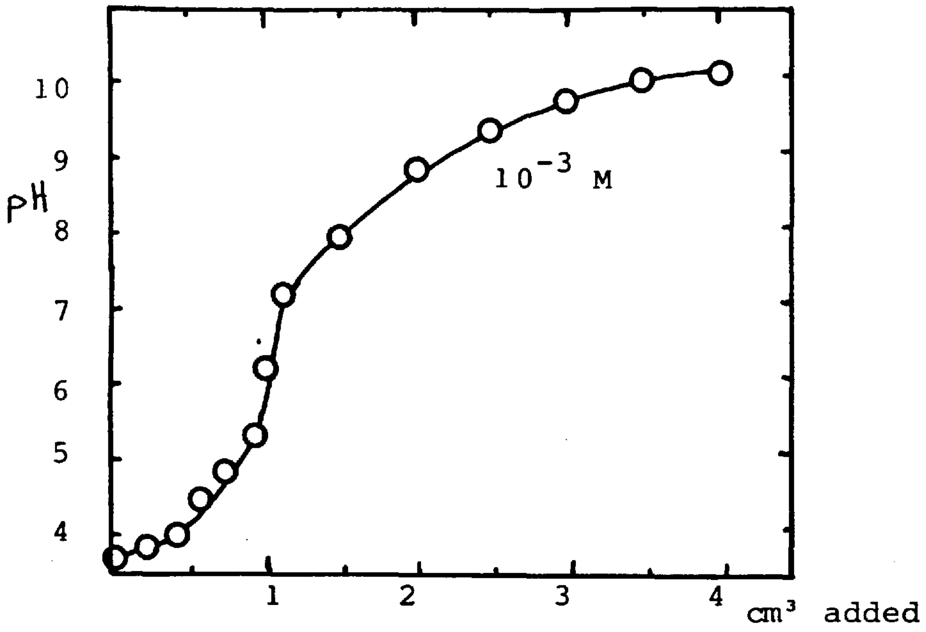


Figure 6.10: Titration of fresh diamond with NaOH

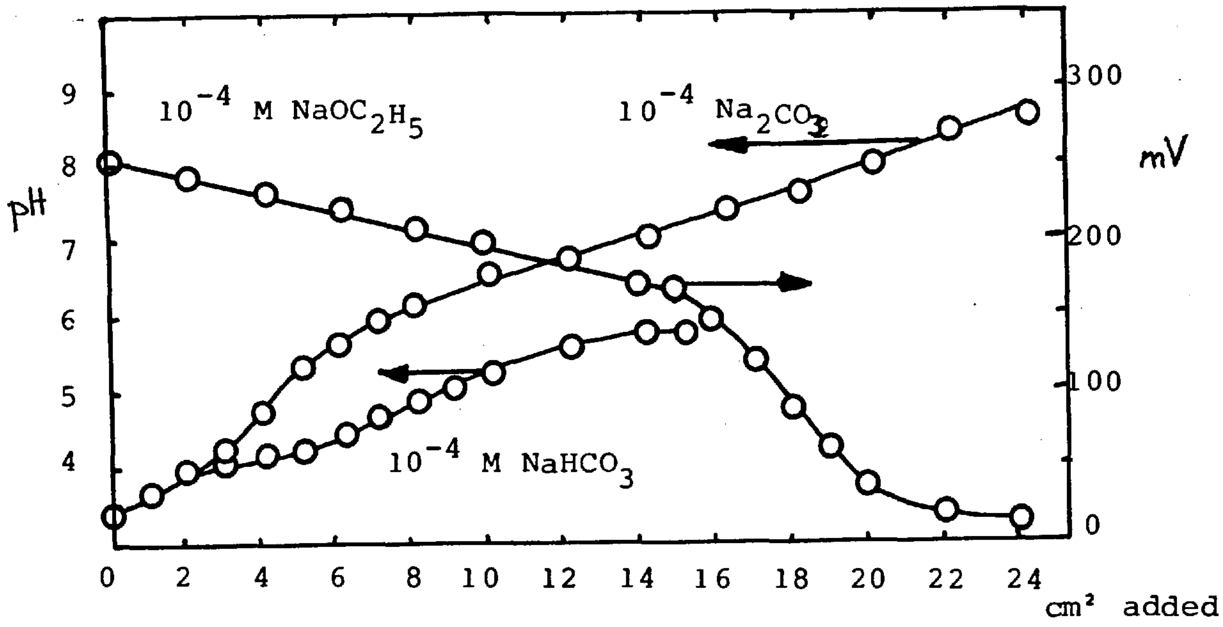


Figure 6.11: Titration of fresh diamond with sodium carbonate sodium bicarbonate and sodium ethoxide.

two groups and quinones. Assuming that the last end point represents the total number of acidic groups on the surface, over 30% of the groups on diamond were carboxylic in nature. This titrimetric method, however, cannot identify surface groups, it can only show that different surface groups are present on the surface.

Table 6.2 Neutralization of acidic surface oxides on unaged diamond.

Base	$NaHCO_3$	Na_2CO_3	NaOH	C_2H_5ONa
Consumption (meq g^{-1})	6×10^{-3}	10^{-2}	1.1×10^{-2}	1.8×10^{-2}

The other method of representing the acid/base properties of solid surfaces, measurement of the net adsorption of hydroxyl ions, has been widely used to study a variety of oxide materials. The results for unaged diamond are presented in Figure 6.12. The net adsorption of hydroxyl ions increased with increasing pH and ionic strength. The titration curves rise sharply at high pH, suggesting very weak acidity. At pH 9 and an ionic strength of 0.1M, the maximum adsorption density of hydroxyl ions corresponds to an area per ion of 57 $\AA^2$. The surface area occupied by one carbon atom on a (111) diamond face is 5.4 $\AA^2$, and on a (100) face 6 $\AA^2$ (96). Therefore at most only 10% of the surface carbon atoms adsorbed hydroxyl ions. The hydroxyl adsorption was reversible, as starting the titration in 1 mM NaOH produced the same adsorption densities as those obtained by starting in 1 mM HCl. Comparison of these results with the zeta-potential data on unaged dimaond shows that, as the zeta-potential becomes more negative with pH, the consumption of hydroxyl ions increases. This indicates that the surface hydroxyl groups ionized (at high pH), to give a negative surface, and protons in solution.

The adsorption of hydroxyl ions was slightly reduced over the whole pH range after washing the diamond with 30% HCl,

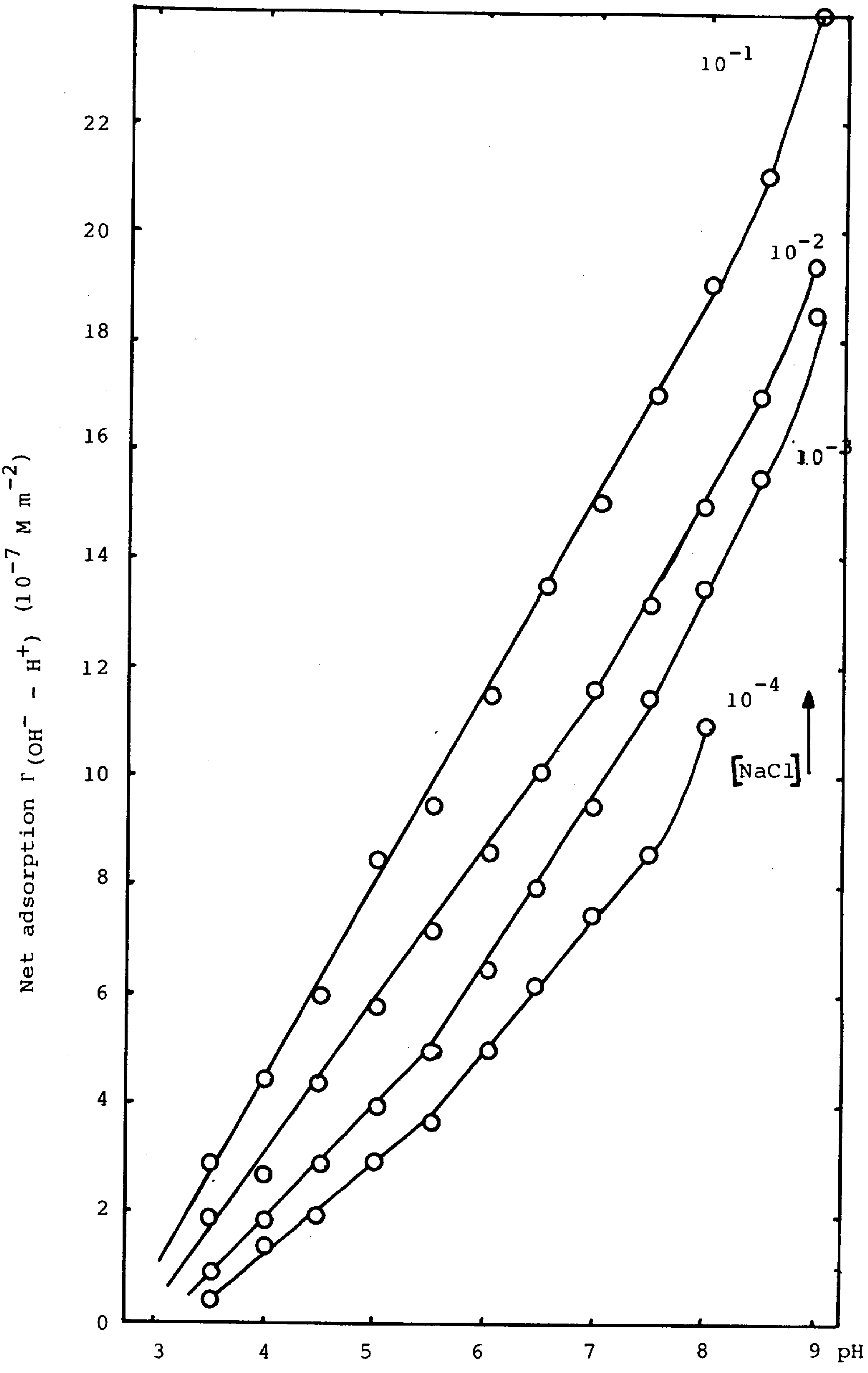


Figure 6.12: Net adsorption of hydroxyl ions by fresh diamond as a function of pH, at four concentrations of support electrolyte.

as can be seen in Figure 6.13, whereas washing with 20% HF markedly reduced the adsorption of hydroxyl ions. These results contrast with the zeta-potential data, where the zeta potential was independent of the acid wash used. There was much less adsorption at low pH values than for diamond washed with 15% HCl, but the adsorption increased with increasing pH after both washed, with a marked rise in adsorption at high pH values indicating weak acidity.

The effect of washing with oxidising and reducing agents on the net adsorption of hydroxyl ions by unaged diamond, is presented in Figure 6.14. Perchloric acid reduced the abstraction of hydroxyl ions from that obtained with diamond washed with 15% HCl. The reduction was most marked at pH values less than 6. The nitric acid washed sample adsorbed much less hydroxyl than either the 15% HCl or the perchloric acid washed samples, and at pH 9 the adsorption was less than 40% of that obtained on the former sample. Sodium borohydride reduced the value of the net adsorption of hydroxyl ions by unaged diamond to 10% of the value for diamond washed with 15% HCl, over the whole pH range.

Methylation of unaged diamond reduced the net adsorption of hydroxyl ions more than treatment with sodium borohydride (Figure 6.15). Above pH 8.5 the adsorption rose sharply, indicating that some of the weak acid groups had not been methylated. A hydrolysed methylated sample showed an increased adsorption compared to the methylated sample. The hydroxyl adsorption was still much reduced, however, compared to that of a diamond sample washed with 15% HCl, and there was a marked rise in the adsorption above pH 9. These results are similar to those obtained by Boehm(42) for a variety of carbons, which nearly always had a residual acidity after reaction with diazomethane, that should have removed all active hydrogen from the carbon surface.

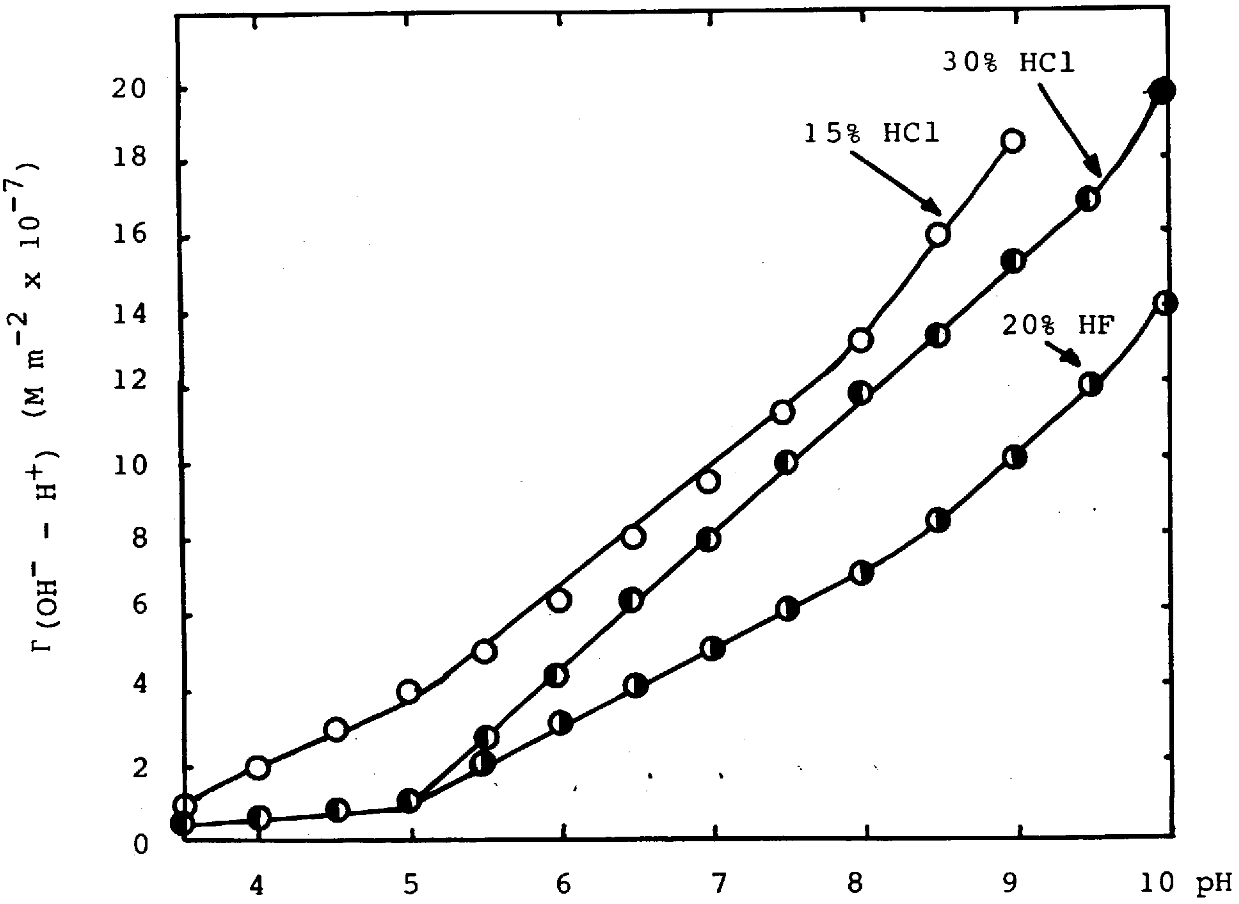


Figure 6.13: Net adsorption of hydroxyl ions by fresh diamond washed with halogen acids, as a funtion of pH.

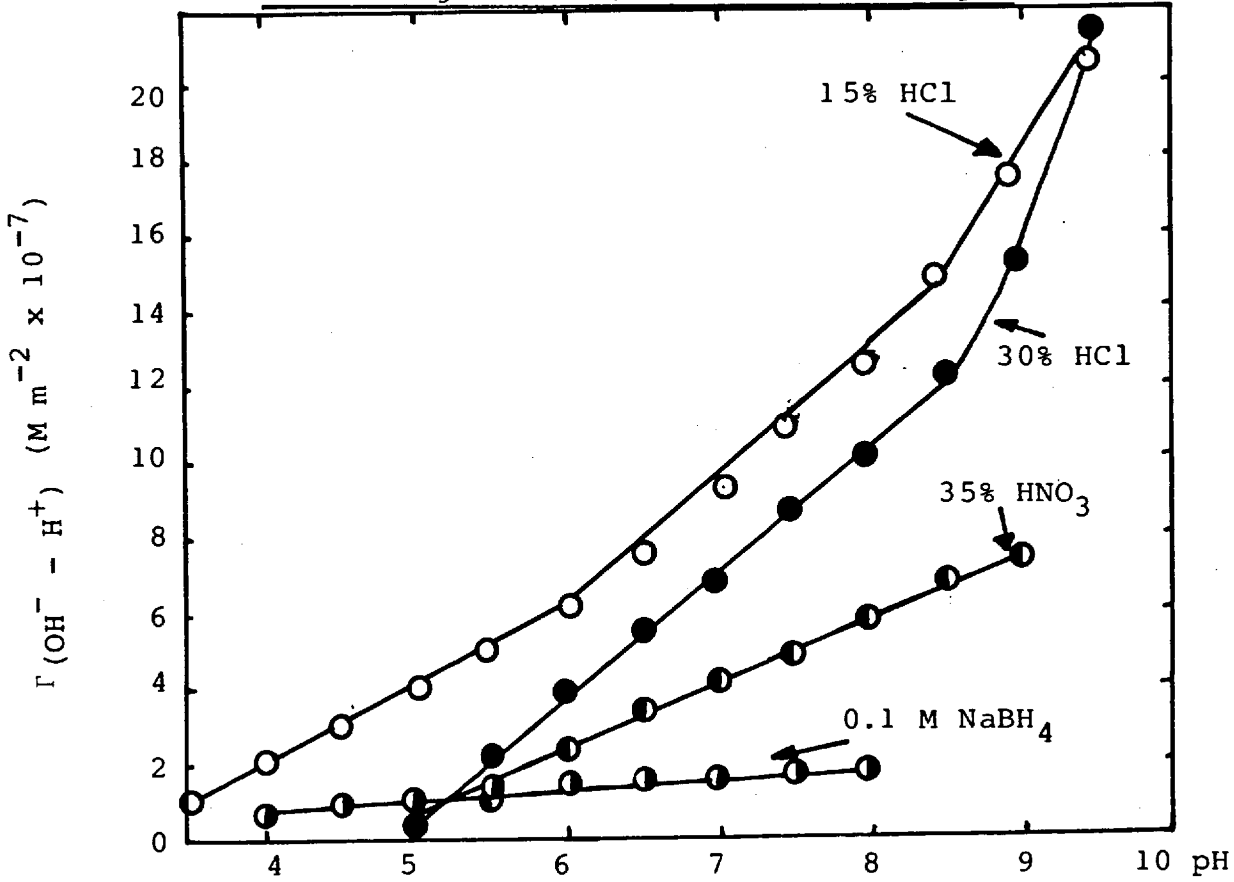


Figure 6.14: Net adsorption of hydroxyl ions by fresh diamond treated with oxidizing and reducing agents as a function of pH.

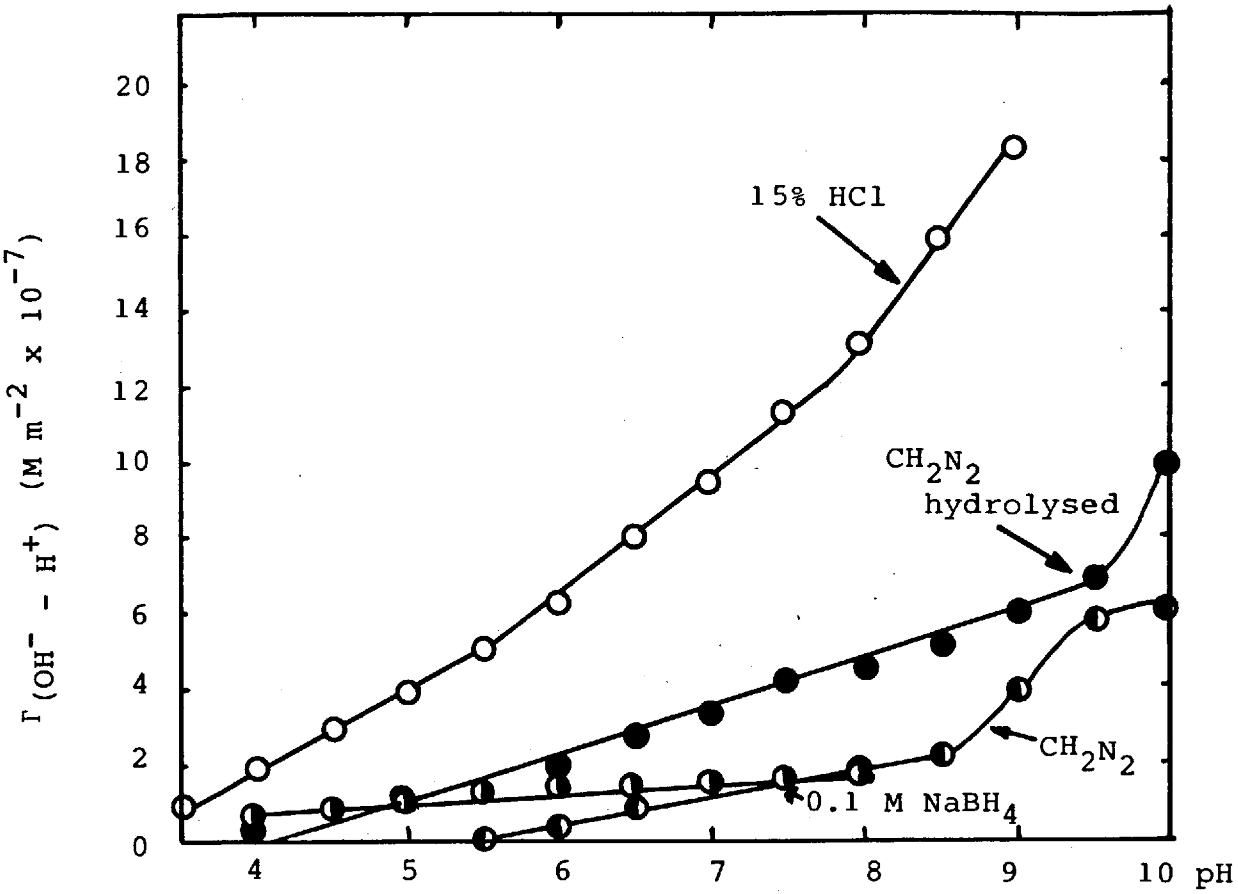


Figure 6.15: Net adsorption of hydroxyl ions by fresh diamond treated with reagents to complex surface groups as function of pH.

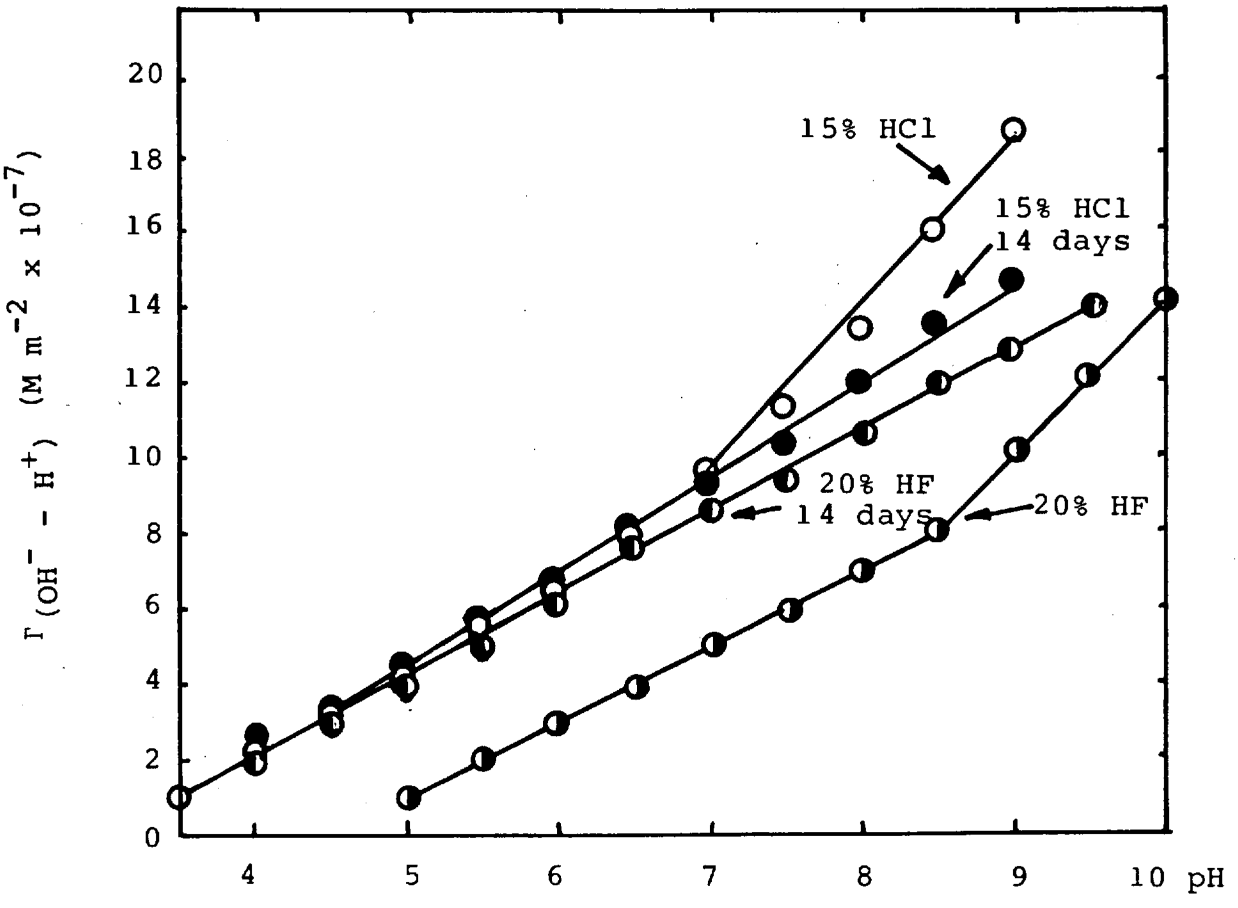


Figure 6.16: Net adsorption of hydroxyl ions by diamond aged in water for 14 days

The effect of ageing on the net adsorption of hydroxyl ions can be seen in Figure 6.16. The adsorption did not change much with respect to time for a sample washed with 15% HCl, but it increased markedly for the diamond sample washed with 20% HF. The adsorption for the two aged samples was not markedly different over the pH range 4 - 9. This effect is similar to that observed with the zeta-potentials, although the value for the uptake of hydroxyl ions did not change as the zeta potential became more negative.

Drying an aged diamond sample caused an increase in the adsorption of hydroxyl ions over the pH range 4 - 9, as shown in Figure 6.17. Reduction by sodium borohydride and methylation of the aged diamond sample both markedly reduced the hydroxyl uptake. There was no sharp rise in the adsorption for the methylated aged sample above pH 8.5, but below that value the adsorption was similar to that of a methylated fresh sample. Reduction, however, did not reduce the adsorption of hydroxyl ions on an aged diamond sample as much as for a fresh sample, and the adsorption increased with increasing pH.

Ageing a diamond sample in 10^{-2} M NaCl solution doubled the abstraction of hydroxyl ions (Figure 6.18). Drying a similarly aged sample of diamond reduced the net hydroxyl uptake, but not to the value obtained for either diamond aged in water or fresh diamond.

There appears to be little correlation between the zeta-potential and hydroxyl adsorption of diamond, as can be seen from Table 6.3.

6.4. Infrared Spectra

The infrared spectra of variously treated diamond powders are presented in Figures 6.19 and 6.20. Ageing had no effect on the spectra obtained. The major problem with the

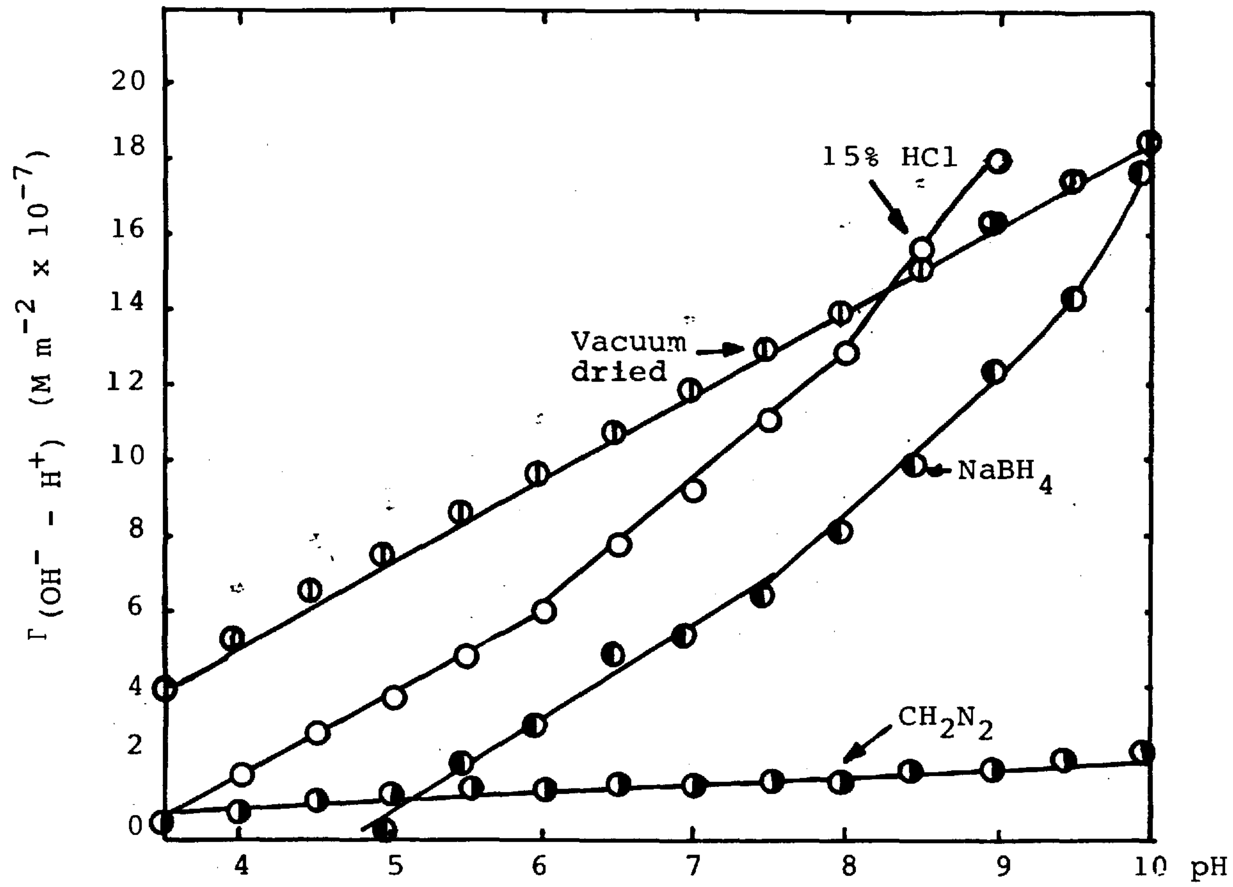


Figure 6.17: Net adsorption of hydroxyl ions by diamond aged in water for 14 days as a function of pH after various treatments.

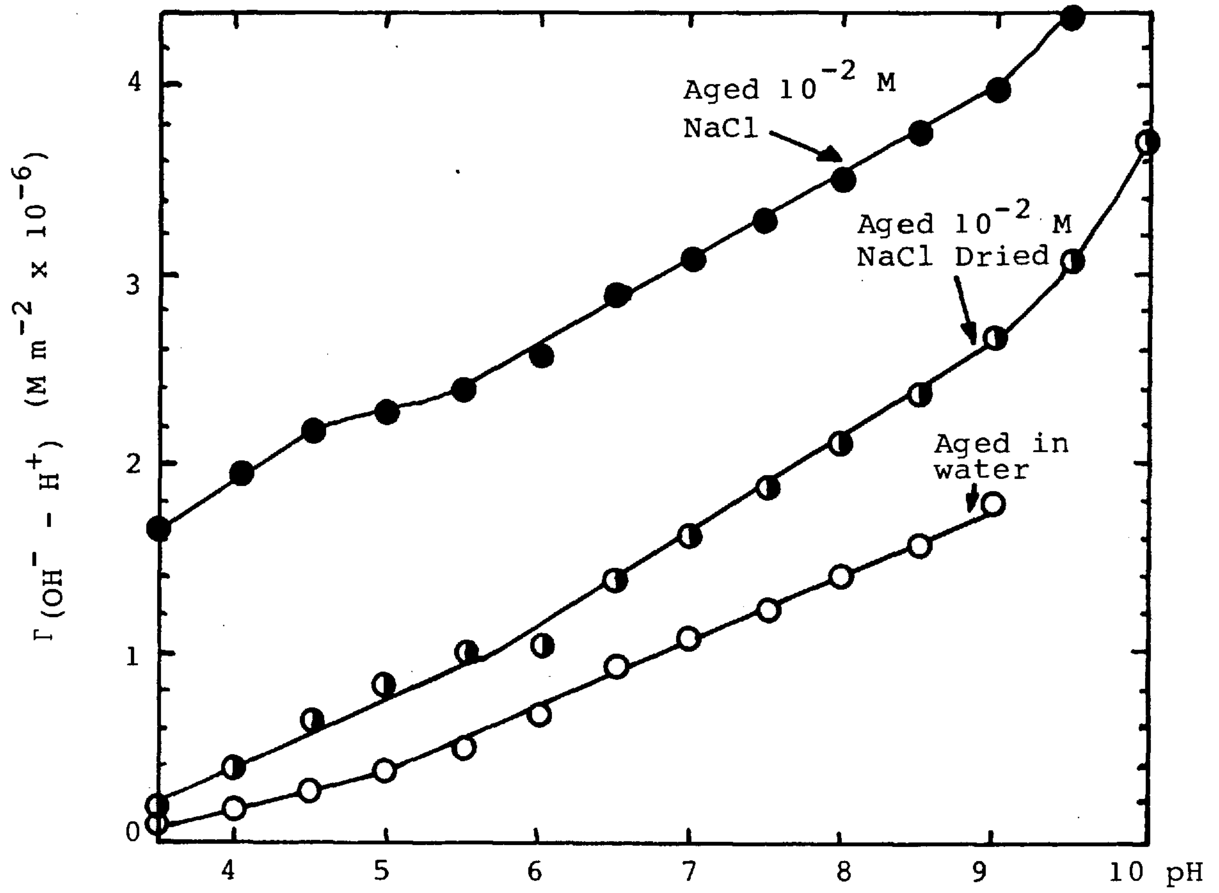


Figure 6.18: Net adsorption of hydroxyl ions by diamond aged in NaCl for 14 days as a function of pH.

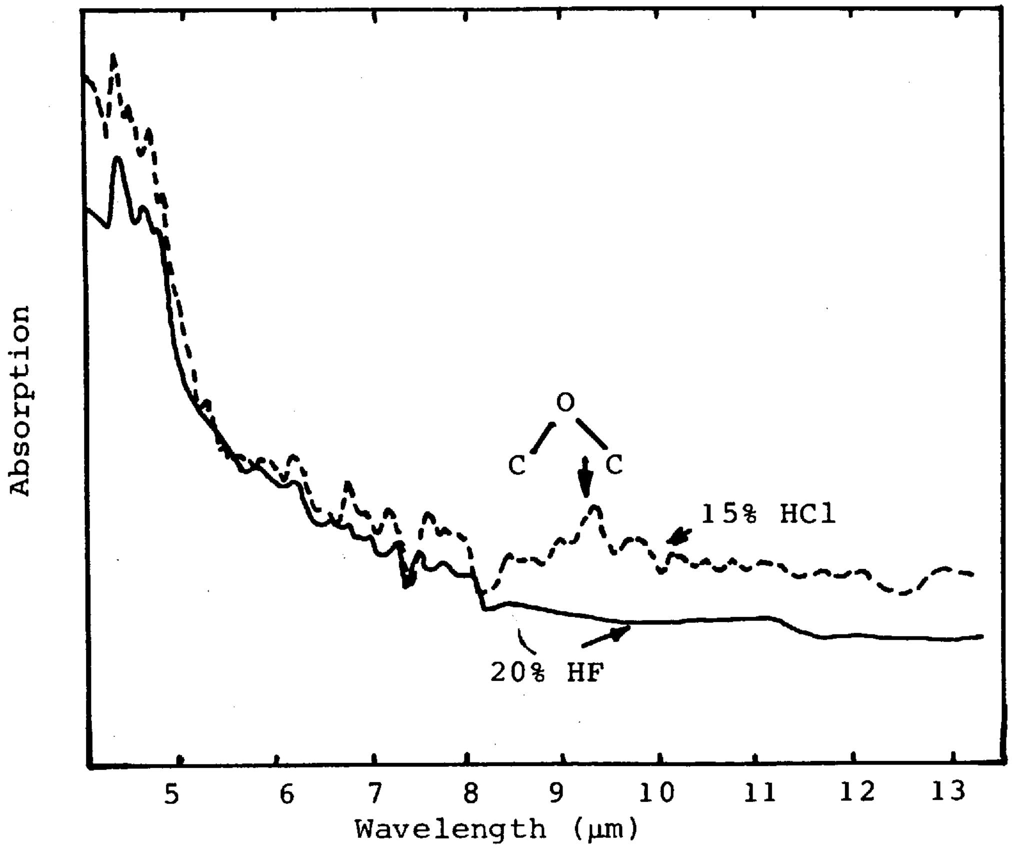


Figure 6.19: Infrared spectrum of diamond washed with HF

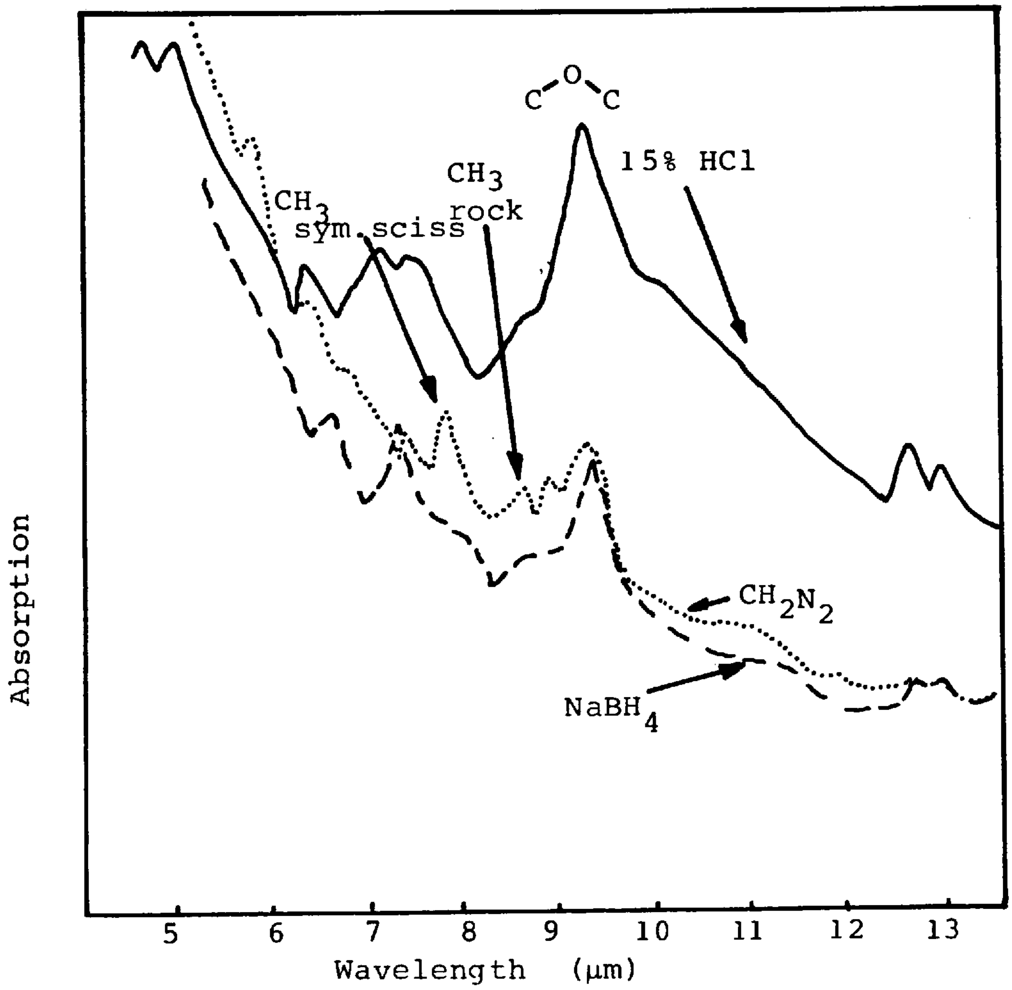


Figure 6.20: Infrared spectra of methylated and reduced diamond

interpretation of these spectra is the high background absorbance of the samples, particularly at wavelengths shorter than 6 µm, which is where the majority of the OH absorption bands occur.

Table 6.3 A comparison of the zeta-potential and hydroxyl adsorption of variously treated diamond powders to those of diamond powder washed with 15% HCl

Diamond sample	Aged		Unaged	
	ζ	$\Gamma(OH^- - H^+)$	ζ	$\Gamma(OH^- - H^+)$
Oxidation	Increased	Decreased	Unaffected	Unaffected
Reduction	Unaffected	Greatly Reduced	Unaffected	Reduced
Methylation	Unaffected	Greatly Reduced	Reduced	Greatly Reduced
Concentrated halogen acids	Increased	Slightly Decreased	Unaffected	Increased

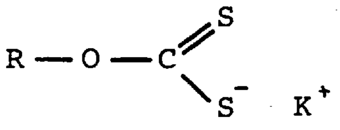
There is one particularly strong absorption band in the diamond spectrum, at 9.18 µm, that is due to C-O-C bands. The intensity of this band was unaffected by methylation, reduction and oxidation, but it was reduced by washing diamond with concentrated halogen acids. Washing a diamond powder with 20% HF caused the band to disappear from the spectrum.

The spectrum of the methylated diamond showed two distinct bands that could be attributed to methyl groups. These occurred at 7.5 µm and 8.4 µm, and they were CH_3 symmetrical scissoring and CH_3 rock respectively.

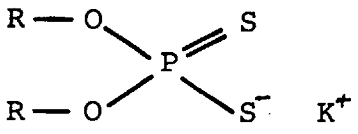
None of the other bands could be identified although the high absorbance at wavelengths shorter than 6 μm is indicative that there are many OH groups on the surface.

7. ADSORPTION FROM AQUEOUS SOLUTION ON DIAMOND

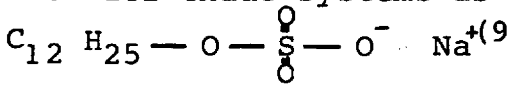
Modification of the wettability of a mineral by adsorption of organic and inorganic substances is the most important step in the recovery of minerals by froth flotation. In general a mineral is made more hydrophobic by the adsorption of a surfactant, usually termed a collector, whereas a mineral is made more hydrophilic by the adsorption of either an inorganic salt or an organic complex, usually termed a depressant. Collectors can be divided into two major types, thiol and non-thiol reagents, and the latter type can be further subdivided into anionic and cationic surfactants. The thiol type reagents are generally short-chain (C_2 - C_5) molecules, the most common being the xanthate series, and the dithiophosphates (97). These reagents adsorb by forming chemical compounds on the mineral surface.

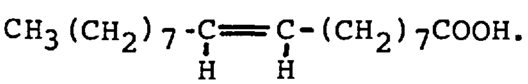


xanthate



dithiophosphate

The anionic non-thiol collectors are generally sodium salts of long-chain (C_{10} - C_{16}) molecules, for example carboxylates, sulphates and sulphonates. An example of an anionic collector that has been widely studied for oxide systems is sodium dodecyl sulphate (SDS),  $C_{12}H_{25}-O-\overset{O}{\underset{O}{S}}-O^{-}\ Na^{+}$ (98).

This surfactant is adsorbed coulombically at the oxide water interface, followed by adsorption due to hydrophobic bonding between the hydrocarbon chains. There is no strong chemical bonding between the ion and the surface. Another example of the anionic collectors that has been widely studied is oleic acid (cis9,10-ene,octadecanoic acid)  $CH_3(CH_2)_7-\underset{H}{C}=\underset{H}{C}-(CH_2)_7COOH$.

This collector is widely used in the flotation of salt type minerals, in which the surfactant forms a surface chemical compound, but however further adsorption of the surfactant can occur by hydrophobic bonding between the hydrocarbon chains of the molecules$^{(98)}$.

Amines are the most widely used of the cationic collectors, particularly in the flotation of oxides and silicates$^{(99)}$. These reagents adsorb by the same mechanism as SDS. A typical example of an amine used in flotation is dodecylamine $C_{12}H_{25}NH_2$.

To determine the effect of commonly used flotation collectors on the surface chemistry of diamond, adsorption, wettability and zeta-potential measurements were made in the presence of aqueous solutions of SDS, DDA, oleic acid and various dithiophosphates.

7.1 Interaction of Sodium Dodecyl Sulphate at the Diamond/Water Interface

The effect of SDS on the diamond/water/air contact angle and the zeta-potential of diamond are shown in Figures 7.1 and 7.2 respectively. In both cases the diamond sample was unaged. At pH 2.8 the contact angle increased from 25°, the value obtained for a hydrophobic diamond in water, to approximately 35° as the SDS concentration was increased to 10^{-5}M. Above this concentration the contact angle remained constant until the critical micelle concentration (c.m.c.) of SDS at 8.2×10^{-3} M (100) was approached, whereupon the diamond became hydrophilic. At pH 5.8 the contact angle increased slightly with SDS concentration, and then also decreased to zero as the c.m.c. was approached. With aged diamond the contact angle increased from zero at 10^{-6} M SDS to a maximum at 10^{-3} M SDS of 27°. At higher concentrations the contact angle decreased to zero.

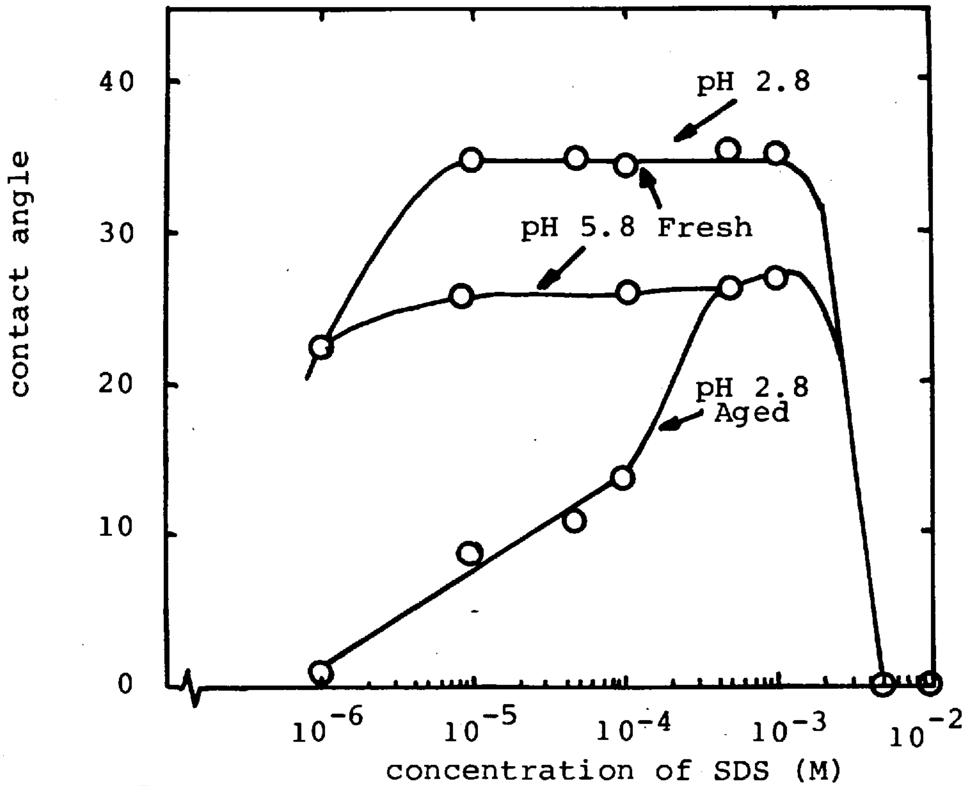


Figure 7.1: Contact angle of diamond as a function of SDS concentration at two pH values.

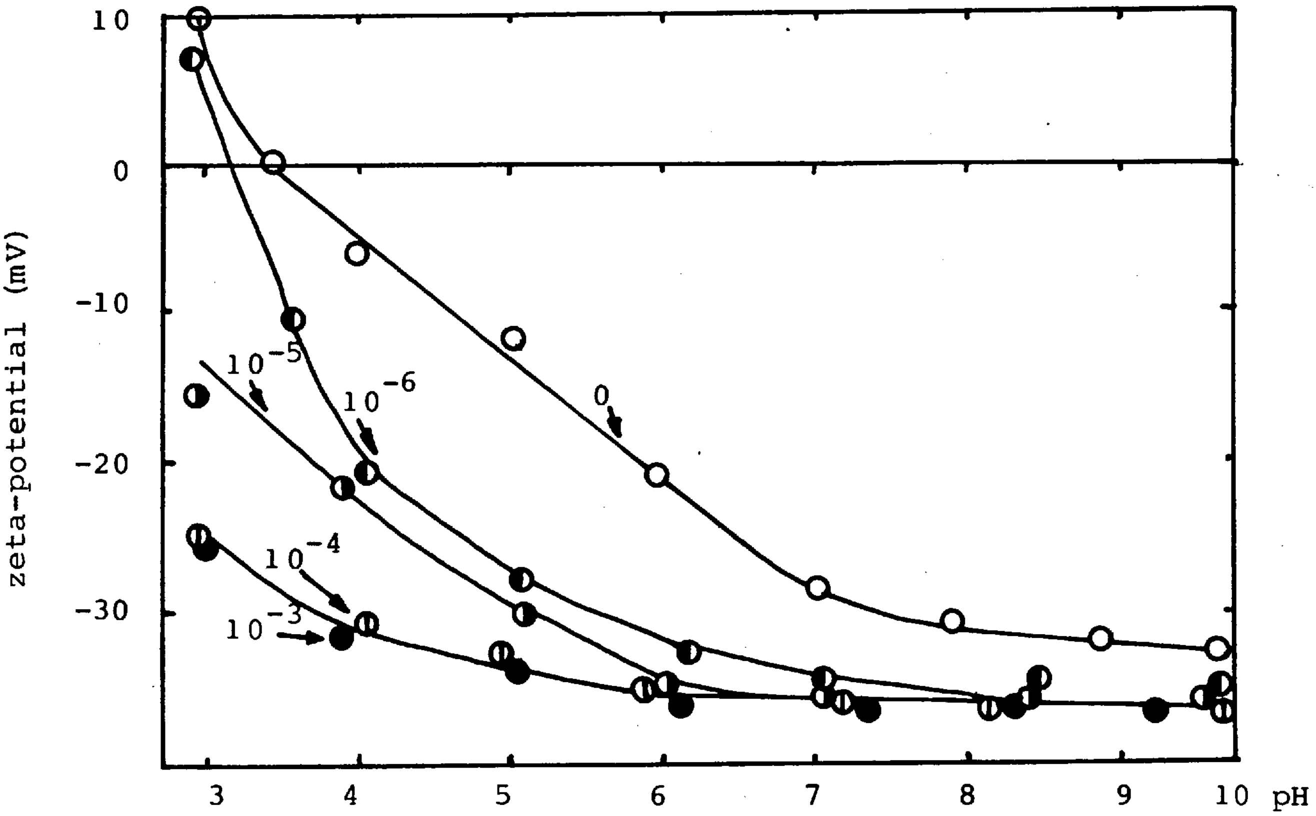


Figure 7.2: Zeta-potential of fresh diamond as a function of pH at various SDS concentrations.

The zeta-potential pH curves obtained in the presence of different SDS concentrations were displaced to more negative zeta-potential values, than those obtained with fresh diamond in the absence of SDS. The zeta-potential became more negative with increasing SDS concentration, especially at low pH values, as shown in Figure 7.3, where the zeta-potentials have been replotted as a function of SDS concentration.

SDS had no effect on the zeta-potential of an aged suspension of diamond.

7.2 Interaction of Amines at the Diamond/Water Interface

The effect of DDA on the air/water/diamond and heptane/water/diamond contact angles is shown in Figure 7.4. The air contact angles increased with amine concentration, for both the 'hydrophobic' and 'hydrophilic' diamonds, to a maximum at approximately 10^{-4} M. Above this concentration the angles decreased to zero. The results obtained with heptane were similar to those obtained with air except the values of the contact angle were higher. As expected the contact angles of the 'hydrophilic' diamonds were lower than those of the 'hydrophobic' ones.

The effect of DDA on the zeta-potential of fresh and aged diamond powders is presented in Figures 7.5, 7.6 and 7.7. At constant pH, the zeta-potential of both fresh and aged powders became more positive with increasing DDA concentration. The zeta-potential of fresh diamond in the presence of DDA was much more dependent on pH, then that of aged diamond. The reversal of zeta-potential for fresh diamond occurred at an amine concentration of 2×10^{-4} M, at pH values greater than 6, whereas the reversal for aged diamond occurred at 7×10^{-5} M, at pH values greater than 3.

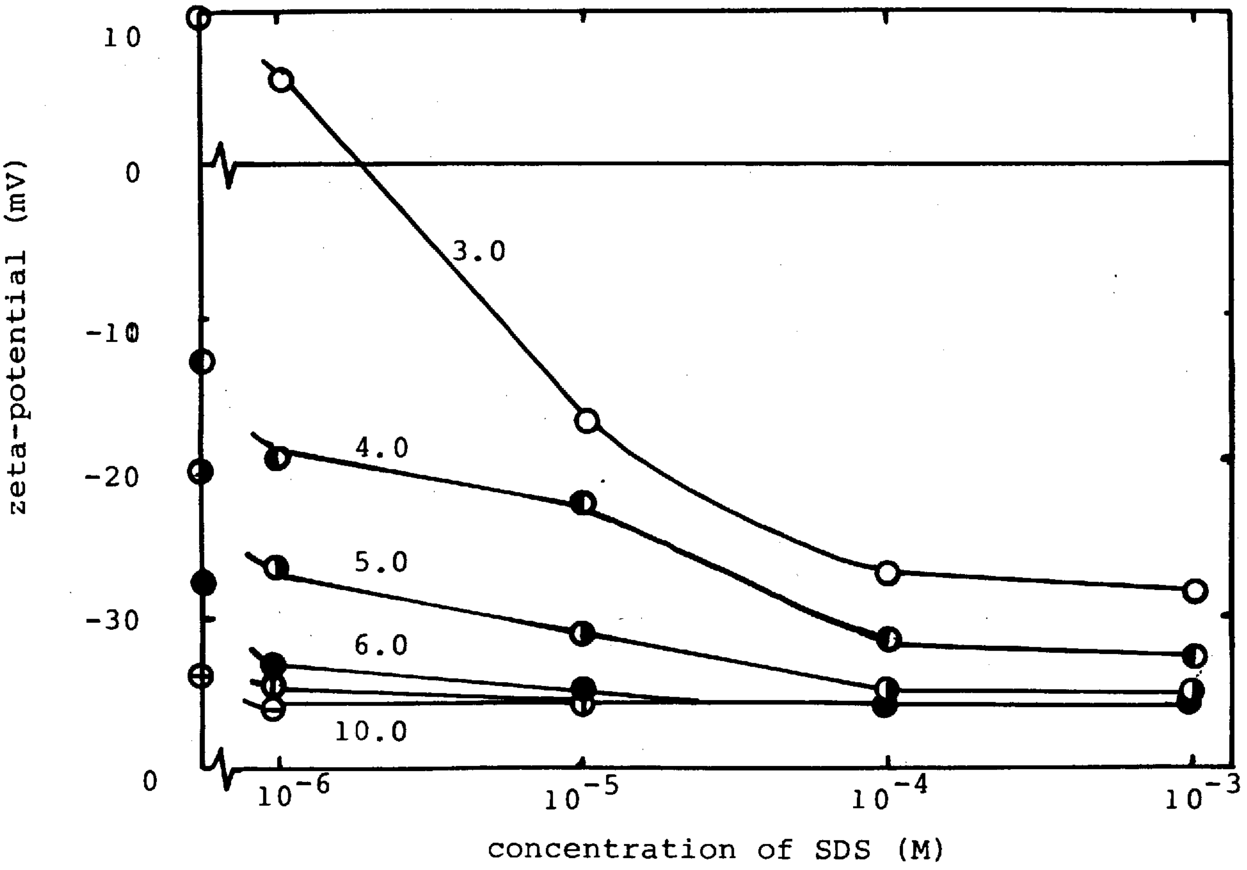


Figure 7.3: Zeta-potential of fresh diamond as a function of SDS concentration at various pH values.

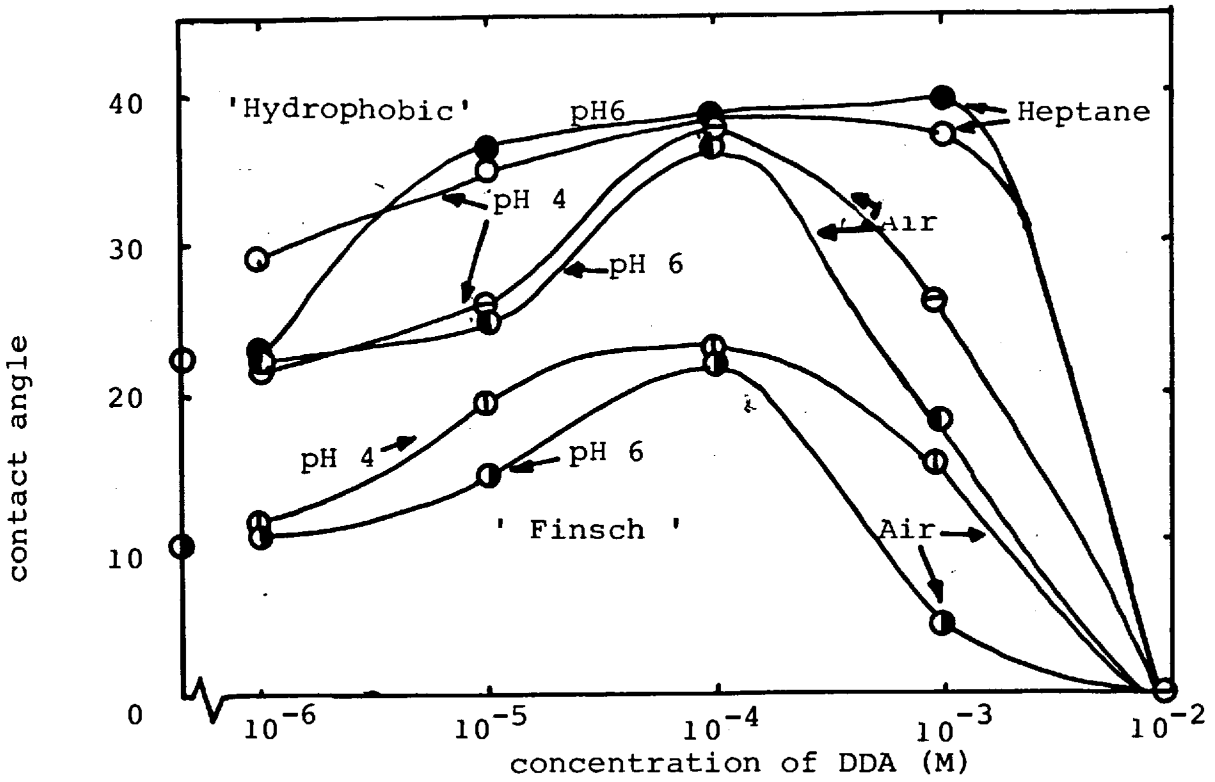


Figure 7.4: Contact angle of fresh diamond as a function of DDA concentration at two pH values.

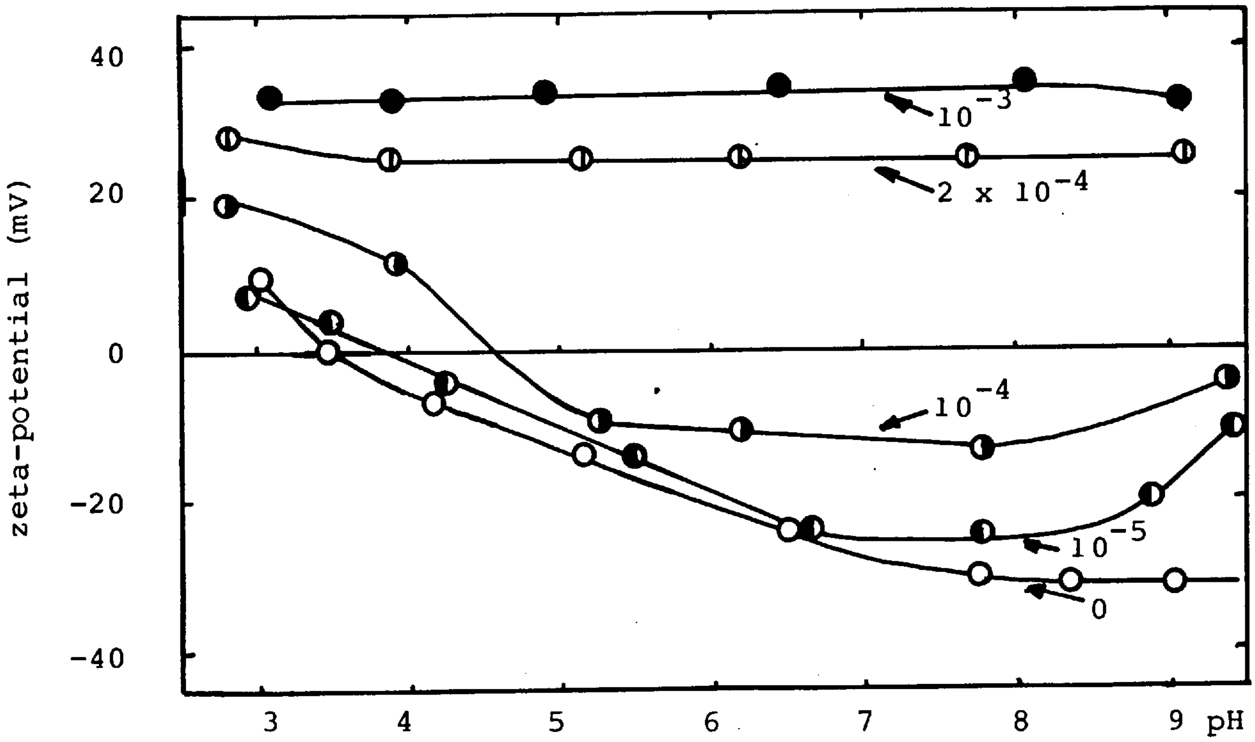


Figure 7.5: Zeta-potential of fresh diamond as a function of pH at various DDA concentrations.

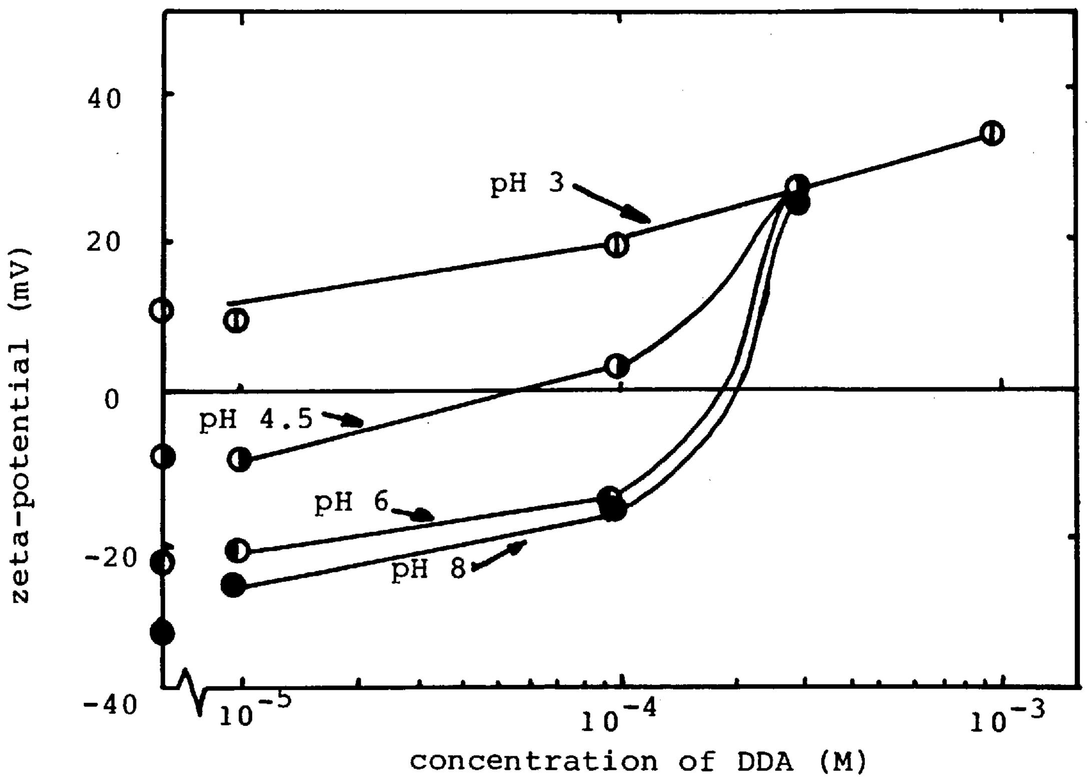


Figure 7.6: Zeta-potential of fresh diamond as a function of DDA concentration at various pH values.

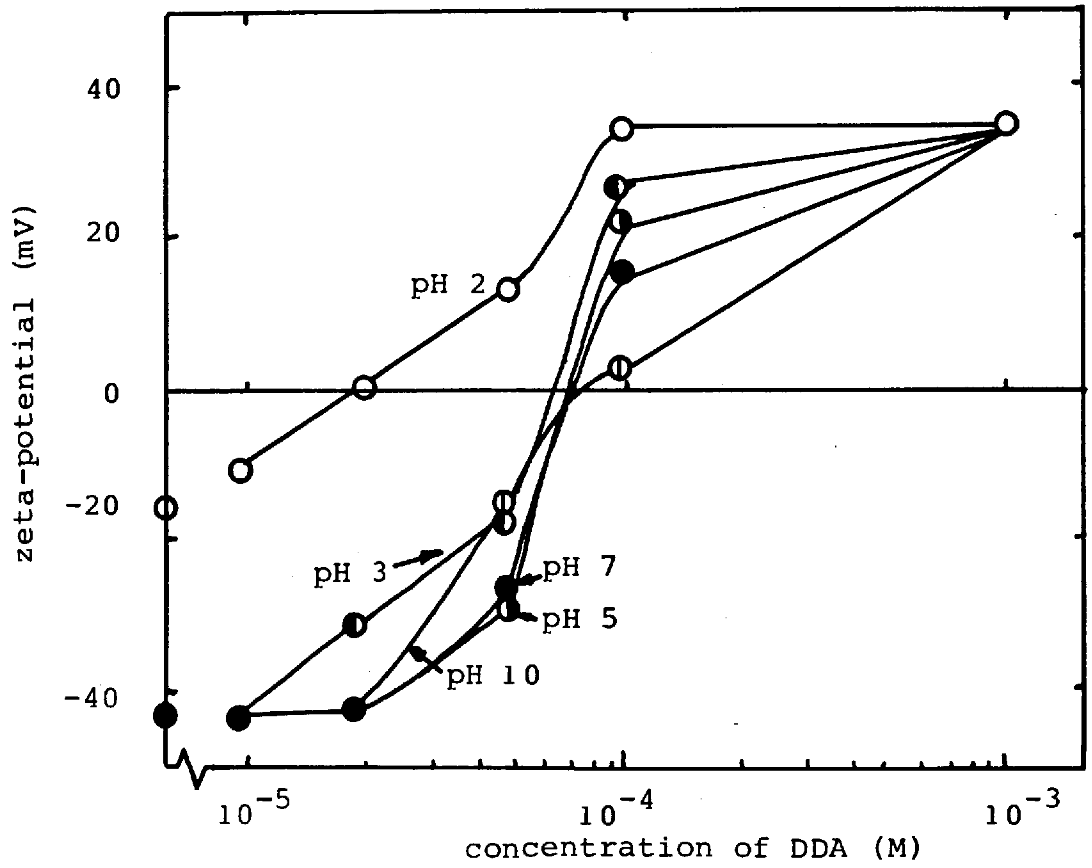


Figure 7.7: Zeta-potential of aged diamond as a function of DDA concentration at various pH values.

Adsorption isotherms of DDA on fresh diamond were measured at three pH values, 2.7, 5.8 and 8.8, these are presented in Figure 7.8. The diamond surface became increasingly covered with DDA, as both pH and DDA concentrations were increased. A maximum coverage of the surface was reached at pH 8.8 and an equilibrium concentration of DDA of 8.0×10^{-4}M, which is equivalent to 95% of a statistical vertically oriented monolayer, assuming a cross-sectional area per molecule of 20 Å²(101). The adsorption isotherms were all S-shaped, and the maximum coverage of the diamond surface increased with increasing pH.

The effect of butylamine (BuA) and benzylamine (BeA) on the air contact angle of diamond is shown in Figure 7.9. BeA had little effect on the contact angle of either the 'hydrophobic' or the 'hydrophilic' diamonds, whereas BuA caused an increase for both types of diamond. The contact angle increased to 40° at 10^{-5} M BuA for a 'hydrophobic' diamond, which is the same value as that obtained in the presence of DDA. The 'hydrophilic' diamonds became equally hydrophobic in the presence of BuA as they did in the presence of DDA. The contact angle did not decrease to zero at high concentrations of BuA or BeA, as it did for DDA.

The zeta-potential of diamond was not affected as much by the presence of BuA as it was by the presence of DDA (Figure 7.10). The zeta-potential reversed only in the presence of 10^{-3} M BuA between pH values of 4.3 and 7, whereas for DDA at concentrations greater than 7×10^{-5} M the zeta-potential was positive at pH values above 3.

7.3 Interaction of Dithiophosphates and Oleic Acid at the Diamond/Water Interface

Some flotation of diamond has been obtained with fatty acids and cresyl dithiophosphates(36). The mechanism of adsorption of these reagents at the diamond/water interface, however,

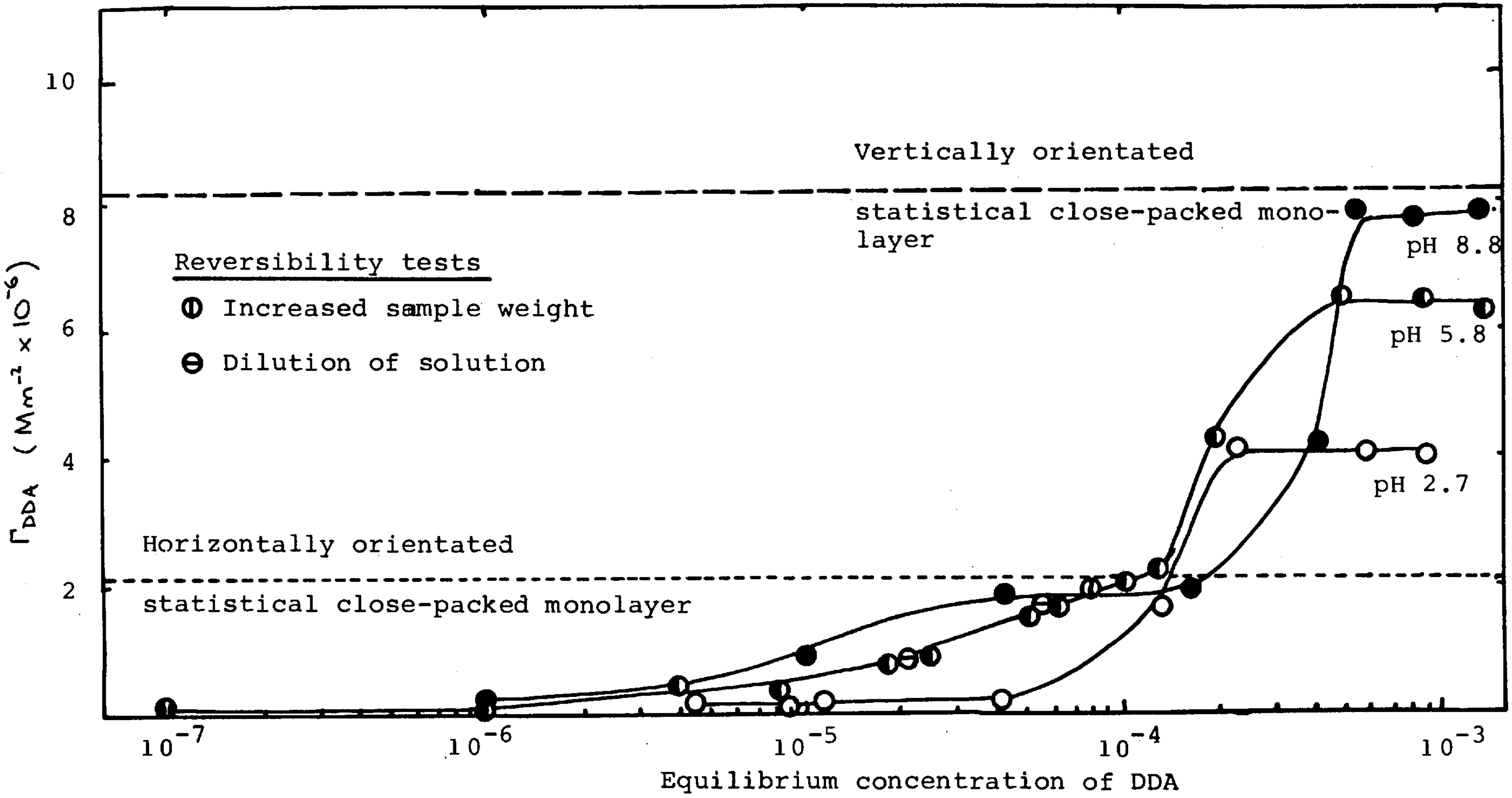


Figure 7.8: Adsorption isotherm of DDA on fresh diamond at various pH values

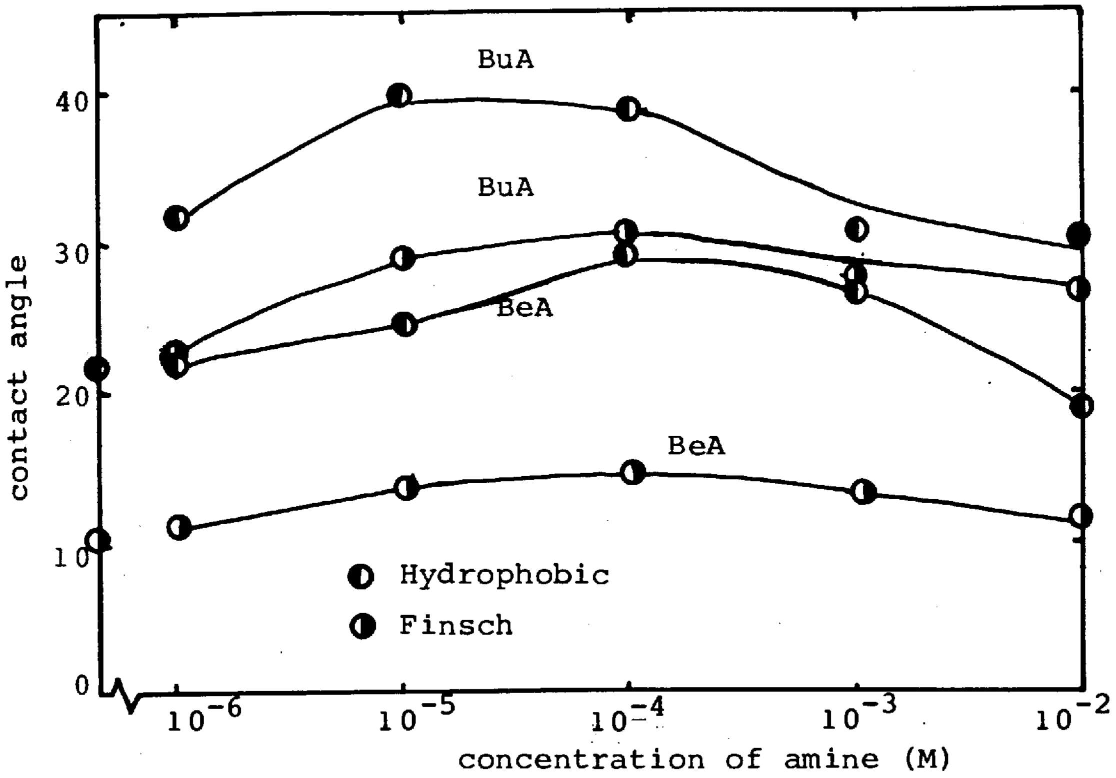


Figure 7.9: Contact angle of fresh diamond as a function of BuA and BeA concentration at pH 6

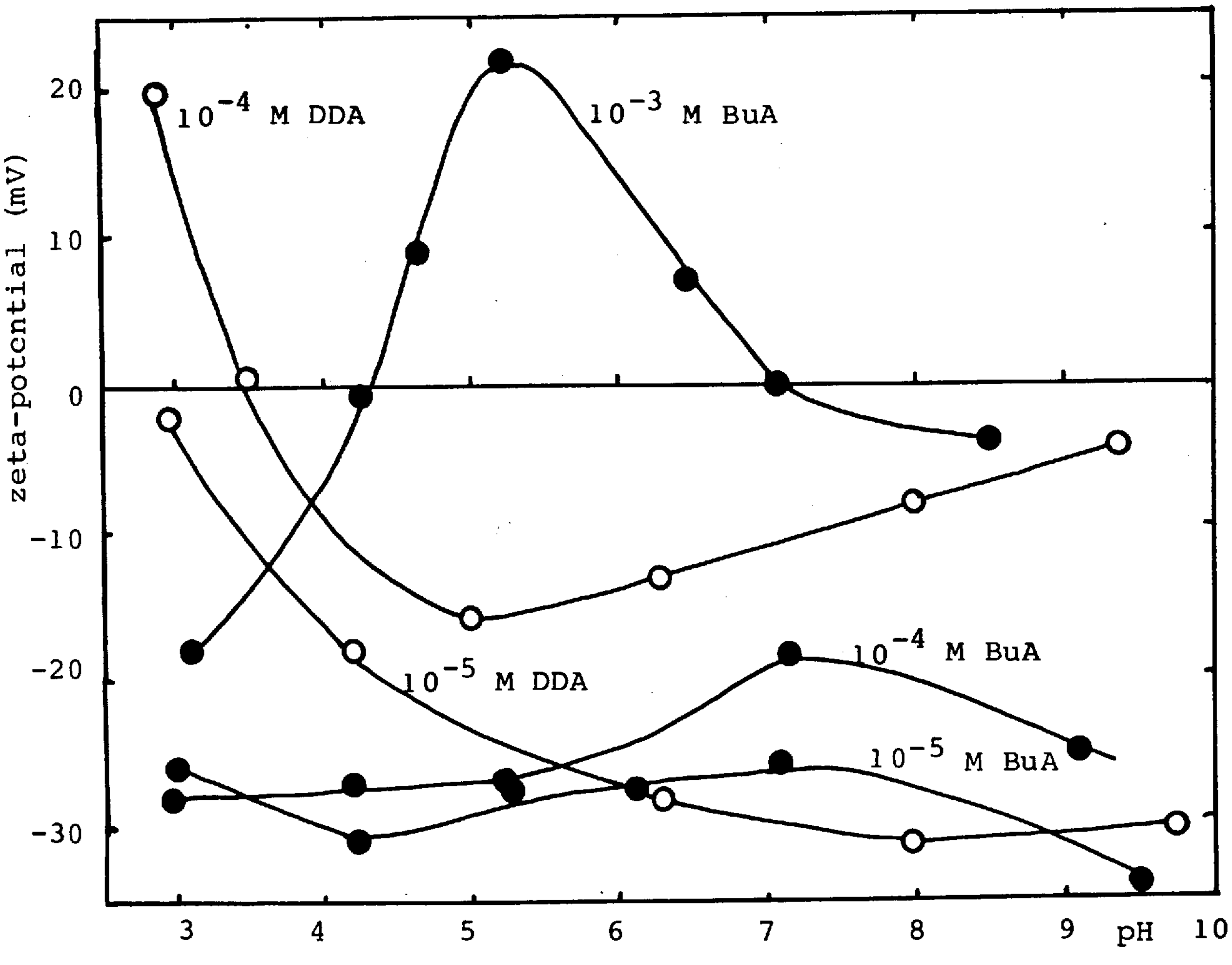


Figure 7.10: Comparison of zeta-potential of aged diamond as a function of pH in the presence of BuA and DDA.

has not been investigated. Both these compounds form chemical compounds with metal ions at the mineral surface, during adsorption at the mineral/water interface. It is unlikely that this type of adsorption mechanism could occur at the diamond/water interface, although some adsorption of xanthates on graphite has been reported(102). This was shown, however, to be due to metallic impurities in the graphite surface.

The effect of oleic acid and dithiophosphates on the contact angle at the air/water/diamond three phase line is shown in Figure 7.11. The contact angle in the presence of oleic acid decreased slightly with increasing oleic acid concentration. Sodium diethyldithiophosphate had no effect on the contact angle, but cresyl dithiophosphate caused the contact angle to increase with increasing surfactant concentration. In this latter case, an examination of the diamond surfaces, after measurement of the contact angle in a 10^{-2}M solution of cresyl dithiophosphate, showed that there were oily patches on the surfaces. As the diethyl dithiophosphate did not affect the contact angle, it seems that the increased contact angle in the presence of the cresyl dithiophosphate was due to smearing of the diamond surfaces by the oily liquid, and not due to an interaction between the anionic head group and the diamond surface.

At constant pH, the zeta-potential of unaged diamond became more negative with increasing oleic acid concentration (Figure 7.12). Below pH 4.5 there was no difference between the zeta-potential in the presence orabsence of oleic acid. Above pH 5, however, the zeta-potential of diamond was more negative in the presence of oleic acid, than it was in the presence of SDS at the same concentration and pH. A possible reason for this is , that there was more adsorption of oleic acid by hydrophobic bonding between the longer octadecyl chains of oleic acid, than there was for the dodecyl chains of SDS. This is supported by the decrease in the

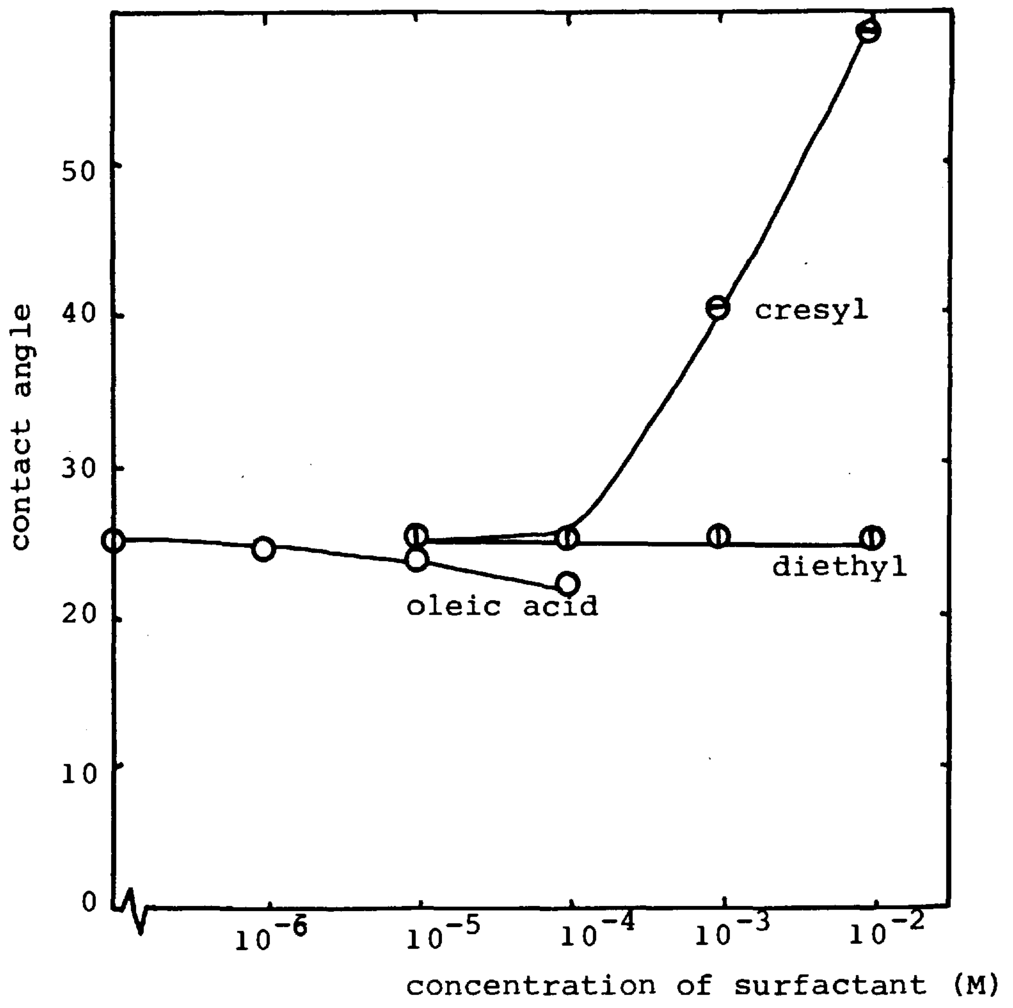


Figure 7.11: Contact angle of fresh diamond as a function of oleic acid, sodium diethyldithiophosphate and cresyl dithiophosphate concentration.

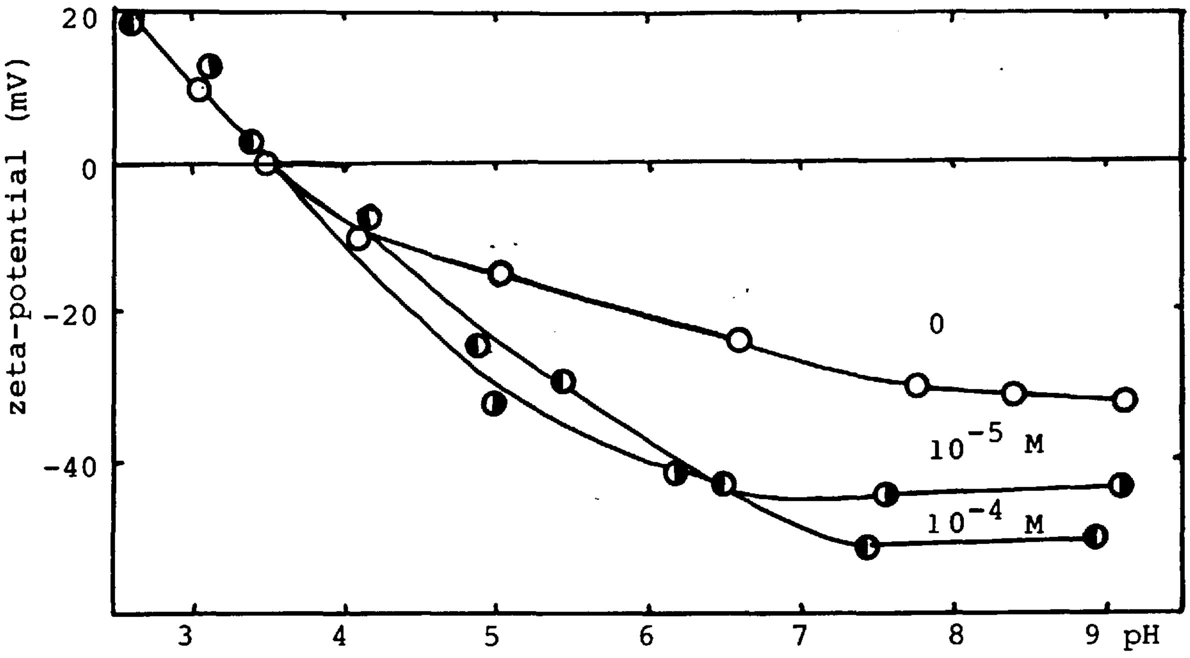


Figure 7.12: Zeta-potential of fresh diamond as a function of pH, at various oleic acid concentrations.

contact angle of diamond with increasing oleic acid concentration, suggesting that the oleate ions were adsorbed with the head group outermost from the diamond surface.

7.4 Discussion of the Adsorption of Surfactants on Diamond

SDS and DDA are reagents that do not show any tendency to become chemically bonded to oxide minerals, and they are adsorbed solely by coulombic attraction. SDS is ionized over the whole pH range, whereas the ionization of DDA is controlled by pH, according to the following equilibrium(99).

$$RNH_{2(aq)} \quad + \quad H_2O \longrightarrow RNH_3^+ \quad + \quad OH^-$$

$$K_b = \frac{[RNH_3^+]\ [OH^-]}{[RNH_{2(aq)}]} = 4.3 \times 10^{-4} M$$

The concentrations of the various amines can be calculated at various pH values, and plotted as shown in Figure 7.13, which shows the distribution of the various amine species in aqueous solution for a 10^{-4} M DDA solution. From this diagram it can be seen that the concentration of RNH_3^+ does not begin to decrease significantly until pH values greater than 10 are reached. Under these conditions neutral amine precipitates because the solubility of the species is exceeded ($K_s = 2 \times 10^{-5}$ moles ℓ^{-1}).

The increase in negative zeta-potential of unaged diamond with increasing SDS and oleic acid concentrations at pH values above the i.p. suggests that there was some adsorption of the surfactant anions under these conditions. This suggests that there was a positively charged site on the unaged diamond surface

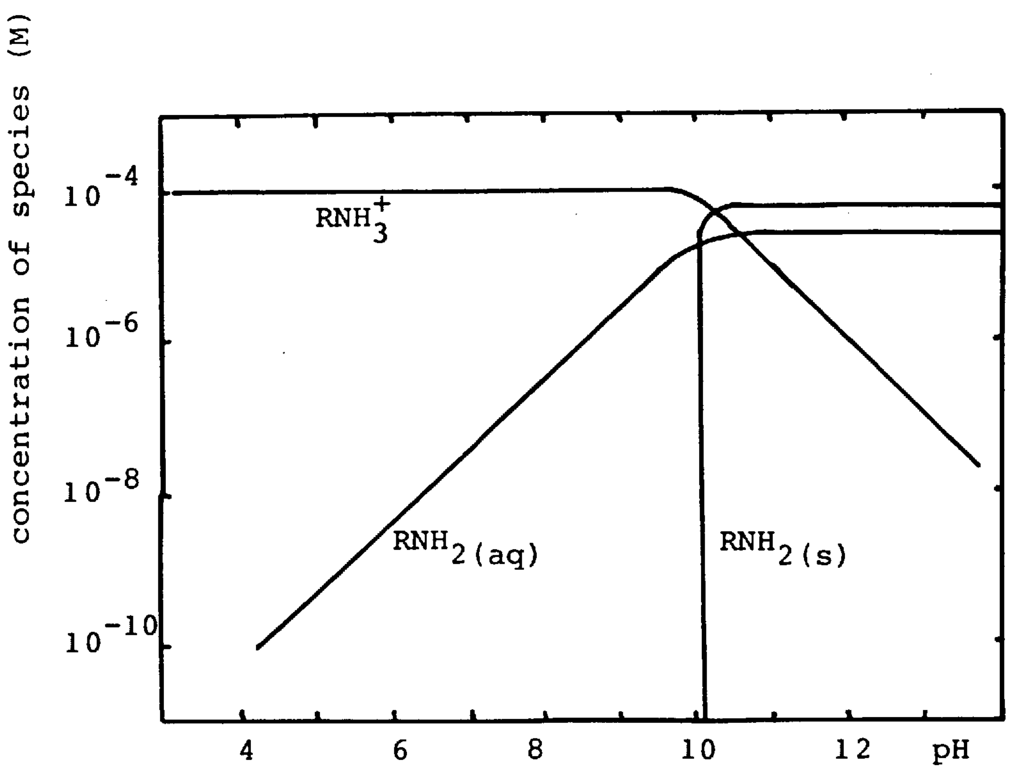


Figure 7.13: Distribution of amine species in aqueous solution as a function of pH.

over much of the pH range. The zeta-potential of unaged diamond in the presence of DDA became more positive at pH values below the i.p. of unaged diamond. This suggests that there was also a negatively charged site at pH values less than the i.p. This behaviour has been observed with some oxide minerals, iron oxide, for example has some negative and some positive sites on the surface at the i.p.; silica, however, is thought to have an almost totally unionized surface at the i.p.(103). The other possible explanation of this adsorption could be the adsorption of surfactant by hydrophobic bonding between the surfactant and the diamond surface. This would give rise to the same zeta-potential effect as those observed, but the surface would also become more hydrophilic. In all three cases the surface did not become hydrophilic until high surfactant concentrations approaching the c.m.c. were reached; and for DDA and SDS the surface became more hydrophobic with increasing surfactant concentration at lower concentrations.

The adsorption isotherm for DDA on fresh diamond is similar to that obtained with oxide minerals(99)(104)(105). The initial portion of the isotherm, at low adsorption densities is typical of the coulombic adsorption of the surfactant ions in the Stern layer. This part of the isotherm is considered to follow a Freundlich type adsorption , which has a reasonably linear relationship between the amount of solute adsorbed (x) and the equilibrium concentrations (c) of the solute, as shown below.

$$\log x = \log K + \frac{1}{n} \log c$$

where k and n are constants.

The isotherms then rise very sharply, at a concentration approximately the same as that at which zeta-potential reversal occurs. This is assumed to correspond to the formation of hemimicelles, by hydrophobic bonding between the hydrocarbon chains of the ions, resulting in the adsorption of the ions into the Stern layer(104). However, the two concentrations may only be similar by coincidence, as the onset of hemimicellization (determined from the electrokinetic data) does not always occur at the same concentration as the sudden increase in the adsorption density(105). The increased surface coverage by DDA with increasing pH is consistent with the theory that the surfactant ions adsorb as clusters around the charged sites(106).

The reversal of the zeta-potential of diamond with increasing SDS and DDA concentrations at pH values below and above the i.p., respectively indicates that adsorption was taking place in the Stern layer after neutralization of the surface sites. The probable mechanism of adsorption under these conditions is hydrophobic bonding between the hydrocarbon chains of the surfactant ions, or alternatively, between the hydrocarbon chains and hydrophobic sites on the diamond surface. Comparison of the contact angle, amine adsorption and zeta-potential of diamond in the presence of DDA, at approximately pH 6, shows that the zeta-potential changes sign at a DDA concentration where the contact angle begins to decrease and the adsorption begins to increase. This suggests that the DDA ions were adsorbed with their polar groups outermost from the surface, rather than adjacent to the surface. A similar comparison of the zeta-potential and contact angle for diamond in the presence of SDS at pH values below the i.p., indicates that adsorption continued after neutralization without affecting the contact angle. In this case the surfactant ions were adsorbed randomly orientated. The reason for difference in the orientation of the SDS and DDA ions on the surface is not known. A similar effect was observed by Stratton-Crawley(107) for the adsorption of alkyl sulphates and amines at the rutile/water interface. In this latter case the results were explained by an armouring effect at the oil/water or gas/liquid interface.

The short chain amines gave rise to different effects at the diamond/water interface than DDA. BeA had little effect on the contact angle, whereas BuA had the same effect as DDA. There was no decrease in contact angle at BuA concentrations greater than 10^{-3} M, as there was for DDA, presumably because there is less tendency for the short chain BuA molecules to associate by hydrophobic bonding. The zeta-potential of diamond in the presence of BuA was less positive at a given pH value than that for DDA at the same concentration. This demonstrates further the lower degree of association of BuA compared to DDA.

The reversal of the zeta potential of diamond between pH 4.2 and 7.5 at a concentration of 10^{-3} M BuA, indicates that some BuA must have been adsorbed by an adsorption mechanism other than coulombic attraction. The contact angle decreased slightly above this concentration, indicating that more BuA was adsorbed with the polar group away from the surface, than with the polar group on the surface. No reversal of the zeta-potential of silica occurs with amines of less than C_8(108), because the intermolecular attraction is too small to allow hydrophobic bonding between the molecules.

The contact angle results show that diamond can be made markedly more hydrophobic by the presence of BuA and DDA. This might be useful in the separation of diamond from kimberlite, because the short chain amines are unlikely to make the silicate minerals hydrophobic(108).

7.5 The Interaction of Metal Ions at the Diamond/Water Interface

The adsorption of metal ions by quartz and other oxide minerals has been widely studied, particularly as they can

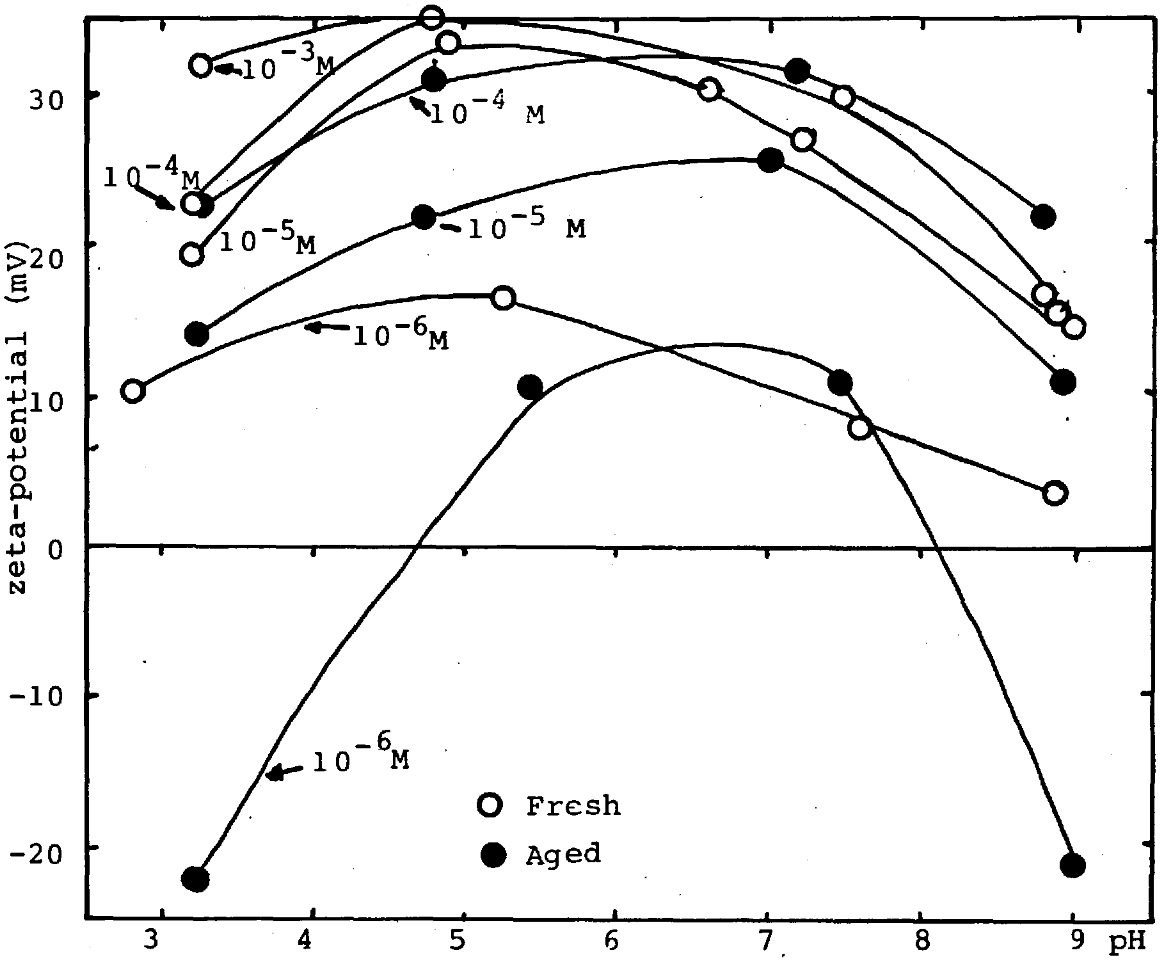


Figure 7.14: Zeta-potential of diamond as a function of pH at various Al^{3+} concentrations.

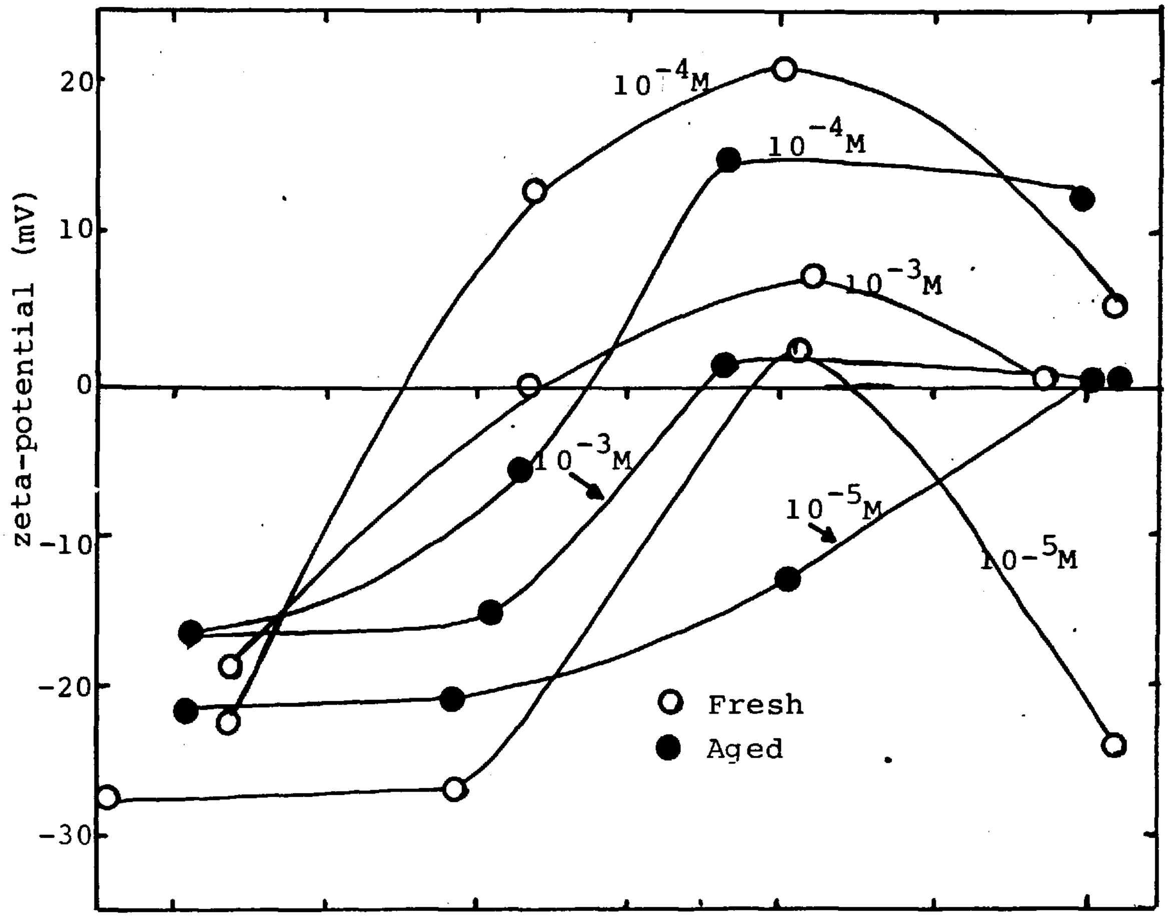


Figure 7.15: Zeta-potential of diamond as a function of pH at various Cu^{2+} concentrations.

significantly affect the flotation response of various minerals (98). It has been suggested, from empirical observations, that alluvial diamonds are hydrophilic because they have adsorbed metal ions during their transportation by water (109). A recent study of the concentration of diamond at the iso-octane/water interface has shown, however that the wettability of diamond is unaffected by the presence of metal ions.

The effect of aluminium and copper II ions on the zeta-potential of diamond is shown in Figure 7.14 and 7.15. The zeta-potential of fresh diamond in the presence of $AlCl_3$ was much less dependent on pH, than in its absence, and it was positive over the pH range 3 - 9. The zeta-potential of aged diamond showed a similar trend, at concentrations of $AlCl_3$ greater than 10^{-5} M. At 10^{-6} M $AlCl_3$, the zeta-potential of aged diamond had a maximum positive value at pH 7, above and below which the zeta-potential became negative. The concentration of $AlCl_3$ at which the zeta-potential became positive was much lower than that reported to reverse the zeta-potential of silica (124). With both aged and fresh diamond, the zeta-potential was essentially independent of concentration of $AlCl_3$ at high concentration.

The zeta-potential of both fresh and aged diamond in the presence of $CuCl_2$ was much more dependent on pH than for $AlCl_3$. The zeta-potential was positive at high concentration and high pH values. At a given pH value the zeta-potential became more positive with increasing $CuCl_2$ concentration up to 10^{-4} M, then became less positive, both for aged and fresh diamond. For fresh diamond the zeta-potential showed a maximum positive value at pH 7 in the presence of $CuCl_2$. The zeta-potential of aged diamond became independent of pH, above pH 7 at CuCl concentrations greater than 10^{-4} M. The concentration of $CuCl_2$ required to reverse the zeta-potential was similar to that which has a similar effect with silica (125).

The reversal of the zeta-potential of both fresh and aged diamond in the presence of both Cu^{2+} and Al^{3+}, indicates that some specific adsorption of the metal ions into the Stern layer occurred.

Ions in aqueous solution become hydrated, usually coordinating four or six water molecules. As the pH of the solution changes, then the ionization of the water molecules surrounding the ion will also change. Taking aluminium as an example, the following equilibria can be written (110).

$$\left.\begin{array}{l}
\left[(Al^{3+})\ (H_2O)_6\right]^{3+} \rightleftharpoons \left[(Al^{3+})\ (OH^-)\ (H_2O)_5\right]^{2+} + H^+ \quad K_1 \\
\left[(Al^{3+})\ (OH^-)\ (H_2O)_5\right]^{2+} \rightleftharpoons \left[(Al^{3+})\ (OH^-)_2\ (H_2O)_4\right]^{+} + H^+ \quad K_2 \\
\left[(Al^{3+})\ (OH^-)_2\ (H_2O)_4\right]^{+} \rightleftharpoons \left[(Al^{3+})\ (OH^-)_3\ (H_2O)_3\right] + H^+ \quad K_3 \\
\left[(Al^{3+})\ (OH^-)_3\ (H_2O)_3\right] \rightleftharpoons \left[(Al^{3+})\ (OH^-)_4\ (H_2O)_2\right]^{-} + H^+ \quad K_4
\end{array}\right.$$

Increasing pH ↓

These equilibria are an over simplification because it is known that particularly with aluminium many different polymeric species are also formed (126). At aluminium concentrations as low as 10^{-5} M, hydroxyl bridges are formed between the hydrated aluminium ions producing soluble species with an OH/Al ratio up to 2.5. Equilibria data on the formation of all of these species are not available and, therefore, it is not possible to calculate the dependency of their concentrations on the pH, nor their effect on the solubility of aluminium hydroxide. However, if the formation of polymeric species is ignored, at concentrations of $AlCl_3$ greater than 10^{-4} M precipitation of $Al(OH)_3$ will occur in the pH range 7 - 8. As the concentration is increased so the pH range for precipitation becomes greater. Figure 7.16 shows the distribution of aluminium species as a function of pH for a 10^{-4} M solution of $AlCl_3$, neglecting polymeric species. The distribution of copper species as a function of pH, in a 10^{-4} M $CuCl_2$ solution is shown in

Figure 7.17. Copper hydroxide is more soluble than $Al(OH)_3$, and precipitation does not occur in a 10^{-6} M solution at pH values less than 8. Data are not available for the existence of polymeric copper hydroxy species.

There are five proposals for the mechanism of adsorption of metal species at the oxide/water interface. The simplest involves the ion-exchange of metal ions with protons from the surface, whereas the other four involve the various hydroxyl complexes formed by the metal ions in solution (111) (127). Fuerstenau and his co-workers propose a mechanism of adsorption involving a condensation reaction. A first or second hydroxy-complex is adsorbed initially by a hydrogen bonding, then a water molecule is eliminated leaving a positive site (98). Healy and his associates propose that a colloidal metal hydroxide is adsorbed by coulombic attraction (112). The fourth model proposes that a hydrolysis product is formed at the surface, from the hydration sphere around the metal ion. Matijevic and his co-workers (124) (127) have proposed that the reversal of the zeta-potential of silica, at low pH values, in the presence of hydrolysable metal ions is caused by the adsorption of polymeric cationic species. This theory, however, has only been suggested for the aluminium-silica system, and it may not be applicable to other metal ions, where the formation of polymeric species is uncertain. No conclusive evidence has been obtained to show that any one of the above types of adsorption occurs uniquely in a given system.

Comparison of Figure 7.14 with 7.16 shows that aluminium species are adsorbed over the pH range used, and that the results did not reflect a change in concentration of any particular species. At low pH values, fresh diamond became only slightly more positive with increasing $AlCl_3$ concentration, whereas the zeta-potential of aged diamond changed from negative to positive. This indicates that aged diamond strongly adsorbs hydrated Al^{3+} ions in excess of the amount required to neutralize the surface charge. It is unlikely that the results obtained at pH 3 - 4 can be explained by the adsorption of polymeric aluminium-hydroxy species. At higher pH values, where both aged and unaged diamonds experienced zeta-potential reversal, it is not possible to determine which species were responsible for the observed effect. However, at high $AlCl_3$ concentrations it is probable that $Al(OH)_3$ was formed on the diamond surface and the zeta-potential reflects that of $Al(OH)_3$. This is consistent with the theory proposed by Healy (112).

The zeta-potential of diamond in the presence of $CuCl_2$ was dependent on the pH and comparison of Figure 7.15 with 7.17 shows that reversal of the zeta-potential corresponded to the presence of positively charged hydroxy species, and a solid hydroxide phase. This is also consistent with the theory of Healy (112), who proposed that colloidal metal hydroxide species are adsorbed, and that the zeta-potential then becomes equivalent to that of the adsorbed metal hydroxide. The i.p. of $Cu(OH)_2$ has been given as pH 7 - 9.5 (128). The zeta-potential of diamond in the presence of 10^{-4} and 10^{-3} M $CuCl_2$ tends to zero at approximately pH 9, indicating that the diamond surface is behaving as a $Cu(OH)_2$ surface. At low pH values, where Cu^{2+} predominates, the zeta-potential of both aged and unaged diamond was little affected by an increase in $CuCl_2$ concentration. This contrasts with the behaviour observed with $AlCl_3$. The reason for the decrease in the zeta-potential as the $CuCl_2$ concentration increased from 10^{-4} M to 10^{-3} M is not known.

8. MODEL OF THE DIAMOND SURFACE

The presence of various oxygen groups on the surface of carbon, including diamond, has been previously established (41), but their effect on the aqueous surface chemistry of carbon has never been fully understood. Analysis of a diamond crystal by ESCA showed that there was oxygen present on the surface, in more than one oxidation state. The various surface groups suggested for carbons may all be present in small quantities, but one particular group appears to determine the surface properties of diamond.

The zeta-potential of unaged diamond became more negative with increasing pH; the net adsorption of hydroxyl ions increased with both pH and ionic strength, and there was a tendency for the isotherms, at different ionic strengths, to converge to a point. The results indicate that H^+ and OH^- ions are potential determining for diamond. Similar results are obtained for oxide/water systems, and in this case, the surface groups are assumed to become hydrated and act as amphoteric sites (112). Hydroxyl groups were detected on the surface of diamond by infrared spectroscopy, therefore a similar model can be proposed for the ionization of diamond surface sites.

$$C - OH_2^+ \overset{H^+}{\rightleftharpoons} C - OH \overset{OH^-}{\rightleftharpoons} C - O^- \qquad (1)$$

These reactions imply that there is an equilibrium between the concentration of surface sites and the concentration of P.D.I.'s. The position of the i.p. at pH 3.5 implies however, that these reactions go far to the right.

The zeta-potential reached a constant negative value in alkaline media, although the hydroxyl adsorption increased with increasing pH and showed no tendency to level off.

It has been suggested that the insensitivity of the zeta-potential to the concentration of P.D.I.'s is attributable either to a reduction of the dependency of the zeta-potential on the charge density in the outer plane or a substantial adsorption of counter ions in the Stern layer(114). There is also the possibility of a limitation to the density of ionizable groups on the surface. The fact that the adsorption of hydroxyl ions did not decrease at high pH values indicates that the latter two possibilities are unlikely, and that, the first suggestion probably accounts for the behaviour of the zeta-potential of diamond at high pH.

The z.p.c. of oxides can be determined from the pH at which the net hydroxyl or hydrogen ion adsorption isotherms at different ionic strengths intersect(115). This method may not be applicable to diamond, but it is useful for a comparison of diamond with oxides. Extrapolation of the adsorption isotherms in Figure 6.12 indicates that the z.p.c. was at approximately pH 2.5. Differences between the i.p. and z.p.c. values of oxides are attributable to surface impurities, or the specific adsorption of ions. for diamond, the difference between the z.p.c. and i.p. indicates that some cationic impurity or site was present on the surface. Detailed analysis of the diamond powder showed that the level of cationic impurity was extremely low. It would appear, therefore that a cationic site might have been present on the diamond surface. It must be stressed, however, that the reactions shown in equation (1) might not be the reactions uniquely responsible for the zeta-potential. Some sites might dissociate independently of pH.

The positive site on the diamond surface may be either a carbon/oxygen group or a carbon site. The former would be unlikely as the existence of a site which involved the capture of proton to become positive would be pH dependent. The latter, however, could be a carbonium ion, which is most stable in the tertiary form, with the positive charge distributed to three neighbouring carbon atoms(116). It may be possible for an electronic vacancy created by the cleavage of a diamond crystal, to become distributed over many atoms by the rearrangement of the sp^3 bonds of the surface atoms.

The effect of SDS on the zeta-potential of fresh diamond provides some further evidence for a positive site on the surface. The zeta-potential increased with increasing SDS concentration up to pH 8, above which the zeta-potential in the absence of SDS was markedly negative, and no adsorption of DS ions would be expected. The contact angle of diamond increased with increasing SDS concentration. The DS ions could not have been adsorbed, therefore, with their polar group outermost from the surface, by hydrophobic bonding between the hydrocarbon chains and the diamond surface.

The existence of a positive site also explains why the adsorption of hydroxyl ions did not become zero after methylation of the diamond surface by diazomethane, which would have complexed all the active hydrogen. A similar effect was observed by Boehm(42), who suggested that the last adsorption of hydroxyl ions was due to very weak acidic groups. These last groups could be complexed by a reaction with a diazomethane solution made up with water saturated ether. This reaction is typical of alcohol groups, but as the methyl groups formed by Boehm were hydrolysable by hot dilute HCl, they could not have been formed from alcohol groups. There was no suggestion as to the origin of this remaining adsorption.

A carbonium ion would be expected to react with nucleophilic agents, for example the halogen ions. The infrared spectra of diamond that had been washed with halogen acids, showed no absorption bands that could be attributed to carbon-halogen bonds. No direct evidence for the presence of fluorine or chlorine on the diamond surface was obtained, therefore, in this work. However, the increased negative zeta-potential and reduced hydroxyl adsorption after treatment with concentrated HCl and HF is consistent with the removal of a positive site.

Similarly ageing of the diamond powder caused the zeta-potential to become more negative, but the adsorption of hydroxyl ions was little changed after ageing. For silica, it has been suggested that a similar effect was due to the hydration of surface sites(94). Changes in zeta-potential with ageing for some oxides are thought to be due to certain cations being leached out of the surface(95). This is most unlikely for diamond, as the surface carbon atoms would not be easily soluble. Any further ionization of existing hydroxyl groups, due to hydration, would result in an increased hydroxyl adsorption, which did not occur with diamond. It is possible, therefore, that the increased zeta-potential is due to the hydroxylation of a positive site. The net abstraction of hydroxyl ions would remain constant after hydroxylation. The positive site would have adsorbed a hydroxyl ion by coulombic attraction, and the hydroxyl group formed by ageing would ionize to give a proton in solution. Therefore, there would be no difference between the net adsorption of hydroxyl by fresh and aged diamonds.

The net uptake of hydroxyl ions by an aged diamond surface after methylation, was reduced more than that of a similarly treated fresh sample. This suggests that some portion of the adsorption of hydroxyl on fresh diamond was due to a positive site, which disappeared with ageing.

The zeta-potential of aged diamond in the presence of SDS was identical to that in the absence of SDS. This further suggests that a positive site was not present on an aged diamond surface.

The zeta-potential of fresh diamond in the presence of DDA, became more positive at pH values less than the i.p. . This suggests that there was a negatively charged site on the surface, when the surface charge was positive. The surfactant ions could not have been adsorbed by hydrophobic bonding between the diamond surface and the hydrocarbon chaines of DDA, as the contact angle increased with increasing DDA concentration.

Oxide materials show similar characteristics to those detailed above for diamond, at pH values around their i.p.(113). It is thought that the acidic and basic ionization reactions shown in equation (1) overlap. At the i.p., the surface is not completely unionized, there are some negative and some positive sites. The dissociation constants for the two reactions indicate the extent of the overlap in ionization of the groups. This type of model fits the data obtained for fresh diamond, and for aged diamond, except that there are very few positively ionizing groups on the aged surface.

The titration of the fresh diamond powder with various bases showed that there were groups of varying basicity on the diamond surface. A third of the total number of acidic groups were found to be equivalent (in strength) to a carboxylic acid. This proportion is very much lower than for graphitic carbons(44). This is not very surprising as carboxylic acid groups can only occur at edge sites on carbons, and there would be many more such sites on graphitic carbons than on diamond.

Titration of a methylated fresh diamond powder after hydrolysis showed that 25% of the total hydroxyl adsorption by fresh diamond powder was by carboxylic acid type groups. This figure is in good agreement with that obtained by the direct surface titration.

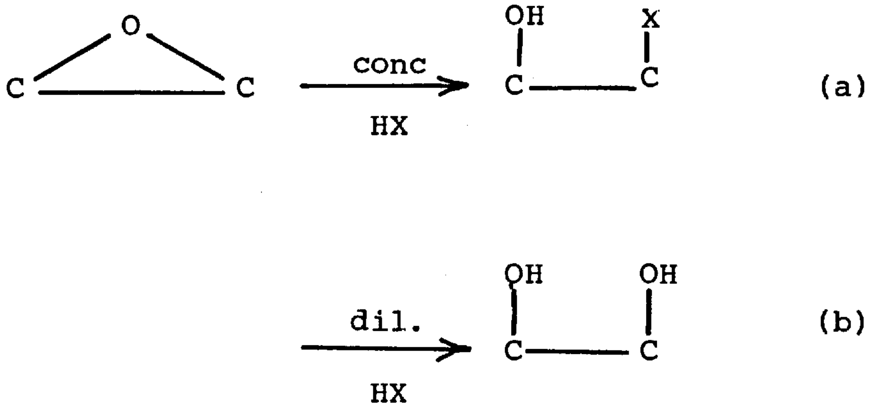
Direct surface titrations showed that slightly more than half of the total active hydrogen on the diamond surface arose from phenolic hydroxyl groups. Approximately 15% of the total number of acid groups of the surface were very weak. This was shown by the titration of diamond with sodium ethoxide, and by the fact that the hydroxyl adsorption curves rose very steeply above pH 8.

The adsorption of hydroxyl ions by fresh diamond was greatly reduced after reduction by sodium borohydride. This reagent reacts with carbonyl groups reducing them to hydroxyl groups. The carbonyl group has a strong dipole, and it may influence the ionization of the hydroxyl groups on neighbouring carbon atoms, in a similar manner to the ionization of carboxylic acid group. The zeta-potential of fresh diamond was not greatly affected after reduction by sodium borohydride up to pH 7. Above this pH value, however, the surface became less negative than an untreated surface. This might be explained by there being less ionization of a reduced surface, coupled with adsorption of counter ions. In contrast a reduced diamond surface was markedly more hydrophilic than a fresh surface, which suggests that the groups became more hydrated. The other data, however, suggest that there was less ionization of the surface groups, compared to a fresh diamond surface. A possible reason for this is that a reduced fresh diamond surface has a high proportion of positive sites, compared to an untreated surface.

The carbonyl group has less effect on the surface properties of aged diamond, than on fresh diamond. The zeta-potential was unaffected, and the adsorption of hydroxyl ions was only markedly reduced at low pH values, after reduction by sodium borohydride. This indicates that the surface hydroxyl groups on an aged diamond surface were ionized to a high degree without the influence of carbonyl groups. The stronger hydroxyl groups, which were responsible for much of the adsorption of hydroxyl ions at low pH values, were removed however by reduction. This is demonstrated by the marked increase in adsorption of hydroxyl ions above pH 7 by a reduced aged diamond.

An oxygen group that is present on the diamond surface that had little direct effect on the acid/base properties or the zeta-potential is the cross-linking oxygen group. The existence of this species is clearly shown in the infra-red spectra of diamond, by a stong absorbance band at 9.18 µm. The geometry of this cross-linking group is such that the oxygen atom is raised from the carbon plane to which it is bonded. The carbon-carbon spacing on a diamond surface is not large enough to allow for the existence of a pure ether linkage$^{(96)}$.

Treatment of a diamond powder with 20% HF caused the absorbance band at 9.18 µm to disappear. The cleavage of epoxides by halogen acids is well known$^{(117)}$, and it follows one of two reaction paths, depending on the concentration of the acid.



(2)

The intensity of the 9.18 µm band was not altered after washing with 30% HCl. This indicates that the cross-linking oxygen was not as reactive as the oxygen atom in an alkene oxide. It is unlikely, therefore, that reaction (2(a)) occurred, and it is probable that the reaction shown in (2(b)) occurred, catalyzed by concentrated HF.

The zeta-potential of fresh diamond was not affected by methylation of the diamond surface. A similar effect was observed with silica(93) and it was suggested that the lone pairs of electrons on siloxane groups were interacting with water to give rise to a zeta-potential. It is possible that a similar interaction occurred with the cross-linking oxygen atoms in diamond.

Aqueous oxidation of carbon results in the breakdown of the surface oxide groups, leaving a hydrophilic, hydroxyl covered surface(42). Oxidation of carbon affects many groups simultaneously, and often CO_2 is evolved. No useful conclusions can be made from the results for oxidised diamond, as the breakdown of particular surface oxygen groups cannot be predicted.

Drying the aged diamond powders at 120°C caused the zeta-potential to become less negative and the hydroxyl adsorption remained unchanged. This shows that some of the hydroxyl groups taken up by diamond on ageing were only physically bound to the surface.

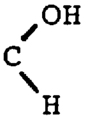
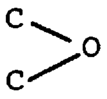
Ageing the diamond in a 10^{-2} M NaCl solution did not affect the rate of equilibration of the surface or the final value of the zeta-potential. However, the adsorption of hydroxyl ions was doubled after ageing for 21 days in an NaCl solution. This suggests that some chloride ions were taken up by the surface during ageing, which were ion-exchanged for hydroxyl ions during the titration. It was hoped to measure the release of chloride from diamond, but the measurement of about 10^{-5} M of chloride against a background of 10^{-3} M NaCl was impossible.

The diamond surface shows many characteristics of an oxide surface, which is not surprising in view of the presence of many oxygen groups in the diamond surface. Many of the models developed for oxide/water systems fit the data obtained particularly its adsorption properties.

Throughout this work it has been assumed that, observations made on the diamond powder reflected changed in the natural diamond surface. In view of the method of production of diamond powder, this may not be true. However,the analyses of the samples did not show any great difference between the powder and diamond.

A summary of the groups present on the diamond surface, and their reactions with certain reagents is presented in Table 8.1.

Table 8.1 Summary of the groups present on the diamond surface

Group	Washing with concentrated halogen acid (HX)	Ageing in water	Methylation by diazomethane	Reduction by sodium borohydride
C - OH	(C - X)	no effect	$C - O - CH_3$	no effect
C = O	no effect	no effect	no effect	 or - C - OH
	C - OH C - OH	no effect	no effect	no effect
C^+	C - X	C - OH	no effect	no effect

CHAPTER 9. SEPARATION OF DIAMOND FROM KIMBERLITE USING A SURFACE SENSITIVE TECHNIQUE

9. THE SEPARATION OF DIAMOND FROM KIMBERLITE USING A SURFACE SENSITIVE TECHNIQUE

The recovery of diamonds by conventional gravity and X-ray techniques is inefficient when the diamonds are smaller than 5 mm. New techniques are required, therefore, to recover fine diamonds. Flotation is a possible process, but its success depends on making the diamonds selectively hydrophobic, and the ability of air bubbles to float particles as coarse as 5 mm. The optimum particle size for conventional flotation is about 20 - 80 µm. Many attempts have been made to recover diamonds by flotation from kimberlite materials, but many problems have been encountered(36). These include the formation of slimes which coat the diamond and gangue minerals alike, and the fact that coarse diamonds are not readily floated. A further problem is that kimberlite rocks contain 10 - 20 % of naturally floatable talc minerals, which would float with the diamond without prior depression.

Kitchener and O'Gorman(118) have identified the major mineral type in kimberlite slimes as saponite, a platey swelling clay. Their sample, form the Premier mine, contained 50 - 60 % of this material. The crystal structure is idealized to being $Mg(OH)_2$ sheets sandwiched between two siloxane sheets, in which some of the Si^{4+} have been replaced by Al^{3+}, leaving a net negative charge on the layer lattice. This charge is neutralized by the presence of freely exchangeable alkaline metal cations between the sheets. A suspension of the slimes showed no tendency to settle after many days, unless a high concentration of electrolyte was present (0.01 M NaCl). The zeta-potential of the slime was found to be strongly negative (>70 mV).

Previous work has shown that extensive desliming of kimberlites is required before flotation of diamond can be commenced. The clays in the kimberlite rock break up in water very easily, and indeed in conventional diamond processing, this property is used to achieve liberation of diamond from the gangue. Although large scale flotation cells have a much less abrasive action than a small laboratory cell, appreciable breakage of the clay minerals in the flotation cells would necessitate desliming.

The data obtained in this project, on the diamond/water interface, indicate that the possibility of separating diamond from kimberlite by flotation is small, because of the similarity of the surface properties of diamond to those of silicates. The adsorption of surfactants and metal ions by diamond is similar to that by silicates(98). It is unlikely that the wettability of diamond could be modified selectively in the presence of kimberlite minerals. The adsorption of short chain amines by diamond, however, indicates that diamond may be made hydrophobic by a reagent that would not significantly affect the wettability of silicates. Flotation tests in the presence of these reagents would indicate the viability of this suggestion, but the problems of sliming by the clay minerals still have to be overcome.

The application of froth flotation to the treatment of the heavy mineral concentrate, obtained by processing the kimberlite ore with various gravity separation processes, may be possible. Some diamonds are already recovered by a technique utilizing the greater hydrophobicity of the diamond compared to the other minerals. It may be possible to enhance the recovery of diamond by the existing grease processes, by utilizing a pH region where selective adsorption of a surfactant onto diamond could occur. The i.p.'s of various minerals commonly present in the heavy mineral concentrate of kimberlites are presented in Table 9.1. Selective adsorption of a cationic surfactant should be possible in acid conditions at approximately pH 4, although this would require testing for each kimberlite, because very little is known about the surface chemistry of the kimberlite minerals. The acid conditions required would cause many design problems, and require large quantities of modifying reagents. However, this should enable recovery of the 'hydrophilic' diamonds which are present in the Finsch deposit, and which may be present in smaller quantities in other deposits.

Table 9.1 The i.p.'s of heavy minerals in kimberlite

Mineral	Chemical Formula	i.p.	Ref.
Diamond	C	3.5	
Ilmenite	$FeO.TiO_2$	4.5-6	119
Garnet	$(Mg,Fe,Ca)_3(Fe,Al)_2(SiO_4)_3$	3.5-6.0	62
Magnetite	$FeO.Fe_2O_3$	6.5	120
Zircon	$Zr\ SiO_4$	5.8	63
Chromite	$FeO.Cr_2O_3$	5.6-7.2	121

The Russians have published two papers on the recovery of diamond by electroflotation(37,122), using a mixture of hydrogen and air bubbles to float diamond. The size range used in their testwork was 0.5 mm - 0.042 mm, the pH was 10 and only a frothing agent was used. The economics of this process are doubtful, and it has never been tried in the West, but it demonstrates that fine diamonds can be floated. In general, diamonds less than 4 mm are recovered by the grease processes, but it is difficult to imagine efficient froth flotation at that particle size.

In recent years attempts have been made to extend the size range of particles amenable to froth flotation, by using organic liquids in place of air(123). This work has been particularly useful for the recovery of very fine particles (<5μm), but no attempt has been made to determine the top size of particle recoverable by an organic liquid based process. It may be possible to adapt this type of processing to recover coarse material.

The information on the flotation characteristics of kimberlite and heavy mineral concentrate minerals needs expanding before any accurate prediction of the possible recovery of diamond by froth flotation may be made.

CHAPTER 10. CONCLUSIONS

10. CONCLUSIONS

A study has been made of the surface chemistry of diamond, with the objective of determining whether or not a surface chemical process might be used to recover fine diamonds. Measurements were made of the wettability, zeta-potential and hydroxyl adsorption of diamond after various pretreatments, and as a function of ageing in water. The zeta-potential and hydroxyl adsorption measurements were conducted on a diamond powder, but both coarse diamonds and powder were used in the wettability studies. Attempts were made to correlate the results obtained with the two different materials.

Measurements of the surface properties before and after treatment of diamond, with reagents such as sodium borohydride and diazomethane, were made, in an attempt to determine the important groups present on the diamond surface.

The influence of surface active agents on the surface chemistry of diamond was determined, and the results compared with those obtained on minerals commonly associated with diamond. Consideration of whether or not the selective flotation of diamond is possible was made.

The results obtained in these studies permit the following conclusions to be made.

1. The 'hydrophobic' natural diamonds, as received, had varied air contact angles, both from site to site on the same diamond and from diamond to diamond. A reproducible contact angle is obtained by washing the diamonds with pure benzene in a Soxhlet apparatus. The value of the contact angle is $25^{\circ} \pm 3^{\circ}$. 'Hydrophilic' diamonds from the Finsch mine have a contact angle of $11^{\circ} \pm 2^{\circ}$ as received. Washing these diamonds with benzene does not affect the contact angle.

2. The surface of the diamond powder shows similar properties to that of the diamond crystals. Changes in the wettability of the diamond crystals after various treatments are reflected by similar changes for the diamond powder.

3. The natural diamond surface is covered with various oxygen groups, which give rise to a negative zeta-potential and a net adsorption of hydroxyl ions over a wide pH range. The isoelectric point (i.p.) of unaged diamond powder occurs at pH 3.5, and the zero point of charge (z.p.c.) at a lower pH (approx. 2.5).

4. The oxygen groups detected on the surface of natural diamond are cross-linked oxygen (C - O - C), carbonyl (C = O) and hydroxyl groups containing ionizeable hydrogen.

5. Most of the surface ionization of diamond is controlled by the carbonyl groups on the surface. Removal of these groups results in a lowering of the hydroxyl adsorption to 10% of the value for a clean diamond surface.

6. The various acid groups on the diamond surface can be titrated to give an indication of the proportion of groups of strengths corresponding to carboxylic acid, lactone, phenol and quinol groups. For the sample of diamond used in this work, 1/3 of the total acid groups on the surface are as strong as carboxylic acid.

7. A diamond surface becomes completely hydrophilic, and the zeta-potential more negative on ageing in water. This is considered to be due to increased coverage of the surface by hydroxyl groups. The i.p. of aged diamond is less than pH 2. Washing the diamond samples with concentrated halogen acids, prior to ageing, does not affect the equilibrium values of the various surface properties, or the rate of equilibration.

8. There is a positively charged site on a fresh diamond surface that ionizes independently of pH, which is considered to be a form of the carbonium ion. This site is destroyed with the ageing of diamond in water.

9. A methylated diamond surface is more hydrophobic than a clean diamond surface, but the zeta-potential is more negative than a clean diamond surface.

10. The mechanism of adsorption of sodium dodecylsulphate (SDS) and dodecylamine (DDA) is consistent with that of coulombic attraction, followed by chain-chain interaction at high adsorption densities.

11. The maximum adsorption density of DDA at pH 8.8 corresponds to 0.95 statistical close-packed vertically orientated monolayers. The properties of diamond in the presence of DDA and SDS, at concentrations approaching the c.m.c. of the surfactants, are consistent with the formation of a reversely orientated bilayer on the surface.

12. A diamond surface can be made appreciably more hydrophobic by the adsorption of short-chain amines.

13. There is no evidence of the specific adsorption of dithiophosphates by diamond. An oily smearing of diamond by cresyl dithiophosphate is observed, which may explain the increased hydrophobicity of diamond, in the presence of this reagent, in previous flotation tests.

14. Metal ions are adsorbed onto the diamond surface, causing a reversal of the zeta-potential.

15. The separation of diamond from kimberlite by froth flotation or a similar process is unlikely to be possible. This is due to the similarity of the surface properties of diamond and silicates. It may be possible to recover diamond from the heavy mineral concentrate of kimberlite, by froth flotation or a similar process.

REFERENCES

REFERENCES

1. EL. GORESY, A. and DONNAY, G., 'A new allotropic form of carbon from the Ries Crater', Science, 161, 1968, 363-4.

2. KURATOMI, T., 'Method of manufacturing diamond crystals', US Patent, No. 3,655,340, 1972.

3. PROFERL, D.J., GARDNER, N.C. and ANGUS, J.C., 'Growth of boron-doped diamond seed crystals by vapor deposition', J. Appl. Phys., 44 (4), 1973, 1428-34.

4. WILKS, E.M. and WILKS, J., 'The hardness and wear of diamond during grinding and polishing', Physical Properties of Diamond, Ed. R. Berman, (Claredon Press, 1965), 221-50.

5. HOWES, V.R., 'Ring cracks on diamond surfaces', ibid, 174-83.

6. DITCHBURN, R.W. and CUSTERS, J.F.H., 'Survey of the physical properties of diamond', ibid, 5 - 11.

7. ROBERTSON, R., FOX, J.J. and MARTIN, A.E., 'Two types of diamond', Phil. Trans. R. Soc. London, Ser. A, 232, 1934, 463-536.

8. CUSTERS, J.F.H., 'Unusual phosphorescence of a diamond', Physica, 18, 1952, 489.

9. CLARK, C.D., DITCHBURN, R.W. and DYER, H.B., 'The absorption spectra of irradiated diamonds after heat treatment', Proc. Roy. Soc. London, Ser. A, 237, 1956, 75-89.

10. KAISER, W. and BOND, W.L., 'Nitrogen, a major impurity in type I diamond', Phys. Rev., 115, 1959, 857.

11. LAX, M., and BURNSTEIN, E., 'Infrared lattice adsorption in ionic and homopolar crystals', Phys. Rev., 97, 1955, 39.

12. CHERENKO, R.M., 'Boron, the dominant acceptor in semiconducting diamond', Phys. Rev. B., 7, (10), 1973, 4560-7.

13. CLARK, C.D., 'Optical properties of natural diamonds', Physical Properties of Diamond, Ed. R. Berman, (Claredon Press, 1965), 295-324.

14. BERMAN, R., 'Thermal properties', ibid, 371-93.

15. TOLANSKY, S., 'Optical studies on diamond', ibid, 135-73.

16. EVANS, T. and SAUTER, D.H., 'Etching of diamond surfaces with gases', Phil. Mag., 6, 1961, 429-40.

17. FRANK, F.C. and LANG, A.R., 'X-ray topography of diamond', Physical Properties of Diamond, Ed. R. Berman, (Clarendon Press, 1965), 69 - 115.

18. PHAAL, C., 'Surface studies of diamond', Indus. Diamond Res., 1972, 259-73.

19. BIBBY, D.M., 'The determination of trace elements in natural diamonds by instrumental neutron-activation analysis', N.I.M.Rep., 1638, 1975, 29 pp.

20. PRYCE, M.H.L., 'Electronic structure of diamond', Physical Properties of Diamond, Ed. R. Berman, (Clarendon Press, 1965), 259-73.

21. OWEN, J., 'Paramagnetic resonance in diamond', ibid, 274-94.

22. TEKUNOVA, T.V. and TESNER, P.A., 'Kinetics of the reaction of diamond powder with oxygen', Khim. Tverd. Topol., 8 (4), 1974, 121-4.

23. BARRER, R.M., 'Sorption processes on diamond and graphite', J. Chem. Soc., 1936, 1261-4.

24. NAIDICH, Yu.V. and KOLESNICHENKO, G.A., 'A study of wetting of diamond and graphite by fused metals and alloys', Poroshkovaya Metallurgiya, 67 (7), 1968, 71-75.

25. GAUDIN, A.M., MIAW, H.L. and SPEDDEN, H.R., 'Native floatability and crystal structure', Proc. 2nd. Cong. Surface Activity, III, London, 1957, 202-19.

26. SCHLOSSIN, H.H., VAN REYNVELD, U.P. and HARRIS, W.F., 'The formation and decay of paramagnetic centres in the Beilby layer on quartz and diamond', Proc. 1st Congr. Int. Soc. Rock Mechanics, II, Lisbon, 1966, 119-20.

27. SAPPOCK, R. and BOEHM, H.P., 'Chemistry of the surface of diamond - I', Carbon, 6, 1968, 283-95.

28. MARSH, J.B. and FARNSWORTH, H.E., 'Low energy electron diffraction studies of (100) and (111) surfaces of semiconducting diamond', Surf. Sci., 1, 1964, 3 - 21.

29. LANDER, J.J. and MORRISON, J., 'Low energy electron diffraction study of the (111) diamond surface', Surf. Sci., 4 , 1966, 241-66.

30. LURIE, P.G. and WILSON, J.M., 'The diamond surface', Surf. Sci., 65, 1977, 453-510.

31. THOMAS, J.M. and EVANS, E.L., 'Surface chemistry of diamond: a review', Indus. Diamond Res., 1975, 2 - 8.

32. PLAKSIN, I.N. and ALEKSEEV, V.S., 'Adsorption of oxygen on freshly exposed diamond surfaces', Tsvetn. Metally, 6, (1), 1963, 32-4.

33. BANSAL, R.C., VASTOLA, F.J. and WALKER, P.L. Jnr., 'Kinetics of chemisorption of oxygen on diamond', Carbon, 10, 1972, 443-8.

34. DAWSON, J.B., 'New aspects of diamond geology', Physical Properties of Diamond, Ed. J.E. Field, (Academic Press, 1978).

35. NAPIER-MUNN, T.J., private communication, 1976.

36. HAMPEL, B.W., unpublished report for DRL, 1974.

37. MAMAKOV, A.A. and AVVAKUMOV, M.I., 'Continuous action electro-flotation apparatus for extracting small diamonds', Elektron Obrab. Mater., 1, 1971, 87-91.

38. DIETZ, V.R., 'The adsorption of carbon dioxide on carbon solids, I. Graphite and diamond at 0°', J. Phys. Chem., 71, (4), 1967, 830-7.

39. LOPEZ-GONZALEZ, J. de D., CARPENTER, F.G. and DIETZ, V.R., 'Adsorption of nitrogen and argon on mineralogical graphite and diamond at 77 and 90°K', J. Phys. Chem., 65 (8), 1961, 1112-9.

40. DAY, R.E., GREENWOOD, F.G. and PARFITT, G.D., 'Effect of heat treatment on the adsorption of Spheron 6', Chem. and Phys. Chem. of Surface Active Substances, 2, (Gordon and Breach, 1967), 1005-13.

41. PURI, B.R., 'Surface complexes on carbon', Chem. and Phys. of Carbon.A Series of Advances, Ed. P.L. Walker, Jr., 6, 1970, 191-282.

42. BOEHM, H.P., DIEHL, E., HECK, W. and SAPPOK, R., 'Surface oxides of carbon', Angew. Chem. Int. Edn., 3 (10), 1964, 669-77.

43. BOEHM, H.P., 'Chemical identification of surface groups', Adv. in Catalysis, 16, 1966, 219-25.

44. DONNET, J.B., 'The chemical reactivity of carbons', Carbon, 6, 1968, 161-76.

45. GARTEN, V.A., WEISS, D.E. and WILLIS, J.B., 'A new interpretation of the acidic and basic structures in carbons', Austral. J. Chem., 10, 1957, 295-328.

46. RIVIN, D., 'Use of lithium aluminium hydride in the study of surface chemistry of carbon black', Rubber Chem. and Technol., 36 (3), 1963, 729-39.

47. STUDEBAKER, M.L., HUFFMANN, E.W.D., WOLFE, A.C. and NABORS, L.G., 'Oxygen-containing groups on the surface of carbon black', Ind. and Eng. Chem., 48, (1), 1956, 162-6.

48. VILLARS, D.S., 'Studies on carbon black. II. Grignard analysis', J. Amer. Chem. Soc., 70, 1948, 3655-9.

49. PENNEY, A.L., private communication 1977.

50. ARNDT, F.G., 'Diazomethane for active H', Organic Analysis, (Interscience, 1956), 198-241.

51. HOFMAN, K.A. and HOFMAN, U.R., Anorganische Chemie, (Friedr. Vieweg und Sohn, Braunschweig, (1939), p272.

52. YOUNG, T.A., 'An essay on the cohesion of fluids', Trans. Roy. Soc., 95, 1805, 65-87.

53. ADAMSON, A.W., Physical Chem. of Surfaces, (Wiley-Interscience, 3rd Edn., 1976), p357.

54. IVANOV, I.B., TOSHER, B.V. and RADOEV, B.P., 'On the thermodynamics of contact angles.,line tension and wetting phenomena', Wetting, Spreading and Adhesion, Ed. J.F. Padday, (Academic Press, London, 1978), 37-82.

55. GRAHAME, D.C., 'The electrical double layer and the theory of electrocapillarity', Chem. Rev., 41, 1947, 441-501.

56. KRUYT, H.R., Colloid Science, 1, (Elsevier, London, 1952), p132.

57. GOUY, G., 'Constitution of the electric charge at the surface of an electrolyte', J. Physique, 4 (9), 1910, 457-67.

58. CHAPMAN, D.L., 'A contribution to the theory of electrocapi-larity', Phil. Mag., 25 (6), 1913, 475-81.

59. VERWEY, E.J.W. and OVERBEEK, J. Th. G., Theory of the Stability of Lyophobic Colloids, (Elsevier, New York, 1948),

60. AVEYARD, R. and HAYDON, D.A., An Introduction to the Principles of Surface Chemistry, (Univ. Press, Camb., 1973), p 43.

61. STERN. O., 'Zur theorie der electrolytischen doppelschift', Z. Elektrochem., 30, 1924, 508-16.

62. FUERSTENAU, D.W., 'The adsorption of surfactants at solid-water interfaces', The Chemistry of Biosurfaces, Ed. M.L. Hair, 1, (Marcel Dekker Inc., New York, 1971),143-76.

63. CASES, J.M., 'On the normal interaction between adsorbed species and adsorbing surface', Trans. A.I.M.E., 245, 1970, 123-7.

64. PREDALI, J.J. and CASES, J.M., 'Thermodynamics of the adsorption of collectors', Proc. 10th I.M.P.C., London 1973, 473-93.

65. FUERSTENAU, D.W. and RAGHAVAN, S., 'Some aspects of the thermodynamics of flotation', Flotation, A.M. Gaudin Memorial Volume, Ed. M.C. Fuerstenau, 1, (AIME 1976), 21-65.

66. GREENWOOD, F.G., PARFITT, G.D., PICTON, N.H. and WHARTON, D.G., 'Adsorption and wetting phenomena associated with Graphon in aqueous surfactant solutions', Amer. Chem. Soc., Adv. in Chem. Ser., 79, 1968, 135-44.

67. ZETTLEMOYER, A.C. and NARAYAN, K.S., 'Adsorption of aliphatic acids at the graphon-aqueous solution interface: effect of chain length on the adsorption and heats of formation of the electrical double layer', Chem. and Phys. Chem. of Surface Active Substances, 2, (Gordon and Breach, 1967), 995-1004.

68. SALEEB, F.Z. and KITCHENER, J.A., 'The electrical double layer at the graphite-surfactant interface', ibid, 129-39.

69. CRAWLEY, S., 'The adsorption of metal species by diamond powder', Unpublished report, Mineral Resources Engineering Department, Imperial College, London, 1978.

70. CLAUSS, C.R.A. and WEISS, K., 'Adsorption of aurocyanide on carbon', CSIR Report CENG 206, (Pretoria, South Africa, 1977), 10 pp.

71. Powder Diffraction Data, ASTM, 6-675, Diamond.

72. ibid, ASTM, 22-1069, Chaoite.

73. ibid, ASTM, 22-1273, Silicon Carbide.

74. ibid, ASTM, 23-64, Graphite.

75. SAUVAN, P. and CHENAUX, G., 'Modifications géochimiques subies par des déblais en cours de forage', Bull. Centre Rech. Pau. SNPA, 9, 1975, 391-405.

76. KITCHENER, J.A. and COOPER, C.F., 'Bubble-persistence test', Quart. Rev., 13, 1959, 71-3.

77. BACHHUBER, C. and SANFORD, C., 'The rise of small bubbles in water', J. Appl. Phys., 45 (6), 1974, 2567-9.

78. GORODETSKAYA, A.,'The rate of rise of bubbles in water', Zh. Fiz. Khim, 23, 1949, 71-7.

79. ANFRUNS, J.P., 'The flotation of small particles', Ph. D. Thesis, University of London, 1976.

80. PASHLEY, R.M., 'Surface forces in wetting phenomena on quartz', Ph. D. Univ. London, 1978.

81. OVERBEEK, J. Th. G., 'Electrokinetic phenomena', Colloid Science, Ed. H.R. Kruyt, (Elsevier, London, 1952), 194-244.

82. ABRAMSON, H.A., MOYER, L.S. and GORIN, M.A., 'Electrophoresis of Proteins and the Chemistry of Cell surfaces, (Rheinhold, New York, 1942), p 50.

83. HENRY, D.C., 'The electrophoresis of suspended particles IV. The surface conductivity effect', Trans. Faraday Soc., 44 (2), 1948, 1021-6.

84. OVERBEEK, J. Th. G., 'Theory of electrophoresis - the relaxation effect', Koll. Beih., 54, 1943, 287-364.

85. BOOTH, F., 'The cataphoresis of spherical, non-conducting particles in a symmetrical electrolyte', Proc. Roy. Soc., A203, 1950, 514-33.

86. WIERSEMA, P.H., LOEB, A.L. and OVERBEEK, J. Th. G., 'Calculation of the electrophoretic mobility of a spherical colloid particle', J. Coll. Int. Sci., 22, (1), 1966, 78-99.

87. PEARCE, A.S. and STREATFIELD, E.L., 'Determination of amines in water', Ger. Pat. 1,190,229,1961, (Anal. Abs., 12, 6766, 1965.)

88. COLE, H.M. and DANNENBERG, E.M., 'Infrared studies of the chemical constitution of carbon black surfaces', Rubber Age, 81, 1957, 96.

89. MANSON, R.S., 'Preparation of diazomethane', Advanced Organic Sunthesis, (Academic Press, 1972), 155-6.

90. FALES, H.M., JAOUNI, T.M. and BABASHAK, J.F., 'Simple device for preparing ethereal diazomethane,without resorting to codistillation', Anal, Chem., 45 (13), 1973, 2302-3.

91. HOPWOOD, J.S., Unpublished report for DRL, 1976.

92. FEDER, D.D. and KOONTZ, D.E., 'Detection, removal and control of organic contaminants in the production of electronic devices', Symp. Cleaning of Electronic Device Components and Materials, (ASTM 1959), 40-65.

93. LASKOWSKI, J. and KITCHENER, J.A., 'The hydrophilic - hydrophobic transition on silica', J. Coll. Int. Sci., 29, (4), 1969, 670-9.

94. GRIOT, O. and KITCHENER, J.A., 'Role of surface silanol groups in the flocculation of silica suspensions by polyacrylaminde', Trans. Farad. Soc., 61, (5), 1965, 1026-37.

95. SMITH, R.W. and TRIVEDI, N., 'Variation of the point of zero charge of oxide minerals as a function of ageing time in water', A.I.M.E. Preprint, 72-B-26, 1971, 17 pp.

96 TABOR, D., 'Some physical aspects of the diamond surface' Indus. Diamond Res., 1975, 9 - 12.

97. POLING, G.W., 'Reaction between thiol reagents and sulphide minerals', Flotation A. M. Gaudin Memorial Volume, Ed. M.C. Fuerstenau (A.I.M.E., 1976), 334-63.

98. FUERSTENAU, M.C. and PALMER, B.R., 'Anionic flotation of oxides and silicates', ibid, 148-96.

99. SMITH, R.W. and AKHTAR, S., 'Cationic flotation of oxides and silicates', ibid, 87-116.

100. MUKERJEE, P. and MYSELS, K.J., 'Critical micelle concentrations of aqueous surfactant systems', Nat. Bur. Stds., NSRDS-NBS 36, 1971.

101. SMITH, R.W., 'Effect of amine structure in cationic flotation of quartz', Trans. A.I.M.E., 254, 1973, 353-7.

102. AFENYA, P.A., Studies in the processing of a carbonaceous gold ore', Ph. D. Thesis, University of London, 1976.

103. DEBRUYN, P.L. and AGAR, G.E., 'Surface chemistry of flotation', Froth Flotation 50th Anniv. Vol., Ed., D.W. Fuerstenau, (A.I.M.E., 1962), 91-138.

104. SOMASUNDARAN, P. and FUERSTENAU, D.W., 'Mechanisms of alkyl sulphate adsorption at the alumina-water interface', J. Phys. Chem., 70 (1), 1966, 90-6.

105. JAYCOCK, M.J. and OTTEWILL , R.H., 'Adsorption of ionic surface active agents by charged solids', Trans. I.M.M., 72, 1963, 477-506.

106. CASES, J.M. and MUTAFTSCHIER, B., 'Adsorption et condensation des chlorhydrates d'alkylamine a l'interface solide-liquide', Surf. Sci., 9, 1968, 57-72.

107 STRATTON-CRAWLEY, R., 'Displacement of water from a titanium dioxide surface by an organic liquid' Ph.D. Thesis, University of London, 1977.

108 APLAN, F.F. and FUERSTENAU, D.W., 'Principles of non-metallic flotation', Froth Flotation 50th Anniv. Vol., Ed. D. W. Fuerstenau, (A.I.M.E., 1962), 170-214.

109. WEAVIND, R.G., 'The treatment and recovery of refractory diamonds', J. Chem. Met. and Min. Soc., Sth Afr., 1952, 243-64.

110. BAES, C. F. and MESMER, R.E., The Hydrolysis of Cations, (Wiley, New York, 1976), p273, 122.

111. JAMES, R.D., STIGLICH, P.J. and HEALY, T.W., 'Analysis of models of adsorption of metal ions at oxide/water interfaces', Farad. Disc., 59, 1975.

112. JAMES, R.O. and HEALY, T.W., 'Adsorption of hydrolyseable metal ions at the oxide/water interface. II', J. Coll. Int. Sci., 40, 1972, 53-64.

113. BOEHM, H.P., 'Acidic and basic properties of hydroxylated metal oxide surfaces', Disc. Farad. Soc., 52, 1971, 264-75.

114. RENDALL, H.M. and SMITH, A.L., 'Surface and electrokinetic potentials of interfaces containing two types of ionizing groups', J. Chem. Soc. Farad. I., 74, 1978, 1179-87.

115. CORNELL, R.M., POSNER, A.M. and QUIRK, J.P., 'A titrimetric and electrophoretic investigation of the pzc and the iep of pigment rutile', J. Coll. Int. Sci., 53, (1), 1975, 6 - 13.

116. FINAR, I.L., Organic Chemistry, 1, (Longman, London, 6th. Edn., 1976), p147.

117. FINAR, I.L., ibid, p 313-5.

118. O'GORMAN, J.V. and KITCHENER, J.A., 'The flocculation and dewatering of kimberlite clay slimes', Int. J. Miner. Process, 1, 1973, 33-49.

119. CHOI, H.S., KIM, Y.S. and PAIK, Y.H., 'Flotation characteristics of ilmenite', Can. Min. and Met. Bull., Feb., 1967.

120. IWASKI, I., COOKE, S.R.B. and KIM, Y.S., 'Some surface properties and flotation characteristics of magnetite', Trans. A.I.M.E., 223, 1962, 113-6.

121. PALMER, B.R., FUERSTENAU, M.C. and APLAN, F.F., 'Mechanisms involved in the flotation of oxides and silicates with anionic collectors. 2.', Trans. A.I.M.E., 258, 1975, 261-3.

122. LAZARENKO, B.R., GLEMBOTSKII, V.A., MAMAKOV, A.A. and AVVAKUMOV, M.I., 'Extraction of small diamonds by electrical flotation', Elektron. Orab. Mater., 30 (6), 1970, 50-4.

123. SHERGOLD, H.L., 'Two-liquid flotation for the treatment of mineral slimes', Indus. Minérale-Minéralurgie, 3, 192-205, 1976.

124. MATIJEVIC, E., MANGRAVITE, Jr, F.J. and CASSELL, E.A., 'Stability of colloidal silica. IV. The silica-alumina system', J. Coll. Int. Sci., 35 (4), 1971, 560 - 8.

125. LECKIE, J.O. and JAMES, R.O., 'Control mechanisms for trace metals in natural waters', Aqueous Environmental Chemistry of Metals, Ed. A.J. Rubin, (Ann Arbor Science, 1974), 1 - 76.

126. STOL, R.J., VAN HELDEN, A.K. and DE BRUYN, P.L., 'Hydrolysis-precipitation studies of aluminium III solutions. 2. A kinetic study and model', J. Coll. Int. Sci., 57 (1), 1976, 115 - 31.

127. ALLEN, L.H. and MATIJEVIC, E., 'Stability of colloidal silica. III. Effect of hydrolysable cations', J. Coll. Int. Sci., 35 (1), 1971, 66 - 76.

128. PARKS, G.A., 'The isoelectric points of solid oxides, solid hydroxides and aqueous hydroxo complex systems', Chem. Rev., 65, 1965, 177 - 98.

111. HAYDEN, P.L. and RUBIN, A.J., 'Systematic investigation of the hydrolysis and precipitation of aluminium III', Aqueous Environmental Chemistry of Metals, Ed. A.J. Rubin, (Ann Arbor Science, 1974), 317 - 81.