THE INFLUENCE OF POLYVINYL ALCOHOL ON THE PHYSICAL PROPERTIES OF SOIL AGGREGATES

A Thesis Submitted

by

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STATEMENT

This thesis contains no material which has been accepted for the award of any other degree or diploma in any University. To the best of my knowledge and belief, the thesis contains no material previously published or written by another person, except when due reference is made in the text of the thesis.

Signed

(B.G. Williams)

INTRODUCTION

Since the work of Ensminger & Giesking (1939) and Hendricks (1941) a considerable amount of effort has been directed towards formulating more precisely the interaction of organic materials with soils and clay minerals. Naturally occurring organic matter has been shown to be a complex mixture of degraded and partially degraded plant material and microbial products. It is largely polymeric in nature and many of the individual components have not yet been characterised satisfactorily.

Most adsorption studies have been carried out using single organic compounds of either natural or synthetic origin. In this way it has been shown that compounds of a polyuronide-polysaccharide nature are of importance in the stability of natural soil aggregates. Organic polymers with similar soil stabilising properties as polyuronides, have been synthesised and are now produced commercially as "soil conditioners".

Many papers have been devoted to the assessment of these conditioners for agricultural use. The main effect of soil conditioners is to increase the stability of soil aggregates to normal cultivation practices. At the same time many other soil properties are modified e.g. water retention, swelling, drainage, porosity and erodibility. Different conditioners have different degrees of influence and different soils have a variable response. Thus a considerable proportion of the literature is concerned with these variables.

Another aspect of soil conditioner investigations has been the attempt to elucidate the mode of action of naturally occurring organic matter by using synthetic polymers of known chemical characteristics. Organic matter is predominantly negatively charged with an exchange capacity of 200-400 m.e. per 100 g. Thus a study of the interaction of anionic polyelectrolytes with soils would seem to be the most appropriate approach. At present a considerable amount is known of the interaction of such polyanions as hydrolysed polyacrylonitrile (HPAN) and the copolymer of vinyl acetate-maleic anhydride (VAMA) and related compounds with clays and puddled soil materials. Panabokke (1956) and Williams (1959) studied the interaction of sodium-HPAN with natural soil aggregates rather than the puddled and remoulded materials used by others. It was found that the polyanion did not readily penetrate into soil aggregates presumably because of repulsion by the negatively charged soil colloids. From this it was inferred that the stabilising components of organic matter would most likely be located in the relatively large pores of natural soil aggregates.

The present work has been designed to study in more detail the penetration of organic polymers into the porous structure of natural soil aggregates and the subsequent stabilisation of the aggregates. For this purpose an uncharged polymer, poly(vinyl alcohol) (PVA), was chosen because earlier work by Williams (1959) showed that this polymer was very effective in stabilising soil aggregates. Furthermore interpretation of the results of stabilisation and adsorption experiments should be more straight forward than would be the case for anionic and cationic polymers. The adsorption of PVA, of varying characteristics, by soil aggregates, and its effect on the water-stability, swelling, porous structure and mechanical stability of the treated soil was therefore studied. From this, some aspects of the movement and interaction of noncharged organic polymers in soil have been elucidated and techniques have been devised that may be useful in extending the work to charged polymers.

CHAPTER I

THE STABILISATION OF SOIL AGGREGATES - A REVIEW

1. Introduction

A desirable property of arable soils is their ability to withstand the physical and physico-chemical stresses that occur as the result of normal cultivation practices. This property is usually described in terms of the stability of soil aggregates as evaluated by laboratory tests that have been specifically designed to simulate the action of natural disruptive forces. The origin of aggregate stability is thus of prime importance as are also methods of inducing and maintaining aggregate stability.

It has long been known that naturally occurring organic matter, apart from being a source of plant nutrients, is associated with the improvement of soil structure. Tests of water-stable aggregation have shown that soils under pastures have a higher mean particle size distribution than arable soils, and also that they are more resistant to slaking in water. Organic matter, consisting of a complex mixture of degraded plant material and microbial by-products, offers a wide range of compounds that may be of importance in soil aggregate formation and stabilisation. However, the complex chemical nature of organic matter has made investigations of specific interactions of it with soil material virtually impossible, so most approaches have been made using single organic species and homoionic clays (Ensminger & Giesking, 1939; Hendricks, 1941; Goring & Bartholomew, 1952; Lynch, Wright & Cotnoir, 1956, 1957). As a result of this work, much is known of the interaction with clays of such materials as proteins, nucleic acids, lignin, cellulose, starch, pectin, alginates and many of their derivatives, although little is known of the extent to which they occur in an unmodified state within soils.

The components of organic matter that have been found to be most effective in soil aggregation and stabilisation are polyuronides and polysaccharides. Such compounds are commonly found in soils. (Forsyth, 1947; Rennie, Truog & Allen, 1954; Whistler & Kirby, 1956; Lynch, Olney & Wright, 1958; Graveland & Lynch, 1961).

Rennie, Truog & Allen (1954) have studied the soil aggregating properties of microbial gums produced _in vitro_ and in the soil. They found a good correlation between the content of gum produced by _Agrobacterium radiobacter_ and the percentage of soil particles greater than 0.1 mm in two silty loam soils. Added plant residues produced an immediate increase in gum content of the soil, reaching a maximum in approximately six days. The type of plant residue however is of importance, as was shown by Schwartz, Freeman & Russell (1958). They showed that additions of wheat straw followed by incubation for a period of a month imparted a greater stability to soil aggregates than did soy bean and cotton stalks. Corn stover applications had an intermediate effect. Similar experiments with additions of dextrans (Smith, Schwartz, Gugliemelli, Freeman & Russell, 1958; Novak, Witt & Hiler, 1955), bacterial polysaccharides (Martin, 1946; Haworth, Pinkard & Stacey, 1946; Geoghegan & Brian, 1948; Swaby, 1949; Smith et al, 1958; Mehta, Streuli, Muller & Deuel, 1960) alginates (Quastel & Webley, 1947) and seed coat mucins (Quartaroli, 1954; and Smith et al, 1958) are useful demonstrations of possible stabilising agents in natural soils and the subsequent beneficial effects on plant growth. It must be remembered however that in natural field conditions a complex and dynamic soil-plant-microorganism-microclimate system exists, and that the above experiments do not really prove a direct relationship between the stability of natural soil aggregates and the organic constituents investigated.

An approach that has produced more positive results has been that of selectively removing organic and inorganic materials from natural aggregates in such a way as not to disrupt the aggregate structure. The stability of the aggregates is then determined before and after treatment.

Mehta et al (1960) used a periodate treatment followed by sodium borate to oxidise selectively the glycol groups of polysaccharides and polyuronides and to disrupt the oxidised polymers. They then tested the resistance of the treated aggregates to wet sieving. Although aggregates artificially stabilised with polysaccharide additives were susceptible to the periodate treatment, natural aggregates were unaffected. Greenland, Lindstrom & Quirk (1962) applied the technique of Mehta *et al.* to a wider range of soils and in particular to soils having very different organic matter contents. They found marked differences in the stability of the treated aggregates to ionic dispersion. The term, "ionic dispersion", refers in this case to the deflocculation of sodium saturated soils following dilution of the external solution electrolyte concentration. Soil aggregates from a crop rotation including pasture phases were more stable than aggregates from rotations that did not include pasture. It was thought that the increase in the stability of aggregates from soils under pasture was probably due to increased amounts of the polysaccharide-type components of the soil organic matter, although the specificity of the periodate treatment to these compounds alone was not conclusively verified. They also showed that some soils were not sensitive to periodate-borate treatment, and suggested that these probably contained other stabilising agents in addition to polysaccharides.

Concurrent with these investigations of the stabilising components of natural organic matter has been the development of synthetic organic compounds that may be used to produce similar increases in the structural stability of soil aggregates. The organic compounds used are mostly polymers and have the capacity to bind soil particles together and make them more resistant to mechanical stress, particularly under conditions of high water content.

One group of polymeric materials, which will not be dealt with in detail in this thesis, are the resin-type compounds such as bitumen and epoxy resin, (e.g. see Ingles, 1962). These are used to stabilise soils by forming a hard-setting matrix in which the soil material is embedded. They have an obvious use in road, dam and channel construction, but are probably of little use for stabilising agricultural soils that require regular cultivation.

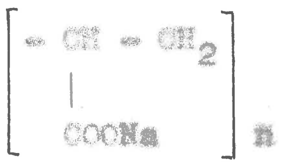
The organic polymers that are of agricultural interest must be able to stabilise soil aggregates to the extent that they can withstand moderate mechanical disruption and yet not interfere with other essential physical soil properties, such as porosity, friability, water-retention and drainage. It is necessary that only small amounts of the polymers be required both from the viewpoint of the above soil properties and from the cost of application. Water-solubility is important as well as resistance to microbial degradation.

The cost of synthetic soil conditioners at the moment prevents their general agricultural use, but there are special instances in which they are of economic importance. Firstly, they may be used in the reclamation of soils that are so physically degraded that plant establishment is very difficult. This may involve only one application after which suitable crop husbandry can carry on the reclamation process. The second case of importance is in areas where cropping is so intense, and profitable, that the use of pasture phases in the rotation to restore structure and fertility is not desirable e.g. market gardening and densely populated rural areas.

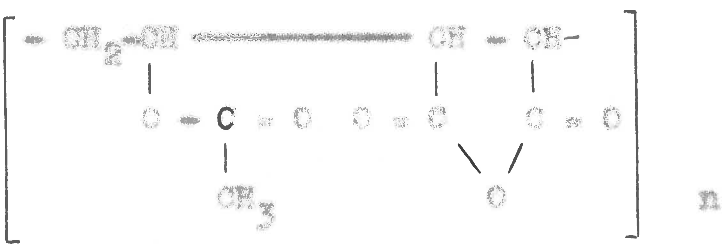
As technical knowledge of synthesising conditioners (especially from existing waste products) and the specific requirements of the chemical constitution of conditioners increase, they should achieve a more important role in agricultural practice. It should be remembered that existing agricultural practices are based on the need to produce and maintain good soil physical conditions, as well as chemical fertility. The present methods need not necessarily be the most economic if the desired soil structure can be produced with synthetic conditioners.

2. The Characteristics of Synthetic Soil Conditioners

A large number of synthetic compounds have been screened for soil conditioning purposes and the most commonly used types are polymers of vinyl derivatives. Although many other compounds can increase the stability of soil aggregates, they frequently do so by water-proofing the aggregates, and it appears that for agricultural purposes this is generally undesirable. Two polyanions in particular have been studied widely viz. hydrolysed poly(acrylonitrile) (HPAN) and a copolymer of vinyl acetate-maleic anhydride (VAMA)[*]. The general formulae of both are shown below



$$\left[-\underset{\substack{|\\ \mathrm{COONa}}}{\mathrm{CH}}-\mathrm{CH_2}\right]_n$$



HPAN or
sodium polyacrylate
Trade name; CRD-189,
or Krilium 9

VAMA
Trade name; CRD-186, or
Krilium 6

The polyacrylic acids and their salts are long chain linear molecules with a high degree of flexibility. The shape of the polyacrylate molecules in solution is very sensitive to pH and the presence of extraneous electrolytes. As the pH is raised, so more of the carboxylic acid groups dissociate, resulting in repulsion between adjacent polymer segments, and an uncoiling of the molecule as a whole. This is evidenced

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[*] A list of the soil conditioners discussed in this review together with their abbreviated or trade names is included at the end of this Chapter.

by a rapid increase in the viscosity of the polymer solutions as the pH increases e.g. the viscosity of a 0.05% solution of Krilium-9 increases from 2.0 centistokes at pH 5.2 to 5.0 centistokes at pH 7.5 (Williams, 1959). Monovalent cations have little effect on the viscosity of the solutions but multivalent cations can suppress the negative charge along the polymer molecules, so reducing the inter- and intramolecular repulsion. This results in a coiling of the molecules and a lowering of the viscosity. This property, as will be seen later, has a considerable influence on the adsorption of polyacrylates and their ability to promote flocculation and aggregate stabilisation.

According to the manufacturing conditions, partially hydrolysed polyacrylamides may possess more or less acid amide groups which have a considerable effect on their soil conditioning properties. Michaels (1954) considers that the main effect of the carboxyl groups is on molecular shape and that by varying the degrees of hydrolysis, a balance between molecular shape and availability of reactive groups for adsorption could be attained.

VAMA is similarly an anionic polyelectrolyte, as in water the maleic anhydride portion of the molecule hydrates to form two carboxyl groups. In addition to the solution properties mentioned for polyacrylic acid, VAMA also has a strong tendency to chelate with multivalent ions due to the close proximity of the carboxyl groups of the maleic acid unit. This feature probably explains the often quoted "high tolerance for calcium" found in the literature, with respect to VAMA.

Cationic polyelectrolytes have achieved very little prominence as soil conditioners, although the reasons for this are rather obscure. It might well be expected that the incorporation of cationic groups in non-charged linear polymers would be effective in flocculating negatively charged soil suspensions and also in the processes of soil aggregate stabilisation. This has been confirmed by Ruehrwein & Ward (1952) using poly(dimethylaminoethylmethacrylate) (DMAEM) and poly(vinylbutylpyridonium bromide). Also Williams (1959) observed that natural soil aggregates treated with poly(4-vinyl pyridinium N - ethyliodide) were stable to rapid wetting with water.

Hoover & Davidson (1956) have screened a number of commercial cationic preparations for use as stabilising agents for engineering purposes. They found that compounds such as primary amine acetates, quaternary ammonium salts and crude amine were most useful in reducing swelling of Iowa loess, but it appears that the mechanism is due principally to waterproofing. Also the compounds used, although strictly polymeric, had molecular weights of less than 10^3 compared with molecular weights of 10^4 to 10^5 for conditioners commonly associated with stabilisation by bridging between soil particles. Other non-polymeric cationic preparations such as cetyl pyridinium bromide (Clare, 1947; Williams, 1959) have been used to alter the water relationships of soils, but these are also water-proofing agents and are generally of little agricultural use.

Non-ionic polymers such as dextrans and methyl cellulose have been investigated as soil conditioners. Dextran is produced commercially for a number of purposes and is a glucose polymer of bacterial origin with a molecular weight varying up to greater than 1,000,000. Novak, Witt & Hiler (1955) have shown that it is useful for aggregation and stabilisation of a wide range of soil types and that its effect persists for at least some months. They investigated the effect of molecular weight and the type of glucose linkages of the polymer in respect to its soil aggregating properties. The water solubility of dextran is of importance as dextrans with a low ratio of alpha 1-6 to non 1-6 repeating anhydro-glucose unit linkages tend to form colloidal suspensions rather than solutions, and consequently are not as effective in forming bridges between soil particles. The aggregating effect of a dextran with a high alpha 1-6 linkage ratio increased with molecular weight up to a value of about 30,000 for a sandy loam, and to 200,000 for a silty loam and a clay loam (Novak *et al*; 1955).

Poly(vinyl alcohol) (PVA) is another synthetic non-ionic polymer that has been used to stabilise soil aggregates (Emerson, 1956; Williams, 1959). Also Michaels (1954) suggested that PVA would be a poor flocculant due to the lack of charged groups, capable of causing the polymer molecules to extend. This latter property has been verified by Greenland (1963) who used a range of PVA of varying molecular weights and degrees of hydrolysis. However, solutions of PVA containing less than 1.5% residual acetyl groups produced a gel-like complex with clay suspensions. This was attributed to the formation of polymer micelles in solution as a result of a high inter-molecular interaction between individual polymer molecules. The groups or micelles of polymer were then capable of enmeshing clay particles within their structure.

Flocculation and stabilisation are discussed in detail in Section 3.2 of this Chapter.

It is considered that PVA molecules in solution are random coils of approximately ellipsoidal shape, the ratio of lengths of the axes varying from 10:1 to 30:1 for molecular weights of the order of 40,000 and 100,000 respectively (Dialer, Vogler & Patat, 1952; Kurosaki, 1954). It is stressed however that this is a statistical description only of the molecular shape and represents the resultant between the tendency for the molecules to assume a shape of minimum free energy and the opposing forces of thermal motion. Extraneous electrolyte had no effect on PVA in solution except at very high concentrations when precipitation occurred.

Quastel & Webley (1947) showed that methylated celluloses were effective aggregating substances, but that they were subject to rapid degradation when incubated with soil. Similar results were found also by Hedrick & Mowry (1952) using a number of carboxy methyl celluloses (CMC) of varying molecular weight. Taylor & Baldridge (1954) found that increasing the degree of substitution of CMC in the range of 0.32-1.28 substitutions of sodium carboxy methyl groups per anhydro-glucose unit, resulted in increased soil aggregation, permeability and plastic limits.

Fiedler (1957) has demonstrated that the degree of substitution of CMC influences its susceptibility to attack by mixed soil and pure micro-organism cultures. CMC containing 1.2 or more substituents per glucose unit showed the highest resistance. A similar figure for the degree of substitution necessary for resistance was obtained by Schwartz, Freeman & Russell (1958), who also showed that with degrees of substitution of less than 0.7, CMC is rapidly degraded. From their results with hydroxy ethyl and methyl celluloses, they came to the conclusion that a high degree of substitution alone is not necessarily an adequate criterion of resistance to microbial degradation, but that the distribution of the substituents along the polymer chain was also important. A uniform distribution of substituents is more likely to confer resistance to enzymatic hydrolyses than an irregular distribution resulting in highly susceptible segments interspersed with resistant segments.

Greathouse, Wessel & Shirk (1951) have reported that vinyl type plastics and resins have a good to excellent resistance to microbial attack. Fuller & Gairaud (1954) found that the biological activity of soils was stimulated by the addition of VAMA but that HPAN and IBMA (copolymer of isobutylene and a half ammonium salt - half amide of maleic acid) had relatively little effect. They concluded that small amounts of the conditioners were immediately available for attack, after which there was little degradation over a period of five months. Addition of other sources of carbon (wheat-straw) made no difference to this situation. Mortensen & Martin (1954) placed carbon-14 with random distribution at the α and β carbons along the vinyl chains of HPAN and VAMA, and so were able to follow with more accuracy the decomposition of the conditioners in soils. After 130 days incubation, radioactive CO_2 equivalent to 2.74% of the added HPAN, and 0.20% of the VAMA was produced. The addition of the polyelectrolyte increased the soil microbial activity. They were careful to point out however that there is no evidence to show that the labelled carbon bonds are attacked at the same rate as the non-radioactive sections of the polymers, and hence no firm conclusions as to the time of effectiveness of the polymers in soils can be deduced from the results obtained.

Wahhab, Khabir, Azim & Uddin (1956) also found increased microbial activity in HPAN treated soil. However, they did not distinguish between the effects of improving the soil physical environment for microbial activity, and the use of the HPAN as a source of carbon for the micro-organisms.

Mortensen & Martin (1956), Simpson & Hayes (1958), McCalla (1959), and de Leenheer & de Boodt (1959) have shown that the effect of soil conditioners may persist in the field over a number of years. Although this is generally interpreted as indicating the resistance of conditioners to microbial attack it may also indicate that only a small portion of the added polymer, located at strategic sites within the soil mass, is necessary for effective stabilisation. Furthermore this portion may be relatively inaccessible to the micro-organisms concerned.

3. Interaction of Synthetic Conditioners with Clay and Soil Suspensions

3.1 Adsorption

For flexible macro-molecules the amounts and rates of adsorption are dependent on a considerable number of variables covering the individual and collective characteristics of the polymer, solvent and adsorbent as well as environmental influences such as concentration ratios, agitation, temperature and extraneous electrolytes. These are dealt with briefly below, emphasis being placed on experiments dealing with clay-polymer interactions where they have been investigated.

3.1.1 Polymer characteristics

The amount of adsorption is molecular weight dependent. This is true for both charged and non-charged polymers. At low molecular weights, the amount adsorbed increases rapidly with molecular size, but this becomes less noticeable at high molecular weights where little dependence may be detected. Ellerstein & Ullman (1961) using a range of polymethacrylates (PMMA) ranging in molecular weight from 23,000 to 2,270,000 with glass and iron powders as adsorbents obtained the relation

$$A_s = K M_w^a$$

where A_s is the amount adsorbed at saturation and K and a are constants.

Greenland (1963) has shown that the adsorption of poly (vinyl alcohol) (PVA) by Na-montmorillonite is molecular weight dependent at least over the range of 25,000 - 100,000.

The shape of the polymer molecules in solution, i.e.

whether extended or tightly coiled, also affects the total amount adsorbed.

In solution the configuration of polymer molecules with a minimum energy is spherical, but any tendency towards this is offset by thermal motion and for a non-charged polymer such as PVA, the resultant may be approximated by ellipsoids with the ratios of the axes varying with the molecular weight. With polyelectrolytes the molecules tend to be more extended due to repulsion between segments carrying like charges. Koral, Ullman & Eirich (1958) found that substituting polar hydroxyl groups on partially α-hydrolysed poly(vinyl acetate) (PVAc) gave increased adsorption of these polymers on iron powder. The effect of the hydroxyls was most pronounced at low degrees of substitution, but increased up to 26% - the highest substitution used. Greenland (1963) using PVA of different degrees of hydrolysis observed that higher adsorptions resulted with polymer carrying less than 1.5% residual acetyl groups than with those having 12% residual acetyls. This was thought to be due to greater intermolecular interaction so that the polymer was adsorbed as "aggregates" rather than as individual molecules.

The type of solvent used also determines molecular shape, as with a poor solvent the polymers tend to a shape of minimum energy. Thus Koral <u>et al</u> (1958) using PVAc and Ellerstein & Ullman (1961) using PMMA were able to demonstrate clearly that the amount of polymer adsorbed increased as the solubility of the polymer decreased. It should be remembered also that the solvent is a source of competition for adsorption sites on the adsorbent surface.

The third factor affecting molecular shape is the presence of extraneous electrolytes in the adsorption solution. Mortensen (1959) studying the adsorption of HPAN on kaolinite found that divalent cations, and especially the transition metals capable of being complexed were more effective in increasing the maximum amount adsorbed, than were monovalent cations. Maximum adsorption took place in the presence of hydrogen ions. This was due to suppression of the like charges between the adjacent segments along the polyanion molecules, with a consequent tightening of the coils. Williams (1959) also observed a 25% increase in the adsorption of Na-HPAN on a clay soil at pH 6 as compared with the adsorption at pH 7. Uncharged linear polymers are relatively unaffected by the presence of extraneous electrolytes, and Michaels (1954) considers that polycations would be less sensitive than polyanions to inorganic ions commonly found in soils.

3.1.2 Adsorbent characteristics

Crystalline clay minerals form the principal adsorbents in soil material and the most common of these belong to the kaolin, illite or montmorillonite groups. Two basic structural units built into the form of sheets are involved in the formation of the plate-like clay crystals. The silicate sheet consists of an hexagonal network of silicon tetrahedrons with oxygen atoms at the apices. The second sheet consists of aluminium atoms in octahedral co-ordination between two layers of closely packed oxygens or hydroxyls.

In the kaolin or 1:1 lattice type group, one silicate and one aluminate sheet combine to form the basic lattice structure. The oxygen atoms at the apices of the silica tetrahedra are shared by both sheets. The illite and montmorillonite groups have a 2:1 lattice structure consisting of one aluminate sheet sandwiched between two silicate sheets. The 1:1 and 2:1 structures are referred to as lamellae and these are stacked face to face to form the clay crystals.

The exchange capacity of clays results mainly from the substitution of trivalent aluminium for tetravalent silica in the silicate sheet and of divalent magnesium or ferrous iron for trivalent aluminium in the aluminate sheet. Each substitution results in one negative charge upon the lattice and this is balanced by free positive ions at or near the clay surfaces.

Kaolinites although having values of surface density of charge similar to montmorillonite, have a much smaller surface area (i.e. larger crystal size) and hence have a lower exchange capacity per unit weight. The lamellae are stacked in such a way that the oxygens of the silicate layer of one lamella are adjacent to the hydroxyls in the alumina layer of another lamella. Hydrogen bonding between these two layers results in a fixed lattice structure.

The illitic clays always have a charge due to substitution in the silicate layer and this is balanced by potassium ions. The potassium ions are partially embedded in the silicate layer and provide such a strong attraction between adjacent lamellae that these ions are usually regarded as not exchangeable.

The montmorillonite group have a similar 2:1 lattice structure as the illites but they possess less charge on the silicate layers, and exchangeable cations occur between the lamellae. The outstanding feature of the montmorillonite type clays is the ability of water and other polar molecules to enter between the lamellae, causing the crystal lattice to expand in the direction of the c-axis. They are known as expanding lattice minerals as compared with the fixed lattice structure of illites and kaolinites.

The amount of polymer adsorbed per unit weight of adsorbent depends largely on the surface area of the adsorbent rather than its cation or anion exchange capacity. Montmorillonites generally adsorb larger amounts of polymer, on a weight basis, than illites, depending on the accessibility of the interlamellar spaces for polymer adsorption. Kaolinites, having the smallest surface area per unit weight of clay, adsorb the least amount of polymer.

Ruehrwein & Ward (1952) using X-ray diffraction data showed that polycations but not polyanions were adsorbed in the interlamellar spaces of montmorillonite. Greenland (1963) has shown that PVA can penetrate partially the interlamellar space (10Å) of calcium montmorillonite, and that some can even penetrate the 4Å spacing of caesium montmorillonite. Also decreasing the interlamellar spacing of sodium-montmorillonite by increased concentration of the external inorganic electrolyte produced a marked decrease in the maximum adsorption of PVA.

Mortensen (1959) found that the addition of anions capable of complexing the lattice aluminium of kaolinite, and/or decomposing the clay crystal, reduced the adsorption of HPAN. The amount of reduction was in the order of

$$OH^- > P_2O_7^{4-} > F^- > H_2PO_4^-$$

also Mortensen (1957) investigated the adsorption of HPAN on kaolinite saturated with various cations. Adsorption increased in approximately the same order as cations reduce the zeta potential of kaolinite viz.

$$Th^{4+} > Ca^{++} > Ba^{++} > H^+ > NH_4^+ > K^+ > Na^+$$

As well as the reduction in zeta potential it was considered that in the case of thorium a reversal of charge could occur on the clay surface. Mortensen also suggested that polyvalent exchange cations can undergo hydrolysis to form a charged mosaic surface, capable of independent cation and anion exchange.

3.1.3 Nature of the adsorption forces

Ion exchange of polyelectrolytes does not fully account for their adsorption on clay minerals. In particular polyanions are adsorbed to a greater degree than can be accounted for by the anion exchange capacity of clays. Positive charges on the edges of the crystal lattice of kaolinite are well known (Schofield & Samson, 1954; Quirk, 1960) but it is doubtful whether they occur to any extent on the edge faces of clays based on a 2:1 lattice (Edwards & Quirk, 1962). However the presence of $Al(OH)_2^+$ on the cleavage faces may give rise to sites capable of adsorbing anions.

Hydrogen bonding of the polymers to lattice oxygens and hydroxyls on the surface of clays has been postulated by many workers. Some evidence for this has been produced by infra-red studies e.g. French, Wadsworth, Cook & Cutler (1954) followed the shift of the carbonyl peak of Lytron 886 (a VAMA type polymer) adsorbed on kaolinite. Fontana & Thomas (1961) have also studied the same type of bonding with polylauryl methacrylate adsorption by various solids. Holmes &

Toth (1957) have shown by infra-red analysis that free hydroxyls of clay minerals disappear on the adsorption of S17 (a half amide, half ammonium salt of a copolymer of methyl vinyl ether and maleic acid) particularly at very high concentrations of polymer (up to 1500% of the cation exchange capacity). Maslenkova (1961) has used infra-red analysis to show that polyacrylamide is H-bonded to kaolinite. She found the greatest amount of H-bonding when the polymer was 30% hydrolysed.

A further mechanism for polyanion adsorption is by coulombic linkage of carboxylate groups through polyvalent cations. VAMA type polymers may have an additional linkage by chelation. Michaels (1954) however, suggests that carboxyls are relatively unimportant in adsorption mechanisms but are rather more important in determining the configuration of the polymer molecules. Aluminium and iron oxides associated with the clay minerals are also possible adsorption sites.

The reversal of charge of clay surfaces in the presence of thorium and the development of independent charged mosaics of hydrated adsorbed cations, suggested by Mortensen (1957), have been mentioned previously.

It is generally agreed that polyanions are adsorbed by only a few segments, the bulk of the molecules extending into the solution phase. This has been shown in electron micrographs (Beutelspacher, 1955, 1957), by infra-red analysis (Fontana & Thomas, 1961) and indirectly by the experiments on flocculation of colloids to be discussed in Section 3.2. Uncharged, flexible polymers, such as PVA, are probably hydrogen bonded to the silicate surfaces of clays, and have a higher proportion of segments in contact with the clay. Silberberg (1962) suggests that approximately half of the segments are adsorbed and this has been supported by Greenland (1963) for PVA adsorption. Greenland was able to show that the most likely form assumed by the adsorbed PVA was that of a single buckled layer of approximately 10Å thickness resulting from the adsorption of alternate segments of the polymer molecules.

3.1.4 Other factors affecting adsorption

The amount of polymer adsorbed per unit area of surface increases extremely rapidly with the polymer concentration of the equilibrium solution. It reaches a plateau value that does not change appreciably with further increases in the solution concentration (Mortensen, 1957, 1959 and Greenland, 1963). However, true equilibrium takes a long time to establish, particularly with high molecular weight polymers (Silberberg, 1962).

It has been shown that polymer molecules adsorbed at a surface are attached by only a limited number of segments and that the remaining segments extend from the surface. The extended segments reduce the accessibility of the surface to other free molecules in solution and hence the final state of equilibrium adsorption is not achieved rapidly.

The concentration of the adsorbent has been shown to be of importance (Greenland, 1963; Theng, 1964). Suspensions of greater than 2% of sodium montmorillonite showed a large decrease in the maximum adsorption, possibly due to the formation of micro-aggregates of clay particles with restricted access to their inner surfaces.

The intensity of agitation markedly affects the maximum adsorption of Separan 2610 (a partially hydrolysed polyacrylamide with a molecular weight of approximately 10^6) on quartz (Healy, 1961). The time of agitation at any one intensity does not affect the adsorption. Healy explained this in terms of the shear force required to detach a sufficient number of polymer segments from the quartz surface at the one time, to allow the molecule as a whole to break free. Such an explanation can also be applied to the apparent irreversibility of polymer adsorption as the probability of a large number of adsorbed segments being released at the one time is not high - unless a better solvent is used.

The dependence of adsorption on temperature is only small, both positive and negative coefficients having been recorded (Silberberg, 1962).

3.1.5 Theoretical treatments of the adsorption process

It has been found that adsorption isotherms of polymers on solids are frequently approximated by the Langmuir adsorption isotherm. However this does not necessarily mean that adsorption occurs in the evaporation - condensation manner proposed by Langmuir. In general, the Simha, Frisch & Eirich (S-F-E) type isotherm (classified as H-type by Giles, MacEwan, Nakhwa & Smith, 1960) have a steeper initial slope than most other L-type Langmuir isotherms. This indicates a strong polymer-surface interaction and a rapid saturation of the adsorbent surface. This has been borne out experimentally in the previously mentioned work of Mortensen (1957, 1959), Koral *et al* (1958) and Greenland (1963), as well as others.

The strong interaction of the polymer with the adsorbent must be reconciled with the commonly invoked mechanism of hydrogen bonding, which gives rise to surface - segment interaction energies of the order of only a few kT. Silberberg (1962b) has pointed out that for flexible, uncharged polymers, the adsorption energy per segment need only be great enough to displace the corresponding solvent molecules from the adsorbent surface. The addition of the individual energies of adsorption of each segment in contact with the surface then results in a large total energy for the molecule as a whole. Also the gain in translational entropy due to the release of solvent molecules acts as a driving force favouring increased adsorption. Thus the isotherms show a very strong initial adsorption.

The same reasoning can be applied to polyanion adsorption but in this case charge interactions, as found between the negatively charged clays and polyanions as well as between segments of the one molecule, prevent the collapse of the polymer to the surface. The result is that relatively few segment-surface contacts are made, compared with the uncharged polymers.

3.2 Mechanisms of Flocculation, Aggregation and Stabilisation

In the literature covering soil conditioners the terms "flocculation", "aggregation" and "stabilisation" have often been used interchangeably, although they do not mean the same thing. In flocculation primary particles are bound loosely together into larger associations known as flocs, and these subside with a clear demarcation between the suspension and the supernatant liquid. With a rapid and complete initial flocculation, the flocs subside according to the following relation (Smellie, & La Mer, 1958)

$$t/(h_o - h) = \alpha + \beta t \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where h_o = initial height of subsidence level

h = height at time t

α and β = constants independent of time.

Aggregation, on the other hand, implies a special case of flocculation in which primary particles are bound closely together into larger particles which sediment as individuals in accordance with Stokes Law. Bradfield (1936) states that "aggregation is flocculation plus!" The "plus" probably refers to the process by which clay particles move from the open card-house structure associated with flocs to positions of minimum potential energy as in close parallel packing. The difference between the two structures would be reflected in the much higher water contents of flocs as compared with that of aggregates.

Both flocculation and aggregation result in "aggregates" of primary particles bound together loosely or tightly as the case may be. In this sense the primary particles are said to have been aggregated.

Stabilisation refers to the process by which material that has all ready been flocculated or aggregated, is rendered more resistant to re-dispersion into primary particles i.e. stable flocs or stable aggregates are formed.

Depending on the degree of dispersion of a soil, an organic polymer may either flocculate or aggregate the soil particles while at the same time it can stabilise the structures so formed. The former case is usually observed only with soil suspensions while the latter is probably the most important process under normal field conditions.

Most of our knowledge of aggregation or flocculation has been obtained from studies of suspensions of primary particles and it is commonly observed that an optimum concentration of polymer exists for flocculating a suspension of primary particles under a given set of conditions. La Mer & Healy (1963, 1964) have derived the following mathematical expression to predict the optimum concentration from adsorption data and from experiments of the filtration rate of suspensions of polymer-adsorbent complexes.

$$P_m = (1 + bk/\beta)^2 . b^{-1} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

where P_m = optimum concentration of polymer for flocculation

b = a constant analogous to Langmuir's constant describing the rate of condensation and evaporation of polymer from the adsorbent surface

k = a constant embracing the number of adsorption sites occupied by each adsorbed polymer segment

β = the number of polymer segments per molecule adsorbed on the surface.

The constants b and β/k may be evaluated experimentally by plotting the adsorption date in the form,

$$P/(P_o - P) = P/k + \beta/kb \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

or the filtration rate data in the form,

$$P_o^{\frac{1}{2}}/(Q - Q_o)^{\frac{1}{2}} = C(1 + bk/\beta)^{\frac{1}{2}}.b^{-\frac{1}{2}} + Cb^{\frac{1}{2}}(1 + bk/\beta)^{-3/2}.P_o \quad \ldots (4)$$

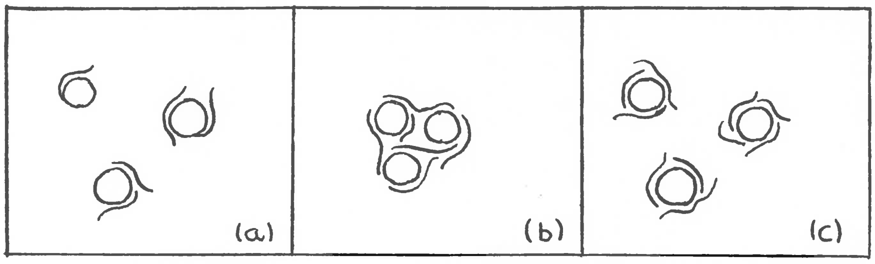
where P_o and P = initial and final polymer solution concentrations respectively

Q_o and Q = filtration rate of adsorbent suspension before and after addition of polymer

C = constant

These two linear equations have been verified experimentally by La Mer and his co-workers in a number of publications and the value of b and β/k when substituted in equation (2) have yielded values for the optimum polymer concentration in good agreement with observed values.

The flocculation mechanism is also discussed by the above authors and they view it in terms of the degree of surface coverage (θ). At low surface coverage one polymer molecule may link a number of adsorbent particles the result being the formation of loose flocs in suspension. As the surface coverage increases, the flocs become more dense and have a faster rate of settling, and also form a less dense layer when settled out from suspensions. At even higher degrees of surface coverage, it is envisaged that the polymer molecules form a "protective coating" around the adsorbent particles and the degree of cross-linking is reduced - resulting in a more dispersed suspension. This is shown schematically below:



(a) Low polymer concentration
(b) Optimum polymer concentration
(c) Excess polymer concentration

○ particle
∼ polymer

As with the adsorption of polyelectrolytes, it has been observed that flocculation depends on the molecular weight, the molecular configuration (and its sensitivity to pH and extraneous inorganic electrolytes), the interaction between polyelectrolyte molecules, adsorbate and adsorbent concentrations, agitation, and the charge density of both adsorbate and adsorbent. All of these factors alter the optimum concentration for maximum flocculation through their effect on the constants of equation (2) and consequently on the degree of surface coverage. It is perhaps in this respect that the semi-empirically derived equations described above may be criticised as they do not specifically take into account each of these factors. Instead they predict the optimum concentration for flocculation from the data of other experiments of adsorption or filtration which in themselves could conceivably be more inconvenient and no more informative than an experimental determination of optimum flocculation. Nevertheless such work is an important step towards describing more precisely the physical state of polymer-adsorbent reactions, a factor which is frequently overlooked when interpreting polymer adsorption experiments.

Flocculation phenomena are of considerable industrial interest, but they have also been investigated to some extent in relation to soil conditioning. Ruehrwein & Ward (1952) distinguished very neatly the difference between the flocculating and floc-stabilising properties of sodium polymethacrylate (PMA). At the polymer concentrations used they found little evidence of flocculation by PMA alone, and concluded that polyanions are poor flocculating agents. However if the clay suspension was first flocculated by the addition of an inorganic electrolyte then PMA stabilised the flocs against redispersion on dilution. Michaels (1954) observed an optimum concentration of polyacrylamide solutions for flocculating clay suspensions and proposed a somewhat similar mechanism of floc formation as in the above figure. Warkentin & Miller (1958), working from the optimum concentrations of polyacrylic acid (PAA) (0.2% by weight of polymer to clay) for flocculating montmorillonite suspensions, have calculated that there were 0.004 and 0.7 molecules of PAA per elementary silicate sheet for the high and low molecular weight fractions respectively. At a 2% concentration there were 7 molecules of low molecular weight polymer per particle, and as would be expected the clay suspension became more dispersed. Packter (1957) has similarly estimated that there was one Wyoming bentonite particle per 4-8 glucose residues of the CMC-clay system investigated. Both authors calculated the number of elementary silicate sheets per unit weight of montmorillonite by assuming sheet dimensions of approximately 1000 x 1000 x 10Å.

Fiedler & Torstensonn (1957) found that although a range of CMC polymers of different molecular weights and degrees of hydrolysis did not produce visible flocculation of soil and kaolinite suspensions, they increased markedly the water-stability of artificial aggregates of a heavy clay soil. Similarly Maslenkova (1961) observed that the formation of water-stable aggregates by polyacrylamide, of varying degrees of hydrolysis was inversely related to the flocculating capacity of the polymer.

It is apparent from the above experiments that although the interaction of polymers with clay suspensions can be studied with some precision, the results do not necessarily have a direct application to soils under field conditions. In the field even the most structurally degraded soils are present as "suspensions" of very high concentration and the mobility of added polymer molecules is severely restricted. It is unlikely that flocculation-deflocculation reactions occur in the manner described above for dispersed clay suspensions. Flocculation or aggregation can proceed by polymer molecules forming bridges between adjacent particles but the effectiveness of this process would depend largely on the size of the particles being bound together. Even soils of poor structure consist largely of aggregated material and the inter-aggregate distances are large compared with the dimensions of polymer molecules. Thus bridging by the polymer would be restricted to points of close approach of neighbouring aggregates. Efficient mixing increases the chances of aggregate stabilisation but even so the efficiency achieved in the field is very much less than that obtained in soil suspensions.

The principal action of soil conditioners under these conditions is probably that of stabilising existing aggregates. The adsorption experiments discussed earlier in subsection 3.1 show that polymer adsorption is in many instances practically irreversible due to the formation of a large number of polymer-surface contacts per molecule. Thus the mechanism of stabilisation is generally thought to be due to polymer bonding between soil particles resulting in increased resistance to separation by mechanical action and the disruptive action of swelling.

This will be discussed in more detail in section 4.

4. The Influence of Soil Conditioners on Soil and Clay Properties

4.1 Water-stable Aggregation

The determination of water-stable aggregation is probably the most commonly used method for testing the effect of soil conditioners on soils. One of the most important problems associated with such studies is the lack of uniformity of the methods used to prepare the treated aggregates and to determine their water-stability. Soil conditioners do not necessarily "aggregate" soils, but rather stabilise existing aggregates against dispersion. Thus quite early in the period of conditioner studies Quastel (1954) remarked that "It cannot be overemphasised that the soil conditioners such as polyuronides or synthetic polyelectrolytes, stabilise soil-crumbs, and that for their effective use, soils must be worked into a good structure before or at the time of application of the conditioner."

Brockman & Allerby (1953, 1955) have studied some of the factors affecting the laboratory evaluation of soil conditioners and conclude that the values obtained vary with the water content of the aggregates during preparation, the manner of incorporating the conditioner, the degree of drying and ageing of the samples, and the source of the soil. Similarly, Toth (1955) reported that the evaluation of six polymeric soil conditioners at eleven different laboratories produced no two sets of identical results.

The methods for incorporating the polymers involve either the use of natural aggregates of a narrow range of size or else finely ground soil that is artificially made into aggregates of known size. The polymers may be added either in solution at different moisture ratios or else as powders followed by wetting. The prepared material is usually allowed to dry to varying degrees before testing by one of the various wet sieving techniques (Toth, 1955; Jones & Martin, 1957; Hedrick, 1954), or with techniques involving cationic dispersion (Emerson, 1956; Bobchenko, 1961). In spite of these differences which make the comparison of results by different workers difficult, the effects of soil conditioners on water-stable aggregation show the same general trends - differing quantitatively rather than qualitatively.

It might be expected that the mechanical composition and structure of soils would have a considerable influence on the development of water-stable aggregates by added polymer, as the polymer-soil interaction is largely dependent on the frequency and accessibility of adsorption sites. The effect of mechanical composition has been investigated by a number of workers (Laws, 1954; Moss, Browning & Southon, 1954; Allison & Moore, 1956; Nath & Nagar, 1960a), and it has been found that generally the largest responses occur with clay loam soils rather than with lighter or heavier textured soils. However, Laws (1954) found good responses to conditioner application on sandy loam soils, which is opposite to that reported by Moss *et al* (1954). Further, he found with artificially prepared soils, that maximum effectiveness was obtained with about 15% clay. It is likely that most differences are based on the accessibility of the polymers to the clay surfaces during the treatment period. Thus in artificial soils, with all components originally separated, it would be expected that the polymer would have free access to reactive sites as compared with natural aggregates that are not readily dispersed under normal mixing conditions. In the absence of any disturbance of the soil Bobchenko (1961) reported that a polyacrylamide conditioner only penetrated the top 3 mm of soil - thus further emphasising the importance of efficient mixing in obtaining responses to conditioners.

It was shown in Section 3 that the presence of various cations can have considerable influence on the adsorption and flocculation of clay systems. With arable soils the presence of moderate amounts of sodium on the exchange complex may result in a strong tendency for dispersion of the soil aggregates. Allison (1956 a & b) used VAMA on soils having from 3 to 47% of the exchange sites occupied by sodium, and found that large increases in water-stable aggregation resulted. An additional effect was increased infiltration rates on the treated soils with a consequent more rapid removal of sodium from the surface soils. The highest degree of aggregation was obtained in the presence of moderate to high amounts of exchangeable sodium. Tamhane &

Chibber (1955) also have reported that HPAN type polymers are effective aggregating agents for sodium soils, at levels of 0.05 to 0.10%. On the other hand, Dhawan, Lal Malhotra & Singh (1958) found that Krilium was not effective in reclaiming soils that had been treated with sodium carbonate. The latter authors however used field applications of 50 lb/acre which would be only about one tenth of the application rates used by other authors.

Martin & Aldrich (1955) showed that different conditioners responded in different ways to the presence of exchangeable sodium and potassium. They observed no effect on the action of VAMA but a considerable reduction in the aggregating effect of IBMA (an isobutylene-maleic anhydride copolymer). Jones & Martin (1957) studied the effect of various inorganic salts on the stabilising properties of HPAN and found similar results to those already mentioned for clay systems viz. the effect of the added cation or anion was in the order of the lyotropic series, and that if the conditioner were added first, the fertiliser salts had little effect. Nath & Nagar (1960b) found no consistent cation (H^+, Ca^{++}, Na^+) influence on the aggregating effects of three polyelectrolytes. The effect of pH on carboxylated polymers was to increase their effectiveness under neutral to slightly acid conditions while liming markedly decreased their effectiveness (Laws, 1954). A similar reduction in the effectiveness of HPAN by $CaCO_3$

and CaSO$_4$ was also observed by Fiedler & Bergmann (1954) on some German soils. From studies with clay suspensions, polyanions are more extended at higher pH values and might well be expected to be more effective in bridging soil particles. This tendency however is offset by the presence of free cations, particularly multivalent ions, and the polymer molecules tighten and may even precipitate. VAMA appears to be more tolerant of the presence of inorganic cations than the HPAN type polymers possibly because of the presence of carboxyl groups in the maleic acid unit capable of chelation.

The presence of organic matter has been reported to reduce the aggregate stabilising properties of VAMA (Laws, 1954). Hanotiaux & Mani (1952) reported a higher "structure coefficient" for a number of soils treated with a HPAN conditioner, following removal of organic matter. Similarly Holmes & Toth (1957) found that of the range of loam soils they used, the two with the highest organic matter (2.53 & 4.26%) had the smallest percentage increase in aggregation in response to a range of soil conditioners. Also the increase was lost more rapidly under cultivation practices. These experiments indicate that the presence of adsorbed organic matter interferes with soil-polymer interactions, presumably by blocking some adsorption sites and by preventing the close approach of polymer molecules to the soil particle surfaces. However they do not really indicate whether the polymer bonds that do form are impaired in any way or whether true comparisons can be made between polymer treatments of soil containing natural organic matter and soil from which the organic matter has been chemically removed. More careful definition of the physical and chemical state of the adsorbent is required if useful inferences are to be drawn from such multi-component adsorption systems.

4.2 Mechanical Strength

The "modulus of rupture" test as described by Richards (1953) has commonly been used to determine the effectiveness of conditioners in preventing crust formation at the soil surface. It consists of applying a load at the centre of a moulded rectangular soil sample of predetermined dimensions and density. The sample is supported at each end and the load applied at failure can be expressed as tensile strength. Jamison (1954) has pointed out that for samples made up of micro-aggregates, as is the case with soils that have not been dispersed completely, the test should give a good indication of the strength of inter-aggregate bonding. Interparticle bonding between primary particles within the micro-aggregates would be expected to have little or no effect on the modulus of rupture value. In fact he showed by treating soils with a number of conditioners that the modulus of rupture of the treated samples was considerably less than that of the control. From this it was inferred that the conditioners, and in particular VAMA, acted through intra-particle bonding. Similar results have been obtained by Allison (1956) and Allison & Moore (1956) who showed that HPAN and VAMA reduced the modulus of rupture of soils with high sodium content, thus ameliorating their crusting tendencies. On the other hand, Pugh, Vomocil & Nielsen (1960) found no consistent correlation between water-stable aggregation and the modulus of rupture for five Californian soils.

Jamison (1954) also determined the rupture values of a soil in which HPAN had been sprayed on to one surface of the prepared briquettes and not mixed throughout the sample. In this case it was found that the modulus of rupture values were approximately twice that of the control briquettes, indicating that when the conditioner was applied as a surface spray, much harder crusts were formed. Plot trials also showed that unless the surface crust was broken up after conditioner application in this manner, cotton seedling emergence was considerably reduced. It was considered that the hard crust was due to slaking of the surface soil during application of the liquid conditioner and that more effective soil-polymer bonds resulted.

Homrighausen (1957) and Modina (1962) determined the crushing strength of artificial and natural soil aggregates treated with a range of soil conditioners and report considerable increases in the strength of the samples. Also Williams (1959) found large increases in the cohesive strength, as determined with an Atterberg balance, of natural aggregates treated with HPAN and PVA, particularly with the latter. Quirk & Panabokke (1962a) also used the Atterberg balance method to measure the mechanical strength of aggregates from a soil having different crop rotations. Aggregates from a soil under pasture which had not been cultivated had a considerably higher cohesive strength than those from the annually cultivated soil which had a lower organic matter content. In contrast to the previously discussed modulus of rupture tests these latter reports emphasize the increased strength of both artificial and natural soil aggregates containing polymeric conditioners or organic matter. The reason for this is found to be not in the test methods used but in the preparation of the samples.

Once organic polymers have been adsorbed and dried on the soil particle surfaces the binding action is not reconstituted if the soil aggregates are ground and remoulded. This has been clearly demonstrated by Laws (1954) using remoulded VAMA treated soils, and by Quirk & Panabokke (1962) using a soil containing natural organic matter. Jamison (1954) and Pugh et al (1960) prepared their briquettes by first treating a sieved soil with the conditioner, drying and grinding it to less than 2 mm aggregates, and then pressing it into moulds after adding the required amount of water. The samples thus represented stabilised aggregates pressed into briquettes and it is not surprising that inter-aggregate bonding values were lower than those observed for the untreated samples. Had the briquettes been moulded from the initial preparation before the samples were dried and the polymer bonds broken by grinding, then it is likely that the modulus of rupture values would have been considerably greater than those for the untreated samples. Allison (1960) and Allison & Moore (1960) do not give sufficient details of their soil-polymer preparations, but it is likely that the lowered modulus of rupture values were a result of the same type of sample preparation.

It is clear then, that organic polymers can increase the mechanical strength of soil by forming strong bonds between the particles. Quirk & Panabokke (1962a) considered that the disposition of organic matter within aggregates is important in respect to mechanical strength. It was suggested that as water enters the coarse pores of an aggregate at the fastest rate these would be the most likely sites for initiation of aggregate breakdown. Similarly, Williams (1959) was able to show that by treating pores of various sizes within aggregates with PVA, that the aggregates were strengthened to different degrees. In particular pores of 15-20 μ radius appeared to be important in this respect for the Urrbrae loam used, rather than finer or coarser pores.

From the above discussion it can be seen that there are a number of methods available for demonstrating the increased strength of soil aggregates with added organic materials. More work is obviously required in evaluating the effects of polymers in terms of the disposition of the organic material and the nature of the bonding forces operating.

4.3 Water Relations

4.3.1 Water retention, porosity, permeability

The water content of soil under any particular set of conditions is dependent on a number of factors, chief of which are the pore structure of the soil sample and the nature and state of the clay mineral fraction.

Croney & Coleman (1954) have shown that a soil can exist in a number of structural states typified by unique water content - energy curves, the positions of which vary with the amount of external work applied to the soil - water system. The effect is most pronounced at low water suction values and less so at pF values of 4 and greater, when the normal shrinkage limit is reached for artificially compressed clay materials. Intensive disturbance of the soil results in a more open particle arrangement and the soil moves from an aggregated or overconsolidated state to one on the normal consolidation curve.

Natural soil aggregates have reproducible water content-energy curves provided that the structure is not disrupted during the wetting process. Rapid wetting can result in structural changes, and hence in the water content-energy relations, of soil aggregates, depending on the ability of the aggregates to withstand this type of applied force.

Quirk & Panabokke (1962a) showed that air-dry aggregates from a continuously cultivated rotation were not stable to rapid wetting at low suctions (2 cm) of water. Although the aggregates retained their identity it was found that they had a gel-like consistency and that on immersion in water the aggregates slaked i.e. the aggregates changed from a state of overconsolidation towards a state of normal consolidation, as defined above. This breakdown of the aggregate structure when wet under suction was referred to as incipient failure. Virgin aggregates of the same soil, taken from a long standing native pasture, were stable to rapid wetting and showed no structural breakdown i.e. the virgin aggregates when subjected to external work of this nature retained their overconsolidated state.

The virgin and cultivated aggregates were structurally very similar and so it was concluded that the higher organic matter content of the virgin aggregates (2.7 and 1.3 per cent for the virgin and cultivated aggregates respectively) was responsible for strengthening the porous structure of the aggregates against the disruptive force of rapid wetting.

Williams (1959) also found that air-dry, cultivated aggregates containing approximately 1g PVA/100g soil, did not show incipient failure when subjected to rapid wetting with water. In fact water-stable aggregation experiments showed that cultivated aggregates containing PVA were able to withstand the forces of rapid wetting and end-over-end shaking in water, much better than virgin aggregates stabilised with natural organic matter. Williams further showed that strengthening large or very small pores of Urrbrae loam aggregates with PVA was not as effective in increasing the stability of the aggregates as was treatment of pores of 15-50 μ radius alone.

The work of the above authors emphasises that water retention by soils depends to a large degree on the disruptive forces applied to the soil at or before the time at which the water content determination is made. This is particularly true at low water suction values but is not as obvious at suctions greater than about pF 4. Also the ability of soil aggregates to withstand the application of external work is intimately associated with the amount, type and disposition of organic materials within the porous aggregates.

Hedrick & Mowry (1952) reported that application of HPAN to a soil of poor structure increased the moisture equivalent (approximately pF 2.7) while the moisture content at the wilting point for tomato seedlings remained unchanged. From this it was inferred that there was an increased amount of water available for plant growth as a result of the polyelectrolyte treatment. Bodman & Hagin (1952) and Hagin & Bodman (1954) reported slight decreases in the moisture in equivalent of soils treated with HPAN and VAMA while Mortensen & Martin (1956), using the same polymers, found that the moisture equivalent was not significantly altered. Taylor & Baldridge (1954), using CMC, also found no difference in the water retention between one third of an atmosphere and 15 atmospheres suction for treated and untreated soils. The variability of these results is probably due to the use of puddled soil material for the water retention determinations and the soils may or may not have been in a state of normal consolidation. Under these circumstances it is difficult to assess the relative values of conditions for increasing the water available for plant growth.

Soil conditioners are generally reported to have the effect of increasing the porosity of treated soils (Haise, Jensen & Alessi, 1955; Mortensen & Martin, 1956; Gussak, 1961). Such determinations are made from measurements of bulk density and as such do not distinguish between an increase in inter-aggregate porosity or an increase in inter-particle porosity, although it is generally inferred that the effect of the conditioner is to reduce bulk density values by increasing inter-aggregate porosity.

If however the conditioner is added to individual soil aggregates, little change in the pore structure of these aggregates is apparent (Bobchenko, 1961; Modina, 1962). Panabokke & Quirk (1962a) have also reported that different levels of naturally occurring organic matter had little effect on the pore structure of natural soil aggregates. There is a need for more information on this aspect of soil-polymer interaction, particularly as the previously described work of Williams (1959) indicates that the disposition of adsorbed PVA has a considerable influence on the stability of aggregates.

Concomitant with increased porosity are increases in permeability or filtration rates due to the more aggregated state of the soil and a higher proportion of coarse pores (Hedrick & Mowry, 1952; Wester, 1955; Pugh, Vomocil & Nielsen, 1960). Allison (1956) has shown that for soils with a high sodium content that VAMA or HPAN treatment increased the filtration rates up to ten-fold and as a consequence the removal of sodium from the top six inches of irrigated soil was approximately twice as rapid.

From the foregoing discussion it can be seen that there is a need for specific definition of the physical state of the soil system when water retention and movement are being considered. The distribution of pores and the durability of that distribution to external forces are parameters of prime importance in evaluating the effect of soil-water interactions.

4.3.2 Swelling

Adsorption and flocculation studies already discussed have shown that polymer molecules form strong bonds between clay particles, and this may be an important mechanism in increasing the stability of aggregates under conditions of high water content.

Water associated with the clay fraction of soils has been studied in considerable detail and is briefly summarised below to provide a background for the understanding of the action of organic polymers on the swelling properties of clay minerals.

Clay minerals of the expanding lattice type such as montmorillonite and vermiculite may swell due to an increase in the separation between crystals (<u>inter</u>crystalline swelling) or by separation of the lamellae which make up individual crystals (<u>intra</u>crystalline swelling). These minerals may further show "limited" or "extensive" intracrystalline swelling, depending on whether the hydration energy of the exchangeable cations is sufficiently large to overcome the potential barrier to extensive swelling caused by the coulombic attractions between the cations and the negatively charged clay lamellae. Non-expanding lattice clay minerals, do not exhibit intracrystalline swelling, but do of course show intercrystalline swelling.

The extent of limited intracrystalline swelling is dependent on the exchangeable cations and the surface density of charge of the clay minerals. Once extensive swelling is achieved, as with the monovalent Na^+ and Li^+ cations, the interlamellar spacing becomes dependent only on the external electrolyte concentration (e.g. Norrish & Quirk, 1954; Norrish, 1954). This latter effect is explained in terms of the development at the clay surfaces of a diffuse layer of hydrated cations, the depth of which is related to the external electrolyte concentration (Schofield, 1946).

Aylmore & Quirk (1960) have studied the intercrystalline swelling of illites and kaolinites and have suggested that the crystals occur in a turbulent array of domains. In monovalent ion systems the swelling was dependent on the external electrolyte concentration and a potential barrier had to be exceeded before the development of diffuse double layers and extensive swelling could take place. In divalent ion systems the domains did not expand extensively and hence the intercrystalline swelling was restricted. Thus it can be seen that there are marked similarities between the swelling mechanisms of both expanding and nonexpanding clay lattice systems. Posner & Quirk (1964) have recently shown that the basic swelling mechanism is essentially the same for both types of swelling for divalent ion systems.

Organic molecules may affect the swelling of clay minerals in two ways. They may be adsorbed in the interlamellar spaces of expanding type clay minerals and so restrict intracrystalline swelling. Also they may be adsorbed on the external surfaces of both expanding and nonexpanding minerals, and reduce intercrystalline swelling by cross linking between particles.

It has been shown that organic polycations but not polyanions are adsorbed in the interlamellar spaces of montmorillonite (Ruehrwein & Ward, 1952; Hagin & Bodman, 1954; Emerson, 1963). As most commercial soil conditioners are anionic in nature it has been concluded that they reduce swelling by interparticle bonding. Also it has been stated previously that, once adsorbed, these polymers do not dissociate readily from the clay surfaces.

With adsorbed anionic polymers there is the possibility that the cation exchange capacity (CEC), and hence the swelling properties, of the clay minerals may be modified considerably by blocking of adsorption sites and/or providing further cation exchange sites on the polymers themselves. This in turn may affect the swelling properties of clays. Archibald & Erickson (1955) studied the changes of CEC of a bentonite and a kaolinite treated with varying amounts of VAMA and IBMA. At very low concentrations of conditioner there was a marked decrease in the exchange capacity. At slightly higher concentrations the exchange capacity increased, but again fell at higher polymer levels. Nath & Nagar (1959) found no change in the CEC of a bentonite and an alluvial soil treated with 0.1% (by weight) of VAMA, HPAN or SMA (a copolymer of styrene and maleic acid). Some decreases in the CEC were noted with a kaolin plus HPAN or VAMA, and also with a black cotton soil when treated with SMA or HPAN. There is little that may be concluded from these results except that there is some indication of the balance of clay and polymer exchange sites mentioned above. So far this type of work has not been included in swelling studies, although Emerson (1960, 1963) has shown that leaching montmorillonite-polymer complexes with N NaCl followed by electrolyte dilution does displace cellulose-type polymers such as sodium alginate and CMC. Sodium polyacrylate, polyacrylamide and PVA were unaffected by this type of treatment.

Uncharged polymers such as PVA and dextrans have been shown to penetrate the interlamellar spaces of montmorillonite (Greenland, 1963; Emerson, 1963). Emerson further showed that PVA reduced both inter and intra-crystalline swelling of montmorillonite. Theng (1964) has studied the effect of a number of PVA samples of varying molecular weight and degrees of hydrolysis on the swelling of montmorillonite. He concluded that PVA controlled swelling chiefly by interparticle bonding, and that the first few cross-links established between crystals or domains were the most effective in reducing swelling. The mean length of the polymer and the mean interparticle distance affected the degree and frequency of cross linking. Fully hydrolysed PVA was more effective in reducing swelling than a partially acetylated PVA (12% acetyl groups), under the same conditions. It was thought that this could be due to greater hydrogen bonding of the polymer molecules, which would strengthen the polymer linkages between clay particles.

Williams (1959) found by treating natural loam aggregates with up to 1% PVA that the aggregates were protected against the disruptive action of rapid wetting at low suctions of water. It was concluded from this and other experiments that the PVA had little if any effect on the total swelling of the aggregates. Quirk & Panabokke (1962a) showed that the instability of aggregates to rapid wetting was not due to extensive swelling of the clay fraction as incipient failure occurred with cultivated aggregates wet at 2 cm suction with 1M $CaCl_2$. They concluded that natural organic matter strengthened the relatively coarse pores against the force of entry of water. Hence it is likely that PVA served a similar function to organic matter in respect to aggregate stability.

5. Summary and Inferences

A considerable amount of information on polymer adsorption has been gained by use of clay suspensions as the adsorbent materials. In general the results obey the predictions embodied in the theoretical considerations of Simha, Frisch & Eirich (1953) and Silberberg (1962), although particular attention has to be paid to the attainment of equilibrium and steric factors. In particular it has been found that the accessibility of adsorption sites modifies the extent to which polymers can interact with clays.

It has been shown that flocculation reactions need to be studied concomitantly with adsorption as they provide an understanding of the changes in physical state of the adsorbent during polymer adsorption. Although there is not such a sound theoretical treatment for flocculation reactions as with adsorption, the work of La Mer and his co-workers has aided the critical analysis of observed flocculation phenomena. It would appear that to understand the complex phenomena involved more emphasis needs to be placed on the physico-chemical properties of the polymers used and the stability of the resulting complexes.

The swelling of clay minerals has received considerable attention in recent years and the modifications to swelling brought about by the adsorption of organic polymers can now be described in terms of the degree and strength of cross-linkages between the clay particles. The information available from adsorption and flocculation studies are particularly important in understanding the swelling behaviour of clay-polymer complexes.

The clay-polymer interactions discussed above can generally be described more precisely than soil-polymer interactions as soil is a far more heterogeneous adsorbent, both physically and chemically. Also the latter studies usually involve the addition of polymers to slurries and pastes of widely varying soil:water ratios rather than to suspensions, and hence the factors of polymer mobility and the accessibility of adsorption sites become increasingly important. In this respect the information obtained from clay suspensions is limited in its application to soils, especially under field conditions. However it does provide a basis for describing the mechanisms by which the addition of organic polymers to soils results in marked changes of the physical properties of soil. Frequently it is only the final effects, such as water-stable aggregation, water retention, mechanical strength etc., that have been reported with little or no attention being accorded to the mechanisms by which they were brought about. This is perhaps a natural result of experiments designed to evaluate commercial preparations for general field use but it is doubtful whether such an approach results in a rapid improvement of the product, especially when the criteria commonly used are themselves imperfectly understood.

Water-stable aggregation has received a considerable amount of attention in assessing the effectiveness of soil conditioners and yet little is known of the theoretical aspects of the test. This is reflected in the large number of water-stability tests available, each reputably being the most useful under the conditions employed. Water-retention is also a commonly observed parameter, but especially where puddled soil material has been used, many of the results need to be reviewed in terms of the variable relation between soil suction and water content as described by Croney & Coleman (1954). Similarly it has been pointed out that wrong conclusions may be drawn from tests of the mechanical strength of soil-polymer complexes by failure to recognise the irreversible nature of polymer adsorption on soil particles.

Throughout this review it has been observed repeatedly that the conditions of mixing polymers with soil affect the results obtained. The formation and extent of effective links between soil particles by the polymer molecules depends largely on the freedom of movement of the polymer within the mass of soil. Thus thorough mixing, as found with suspensions and slurries of dispersed soil material, results in increased soil particle-polymer linkages. However in the field it is not usually possible to achieve these conditions and so it is desirable to know more of the movement of polymers into relatively undisturbed, aggregated soil material and to relate these to the changes in the physical properties of the aggregates. The use of natural soil aggregates (Quirk & Panabokke, 1962; Williams, 1959) rather than artificial aggregates or slurries obtained from finely ground material can provide useful information in this respect.

In this Thesis an attempt has been made to describe the movement and to determine the location and mode of action of poly(vinyl alcohol) within natural soil aggregates.

Attention has been paid also to the theoretical aspects of water-stability tests used to describe the aggregate stabilising properties of the polymer. Mechanical strength tests were designed to determine the tensile strength of soil-PVA complexes and, as with the other studies, they have been interpreted in terms of the physico-chemical properties of the polymer. From these studies it has been possible to draw inferences relating to the structure and stability of natural soil aggregates.

	Compound	Abbreviated Name
1.	hydrolysed poly(acrylonitrile)	(HPAN, CRD-189, (Krilium 9
2.	copolymer of vinyl acetate-maleic anhydride	(VAMA, CRD-186, (Krilium 6
3.	poly(dimethylaminoethylmethacrylate)	DMAEM
4.	poly(4-vinyl pyridinium N-ethyl iodide)	PVPI
5.	poly(vinyl alcohol)	PVA
6.	carboxy methyl cellulose	CMC
7.	copolymer of isobutylene and a half ammonium salt - half amide of maleic acid	IBMA
8.	poly(vinyl acetate)	PVAc or PVA
9.	polymethacrylates	PMA or PMMA
10.	VAMA type polymer	Lytron 886
11.	half amide, half ammonium salt of a copolymer of methyl vinyl ether and maleic acid	817
12.	partially hydrolysed polyacrylamide	Separan 2610

CHAPTER II

THE ADSORPTION OF PVA BY SOIL AGGREGATES

1. Materials

1.1 Soils

The soil samples used were taken from the Urrbrae loam, a red brown earth. The surface horizons consist of a fine sandy loam which is free of calcium carbonate. The subsoil is a red-brown clay, having a field structure that is strongly prismatic with marked horizontal cracking (Piper, 1938). The surface samples (0-4") and the sub-surface samples (14-20") are referred to as Urrbrae A and Urrbrae B respectively in the following work. Some of the analytical data of the samples used in this work are given in Table 1.

Table 1

Properties of Urrbrae Soils

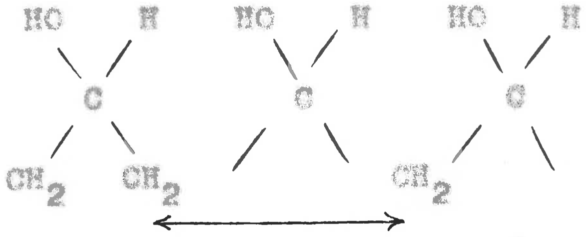
Sample	Sampling Depth	pH	%C	%N	C/N	% Clay
Urrbrae A	0- 4"	5.0	1.28	0.091	13.5	17
Urrbrae B	14-20"	6.6	0.74	0.086	8.6	60

These samples were collected in the form of clods and after air drying were ground and sieved to obtain aggregates of 0.063-0.125, 0.25-0.50, 0.50-1.0, 1.0-2.0 and 2.0 to 5.0 mm diameter. Some Urrbrae B samples were collected in the form of cores of 2 cm diameter, by use of a tube sampler inserted vertically into the ground. The portion of the cores corresponding to 14-18 inches depth were retained for use in adsorption experiments.

1.2 Chemicals

The poly(vinyl alcohols) (PVA) used were the Gohsenol products of the Nippon Synthetic Chemical Corporation, Japan. PVA is prepared by the hydrolysis of poly (vinyl acetate) and the polymers used contained either 12% residual acetyl groups per 100 segments (G-series) or less than 1.5% residual acetyls (N-series).

Fibre diagrams obtained by X-ray analysis (Bunn, 1948) show that PVA has a zig-zag configuration with a repeat distance of 2.5-2.53Å, as shown below.



Repeat distance 2.5Å

The OH groups may all be on one side of the carbon chain or there may be a succession of hydroxyls on one side followed by a number on the opposite side. Such differences depend on the precise conditions of polymerisation and cause minor differences in the properties of the PVA. No information is available on the Nippon products in this respect.

PVA solutions, up to 2% concentration, were prepared by adding small amounts of the solid at a time to vigorously stirred water maintained at approximately 70°C. The polymers containing 12% acetyl groups were more readily soluble than the fully hydrolysed samples. Stock solutions stored in closed vessels at 20°C showed some tendency to come out of solution after periods of 3 months and care was taken to remove the gel so formed, by filtering before use.

Some of the properties of the polymers used are listed in Table 2. The estimation of molecular weight obtained from the manufacturer's data has been used in preference to the relations between intrinsic viscosity and molecular weight found in the literature. The latter result in a wide range of molecular weights depending on the values given to the constants (K and a) in the general relation $[\eta] = K M^a$. For example molecular weights obtained using Berezniewicz's (1959) formula for partially alcoholised poly(vinyl acetates) were approximately twice the values shown in Table 2. The differences probably arise through the use, by different authors, of PVA containing unspecified degrees of molecular branching.

Table 2

Properties of Poly (vinyl alcohols)

Sample	Residual acetyl groups per 100 segments	Polymerisation Number	Molecular Weight (*)	Molecular Weight (**)	Intrinsic Viscosity (***)
Gohsenol					
GL05	12	500	25,000	25,000	0.40
GM14	12	1400	70,000	-	0.80
GH20	12	2000	100,000	80,000	0.95
NL05	1.5	500	22,000	-	0.48
NM14	1.5	1400	64,000	-	0.85

* calculated from the data supplied by the manufacturer using the relation

$$\eta = 7.50 \times 10^{-4} P^{0.64}$$

where η = viscosity of a 4% solution at 30°C (falling sphere method)

P = polymerisation number

** calculated from sedimentation values obtained by ultracentrifuge method (Greenland, 1963).

*** obtained by determining the viscosities of PVA solutions at 25 ± 0.01°C using a No. 1 Ostwald U-tube viscometer.

Intrinsic viscosity $[\eta] = \lim_{c \rightarrow 0} (\eta \text{ specific/concentration})$

2. Methods

2.1 Quantitative estimation of PVA

Standard solutions of PVA were made by dissolving the solid as previously described, allowance being made for the water content as determined at 70°C. Aliquots of the solution were then oxidised with an excess of a mixture of 1N potassium dichromate-concentrated sulphuric acid mixture. The excess dichromate was determined by titration with approximately 0.2N ferrous ammonium sulphate, with Ferroin indicator (0.025M tri-ortho-phenanthroline ferrous sulphate).

The oxidations were not complete (83% for the G-series, 99.5% for the E-series) but were highly reproducible provided that standard conditions were used. It appears that the presence of acetyl groups lowers the efficiency of the oxidation under the conditions used. Standard curves were constructed of dichromate consumed (m.e.) : PVA (mg) and the slope of this relation was then used for subsequent calculations. The concentration of the polymer solutions could be determined to within ± 0.1 mg.

A Fisher high frequency induction furnace was used to determine the amount of PVA adsorbed on soil samples in experiments where it was not possible to analyse the polymer solution. The soil-polymer complexes were ground to pass a 70 mesh sieve and then approximately 0.5 g samples were combusted in the furnace. The CO_2 formed was collected and weighed. Duplicate samples agreed to within 20 mg of carbon per 100 g of soil. The method of using a high frequency induction furnace for soil carbon determinations has been described by Jackson (1958), and more recently by Young & Lindbeck (1964).

2.2 Adsorption of PVA

2.2.1 Adsorption by soil aggregates

Samples of soil aggregates equivalent to 1 ± 0.001 g oven dry material were placed in poly(vinyl chloride) rings (12 mm diameter) with one end covered with filter paper. These were wet slowly at 50 cm suction of water under vacuum for one week to ensure that no structural damage occurred to the aggregates (Quirk & Panabokke, 1962) and to reduce the possibility of entrapped air remaining in the pores. The solution contained 10^{-2} g Hg/litre in the form of methyl mercury dicyandiamide to inhibit fungal growth.

The partially wet aggregates were then washed carefully into 3" x 1" polystyrene tubes with distilled water and the excess water removed with the aid of a fine tube attached to a vacuum pump. The amount of water in the sample and the tube was then determined by weighing.

20 cc of PVA solution of known concentration were pipetted into the tubes, care being taken to avoid unnecessary disturbance of the aggregates. The tubes were stored at 20°C for the required adsorption period, after which the supernatant solution was decanted for subsequent analysis.

Adsorption was determined by the difference between the initial and final concentrations of the PVA solution. Correction was made for the initial water content of the aggregates by assuming that it came to equilibrium with the added PVA solution. This was not a strictly valid procedure as it will be shown later that PVA molecules are not able to penetrate into all of the pores of an aggregate. However it was considered that the error introduced into the calculated values of adsorption were of the same order as those of the analytical procedures.

2.2.2 Adsorption by soil cores

In the experiments with Urrbrae B cores PVA was introduced under suction by wetting the cores on a Grade 4 Buchner type sintered glass funnel filled with PVA solution. One such core was wet from an air-dry state with a 1% PVA solution supplied at a suction of 100 cm. The suction was reduced gradually to 0.5 cm over a period of a week. Another core was first saturated with water by a similar method before it was placed on the sinter containing the PVA solution at 0.5 cm suction for one week.

After removal and partial air drying the cores were sliced into segments 2 mm thick with a sharp blade. The amount of PVA in the samples was then obtained from the increase in carbon content over the untreated soil as determined with an induction furnace.

3. Results and Discussion

The conditions under which polymer adsorption experiments are carried out have a marked influence on the results obtained (Smellie & La Mer, 1958; Silberberg, 1962; Greenland, 1963). The amount and rate of polymer adsorption depends on such factors as the adsorbate-adsorbent ratio, the concentration and molecular weight of the adsorbate and the amount and rate of agitation. These factors are particularly important when using finely divided adsorbent material as flocculation of the particles by the polymer can rapidly reduce the accessibility of the surface for further adsorption.

In the present work, a study was made of the adsorption of a range of poly(vinyl alcohols), of varying molecular weight and degrees of hydrolysis, by virtually undisturbed soil aggregates. The majority of the experiments were carried out with Urrbrae B aggregates because of their high clay, and low organic matter contents.

No experiments were carried out to determine the effect of varying the adsorbate-adsorbent ratio as it was considered that there would be no restriction to the diffusion of PVA to the surfaces of the aggregates in the shallow beds of aggregates used. A ratio of 1 g of soil to 20 cc of polymer solution was used throughout.

Urrbrae B soil is calcium saturated and naturally well flocculated so that PVA is unlikely to have caused any further flocculation of clay particles within the aggregates. Thus the following adsorption experiments were essentially a study of the diffusion of PVA into the porous network of the aggregates so that a comparison can be made with the well known laws of ionic diffusion into porous ion-exchange resins. To simplify the discussion of PVA diffusion in these terms, the experimental work is described first and is followed by a summary in which the rate of diffusion and the rate controlling processes are discussed in more detail.

3.1 Adsorption by Aggregates

3.1.1 Aggregate size

Preliminary experiments using a range of Urrbrae B aggregates of different sizes, 0.063-0.125, 0.25-0.50, 0.50-1.0, 1.0-2.0 and 2.0 to 5.0 mm were carried out to determine which aggregate size would be most suitable for studying the adsorption of PVA by this material.

There were three factors to consider, viz.,

(a) the smaller the aggregates the less likelihood there would be of aggregate disruption in the polymer solutions.

(b) the smaller the aggregates the more chance there would be of the polymer being able to penetrate the aggregates completely.

(c) the larger the aggregates the more representative they would be of field structure.

It was found with adsorption periods of one to three days that clear differences in the amount of GM-14 adsorbed were obtained. The smallest aggregates adsorbed the most. With longer periods (14 days) there was little difference in the adsorption by (¼-½), (½-1) and (1-2) mm aggregates, while the smallest and largest aggregates adsorbed approximately 10 per cent more and 10 per cent less PVA respectively.

The (½-1) mm fraction was then chosen for subsequent work, as the best compromise between the factors mentioned above.

3.1.2 Agitation

The effect of gentle agitation of the adsorption tubes on a slowly rocking table was to increase considerably the amount of PVA adsorbed, e.g. the amount of GM-14 adsorbed from 20 cc of 0.5% solution over a 7 day period, with and without agitation, was 1.82 and 0.98 g/100g soil, respectively. It was observed that even with this gentle agitation some breakdown of the aggregates occurred and hence increased the surface available for adsorption. However it is unlikely that all of the increase was due to aggregate breakdown as it would be necessary to have at least 10% of the aggregates dispersed to particles of less than 2 μ size to account for the increase of 0.84 g/100g. It will be shown that at least part of the increase was due to disturbing the film of PVA solution held at the surface of the

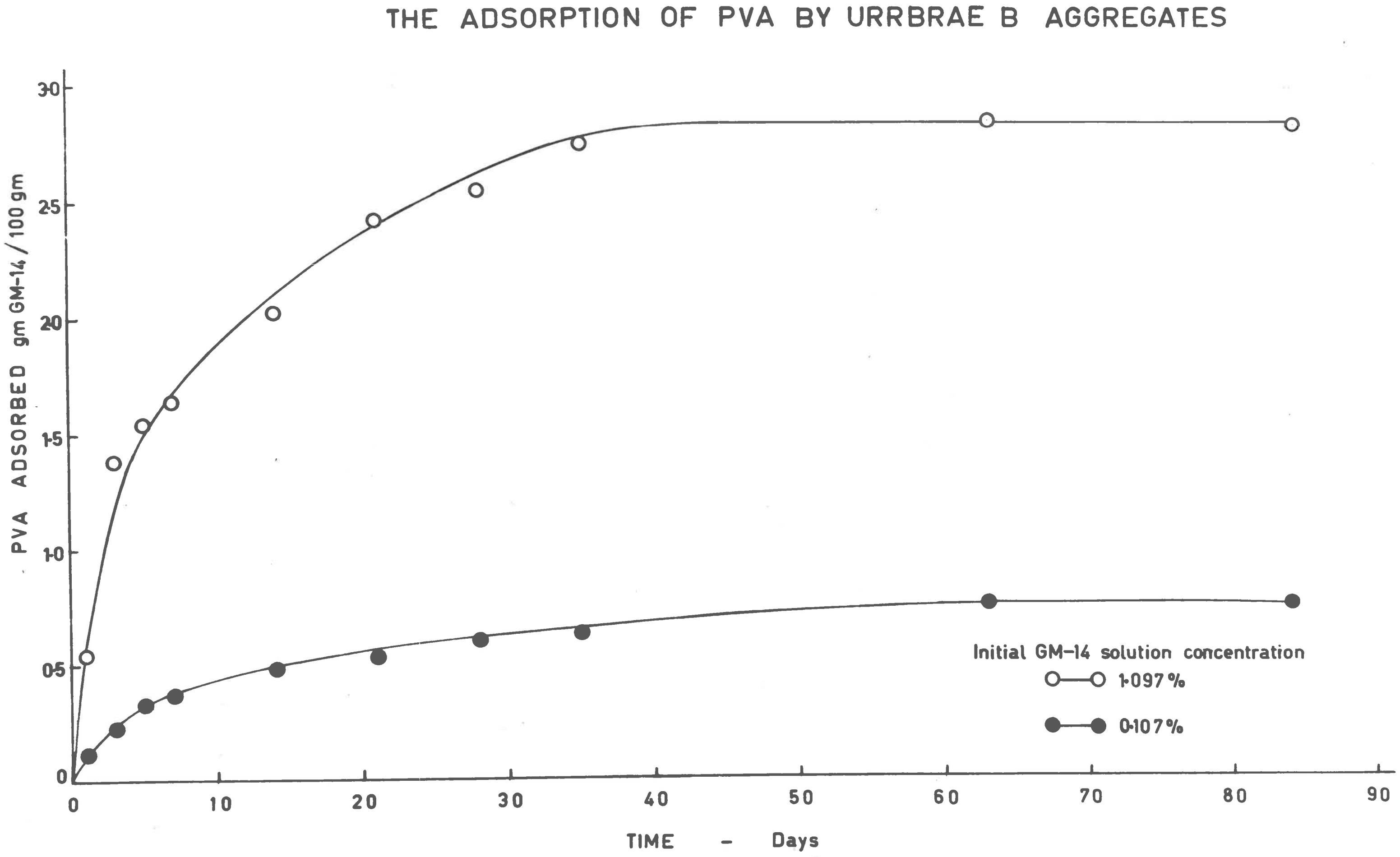
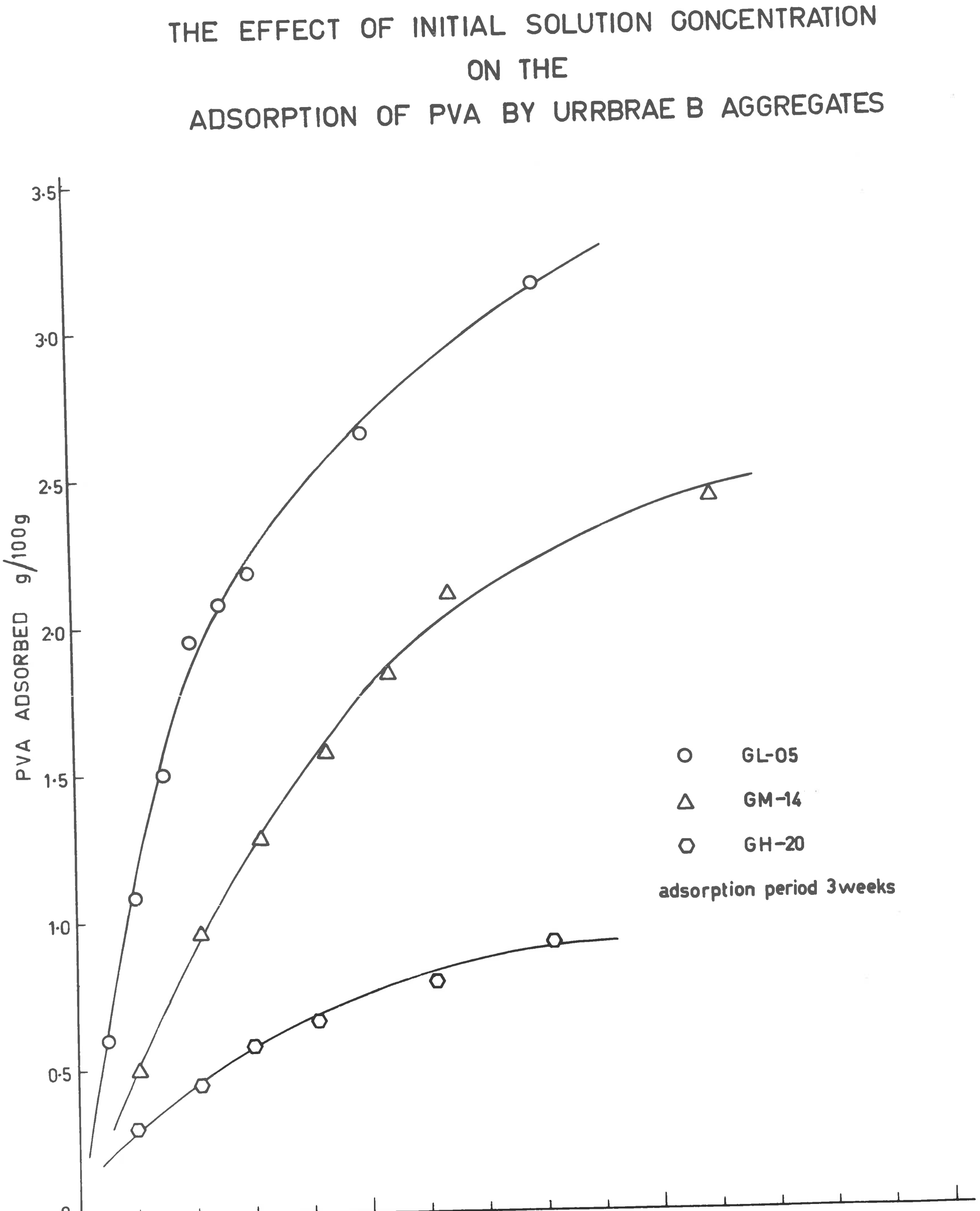
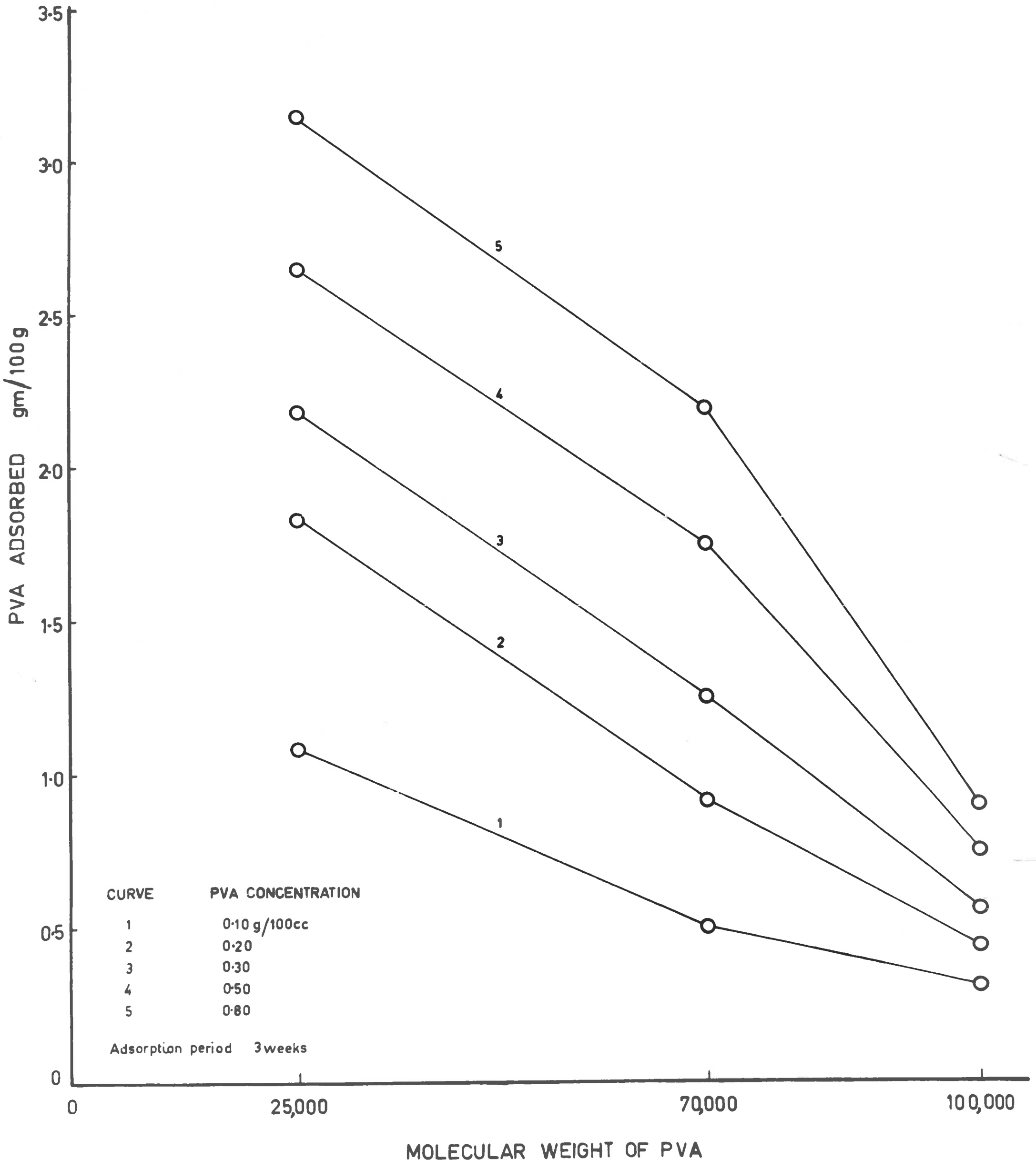

THE ADSORPTION OF PVA BY URRBRAE B AGGREGATES
PVA ADSORBED gm GM-14 / 100 gm
3·0
2·5
2·0
1·5
1·0
0·5
0
0
10
20
30
40
50
60
70
80
90
TIME - Days
Initial GM-14 solution concentration
○—○ 1·097%
●—● 0·107%

Figure 1.



THE EFFECT OF INITIAL SOLUTION CONCENTRATION
ON THE
ADSORPTION OF PVA BY URRBRAE B AGGREGATES

Figure 2.



THE EFFECT OF MOLECULAR WEIGHT ON THE ADSORPTION OF PVA BY URRBRAE B AGGREGATES

Figure 3.

aggregates. This boundary film may or may not control the rate at which PVA molecules are able to diffuse into the soil aggregates. Without detailed studies of the quantitative effects of agitation on PVA movement, especially under conditions of partial breakdown of the aggregates and of the film, interpretation of the adsorption data in terms of the diffusion of the polymer is difficult to make. Thus to assist in interpreting the results, all further experiments were carried out with no agitation and precautions were made also to avoid disturbing the adsorption tubes by normally occurring vibrations in the laboratory.

3.1.3 Time to reach equilibrium

The adsorption of the medium molecular weight polymer, GM-14, at two concentrations (1.097% and 0.107%) on Urrbrae B aggregates was determined over a period of 12 weeks. The rate of adsorption was very slow as can be seen from Figure 1. Under the conditions used the time to reach maximum adsorption was 5-6 weeks, and 8-9 weeks for the high and low concentrations respectively.

In the remaining experiments an adsorption period of 3 weeks was used. In most instances this represented greater than 80% of the maximum adsorption values that might have been expected from the above results and as such true equilibrium values were not obtained. However for the purposes of demonstrating the factors affecting adsorption it was sufficient to have values of adsorption approaching the plateau values, and the additional details derived from much longer adsorption periods would not add significantly to the information from the 3 weeks adsorption data.

3.1.4 Adsorption dependence on initial polymer concentration

In Figure 2 the amount of PVA adsorbed by Urrbrae B aggregates is shown as a function of the initial solution concentration for the GL-05, GM-14 and GH-20 polymers.

There is a rapid rise in the adsorption with increasing initial polymer concentration, the rise being greatest with the polymer of lowest molecular weight. The isotherms appear to conform with the L-type classification of Giles *et al* (1960) rather than the H-type isotherms obtained with the adsorption of PVA on montmorillonite suspensions (Greenland, 1963). However a precise classification cannot be made from ~~this~~ these data as the adsorption period of three weeks is considerably less than that previously shown to be necessary to reach equilibrium.

3.1.5 Effect of molecular weight of polymer on amount adsorbed

In Figure 3 the data from Figure 2 have been re-arranged to show the amount of PVA adsorbed, from solutions of different initial concentrations, as a function of the molecular weight of the polymer. The relationship is curvilinear, being convex to the X-axis at high solution concentrations and concave to the X-axis at low concentrations. A linear relationship occurs in the vicinity of an initial PVA concentration of 0.30 g/100 cc.

Silberberg (1963) considers that provided equilibrium is attained noncharged macromolecules should be adsorbed in increasing amounts with increasing molecular weight, at least for the relatively low molecular weights used in this work. This is borne out by the work of Miller (1961) using poly(methacrylic acid), (PMA), and Greenland (1963) using PVA. The reason for the increased adsorption is thought to be due to a larger proportion of the polymer segments per molecule extending from the adsorbent surface rather than a closer packing on the surface.

The results of this present experiment are opposite to what would be expected from the preceding paragraph in that the low molecular weight PVA is adsorbed to the greatest extent. This difference can be explained in terms of the reduced accessibility of adsorption sites within the fixed structure of soil aggregates as compared with dispersed clay suspensions where all surfaces are available for adsorption.

A large proportion of adsorption sites within Urrbrae B aggregates are located in small pores which can readily become blocked with large organic molecules such as PVA. This prevents, or greatly reduces, the movement of other PVA molecules throughout the aggregates and hence the amount of polymer adsorbed is considerably reduced. Furthermore the adsorption of PVA is virtually irreversible because the large number of polymer-particle contacts per molecule greatly reduces the possibility of an adsorbed molecule breaking free from the surface and moving along a pore by surface diffusion processes. The reduced adsorption of PVA on soil aggregates is clearly demonstrated by the observation that the extent of GL-05 (molecular weight, 25,000) adsorption on whole Urrbrae B aggregates was only about 30% of the amount adsorbed when the soil was completely dispersed.

The movement of PVA of higher molecular weight within soil aggregates would be expected to be even less than that observed for GL-05 and this is reflected in the smaller amounts of GM-14 (50,000) and GH-20 (100,000) adsorbed by whole Urrbrae B aggregates, as shown in Figure 3.

A similar observation was made by Greenland (1963) when it was found that adding PVA to an incompletely dispersed clay suspension resulted in a reduction in the total amount of PVA adsorbed and also that the lowest molecular weight polymer was then adsorbed to the greatest extent.

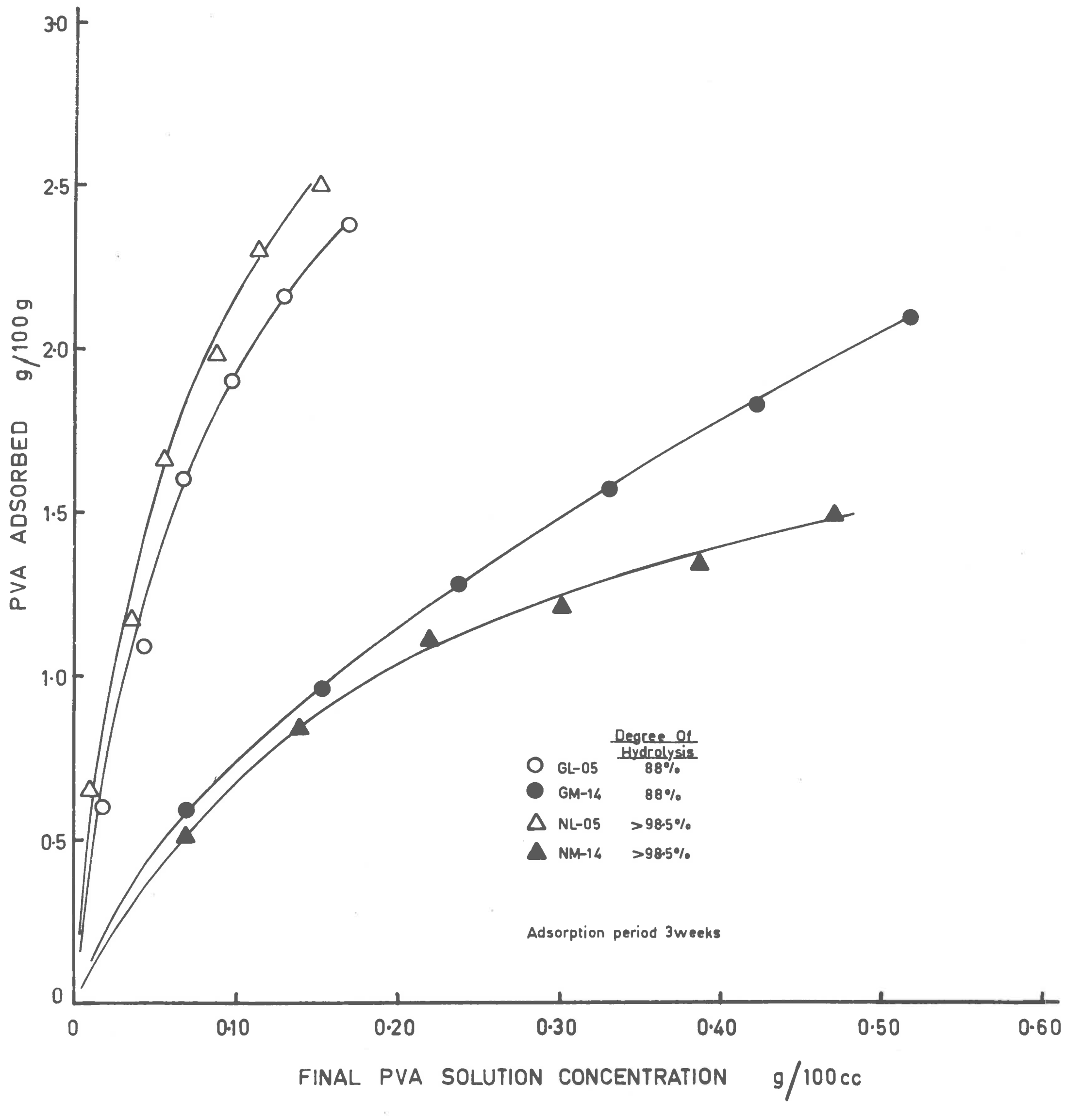
The accessibility of adsorption sites within aggregates to PVA molecules, or to other stabilising agents, is of considerable importance in respect to aggregate stability, and this aspect is discussed in more detail in Chapter III and V of this thesis.

3.1.6 Adsorption of PVA with varying degrees of hydrolysis

To determine the effect of residual acetyl groups in the PVA molecules, the adsorption on Urrbrae B aggregates of GL-05 and GM-14 (12% residual acetyls) was compared with that of NL-05 and NM-14 (less than 1.5% residual acetyls). The results are shown in Figure 4.

NL-05 was adsorbed to a slightly greater extent than GL-05 while the reverse occurred with NM-14 and GM-14. This is probably due to the resultant of two factors having opposing effects on the amount of adsorption viz. the molecular weight and the state of the polymer molecules in solution.

The manufacturer's data indicate that NL-05 and GL-05, and similarly NM-14 and GM-14, are prepared from the same parent poly(vinyl acetate) fraction. Thus each pair have the same degree of polymerisation, but the N-series have a molecular weight of approximately 8.5% less than that of the G-series. However the work of Greenland (1963) shows that the N -series polymers probably occur in an aggregated form in solution and so tend to behave as large molecules. This is supported by Dieu (1959) who showed that some of the PVA samples he used formed molecular aggregates in solution. To investigate this factor further the intrinsic viscosities of the polymers used in this work were determined and are shown in Table 3 below.



THE ADSORPTION OF PVA HAVING DIFFERENT
DEGREES OF HYDROLYSIS
BY URRBRAE B AGGREGATES

Figure 4.

Table 3

The Intrinsic Viscosity of PVA

Sample	Molecular Weight	Intrinsic Viscosity
GL-05	25,000	0.40
NL-05	22,000	0.48
GM-14	70,000	0.80
NM-14	64,000	0.85

It can be seen that although the N-series polymers have a lower molecular weight than their G-series counterparts, they have higher values of intrinsic viscosity, i.e. the N-series polymer molecules form associations which cause them to behave as polymers of higher molecular weight.

It was previously shown that PVA with the lowest molecular weight is adsorbed to the greatest extent. This is also seen with NL-05 (22,000) and GL-05 (25,000). However because of their aggregated form in solution it would be expected that the N-series polymers would be adsorbed to a smaller extent than the G-series having the same degree of polymerisation. This was found to be the case with NM-14 (64,000) and GM-14 (70,000).

Thus the results shown in Figure 4 may be regarded as being due to a combination of these two molecular characteristics. It appears that aggregation has little effect on the low molecular weight PVA while the effect on GM-14 is quite pronounced.

3.1.7 The adsorption of PVA on Urrbrae A aggregates

The adsorption of GM-14 and GH-20 on (½-1) mm aggregates of Urrbrae A is shown in Figure 5, together with the adsorption of these polymers on Urrbrae B.

The adsorption isotherms for the surface soil are quite different to those for Urrbrae B in that the amount adsorbed is much less dependent on the concentration of the polymer solution. Also the GH-20 isotherm for Urrbrae A shows a marked decline in the adsorption at final solution concentrations above 0.19 g/100 cc. This effect is not apparent when Urrbrae B aggregates are the adsorbent. A similar, but more weakly developed, tendency can also be seen with the adsorption of GM-14, at the highest solution concentrations used.

The difference in the amounts of GM-14 adsorbed cannot be directly related to the clay content of the two soils as the surface area of Urrbrae B is approximately four times that of Urrbrae A, while the ratio of the amounts adsorbed is more than 5:1 at the maximum adsorptions observed. Also, the pore-size distributions of these soils (Aylmore, 1950; Quirk & Panabokke, 1962) show that Urrbrae B has a large proportion of fine pores (radius < 20Å) compared with a high proportion of pores greater than 200Å radius in the

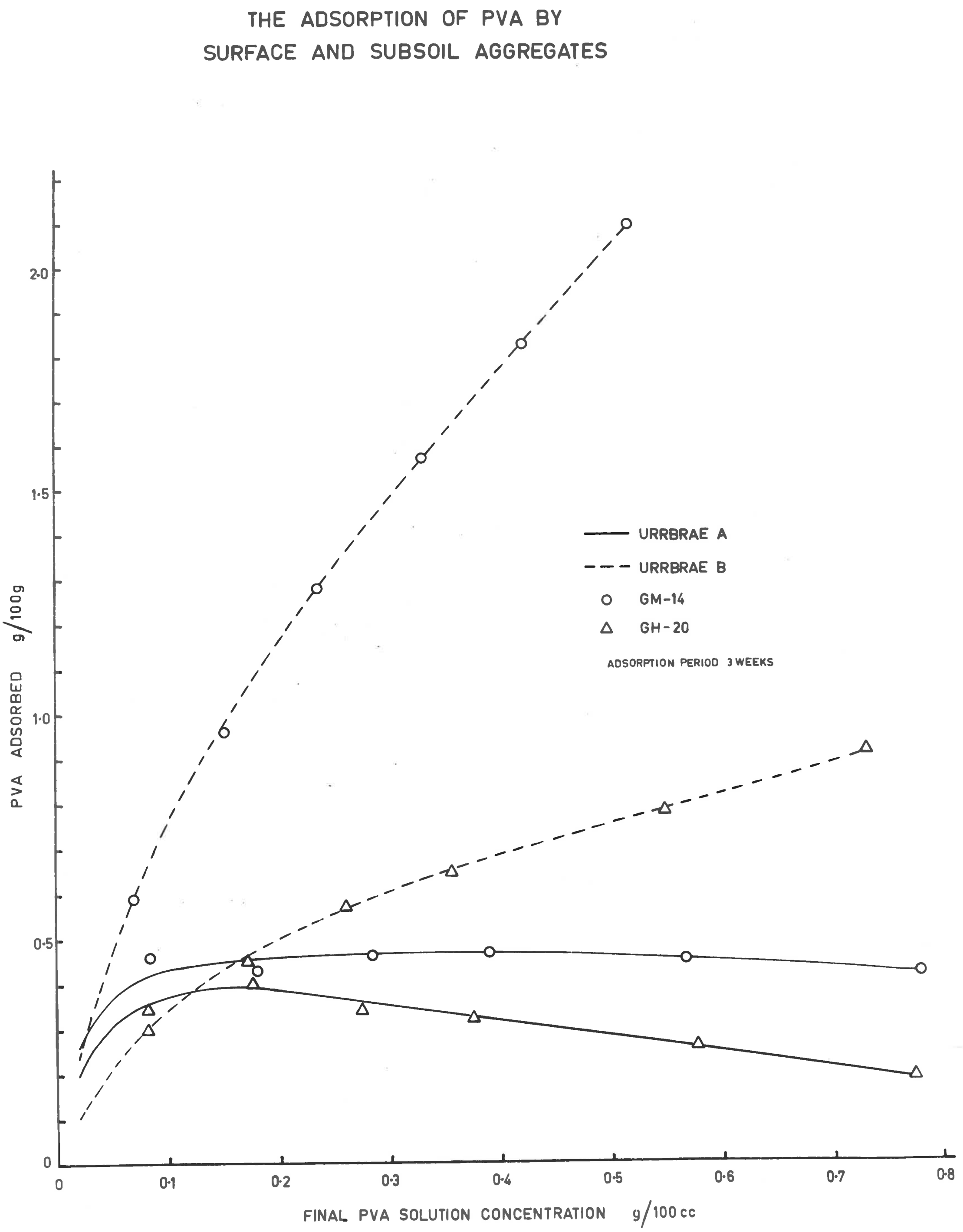

THE ADSORPTION OF PVA BY
SURFACE AND SUBSOIL AGGREGATES
PVA ADSORBED g/100g
2·0
1·5
1·0
0·5
0
0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
FINAL PVA SOLUTION CONCENTRATION g/100 cc
URRBRAE A
URRBRAE B
GM-14
GH-20
ADSORPTION PERIOD 3 WEEKS

Figure 5.

Urrbrae A aggregates. This would be expected to increase the accessibility of adsorption sites within Urrbrae A aggregates and so reduce the difference expected by consideration of total surface area alone.

The large difference observed is probably due to the presence of organic matter in the Urrbrae A sample. Organic matter can block adsorption sites and also prevent the adsorption of other organic species by hindering penetration of the introduced polymer throughout the aggregates. In fact, organic matter has been shown to prevent to a considerable degree the adsorption of such relatively small molecules as cetyl pyridinium bromide on Urrbrae A (Burford, Deshpande, Greenland & Quirk, 1964). Such an explanation would also account for the observation that there is little difference in the maximum amount of GM-14 and GH-20 adsorbed on Urrbrae A, whereas there are marked differences in the amounts adsorbed by the aggregates of Urrbrae B.

The decrease in the amount of GH-20 adsorbed by Urrbrae A at solution concentrations greater than 0.19 g/100 cc may be due to greater intermolecular interaction between the high molecular weight polymer molecules as the solution concentration is increased.

3.2. Interpretation of adsorption results in terms of the Diffusion of PVA into soil aggregates

In the foregoing experiments a number of factors affecting the adsorption of PVA by soil aggregates have been investigated. It has been shown that the size of the soil aggregates, the concentration of the polymer solution, and the molecular weight and configuration of the polymer molecules in solution have a marked effect on the adsorption of PVA by soil aggregates. The experimental data, considered in relation to adsorption by dispersed materials, enables inferences to be drawn about the movement of PVA into soil aggregates.

The rate controlling steps for ion diffusion into porous media are usually termed "film diffusion" and "particle diffusion" (Helfferich, 1962). They arise from the observation that a thin film of liquid adheres to the adsorbent bead surface and that under some circumstances the diffusion of ions through this film may control the overall rate of ion uptake by the exchange resin. Where this occurs the process is termed "film diffusion control" whereas if the diffusion of ions through the porous beads is much slower than through the adhering film then it is regarded as "particle diffusion control".

Helfferich considers that the best technique for distinguishing between particle and film diffusion control is the "interruption test". In this the adsorbent particles are removed from the solution for a short period of time and then re-immersed. The interruption allows any concentration gradients within the adsorbent to even out. Thus with particle diffusion control the rate immediately after re-immersion is greater than just before the interruption whereas the rate with film diffusion is unaffected because no concentration gradients exist within the adsorbent.

For the PVA - soil aggregate system used here this test was applied by interrupting the adsorption of GM-14 from a 1.097% solution after a period of one week. Two adsorption tubes were disturbed by carefully inverting them so that the aggregates were free from the bulk solution for a period of twenty minutes. The tubes were then returned to their normal position and the adsorptions were continued for a further one and two weeks. The amounts adsorbed compared with similar undisturbed samples are shown in Table 4 below. The values shown are for a single unreplicated determination.

Table 4

Interruption Test For PVA Adsorption

Adsorption time (weeks)	GM-14 adsorbed mg/g	
	Undisturbed	Disturbed
1	16.4	
2	20.3	22.4
3	24.2	25.5

Thus the increased adsorption following the interruption would seem to indicate that particle diffusion control operates in this system.

However the experiments in which the adsorption of PVA increased with increases of solution concentration and with gentle agitation are usually indicative of film diffusion control as both of these factors can affect the concentration gradient across the adherent film of solution but have little or no effect on the interior of the aggregates. To obtain a better indication of which of the two processes was more dominant the results obtained in subsection 3.1.3 have been tested by using the quantitative expressions for particle and film diffusion processes.

If the data in Figure 1 are arranged as in Figure 6 (where <u>absolute</u> values of adsorption and time are eliminated) it can be seen that the two isotherms reduce to approximately the same relationship of A' : T' where

$$T' = \frac{t}{T} = \text{fractional time to reach equilibrium}$$

$$A' = \frac{\text{a (amount adsorbed at T')}}{\text{A (maximum adsorption)}}$$

$$= \text{fractional attainment of equilibrium}$$

There is some uncertainty in the values of T (time to reach equilibrium) as read from the isotherms because of the

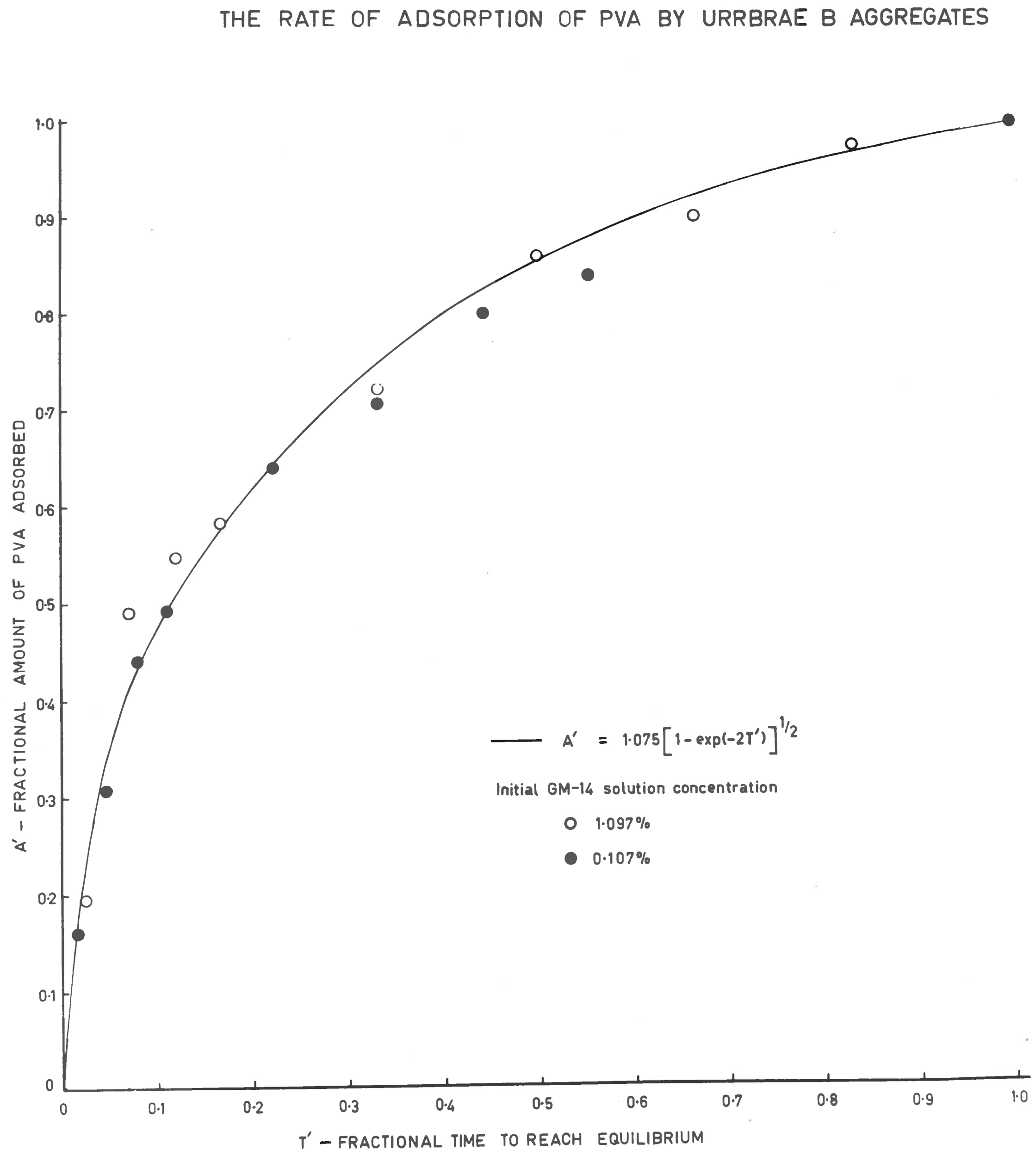

THE RATE OF ADSORPTION OF PVA BY URRBRAE B AGGREGATES
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0
A′ – FRACTIONAL AMOUNT OF PVA ADSORBED
0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9
1·0
T′ – FRACTIONAL TIME TO REACH EQUILIBRIUM
A′ = 1·075[1 - exp(-2T′)]^1/2
Initial GM-14 solution concentration
○ 1·097%
● 0·107%

Figure 6.

limited number of determinations made; so values of 6 weeks and 9 weeks were chosen. Varying these values by one week does not introduce any serious errors.

The following equation was found to describe the experimental results.

$$A' = \left[\frac{1 - \exp(-2T')}{1 - \exp(-2)}\right]^{\frac{1}{2}} \quad \ldots\ldots\ldots\ldots \quad (1)$$

$$= 1.075 \left[1 - \exp(-2T')\right]^{\frac{1}{2}} \quad \ldots\ldots\ldots\ldots \quad (2)$$

This is similar to Vermeulen's (1953) approximation for the law of the rate of ion exchange with porous bead exchange resins where particle diffusion is rate controlling, viz.

$$U_t = \left[1 - \exp\left(-\frac{D\pi t}{r^2}\right)\right]^{\frac{1}{2}} \quad \ldots\ldots\ldots\ldots\ldots \quad (3)$$

where U_t = the fractional attainment of equilibrium at time t,

D = diffusion coefficient,

r = radius of ion exchange beads

From equation (2) a value for the diffusion coefficient of PVA in the soil aggregates may be obtained. This value is of the order of 10^{-10} cm^2/sec, its exact value depending on the value used for T.

Hosono & Sakurada (1952) have shown that a PVA with similar properties to the GM-14 fraction used in these experiments had a self diffusion coefficient in aqueous solution of approximately $10^{-5} cm^2/sec$. The value obtained here should be regarded as an "apparent diffusion coefficient" rather than a true diffusion coefficient as the PVA molecules are, for all practical purposes, irreversibly adsorbed as they diffuse into the aggregates. Once adsorbed they would restrict the movement of incoming molecules, especially in the smaller pores.

It appears then that particle diffusion control dominates the movement of PVA into soil aggregates although there is an indication that film diffusion control operates to some extent. This latter is readily understood when it is considered that PVA molecules adsorbed on the external surface of the aggregates would tend to block the entrances of pores and so add to the restrictive factor of an adhering of film of solution at the surface.

3.3. Adsorption by Soil Cores

The results of the experiments on the adsorption of PVA by soil cores placed with one end in contact with the PVA solution are shown in Figure 7. The amount of PVA in the core after 1 week is plotted from the plane of contact with the polymer solution.

The penetration of GM-14 into an air dry core diminished rapidly with distance from the wetting front until at

THE PENETRATION OF PVA INTO URRBRAE B CORES

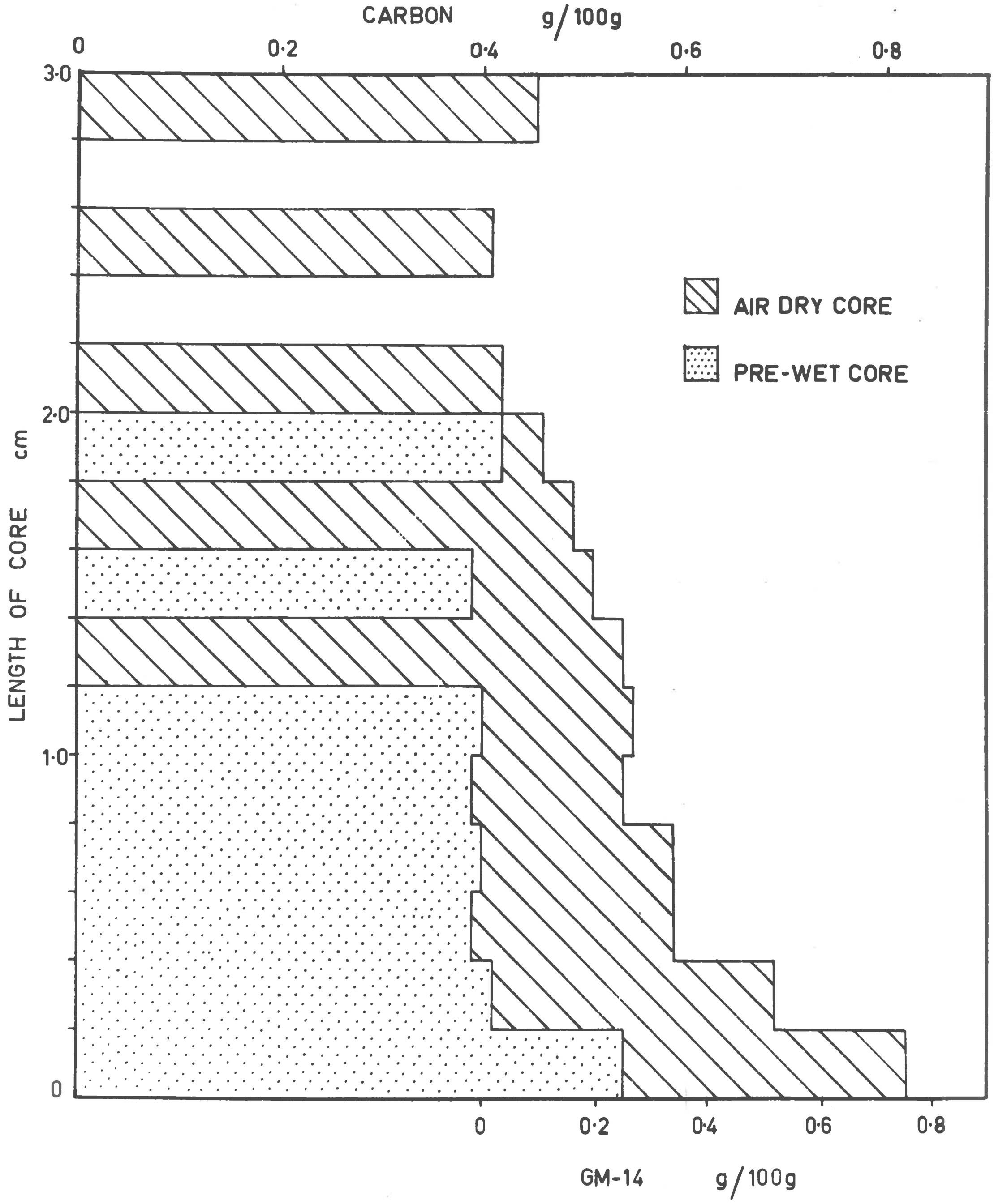


Figure 7.

a distance of 2 cm virtually no PVA could be detected. The penetration of PVA into a core previously saturated with water was restricted to the first 2 mm of soil.

This experiment demonstrates two extreme conditions for the movement of PVA molecules into soil. In the first case PVA solution moved by diffusion and by mass flow caused by the capillary suction exerted by the drained soil pores. It can be seen that as the PVA solution advanced into the core the concentration of the polymer was reduced by adsorption, so giving rise to the decreasing carbon contents shown in Figure 8.

In the second case the movement of PVA was restricted to diffusion processes alone as the soil had been previously saturated with water. As with previously described experiments on the diffusion of PVA into (½–1) mm aggregates, the diffusion process was shown to be very slow. The amount adsorbed in 7 days by diffusion alone was only 8% of that adsorbed by diffusion and capillary suction combined. Also it can be seen that PVA was detected only in the first 2 mm of the core. This suggests that there is little differential movement of PVA through the largest soil pores, although this could be due to,

(1) the difficulty of detecting very small quantities of PVA in soil

(2) the lack of pores large enough to allow the free move-

ment of PVA throughout the length of the soil core.

This experiment clarifies some aspects of the work of Williams (1959) in which Urrbrae A aggregates of approximately 1 cm^3 were treated in a similar fashion with PVA from a sintered funnel. It was observed that dry aggregates when wet from one face with a PVA solution were not stabilised throughout their whole depth. It was found necessary after the first treatment to dry the aggregates and then to wet them again with PVA solution from the opposite side. In this way it was assumed that an even distribution of PVA throughout the aggregates was achieved. However it now appears likely that although the external surfaces of the aggregates contained approximately the same amounts of PVA the centre of the aggregates could have contained a somewhat lower amount. This uneven distribution of PVA apparently had no effect on the stability of the aggregates as determined by their rate of wetting, breakdown during end-over-end shaking in water and cohesive strength measurements, as differences in treatments were clearly demonstrated. It is likely however that the differences would have been greater if the PVA had been distributed evenly throughout the aggregates.

The method of carbon analysis described above could well be used more extensively to examine the distribution of organic materials added to soils. It should also prove useful in following the profile distribution and seasonal variations of organic matter added to soils by growing plants, as relatively small samples are required. The cores are obtained easily and triplicate samples can be analysed from each 2 mm slice if required.

It is apparent that the degree of saturation of a soil with water, prior to adding PVA, can have a large effect on the subsequent movement and distribution of the polymer. This has important practical implications both in the field and in the laboratory, since (as will be shown subsequently) the distribution of the polymer within soil aggregates can largely determine the magnitude and persistence of the stabilising effect.

The information obtained from the study of PVA adsorption by soil aggregates and cores has been used in the preparation of samples for subsequent investigations of the effects of PVA on the stability of aggregates. In most cases aggregates of ($\frac{1}{2}$-1) mm size have been immersed in polymer solutions for periods of three weeks to ensure an even distribution of PVA throughout the aggregates. Where the $< 2\ \mu$ clay fraction or puddled soil was used attention has been paid to the conditions of adsorption and the manner in which the treated samples were prepared. In this way it has been possible to define the soil-system used more precisely than in earlier experiments and so a better appreciation of the results of the tests applied has been obtained.

CHAPTER III

THE WATER-STABILITY OF SOIL AGGREGATES

1. Introduction

The stability of an aggregate of soil may be defined as the resistance to changes in particle arrangement. Water-stability tests are concerned with the breakdown of aggregates in the presence of a large excess of water. A twofold problem arises from the definition viz.

(1) determining the nature of the soil particle arrangement

(2) determining the permanence, or resistance, of that arrangement to applied forces.

Many investigations of the latter are empirical, in that little regard has been paid to defining the system to which the tests are applied. It is partly for this reason that such a large number of stability tests have been devised.

Water-stability tests fall roughly into two classes viz. particle size distribution and pore size distribution measurements. Particle size distributions or aggregate analyses are further subdivided into determinations of macro-aggregates ($> 50\ \mu$ diameter) and micro-aggregates ($< 50\ \mu$ diameter). There does not appear to be any clearly defined reason for this particular division although Russell (1938) considers that it arose from the observations of a number of workers (Baver & Rhoades, 1932; Pavlov, 1932; Tiulin, 1936) that mechanical and aggregate analysis curves cross over at approximately the 50 μ level. It may also be that 50 μ represents the upper level for which hydrometer and pipette methods can conveniently be used.

By far the most variable feature of all the methods for determining macro- and micro-aggregation is the amount of work applied to the aggregates. Yoder (1936) specified the amount of soil, the size of sieves used and the amplitude, rate and time of vibration used, so as to obtain comparable results for macro-aggregation determinations by wet-sieving. Quirk (1950) after studying such variables as shaking cylinder characteristics, method of wetting, time of shaking and initial aggregate size, has also proposed a standard method for micro-aggregation determinations by end-over-end shaking. Even so the amount of work applied to aggregates is fairly arbitrary in that as long as uniform amounts of work are used in any one experiment, the results between treatments remain comparable. Other variations of particle distribution techniques include

(1) Freezing and Thawing or Wetting and Drying cycles

Sillanpan & Webber (1961) combine these cycles with wet sieve analysis.

(2) Dry sieving. Chepil (1962) claims that dry sieving detects smaller physical differences than the wet method.

(3) <u>Turbidimetric Technique</u>. Davidson & Evans (1960) measured the breakdown of aggregates after shaking in water-glycerol mixtures by determining the turbidity of the suspension.

The pore structure methods have been developed to a greater degree since the work of Bradfield & Jamieson (1938) and Leamer & Lutz (1940), who noted that pore size distribution curves of soils frequently showed that a large proportion of the soil pores occurred within a small range of pore radii e.g. a medium sand was found to have a large proportion of pores with diameters of 100-200 μ diameter while for a silt soil the pores were mainly of 10-20 μ diameter.

Childs (1940, 1942) using beds of aggregates, followed the changes in the size and distribution of the inter-aggregate spaces when disintegrating forces, such as flood wetting, were applied to the soil. The less stable aggregates were disrupted and blocked many of the inter-aggregate spaces and this resulted in changes in the original pore size distribution of the bed. From this an index of aggregate stability was obtained.

Using the same principle of porosity change, Dettman & Emerson (1959) used the method of cationic dilution to disperse a bed of soil aggregates and obtained a stability index by determining the change in permeability of the sample. This method has been shown to be very sensitive and has been modified by Williams, Lindstrom, Greenland & Quirk (1964) to demonstrate the importance of polysaccharide-polyuronide type compounds in stabilising natural soil aggregates.

Numerous variations and combinations of all of these methods have been devised and although the wet sieving methods are used most commonly they do not have the sensitivity and are not as readily amenable to theoretical analysis as are the pore size distribution - permeability techniques.

2. Experimental

2.1. Materials

The Urrbrae B aggregates of ($\frac{1}{2}$-1) mm size described earlier and the PVA's of varying molecular weights and degrees of hydrolysis, were used to determine the effect of PVA on the water stability of soil aggregates.

2.2. Methods

It was desirable to use a method that required only small samples of aggregates so that aggregates from the adsorption studies could be used for water-stability measurements. An attempt was made to adapt various methods for determining changes in the pore structure of aggregates or the particle size distribution of disrupted aggregates, to examine the stability of small samples (1g) of aggregates.

These included the rate of water uptake (Quirk & Panabokke, 1962), an oscillating permeameter (Childs & Poulovassilis, 1960), hydrometer (Bouyoucos, 1927), hydrocyclone and ultrasonic dispersion. None of these methods could be readily adapted for use with such small samples. However the determination of the turbidity of a dispersed soil suspension (Davidson & Evans, 1960) proved to be satisfactory and a variation of their method was used in the following experiments.

The turbidity of a clay suspension, as determined with a Hilger Biochemical Adsorptiometer, was found to obey the theory of light scattering by inhomogenous solutions, as described by West (1949), so it was possible to use the relation -

$$\log \frac{T\ (\text{clay suspension})}{T\ (\text{water})} = K.C. \ldots\ldots \quad (1)$$

where T = percentage light transmission

C = concentration of clay suspension

K = a constant

The derivation of this relation is discussed in Appendix I.1. The calibration and use of the variable aperture of the Hilger Adsorptiometer is discussed in Appendix I.2.

In the method employed, 0.25 g samples of air-dry aggregates were poured into 3" x 1" clear, polystyrene tubes containing 20 cc water. The tubes were placed on an end-over-end shaker (13.4 rpm) for the required time - usually 2 hours. The suspensions were allowed to stand for 2 hours and 18 minutes until all particles of diameter greater than 2 μ e.s.d. had settled below the depth of the light beam (3 cm). The percentage light transmission was then determined at three apertures, using a No. 70 red filter to gain maximum transmission. The determinations were carried out in triplicate and the results averaged.

Where the rate of aggregate breakdown was followed, the tubes were shaken for further periods of time and the concentration of less than 2 μ particles in suspension determined as above.

In some instances the amount of material greater than 0.25 mm remaining in the tubes after 10 hours end-over-end shaking was determined. This was done by bulking the triplicate samples and gently washing them on a 0.25 mm sieve, before drying at 70°C and weighing.

An investigation was also made to determine if the manner in which PVA was adsorbed on to the aggregates produced any difference in the subsequent water-stability determinations. The adsorption methods used were -

(1) 0.50 to 1.0% GL-05 solutions for periods of ½ to 7 days

(2) 0.05 to 0.30% GL-05 solutions for a period of 21 days.

These treatments resulted in two sets of aggregates containing similar ranges of adsorbed PVA.

It should be noted that following the adsorption treatment all the aggregates were washed free of excess PVA solution and thoroughly dried over P_2O_5 before storing in an air-dry state. The severe drying was used to ensure that all of the adsorbed PVA was collapsed onto the soil surfaces and to remove any doubt as to the state of the adsorbed PVA that may have arisen with varying degrees of des~~s~~iccation.

Panabokke & Quirk (1957) have shown that the initial soil water energy status of aggregates at the time of immersion in water can have a marked influence on the values obtained for macro-aggregation by wet-sieving. However they did not observe the same degree of variability with determinations of micro-aggregation (< 0.05 mm). Thus in this work it was not considered necessary to prewet the aggregates to overcome changes in water content that may have arisen with the varying relative humidity values experienced in the laboratory.

3. Results and Discussion

3.1. Water-Stable Aggregation

3.1.1 Comparison of different PVA's

The relative water-stabilities of Urrbrae B (½-1) mm aggregates containing different amounts of GL-05, GM-14, GH-20, NL-05 and NM-14 are shown in Figures 8a & 8b. In

THE WATER STABILITY OF URRBRAE B AGGREGATES CONTAINING PVA

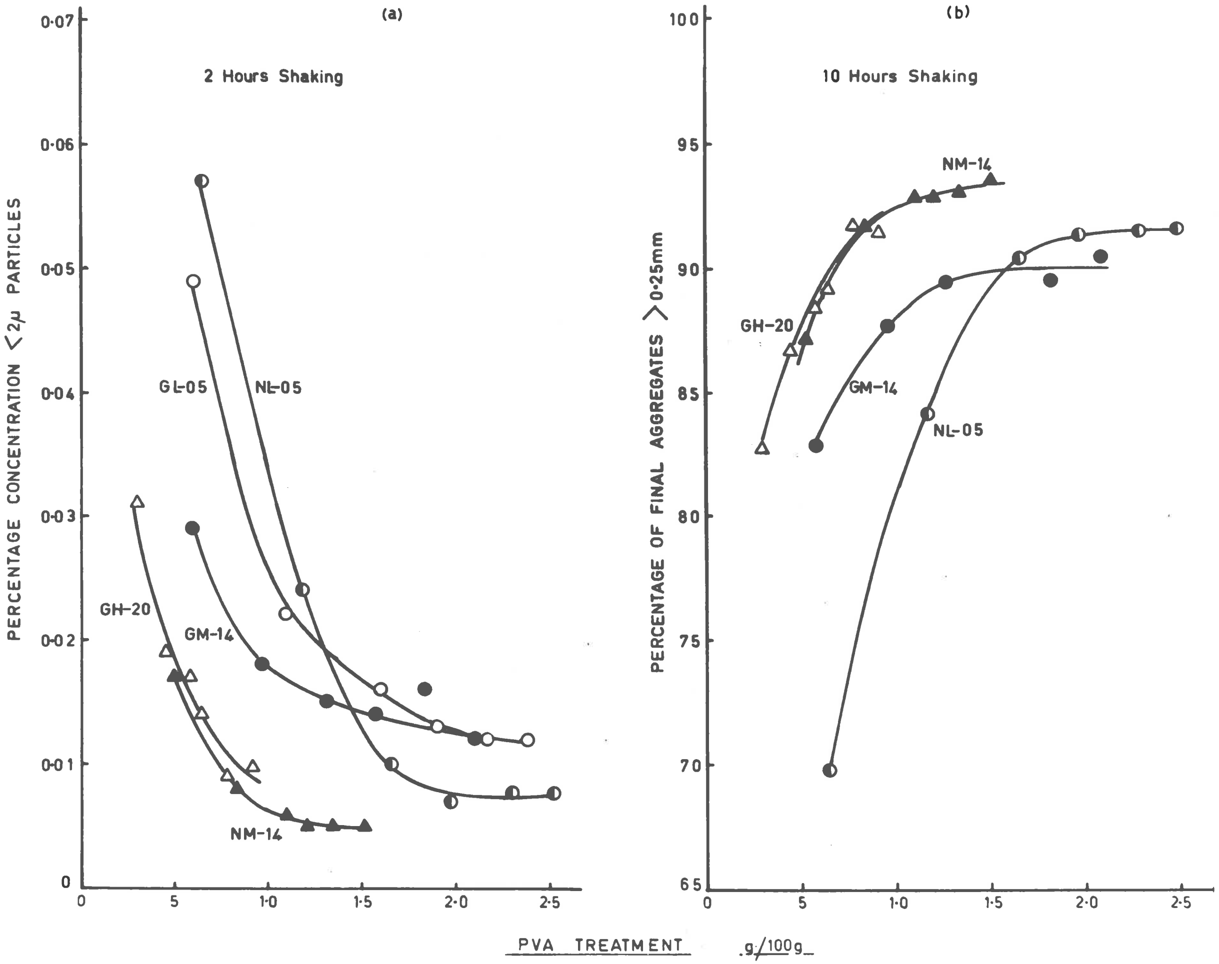


Figure 8.

Figure 8a the degree of aggregate breakdown is shown in terms of the percentage concentration of 2 μ particles in suspension after 2 hours end-over-end shaking. In Figure 8b the percentage of particles (by weight) greater than 0.25 mm, remaining after 10 hours end-over-end shaking, are shown.

It may be seen from these results that

(a) All of the PVA fractions reach a maximum level of effectiveness in reducing the breakdown of aggregates. That is, above a certain level of adsorbed polymer there is little or no further reduction in the breakdown of aggregates by this treatment.

(b) GH-20 is more effective in reducing the breakdown of aggregates than are equal amounts of adsorbed GL-05 and GM-14.

(c) GM-14 is more effective than GL-05 with small amounts of adsorbed polymer, but they approach the same value at a level of about 2.0 g/100 g. A similar situation occurs with the NL-05 and NM-14 treatments.

(d) NM-14 is more effective than GM-14 at all levels, while NL-05 is less effective than GL-05 up to a level of 1.3 g polymer/100 g soil, after which it is more effective.

(e) NM-14 and GH-20 have very similar effects and reach a maximum at a treatment level of approximately

1.2 g/100 g compared with 2.0 g/100 g for the other three polymers.

(f) NL-05, NM-14 and GH-20, at their maximum level of effectiveness, reduce the amount of breakdown somewhat more than GL-05 and GM-14.

(g) There is little breakdown of the (½-1) mm aggregates to particles of less than 0.25 mm after a long period of end-over-end shaking, except with the smallest amounts of polymer adsorbed.

The failure to form particles of less than 0.25 mm diameter indicates that the breakdown of PVA treated aggregates is essentially an abrasive action i.e. the surface of the aggregates is worn away and the aggregates do not subdivide into successively smaller fragments. Some subdivisions of aggregates does occur, particularly with small amounts of adsorbed polymer, but to describe this would require the determination of a complete particle size distributions which for samples of this size is not practical.

The results of Figure 8a may be converted to absolute amounts as a 0.100% suspension represents 20 mg of less than 2 µ particles as compared with 150 mg of less than 2 µ particles in the original (½-1) mm aggregates being tested.

The effects of the different polymers on aggregate stability can be explained in terms of the size of the adsorbed molecules and also on the interaction between the molecules themselves.

It is considered that stable aggregates are formed by the attachment of individual polymer molecules to several soil particles and that the degree of stability increases with the extent of cross linking (Ruehrwein & Ward, 1952; Michaels & Morelos, 1955). Thus the present work in which it is shown that a maximum stability is attained with amounts of polymer less than the highest amounts adsorbed indicates that at higher polymer levels some molecules do not form effective bridges between adjacent soil particles. The apparent ineffectiveness of these "excess" polymer molecules could be due to either or both of the following situations -

(1) The "excess" molecules may have only a few points of contact with the soil particle surfaces, in between molecules already collapsed on the surface.

(2) It may be necessary to have only a certain number of polymer bonds, located at critical points of weakness within an aggregate, to confer stability to the aggregate as a whole.

The second alternative is supported by the work of Williams (1959) in which strengthening pores of 15-50 μ radius in Urrbrae A aggregates increased the ability of the aggregates to withstand rapid wetting with water, more than strengthening either smaller or larger pores. It was thought that the 15-50 μ pores represented the major points of weakness for those particular aggregates and that strategic placement of the PVA strengthened the aggregates against the force of rapid entry of water.

There is a clear distinction between the effects of GL-05, GM-14 and GH-20 up to a level of about 1.6 g/100 g. GH-20 with a molecular weight of 100,000 is more effective than GL-05 (25,000), while GM-14 (70,000) is intermediate. The greater effectiveness of the largest polymer molecules is probably due to an increased number of soil-polymer linkages per unit of polymer - assuming of course that all of the polymers act at similar sites. It might well be expected that there is a limiting size of a polymer molecule above which it would be excluded from sites that are important in respect to the stability of an aggregate. The present results show that this limit would be in excess of a molecular weight of 100,000.

Above a level of 1.6 g of PVA per 100 g of soil, GL-05 and GM-14 have been found to have similar stabilising effects. The maximum degree of stability imparted by these polymers is somewhat less than that observed with the higher molecular weight fraction, GH-20. The reasons for this are somewhat obscure. If it were simply a matter of the largest molecules being able to form bridges between more widely separated soil particles then it would be expected that GM-14 would be more effective than GL-05 irrespective of the amount adsorbed. It may be that the smaller molecules have an increased stabilising effect due to their ability to penetrate into pores from which the larger molecules are excluded on grounds of their size. There would be less difference in this respect between the GM-14 and GH-20 polymers, than between the GL-05 and GM-14 polymers. Added support for this argument is obtained from the similarity between the maximum level of stability of the NL-05 and NM-14 polymers which also have a similar size difference to GL-05 and GM-14.

The NL-05 and NM-14 polymers produce a greater level of stability than the corresponding GL-05 and GM-14 fractions. The reason for this is thought to be due to the higher intermolecular forces acting between the fully hydrolysed polymers so that as well as imparting stability by bridging soil particles they probably form stronger bridges. This reasoning can also be used to explain the similarity between the results for NM-14 (64,000) and GH-20 (100,000).

In comparing GL-05 (25,000) and NL-05 (22,000) a mixture of the effects due to molecular weight and intermolecular bonding occurs. At low levels of adsorption, the lower molecular weight polymer is less effective. As more molecules are packed on to the surfaces, so the intermolecular bonds have an added effect and the NL-05 becomes the more effective stabiliser.

3.1.2 The effect of conditions in which PVA is adsorbed on water-stability

The conditions used to introduce PVA into soil aggregates have a marked effect on the resultant water-stability of the aggregates. In Figure 9 the water-stabilities of GL-05 treated aggregates prepared using different periods of adsorption are compared. When the polymer was adsorbed over 21 days from solutions of lower concentration, as compared with ½-7 days and higher concentrations, there was a considerable increase in water stability.

It is to be expected that when PVA is adsorbed slowly from a dilute solution it will be distributed more evenly throughout the aggregate and so results in a higher water-stability of the aggregates. This will be discussed in more detail in Chapter VII when other evidence on the location of adsorbed polymer is presented.

3.2 The Rate Of Breakdown Of Soil Aggregates Due To Shaking In Water

In the previous Chapter it was shown that the movement of PVA into soil aggregates was likely to be small and an uneven distribution of PVA throughout the aggregates might be expected, with polymer concentrated near the surface. Thus the rate of breakdown of aggregates treated

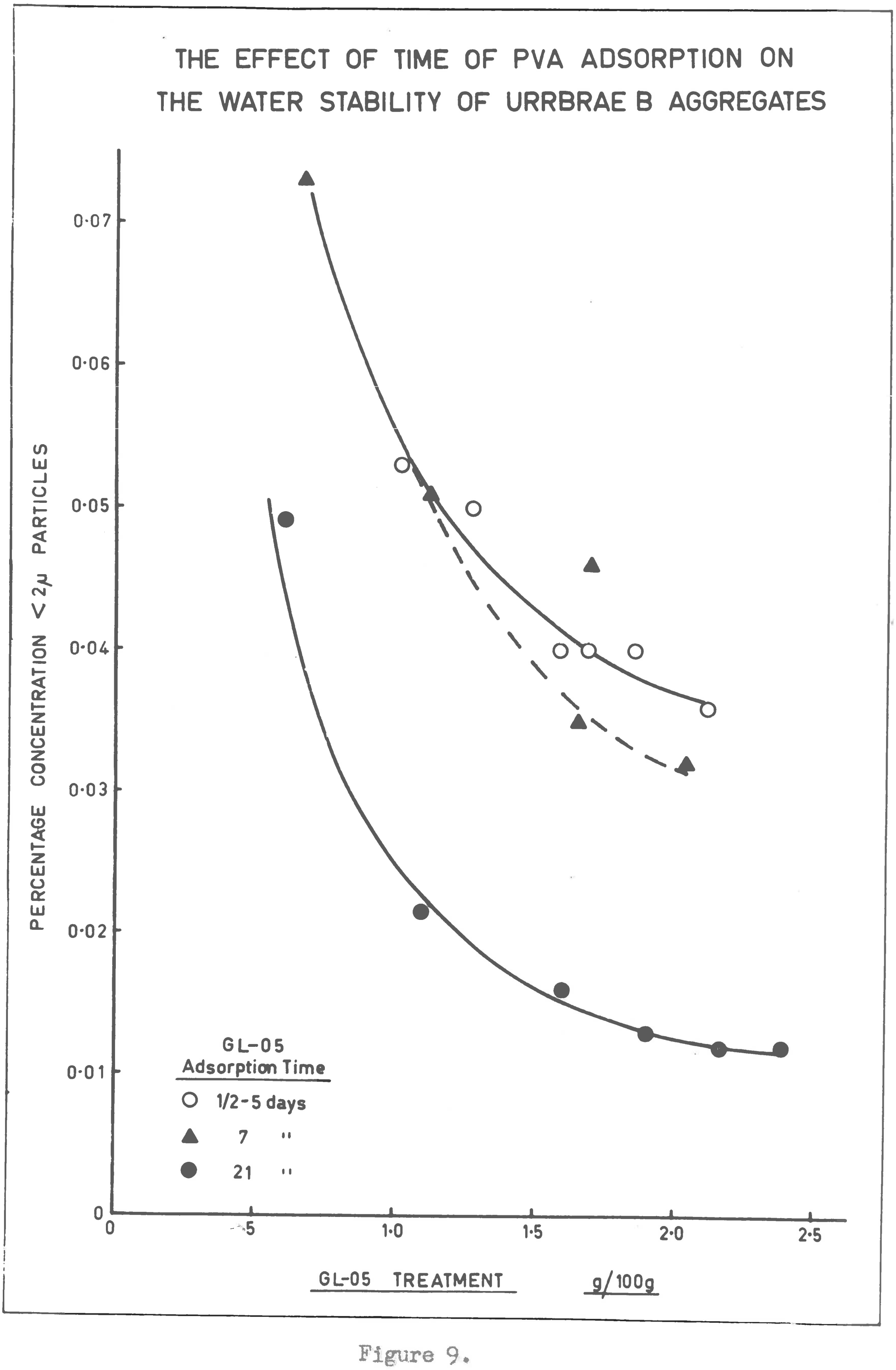

THE EFFECT OF TIME OF PVA ADSORPTION ON THE WATER STABILITY OF URRBRAE B AGGREGATES
PERCENTAGE CONCENTRATION < 2μ PARTICLES
0·07
0·06
0·05
0·04
0·03
0·02
0·01
0
0
·5
1·0
1·5
2·0
2·5
GL-05 TREATMENT g/100g
GL-05
Adsorption Time
○ 1/2-5 days
▲ 7 "
● 21 "

Figure 9.

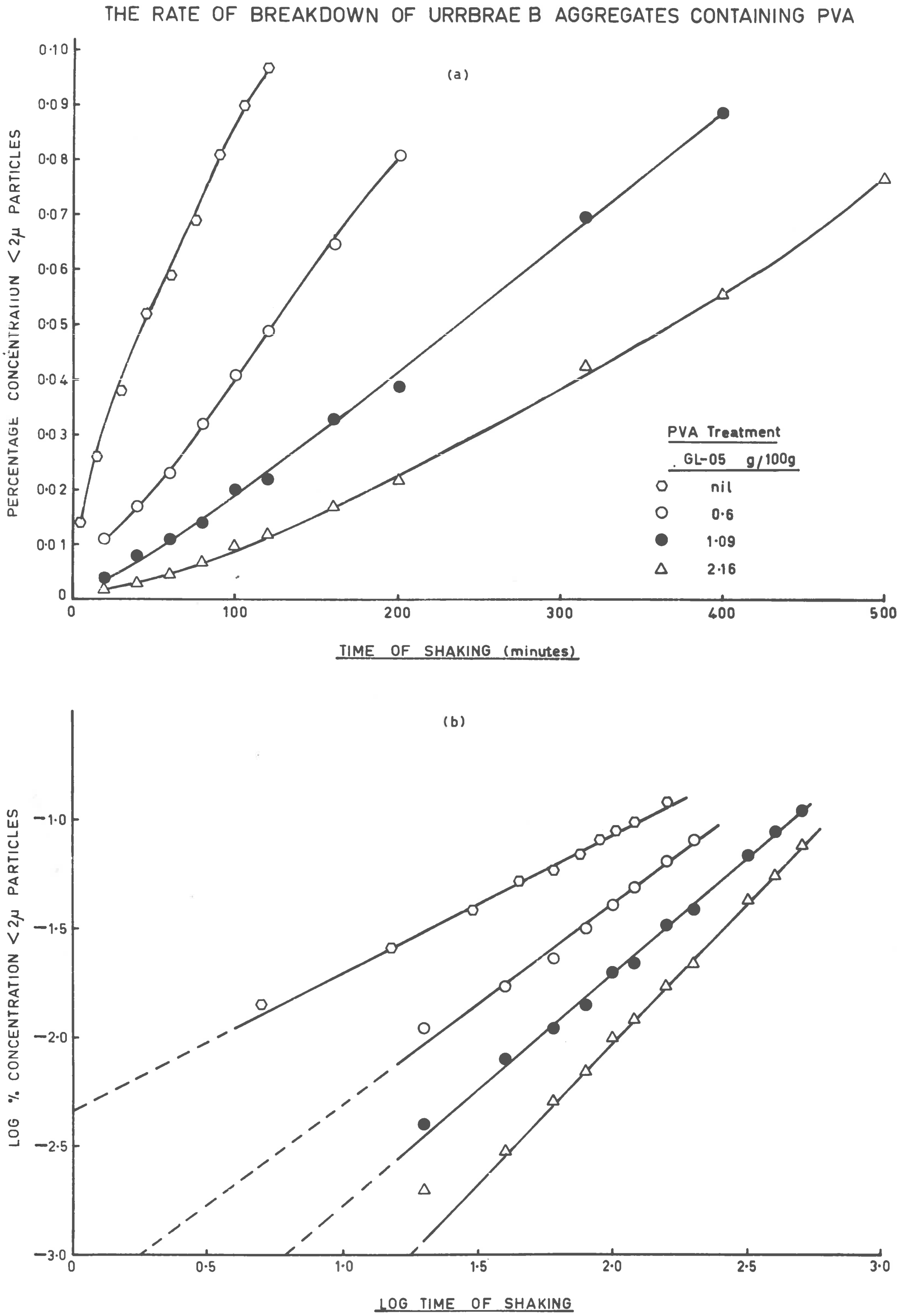

THE RATE OF BREAKDOWN OF URRBRAE B AGGREGATES CONTAINING PVA
(a)
PERCENTAGE CONCENTRATION <2μ PARTICLES
0·10
0·09
0·08
0·07
0·06
0·05
0·04
0·03
0·02
0·01
0
0
100
200
300
400
500
TIME OF SHAKING (minutes)
PVA Treatment
GL-05 g/100g
nil
0·6
1·09
2·16
(b)
LOG % CONCENTRATION <2μ PARTICLES
−1·0
−1·5
−2·0
−2·5
−3·0
0
0·5
1·0
1·5
2·0
2·5
3·0
LOG TIME OF SHAKING

Figure 10.

with different amounts of PVA was followed for periods of up to 10 hours end-over-end shaking. If only an outer shell of the aggregates were stabilised it might be expected that with continued shaking this could be worn away and then the rate of breakdown should increase to a value similar to that of untreated aggregates. With shaking periods of up to 10 hours this hypothesis was not confirmed but other information relating to the structure of soil aggregates and the location of adsorbed PVA was obtained and is reported in the remainder of this section.

In Figure 10a it can be seen that for aggregates treated with GL-05 a curvilinear relation exists between the amount of aggregate breakdown and the time of shaking. The rate of breakdown is considerably reduced as the amount of adsorbed PVA is increased. Similar results were obtained for aggregates treated with the GM-14, GH-20, NL-05 and NM-14 polymers.

Other experiments of this nature have been reported in the literature and various parameters have been used to express aggregate breakdown in water as a function of the time for which work was applied.

Puri & Keen (1925) using end-over-end shaking for up to 100 hours obtained the relation

$$d = a + m \log t \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where t = time

d = dispersion factor

= weight of particles/100 cc in the top 8.5 cm of the cylinder after 24 hours settling, expressed as a percentage of the initial soil concentration.

Woodruff (1939) using complete aggregate analysis by wet sieving for periods of 2 hours, obtained -

$\log P = \log A - n \log t$ .... (2)

where P = state of aggregation

= the difference in areas between the dispersion and aggregation curves expressed as a percentage of the area below the dispersion curve.

Russell & Feng (1947) using wet sieving for periods of 64 minutes obtained -

$\log W = \log a - b \log t$ .... (3)

where W = weight of soil retained on a 0.25 mm sieve.

Quirk (1950) using end-over-end shaking for up to 100 minutes, obtained -

$A = c - k \log t$ .... (4)

where A = 0.05 mm aggregation i.e. the percentage of particles less than 0.05 mm in aggregates greater than 0.05 mm.

Allison (1956) followed the natural degradation of VAMA treated soils over a number of years under field conditions. Using a wet-sieve analysis he obtained the relation -

$$\ln M = \ln a - \frac{1}{b} . t \text{ .... } (5)$$

where M = the geometric mean size of the sieved aggregates.

t = time in years after application of the conditioner to field plots.

Thus the dispersion parameters used have been particles of $< 0.01\ \mu$ (Puri & Keen), $50\ \mu$ (Quirk), 0.25 mm (Russell & Feng) and values involving total aggregate analyses (Woodruff, Allison). The time for which the effect of the degradative forces have been followed vary from minutes up to a number of years.

It will be noticed that Puri & Keen, and Quirk, used a relation of dispersion : log time, while Woodruff and Russell and Feng used log dispersion : log time. Allison obtained yet another linear relation using log dispersion : time. The positive and negative gradients obtained depend simply on the manner of expressing the dispersion parameter.

In the present work particles of $< 2\ \mu$ diameter were used to describe the breakdown of aggregates. In figure 10b the relation between the concentration of $< 2\ \mu$ particles and the time of end-over-end shaking for aggregates containing different amounts of GL-05 are shown on a log : log scale. It is seen that the relation may be expressed in the form -

$$\log c \quad = \quad \log a + b \log t \ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

where c = percentage concentration of $< 2\ \mu$ particules in suspension.

t = time in minutes

a & b = constants

Similarly, graphs for the remaining treatments show the same relation. There is some tendency for values at less than 60 minutes shaking to deviate from the straight line, the variation being irregular in direction and magnitude. Thus the 'best fit' straight lines were computed by a simple regression using values of 100 minutes shaking and greater. In most cases the number of observations used for calculating the straight lines was 8 - 11 per polymer treatment. All of the triplicate values were used individually in the calculations. The computed values of the Y-intercept (at log t = 0) and the slope, i.e. 'a' and 'b' values, are shown in Table 5. A very high correlation coefficient between log concentration and log time was found - all but one value being greater than 0.99.

Previous workers have referred to these constants as indicating the 'initial state of aggregation' (Y-intercept) and 'the rate of breakdown' (slope). The initial state of aggregation is obtained by extrapolating the graphs to short time intervals and the values obtained represent the amount of aggregate breakdown upon immersion in water or with short periods of agitation. The 'rate of breakdown' is strictly the differential (dc/dt) of the curvilinear relation shown in Figure 10a, at a particular time, rather than the slope of the straight line relations (d log c/d log t) in Figure 10b.

Table 5

Regression Constants of Water Stability Data

PVA	Amount adsorbed g/100 g	Intercept Initial aggregation	Slope	Rate of breakdown $(dc/dt)10^4$	S.E. of slope	Correlation Coefficient (R)
GL-05	0.6	-3.3629	0.9875	4.042	0.1080	0.9451
	1.09	-3.9707	1.6209	2.127	0.0217	0.9964
	1.60	-4.2512	1.8395	1.665	0.0277	0.9949
	1.90	-4.4427	1.9968	1.337	0.0232	0.9966
	2.16	-4.6467	2.1928	1.213	0.0310	0.9947
	2.38	-4.4981	2.0302	1.309	0.0262	0.9959
GM-14	0.59	-3.8689	1.1146	2.557	0.0241	0.9949
	0.96	-4.3183	1.2276	1.683	0.0258	0.9938
	1.28	-4.4234	1.2299	1.338	0.0283	0.9918
	1.57	-4.3557	1.2025	1.348	0.0156	0.9974
	1.83	-4.2289	1.1612	1.440	0.0147	0.9975
	2.10	-4.5408	1.2468	1.119	0.0254	0.9936
GH-20	0.30	-3.8936	1.1301	2.628	0.0358	0.9920
	0.45	-4.1874	1.1552	1.553	0.0796	0.9395
	0.58	-4.2345	1.1657	1.457	0.0190	0.9959
	0.64	-4.5051	1.2570	1.283	0.0180	0.9968
	0.78	-4.9554	1.3711	0.839	0.0276	0.9937
	0.92	-4.9161	1.3575	0.855	0.0325	0.9912
NL-05	0.65	-3.0170	0.8452	3.985	0.0195	0.9957
	1.17	-3.8418	1.0659	2.078	0.0140	0.9975
	1.66	-4.7200	1.3018	0.996	0.0157	0.9957
	1.98	-5.1152	1.4190	0.750	0.0259	0.9948
	2.30	-4.7960	1.2870	0.772	0.0220	0.9955
	2.50	-4.7683	1.2781	0.784	0.0270	0.9931
NM-14	0.51	-4.3102	1.2123	1.577	0.0187	0.9963
	0.84	-5.0557	1.3906	0.739	0.0285	0.9935
	1.11	-5.0320	1.3510	0.632	0.0351	0.9896
	1.21	-5.2003	1.3927	0.536	0.0372	0.9891
	1.34	-5.1964	1.4062	0.583	0.0247	0.9952
	1.51	-5.1483	1.3781	0.559	0.0268	0.9941
N11		-2.3314	0.6299	5.342	0.0096	0.9971

Intercept value at log t = 0

It has been noted above that the relation between the concentration of $< 2\ \mu$ particles (c) appearing in suspension with the time of end-over-end shaking (t) is of the form -

$$c = at^b \quad \text{.....................} \quad (7)$$

differentiating c with respect to t,

$$dc/dt = abt^{b-1} \quad \text{............} \quad (8)$$

or $$dc/dt = b \cdot c/t \quad \text{.............} \quad (9)$$

The rate of breakdown depends on both the time of shaking and the concentration of particles in suspension. Thus to compare the rates of breakdown of aggregates containing different amounts of adsorbed PVA it is necessary to choose either a particular time of shaking or a particular concentration of $< 2\ \mu$ particles, at which to make the comparison. As the computed constants for the relation $c = at^b$ were obtained with shaking periods of greater than 100 minutes, the rates of breakdown of aggregates containing PVA were calculated by substituting t = 100 minutes in equation (8) and using the values for 'log a' and 'b' (slope) shown in Table 5.

The values for the 'rate of breakdown', so calculated, are also included in Table 5.

Before discussing the results in Table 5 in detail it is desirable to know if the values of dc/dt calculated from the relation $c = at^b$ for 100 minutes shaking present the same picture of aggregate stability as do values of dc/dt for shorter time intervals. The latter can be obtained by differentiating geometrically the curvilinear relationships between concentration and time of shaking.

The geometrical differentiation of the graphs describing the breakdown of aggregates containing GL-05 was carried out at points corresponding with 60 and 100 minutes end-over-end shaking, by constructing normals to the curves at these points with the aid of a mirror. There were not sufficient experimental points to differentiate acurately the curves at shorter time intervals. The geometrical and calculated values of dc/dt can best be compared by expressing the values for the aggregates containing PVA as a ratio of the values for the untreated aggregates. The comparison is made in Table 6 below.

Table 6

The Relative Rates of Breakdown of Urrbrae B Aggregates

PV adsorbed g GL-05/100 g	Relative dc/dt at shaking times of		
	60 min. *	100 min. *	100 min. **
0	1.00	1.00	1.00
0.60	0.91	0.81	0.76
1.09	0.39	0.39	0.40
1.60	0.31	0.32	0.31
1.90	0.24	0.24	0.25
2.16	0.25	0.24	0.23
2.38	0.25	0.25	0.25

* obtained by geometrical differentiation

** calculated from the relation $c = at^b$

It can be seen that except for the aggregates containing the least amount of PVA, there is a very good agreement between the calculated values of dc/dt and those obtained geometrically. Thus the calculated values can be taken as a true representation of the relative rates of breakdown of aggregates for both long and short periods of shaking, even though these values are obtained only with the data for periods of greater than 100 minutes shaking.

From Table 5 it can be seen that the values of 'initial aggregation' and 'rate of breakdown' vary for the different PVA's and also with different amounts of any one polymer. These parameters of aggregate stability are shown as functions of the amount and type of PVA adsorbed in Figures 11(a) and (b). The points of immediate interest are -

(1) With increased amounts of adsorbed PVA the values of 'log a' and dc/dt decrease to a minimum value which remains relatively unchanged as the amount of polymer adsorbed increases. There is some tendency for the 'log a' values to attain a minimum value and then to increase slightly, particularly with aggregates containing NL-05. However without further investigation in this region of polymer treatment the plateau type relation generally appears to be the more correct form.

(2) The plateaux in the 'log a' and dc/dt curves for

THE EFFECT OF PVA ON THE BREAKDOWN FACTORS IN THE RELATION $c = at^b$

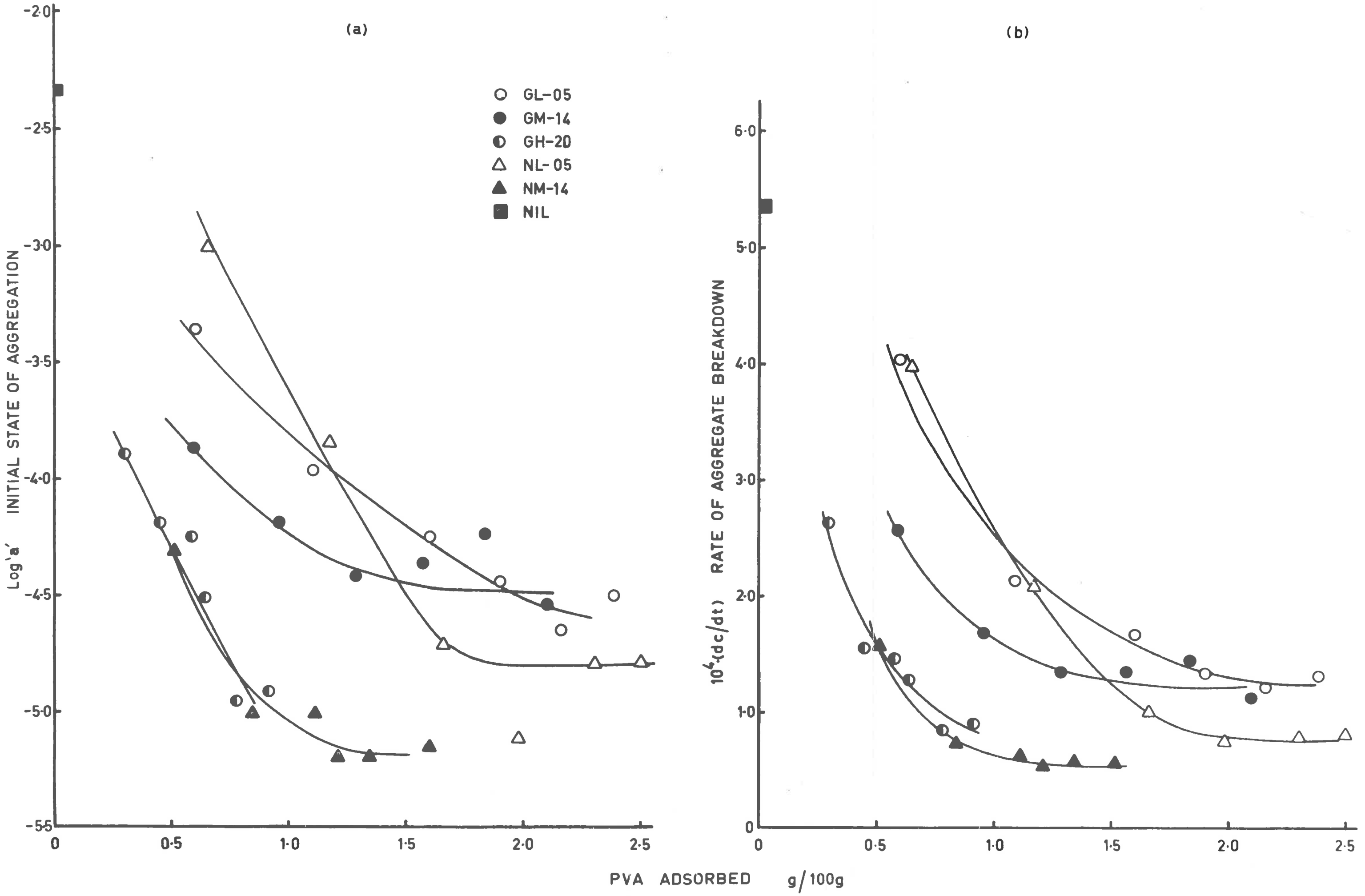


Figure 11.

any one polymer, occur at the same level of polymer treatment.

(3) The plateaux in the GM-14, GH-20 and NM-14 curves occur at a treatment level of approximately 1.0 g polymer/100 g of soil, while those for the NL-05 and GL-05 treatments occur at 1.8 and 2.0 g/100 g respectively.

The lowering of the values of 'a' with increasing PVA indicate that the initial state of aggregation is improved by the polymer treatment. That is, aggregates containing higher amounts of PVA are better able to withstand the initial rapid wetting used. This is in agreement with the work of Quirk & Panabokke (1962) and Williams (1959) who showed by rate of water uptake studies that Urrbrae loam aggregates stabilised with either natural organic matter or synthetic polymers were better able to withstand wetting at low suctions (2 cm) of water, than untreated aggregates.

The decrease in the 'rate of breakdown' values with increasing amounts of adsorbed PVA may be due to either one of two factors or a combination of both. Firstly equation (9) shows that the value of dc/dt at a given time depends on the number of particles in suspension. Aggregates which break down into a number of smaller particles on immersion in water, as in the case of untreated aggregates and those containing only small amounts of PVA, might be expected to have a faster rate of breakdown with further shaking than those which retain their original identity on immersion. Secondly, PVA links adjacent soil particles together and this might reduce the rate at which such particles can be abraded from the aggregate surfaces.

Some indication of the importance of the first alternative can be seen from the values of 'log a' or 'initial state of aggregation'. After immersion and shaking for one minute, untreated aggregates and those containing small amounts of adsorbed PVA are broken down to a considerably greater degree than those containing larger amounts of PVA. The weakest aggregates subsequently have a faster rate of breakdown.

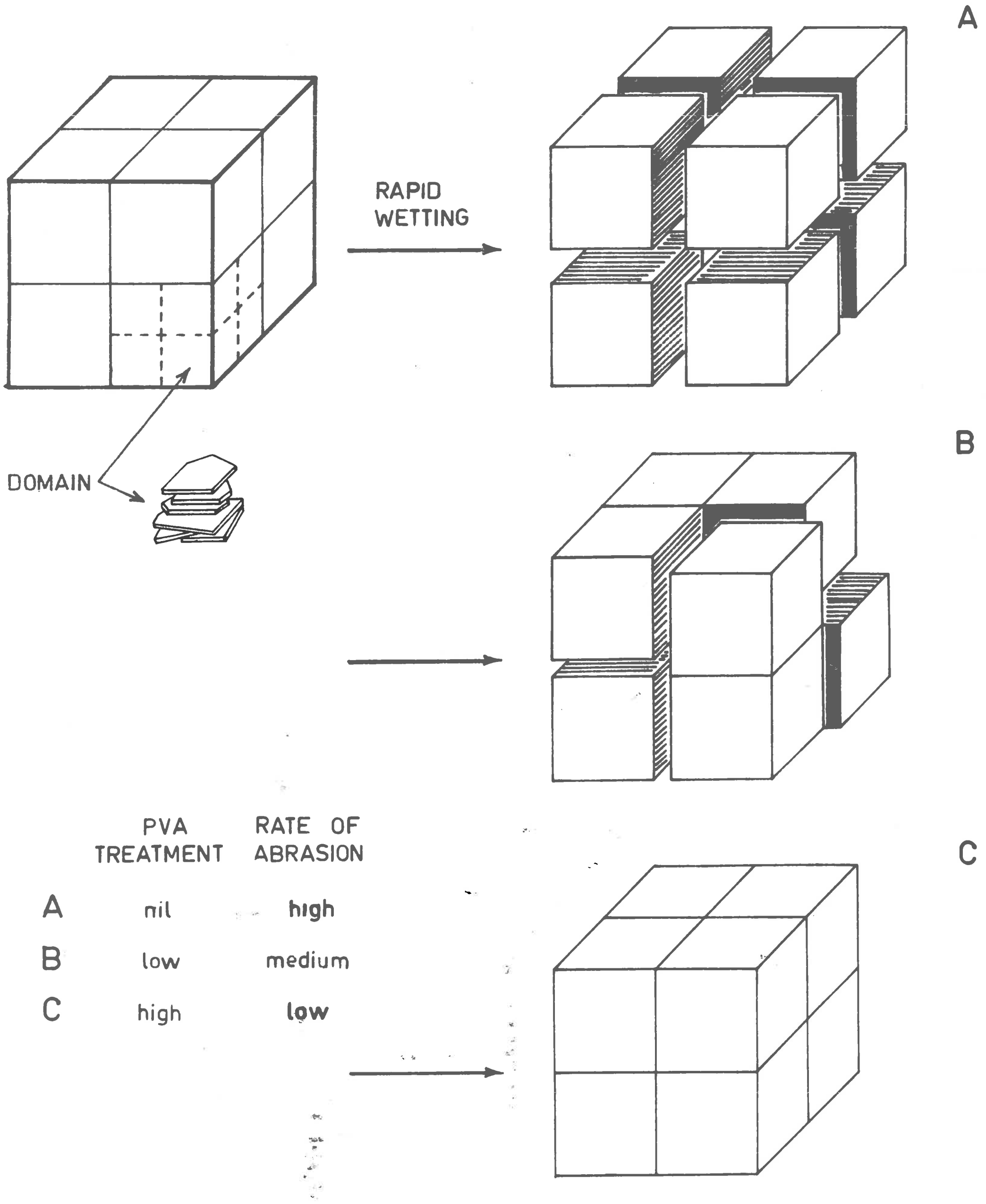
Evidence concerning the second alternative is not so available because the rate of breakdown in controlled not only by the resistance of the aggregate surface to abrasion but also by the number of particles in suspension resulting from the initial immersion treatment. In Chapters IV and VI it is shown that adsorbed PVA hydrates very rapidly and that with increasing water contents the tensile strength of soil-polymer complexes diminishes rapidly. This appears to indicate that the polymer bonds between soil particles have a low tensile strength when wet and that the reduced rates of breakdown observed in these experiments may be due primarily to the number of particles in suspension. It should be remembered, however, that the magnitude of the forces used in the tensile strength measurements (greater than 1 Kg/cm^2) are much larger than those experienced by small aggregates in suspension.

It is not possible from the present evidence to state which factor, of the two discussed, controls to the greatest extent the rate of breakdown of aggregates with shaking in water.

So far this work has not been discussed in terms of the location of adsorbed PVA within the aggregates and to do this it is necessary to propose a simplified model of aggregate structure. In Figure 12 an idealised situation is shown in which a soil aggregate is built up of structural units of various sizes. The smallest unit corresponds with the 'domain' structure proposed by Aylmore & Quirk (1960). A number of domains are grouped together to form a microaggregate and these in turn are grouped to form larger structural units. The building process is continued until aggregates of the size commonly observed in the field are obtained.

The spaces, or pores, between the structural units also occur in various sizes, the smallest corresponding to the intercrystalline spaces within domains. Thus the overall structure can be considered either in terms of structural units of various sizes or conversely, as pores of varying sizes.

MODEL OF AGGREGATE STRUCTURE AND BREAKDOWN IN WATER



	PVA TREATMENT	RATE OF ABRASION
A	nil	**high**
B	low	medium
C	high	**low**

Figure 12.

The strength of an aggregate depends on the degree of association between the various structural units i.e. the strength of the pores separating the units. The smallest pores would be expected to have the greatest mechanical strength due to the close approach of the solid particles and the consequently greater liquid film and electrostatic forces of attraction. The largest pores are regarded as being the weakest and hence are sites for the initiation of aggregate breakdown.

Evidence of this type of structure described above was obtained from the available data of the pore size distribution of Urrbrae B soil. Quirk & Panabokke (1962) using a non-polar liquid (benzene) desorption isotherm showed that there are three major peaks in the pore size distribution curves for Urrbrae B aggregates. The largest peak corresponded to pores having a diameter of less than 30Å. and the two smaller peaks corresponded with pore diameters of approximately 300Å and 3,000Å. Aylmore & Quirk (1962) using low temperature nitrogen adsorption were able to describe the group of smallest pores with greater accuracy than was possible using benzene adsorption. They concluded that these pores corresponded to the intercrystalline spaces of clay particles which occurred in highly organised domain structures.

These results can be interpreted as indicating the presence of structural units of various sizes. The smallest pores would be associated with the clay domains while the larger pores would represent the spaces in between other larger structures.

The proposed structure is also in accord with the observation that when a non-stabilised, air-dry aggregate is immersed in water it swells and disperses into smaller fragments of various sizes. The fragments are generally microscopic and considerable forces are required to disperse them completely into primary particles.

The non-stabilised aggregates are found to have a low "initial state of aggregation" in comparison with stabilised aggregates which retain their original identity on immersion in water. Stabilised aggregates may or may not subsequently fragment with additional mechanical agitation, depending on the degree of stabilisation. Thus a range of 'initial states of aggregation' ~~are~~ is observed with increasing amounts of adsorbed PVA and it is thought that this is due to the polymer stabilising some or all of the weakest pores mentioned above.

The positions of the plateaux in Figure 11 (a) and (b) indicate that GM-14, GH-20 and NM-14 are all restricted to approximately the same sites within the aggregates, while the GL-05 and NL-05 are able to penetrate into smaller pores. The strength of the GH-20 and NM-14 bonding is greater than that for GM-14 in equivalent sites. As was suggested previously this is probably due to the largest molecules being able to bridge more soil particles per molecule, while the NM-14 polymers gain additional strength through greater intermolecular bonding. Both the NL-05 and GL-05 bonds at high levels of treatment are stronger than that of GM-14, because of their ability to penetrate into finer pores. At lower treatments they are weaker than GM-14, as for equivalent amounts by weight they are spread over a larger surface area.

4. Summary and Conclusions

It has been shown that PVA increases the water-stability of Urrbrae B aggregates and that this can be related in a general way to the number and strength of the inter-particle bonds formed. Above a certain amount of adsorbed PVA, further additions of polymer do not result in increased aggregate stability. This is thought to indicate that there are only a certain number of sites within the aggregates that are critical for producing maximum stability. Once these sites are strengthened with PVA then any further adsorption does not result in increased stability. It is also possible that at higher amounts of adsorbed PVA there ~~are~~ is a lack of adsorption sites suitable for cross linking.

The water-stability depends on such molecular characteristics of the PVA as molecular weight and intermolecular bonding between the polymer molecules. These factors determine the ability of PVA molecules to diffuse into small pores and also determine the strength of the interparticle bonds formed.

Aggregates containing PVA do not slake on immersion in water and with shaking they are abraded at a slower rate than untreated aggregates. The addition of PVA resulted in a slowing down of the disintegration processes to an extent where the important features of aggregate breakdown could be distinguished. Thus it was shown that the water-stability of soil aggregates is a function of both their ability to withstand the initial wetting treatment and their resistance to abrasion. The two mechanisms are closely related in that a low initial stability results in a larger number of particles in suspension which in turn increases the rate of abrasion and breakdown.

The fact that small particles are removed from the surfaces of the stabilised aggregates by abrasion indicates that PVA does not penetrate into pores surrounding particles of the order of 2 μ diameter in sufficient amounts to greatly increase the resistance to abrasion of the aggregate surfaces.

A model of the physical structure of Urrbrae B aggregates has been proposed. It is suggested that clay particles arranged into domains are built up into micro-aggregates and that these in turn are formed into larger structural units. The spaces or pores between these structures are of varying orders of size and strength. The largest pores are regarded as being the weakest and hence are the sites at which aggregate breakdown is initiated.

Addition of PVA strengthens the aggregates by forming a tough continuous or semi-continuous film along the pore 'walls'. If sufficient of the pores, or certain critical pores, are stabilised in this way the aggregates do not disperse on immersion in water or even with additional mechanical work.

These concepts may add further meaning to the widely used water-stable aggregation tests which so far have received little theoretical consideration in terms of soil aggregate structure. Further work with larger samples and complete aggregate analyses at each shaking period would define the abrasion process more accurately, particularly in respect to the size of the particles that are plucked from the surfaces of the stabilised aggregates. Such studies with aggregates containing different amounts of natural organic matter would also be useful in determining the location of the stabilising components of organic matter.

CHAPTER IV

THE SWELLING OF URRBRAE B (< 2 μ) - PVA COMPLEXES

1. Introduction

In this chapter the influence of relatively small amounts of PVA on the total swelling and the rate of swelling of pressed cores of the clay fraction from Urrbrae B soil was investigated with a view to determining if these factors are important in stabilizing natural soil aggregates.

Williams (1959) observed that natural aggregates of Urrbrae A containing 0.5% PVA showed little difference in swelling to the untreated aggregates. Also puddled Urrbrae B soil treated with PVA had similar water relations to the control samples. These results indicated that PVA had little effect on the equilibrium water content of either natural aggregates or puddled soil material, over a range of suctions from pF 0.3 to 4.2. On the other hand Emerson (1956) demonstrated quite clearly that artificial soil aggregates treated with PVA, when immersed in water did not swell and disrupt as did the control samples.

The difference between these results can be attributed to the manner in which the soil - PVA complexes were allowed to swell. In the case of the Urrbrae soils, the samples were wet slowly from a high to a low suction while those of Emerson were immersed in water from an air-dry state. This latter method cannot really be interpreted just in terms of swelling as Quirk & Panabokke (1962) have shown that the rapid entry of water into soil aggregates can cause a breakdown of the internal structure of the aggregates and additional water is adsorbed by the aggregates. In the extreme cases of instability the aggregates are disrupted while more stable ones retain their original shape. It was shown that strengthening of the porous structure of aggregates with organic matter controlled the amount of structural breakdown. With rapid wetting some aggregates are disrupted, some retain their original shape but develop internal planes of failure, while the strongest are unaffected structurally by the treatment. Each particular state of the aggregates results in a different water content depending on the amount of structural breakdown.

Thus in interpreting the water relations of soil-polymer complexes it is necessary to take into account the wetting conditions to ensure that the factor being determined is swelling (in the sense of water associated with the clay surfaces and the structural water held in pores) as compared with the ability of the forces of cohesion between the clay particles to withstand rapid swelling and the development of a gel structure.

Theng (1964) has studied the effect of a number of PVA samples of varying molecular characteristics on the swelling of montmorillonite cores. The water content (pF 1.1) of calcium montmorillonite was progressively reduced from approximately 200 cc/100 g to 125 cc/100 g by amounts of up to 6 g of adsorbed PVA per 100 g of clay. Further amounts of PVA did not result in further reductions in the swelling of the cores. As the silicate layers of calcium montmorillonite do not expand beyond a spacing of 19Å only 30 cc of water per 100 g of clay was located in the interlamellar spaces. Thus it was considered that the greatest effect of the adsorbed PVA was in reducing the water associated with the external surfaces of the clay crystals and the water held in the pore structure of the clay mass (gel or structural water). The progressive decrease in swelling with increased amounts of adsorbed PVA indicated that interparticle bonding between clay particles or domains restricted gel formation. Also as 6 g PVA/100 g clay represented only 50 per cent coverage of the external surfaces of the clay (assuming an adsorbed layer 10Å deep), it appeared that the polymer linked domains of crystals together rather than individual crystals, as the external surface of domains would be much smaller than that of an equivalent amount of individual crystals.

Emerson (1963) and Emerson & Raupach (1964) have also demonstrated that PVA reduces the swelling of montmorillonite flakes in dilute salt solutions. They observed that when the clay suspension was flocculated before the addition of PVA, the polymer was not as effective in reducing swelling. This latter effect was thought to be due to a reduced number of polymer-particle linkages. However more adsorption data would be required to make a precise comparison of the flocculated and dispersed clay-organic systems used.

The above results of the swelling of montmorillonite - PVA complexes are opposite to those reported by Williams (1959) for the essentially illitic system of Urrbrae B. Further investigations have therefore been made using the < 2 μ clay fraction of Urrbrae B treated with the medium molecular weight polymer, GH-14.

Quirk & Panabokke (1962) also investigated the possibility that organic matter in soil aggregates may cause temporary physical blocking of pores and so protect the aggregates against the disruptive force of rapid swelling at low wetting suctions. However they found at wetting suctions of ~~(~~30 cm of water~~)~~ and by using a non-polar wetting liquid, that the wetting curves of aggregates, containing either high or low amounts of organic matter, were very similar. This tended to discount the suggestion of any major change in the pore structure of aggregates due to the presence of organic matter.

In the present work in which artificial clay cores were used, the question of physical blocking of the clay surfaces to water by adsorbed PVA again arose with the observation that there is a marked reduction in the surface area of cores containing PVA. In Chapter V it is shown that the surface area of compressed cores of the < 2 µ fraction of Urrbrae B, similar to those used in the swelling studies, was reduced from 124 m^2/g to approximately 100 m^2/g by the incorporation of 3% PVA. This was attributed to the PVA forming a film around groups of the clay particles and so preventing access of nitrogen molecules to all the clay surfaces. Thus the work on the swelling of clay-PVA complexes was extended to determine the rate of swelling, as such measurements should give a better indication of the accessibility of the clay surfaces to water than total swelling measurements.

2. Methods

2.1. Preparation of Urrbrae B (< 2 µ) Cores

To avoid the use of chemical dispersing agents the < 2 u Urrbrae B sample was prepared by dispersing a suspension with an ultrasonic probe. Approximately 5 g of air-dry aggregates were placed in a tube with 25-30 cc of water and this was dispersed for 2 minutes using a model S-75 Branson Sonifier. A number of samples were dispersed in this fashion and were then bulked and made up to a 2.5% suspension with water. The < 2 µ fraction was collected by sedimentation and decantation and was finally dried at 70°C and ground to pass a 70-mesh sieve. It was thought that this procedure would result in clay samples more closely resembling the natural chemical state of the clay as it occurs in aggregates, than would methods involving the replacement of cations with sodium.

Samples of 2 g of oven-dry material were suspended in 50 cc water and then 15 cc of the required GM-14 solution were added. The adsorptions were carried out on an end-over-end shaker for 6 days, after which the clay was recovered and washed by centrifuging. The amount of PVA adsorbed was determined by analysis of the supernatant solution, as described previously. The samples were dried at 70°C, ground to pass a 70-mesh sieve, and returned to a vacuum des~~s~~iccator to equilibrate at 96% R.H. Cores of approximately 0.2 g were made at a pressure of 1200 atmospheres. These cores were then used to investigate the swelling, the rate of swelling, and in a later chapter, the surface area, of the complexes.

2.2. Swelling Determination

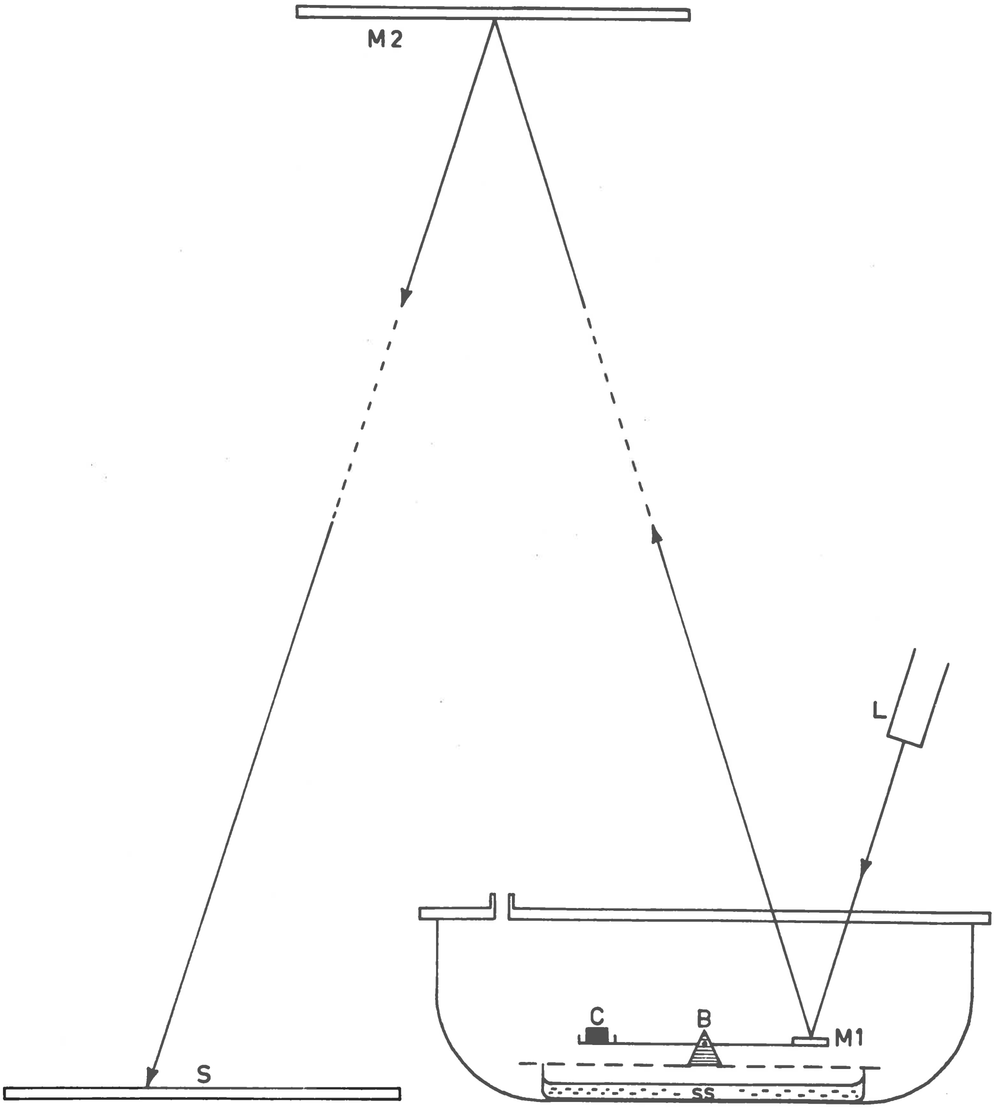
Cores containing different amounts of polymer were wet slowly at 700 cm suction of water using a pressure plate apparatus. The suction was then reduced to 100 cm and finally to 15 cm. The equilibrium water content was determined on duplicate samples at each suction and the water content expressed as cc/100 g oven-dry (70°C) material.

2.3. Rate of Swelling Determination

A torsion balance was designed to measure the rate of water vapour adsorption of the cores described above and is shown in Figure 13. It consists of a beam supported at its centre by a piece of watch spring. A pan at one end holds the clay core and is balanced at the other end by a small mirror. The whole balance is placed in a vacuum desiccator bowl fitted with a flat ⅛" perspex top. A collimated beam of light having a superimposed hairline graduation is directed through the perspex on to the mirror and is reflected up to a ceiling mirror and thence back to a scale graduated in millimetres. Small movements of the torsion balance mirror can be considerably magnified by suitable positioning of the mirror system. The particular arrangement used had a sensitivity of 1 mg which was sufficient for the required purposes. Considerably higher sensitivities could be obtained by replacing the watch spring by a fine tungsten torsion filament e.g. Barret, Birnie & Cohen (1940).

An oven-dry core (70°C) was placed on the balance which was supported over a saturated potassium sulphate solution, and the desiccator rapidly evacuated with a Speedivac pump. The rate of water vapour adsorption, from an atmosphere of 96% RH, was then followed at short time intervals over a period of 12 hours. At the end of the run the core was weighed and the oven-dry weight determined as a further check on the

TORSION BALANCE FOR SWELLING DETERMINATIONS



L	light source
M1,M2	mirrors
B	balance
C	clay core
ss	saturated salt solution
S	graduated scale

Figure 13.

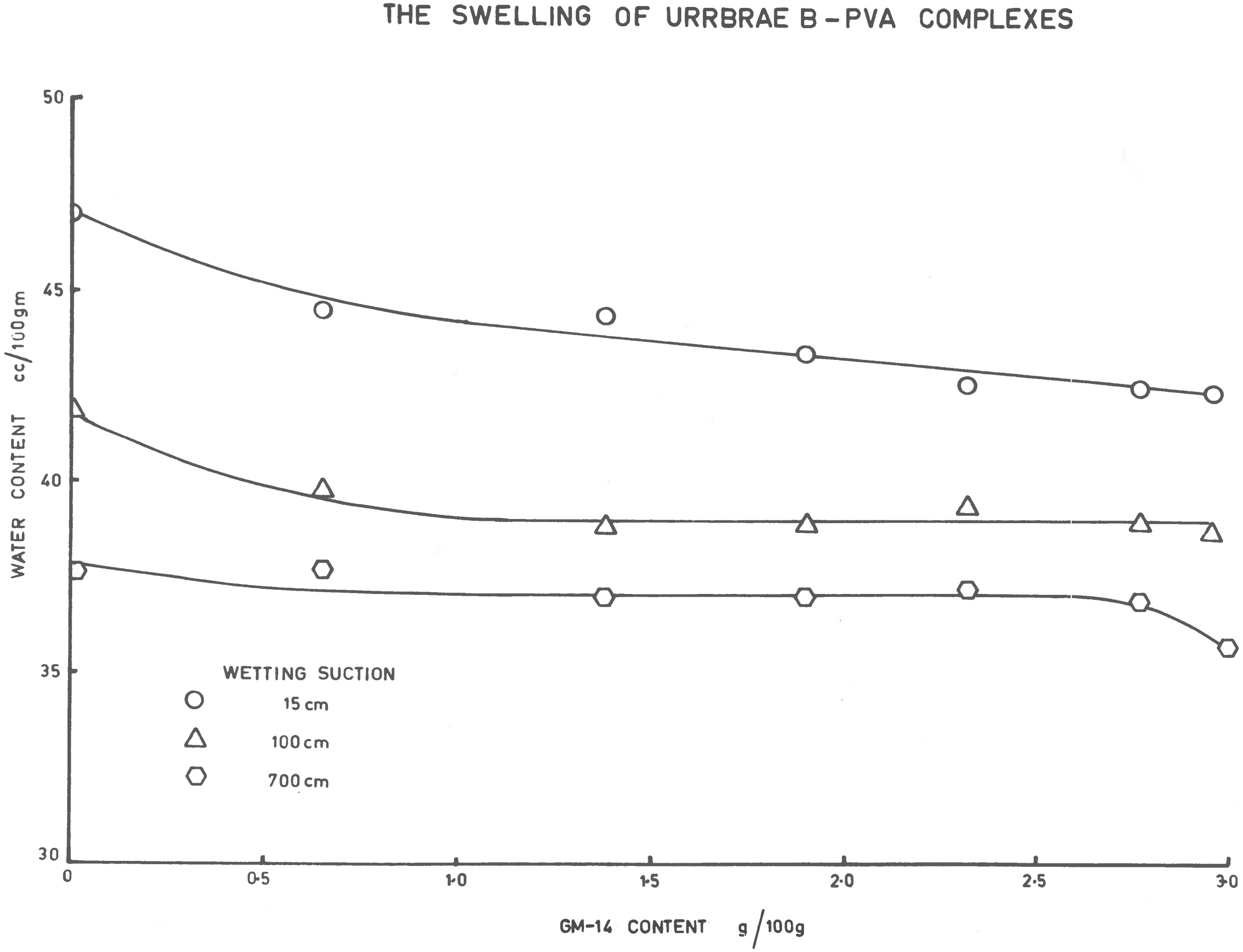

THE SWELLING OF URRBRAE B - PVA COMPLEXES
WATER CONTENT cc/100gm
50
45
40
35
30
0
0·5
1·0
1·5
2·0
2·5
3·0
GM-14 CONTENT g/100g
WETTING SUCTION
○ 15 cm
△ 100 cm
⬡ 700 cm

Figure 14.

total water uptake as determined from the calibration curve.

The method proved to be quite satisfactory and is capable of being adapted for use under a wider range of conditions than used here, as other modifications could easily be incorporated to vary the relative humidity of the atmosphere inside the desiccator.

3. Results and Discussion

3.1. Swelling

The water-contents of Urrbrae B clay cores containing 0 - 2.96 g GM-14/100 g are shown in Figure 14.

There is little reduction in the swelling of the clay cores with amounts of adsorbed PVA of up to 2.96 g/100 g over a range of wetting suctions from 15 - 700 cm of water. The water content (15 cm suction) at the highest PVA treatment is 4 cc/100 g less than that of the untreated sample. Assuming that the porosity of the dry cores is 14 cc/100 g and the density of the clay particles is 2.72 g/cc (Panabokke, 1956) it can be calculated that 100 g of untreated clay increases in volume from 51 cc to 84 cc at 15 cm suction of water. A similar amount of clay containing 3 g PVA/100 g swells to a volume of 80 cc. Thus there is little difference in the swelling behaviour of the treated and untreated samples.

This result is markedly different to the relatively large reductions in swelling reported by Theng (1964) for sodium and calcium Wyoming bentonite systems. The reason for this difference in swelling behaviour may be due to the presence of some other forces capable of restricting the swelling of Urrbrae B, and so masking the effect of PVA.

Aylmore & Quirk (1962) have shown that there is a force operative within Ca^{++} - Urrbrae B systems that restricts swelling to a level considerably below that which might be expected from considerations of its specific surface area. The exact nature of this force is not known but it appears to be associated with a high degree of orientation of the clay crystals (illite) into domains which would provide suitable conditions for the operation of strong electrostatic forces between the clay crystals (MacEwan, 1948). The domains are apparently very stable in the divalent ion system and either through this mechanism, or through a stable association between individual domains, the amount of swelling is restricted. Furthermore, Edwards, Posner & Quirk (in preparation) have shown that diffuse double layers are not developed on the entire surfaces of illite crystals in suspension, whereas this is the case for the external surfaces of montmorillonite crystals.

This observation probably explains why PVA forming links between the domains of Urrbrae B clay crystals has much less effect on swelling than when the PVA links together domains of calcium montmorillonite in which there is no naturally occurring restriction to intercrystalline and interdomainal swelling.

In view of these observations in these experiments and those of Aylmore & Quirk (1962) it appears that PVA does not contribute appreciably to the water stability of PVA treated Urrbrae B aggregates through restrictions of swelling by interparticle bonding.

The possibility that the rate of swelling, rather than the total swelling, of the clay fraction is important in this respect is discussed in the next section.

3.2. Rate of Swelling

The rates of wetting of a clay core (diameter 0.76 cm, depth 0.24 cm) and a similar core containing 2.96% GM-14 by weight, are shown in Figure 15a. The two cores exhibited very similar rates of water vapour adsorption, showing that the presence of PVA had little or no effect on the penetration and distribution of water throughout the cores.

This result is quite different to that obtained for PVA-treated Urrbrae loam aggregates (Williams, 1959) in which the presence of PVA reduced the rate of water uptake by the aggregates. However there is an important difference between the clay cores used here and the natural aggregates used by Quirk & Panabokke (1962) and Williams (1959). The cores do not represent a stabilised natural structure but rather individual clay particles bound together in small groups

THE RATE OF WATER UPTAKE BY URRBRAE B CLAY
AT pF 4·69

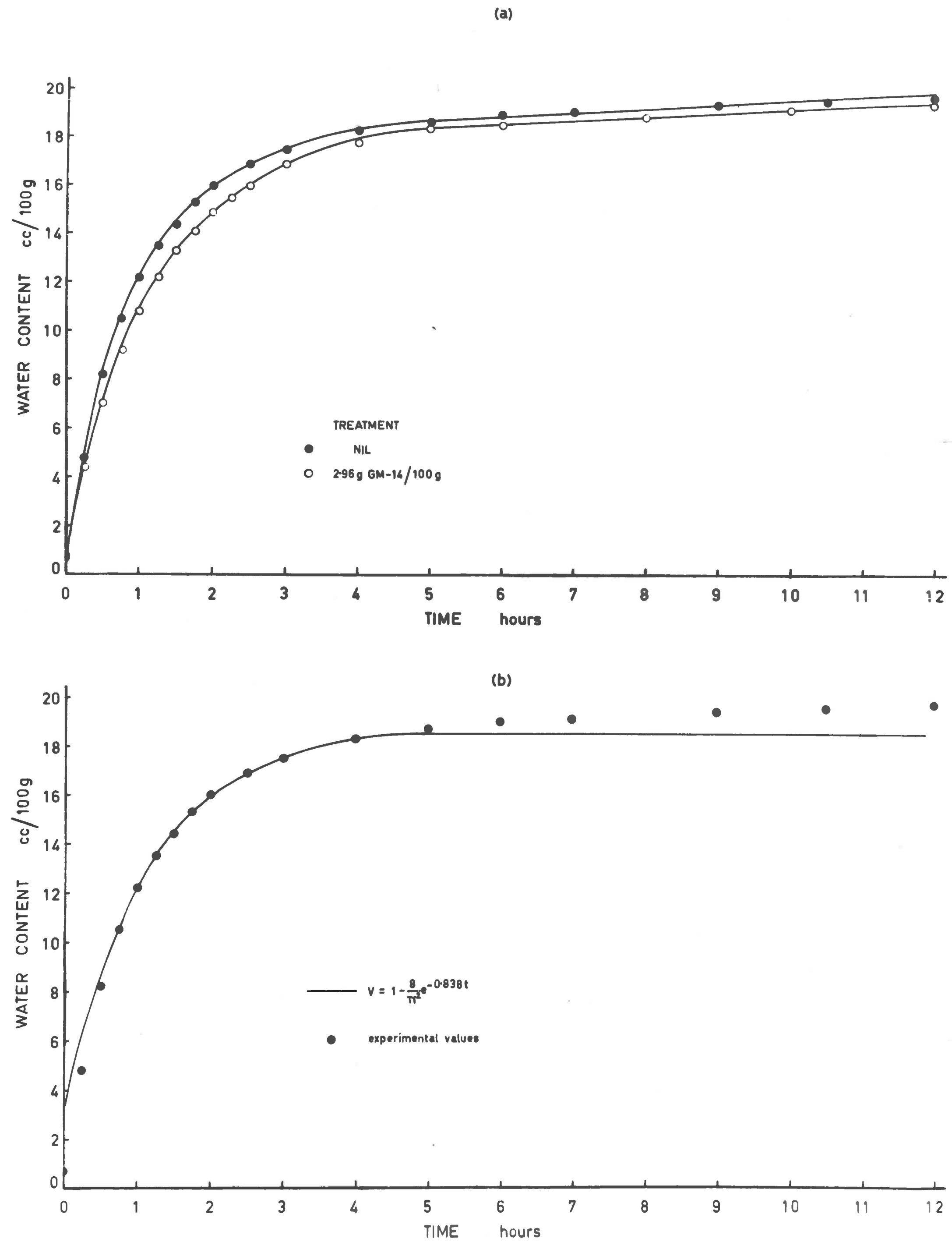


Figure 15.

(70-mesh sieve size) that have been pressed together in the form of a core. It is unlikely that there is any polymer cross-linking between the micro-aggregates as polymer linkages once broken by grinding do not reform on wetting and compression (Jamison, 1954; Quirk & Panabokke, 1962). Thus any attempt to measure the rate of water uptake by the cores from a free water surface could not be interpreted in terms of strengthening the macro-pores of the cores. In fact preliminary experiments with the sintered glass funnel apparatus used by the previous authors showed that the clay cores were unstable to wetting by capillarity, even at wetting suctions of 100 cm of water. At higher wetting suctions this method was unsuitable because of the rate of evaporation of water from the sintered funnel.

For these reasons the rate of water-vapour adsorption was determined at 96% Relative Humidity (approximately equal to 5×10^4 cm suction of water) rather than the low wetting suctions discussed above. The results shown in Figure 15a should now be interpreted in terms of the accessibility of water to the clay particle surfaces, contained within the micro-structures described above.

Nitrogen adsorption studies show that PVA adsorbed on clay particles reduces the accessibility of non-polar molecules to the clay surfaces while the present study shows that water molecules of similar molecular dimensions may readily penetrate the adsorbed PVA. Although the observation of Greenland (1963) showed that PVA adsorption is virtually irreversible, the dried polymer must hydrate rapidly on contact with water and become permeable to water molecules. The rapidity with which it hydrates is indicated by the similarity of the wetting curves for the treated and non-treated cores. Thus it is unlikely that PVA deposited in the pores of natural aggregates can have a significant effect on the water-stability of the aggregates through reducing the rate at which water can penetrate to the clay surfaces.

This result and those of the previous section indicate that adsorbed PVA forms strong, flexible (in the wet state) bonds between clay particles and it increases the ability of aggregates to withstand rapid wetting by buffering the disruptive forces of swelling and rapid entry of water, rather than by water-proofing or increasing the rigidity of the aggregates.

Apart from the results concerning the presence of adsorbed PVA - two items of interest may be obtained from the determined rate of water vapour adsorption viz. the time to reach equilibrium, and the relationship of the experimental results to theoretical studies on the rate of adsorption.

Brunauer (1943) summarising the results of a number of different investigations concludes that the rate of adsorption of gases by adsorbents possessing very fine pores is virtually complete in a matter of hours although small increases may occur over weeks and even months.

The present study agrees with this in that approximately 95% of the total water uptake takes place during the first 5 hours. Patrick & Cohan (1937) have clearly demonstrated the importance of the presence of gaseous impurities on the rate of adsorption of water vapour on silica gel. They concluded that with air pressures of less than 0.5 mm, equilibrium is reached within 2-3 hours, whereas if the pressure reaches 3.6 mm, equilibrium is not attained even in 25 hours. This is of practical importance in studies on the swelling of clay materials where clay cores are frequently left to equilibrate in constant humidity desiccators for periods of one to several weeks. By using more complete evacuation than is usually obtained with water main vacuum pumps, this period could be reduced confidently to 1-2 days.

McBain (1907) was one of the first to investigate the theory of adsorption rates of gases on porous materials and this has been followed by various refinements - all of which reduce to basically the same expression. The following expression of Damkohler (1935) for porous adsorbent particles is typical of the form of equation obtained.

$$V = 1 - \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{e^{-\delta(2m+1)^2}}{(2m+1)^2} \quad \ldots\ldots\ldots\ldots (1)$$

where V = fraction of the equilibrium amount adsorbed at time t

δ = a constant that includes the time t, as well as the diffusion coefficients of the molecules in the liquid and vapour phases, and the geometry of the adsorbent.

m = an integer.

If the first term only is considered, the resultant errors are not great and the equation becomes

$$V = 1 - \frac{8}{\pi^2} e^{-kt} \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

This expression has been tested with the data obtained for the water vapour adsorption by Urrbrae B cores. It is necessary to know the equilibrium water content and as shown earlier, this continues to increase over long periods. An inspection of the adsorption isotherm shows that it consists of two parts - an initial exponential relation for the first 5 hours followed by a relatively linear increase. Thus the equilibrium water content at a time of 5 hours was chosen and this value was used in equation 2. In figure 15b it can be seen that the experimental points lie fairly close to the curve calculated using a value of k = 0.838. The agreement is not as good during the first 30 minutes but this is probably due to using only the first term of Damkohler's expression. Use of further terms would lower the theoretical curve in this region. The experimental values do not reach a plateau at 5 hours, but continue to increase slowly. It is thought that the most likely explanation is not that water diffuses slowly into extremely fine pores but rather that the core begins to swell as a whole at this water content (18.7 cc/100 g) and so extra water is taken up. Holmes (1955) has shown that moulded Urrbrae B clay blocks commence to show normal swelling at a water content of approximately 17 cc/100 g. The present results are in general agreement with this, considering the differences in the samples - 100% clay as compared to 60% clay for the blocks used by Holmes.

CHAPTER V

THE EFFECT OF PVA ON THE PORE STRUCTURE OF SOIL AGGREGATES

1. Introduction

Burford, Deshpande, Greenland & Quirk (1964) have shown that the presence of naturally occurring organic matter and also PVA can cause a considerable reduction in the specific surface area of clays as determined by low temperature nitrogen adsorption. It was suggested that this was due to the formation of a film of large organic molecules, blocking fine pores between soil particles and so restricting the entry of nitrogen molecules. Removal of the organic matter resulted in large increases in the measured surface areas e.g. reducing the carbon content of a Terra Rossa surface soil from 4.16% to 0.30% carbon using 6% hydrogen peroxide treatment resulted in an increase in surface area from 6.4 to 27.0 m^2/g, as determined by low temperature nitrogen adsorption.

It was thought that a detailed analysis of the nitrogen adsorption and desorption isotherms obtained with aggregates of Urrbrae B before and after the adsorption of PVA would provide additional data on the location of adsorbed polymer molecules.

2. Materials

The soil-polymer samples used were taken from the adsorption and swelling experiments described in Chapters II and IV.

3. Methods

The apparatus used in these experiments has been described in detail by Aylmore (1960) and is similar to that of Culver & Heath (1954). It consists essentially of a sample bulb, containing the clay adsorbent, attached to a gas burette, a mercury cut-off manometer and a high pressure mercury manometer. The gas burette and the cut-off manometer are thermostated at 25°C. The whole system is evacuated to less than 10^{-5} mm Hg with a mercury diffusion pump backed by a rotary oil pump. The sample bulb is heated with a portable furnace to assist in evacuation of the sample. In this present work an outgassing temperature of 70°C was used. The furnace is replaced with a thermos of liquid nitrogen during the adsorption determinations to keep the sample at a temperature of -195°C.

The volume of nitrogen gas admitted to the calibrated system is known and the change in pressure as the gas is adsorbed or desorbed is recorded using the high pressure mercury manometer. By use of the Gas Laws the changes in volume and pressure can be used to calculate the quantities of nitrogen adsorbed or desorbed by the sample.

The amount of nitrogen adsorbed by the sample at the temperature of liquid nitrogen (-195°C) is determined over a range of vapour pressures and the amount forming a monolayer on the surface is then calculated using the relation derived by Brunauer, Emmett & Teller (1938).

The B.E.T. equation was derived from a generalisation of the Langmuir monolayer adsorption theory and has been found to hold for most adsorbents over the range of P/P_o = 0.05 to 0.35.

$$\frac{P}{v(P_o-P)} = \frac{1}{v_m c} \cdot \frac{c-1}{v_m c} \cdot \frac{P}{P_o} \quad \text{..........} \quad (1)$$

where v = the quantity of nitrogen adsorbed at pressure P

v_m = the quantity of nitrogen required to form a monolayer

P_o = the saturation vapour pressure of liquid nitrogen

c = a constant related to the heat of liquefaction of the first layer (E_1) and the heat of liquefaction of the gaseous N_2 (E_L)

$$c = \frac{a_1 b_2}{b_1 a_2} \cdot e^{(E_1 - E_L)/RT} \quad \text{..............} \quad (2)$$

where a_1, b_1 and b_2 are rate constants.

Equation (1) is written in a linear form and a plot of $\frac{P}{v(P_o-P)}$ against P/P_o allows the evaluation of the constants c and v_m from the intercept ($\frac{1}{v_m c}$) and the slope ($\frac{c-1}{v_m c}$). Assuming that the packing area of a nitrogen molecule is 16.2 Å at 78°K, the surface area of the adsorbent may be calculated from v_m.

It has been shown in equation (2) that c depends on the energy of adsorption of the first layer and also that of successive layers. The energy of adsorption of the monolayer is not constant over its entire range as the most reactive sites are filled first. However above a relative pressure of about 0.05 the reactivity of the sites, although not constant, do not change very rapidly. The B.E.T. theory assumes that the energy of adsorption of successive layers beyond the first is equal to the energy of condensation of the liquid adsorbate. This has since been shown to be not strictly correct (Clampitt & German, 1957). Their modification of the energies of adsorption of successive layers produces a considerable improvement in the value of c obtained by use of the B.E.T. equation. In practice the relative differences between E_1 and E_L remain remarkably constant for any one gas as was originally demonstrated by the authors of the equation.

The value of v_m depends on the closeness of packing of the adsorbed molecules and in particular on their thermal motion. Much is said in the literature of the lack of uniformity of the adsorbent surface and the lateral interaction between the adsorbed molecules but as yet these factors have not been sufficiently characterised to require any major change in the present form of the B.E.T. equation. Brunauer (1961) points out that their theory did not include assumptions of the uniformity of the adsorbent surface or the non-interaction between the adsorbate molecules as is commonly suggested, but admits that such considerations should produce improvements in the characterisation of adsorption processes.

It might be expected that the values of both c and V_m would be altered by the presence of organic molecules already at the surface of the adsorbate. It appears however that this aspect has received little attention, possibly because outgassing temperatures commonly used are sufficiently high to remove, or char, organic materials. Carbon from a variety of sources has been used frequently as an adsorbent at low outgassing temperatures and there is no indication that the process of adsorption is markedly different to that of inorganic solids. Organic molecules present as impurities would affect the heat of adsorption of a gas but in the quantities in which they are likely to persist, after sample preparation, are probably only of importance at relative pressures below 0.05 to 0.10. Hence surface area determinations should not be unduly affected.

The author is unaware of any detailed investigation into this aspect of solid-organic complexes and the lack of any mention of it in such reviews as that of De Boer (1951) and the American Chemical Society symposium on "Solid Surfaces and the Gas-Solid Interface" (1961) suggests that it has received no particular attention.

To describe the micro-structure of the soil aggregates, complete nitrogen adsorption - desorption isotherms were obtained. By differentiating the desorption curve the relative frequency distribution of pores within aggregates can be obtained as a function of the relative vapour pressure. The equivalent cylindrical radii at any relative vapour pressure (P/P_o) can then be obtained by the Kelvin equation:-

$$\ln(P/P_o) = \frac{2V\gamma\cos\theta}{R.T.}\frac{1}{r} \quad \ldots\ldots\ldots\ldots\ldots (3)$$

where P and P_o have the same meaning as in equation (1). V is the molar volume of liquid nitrogen at temperature T, R is the gas constant, γ is the surface tension of the liquid, θ is the angle of contact and r is the Kelvin radius.

There is reason to believe that the molar volume and surface tension of the liquid condensed in fine pores is different from those in the bulk phase as the density of adsorbed liquid is somewhat greater than in the bulk phase. θ is assumed to have a value of 0°, i.e. the solid is completely wetted by liquid nitrogen. Various semi-empirical substitutes have been used but it has been found that the use of the normal values of the bulk phase do not introduce any serious error in describing the desorption branches of adsorption-desorption hysteresis loops.

It should be noted that the equivalent cylindrical radii calculated in this way are probably more correctly estimates of the average crystal separations as the conventional Kelvin equation is based on the vapour pressure lowering over a hemispherical meniscus that occurs between plate-like clay crystals (Aylmore & Quirk, 1960). Foster (1932) suggests that a more correct value of crystal separation is obtained by adding twice the thickness of an adsorbed monolayer to the Kelvin radius; In this case nitrogen has a molecular diameter of 4.2Å so the crystal separations are approximately $(r + 8)$ Å.

In the experiments in which only a surface area determination was made, approximately 0.60 g of treated aggregates were moulded into a cylindrical core to prevent fine particles being drawn from the sample bulb into the vacuum system during evacuation. This precaution was later shown to be unnecessary although it did not affect the results

THE N_2 SURFACE AREAS OF URRBRAE B-PVA COMPLEXES

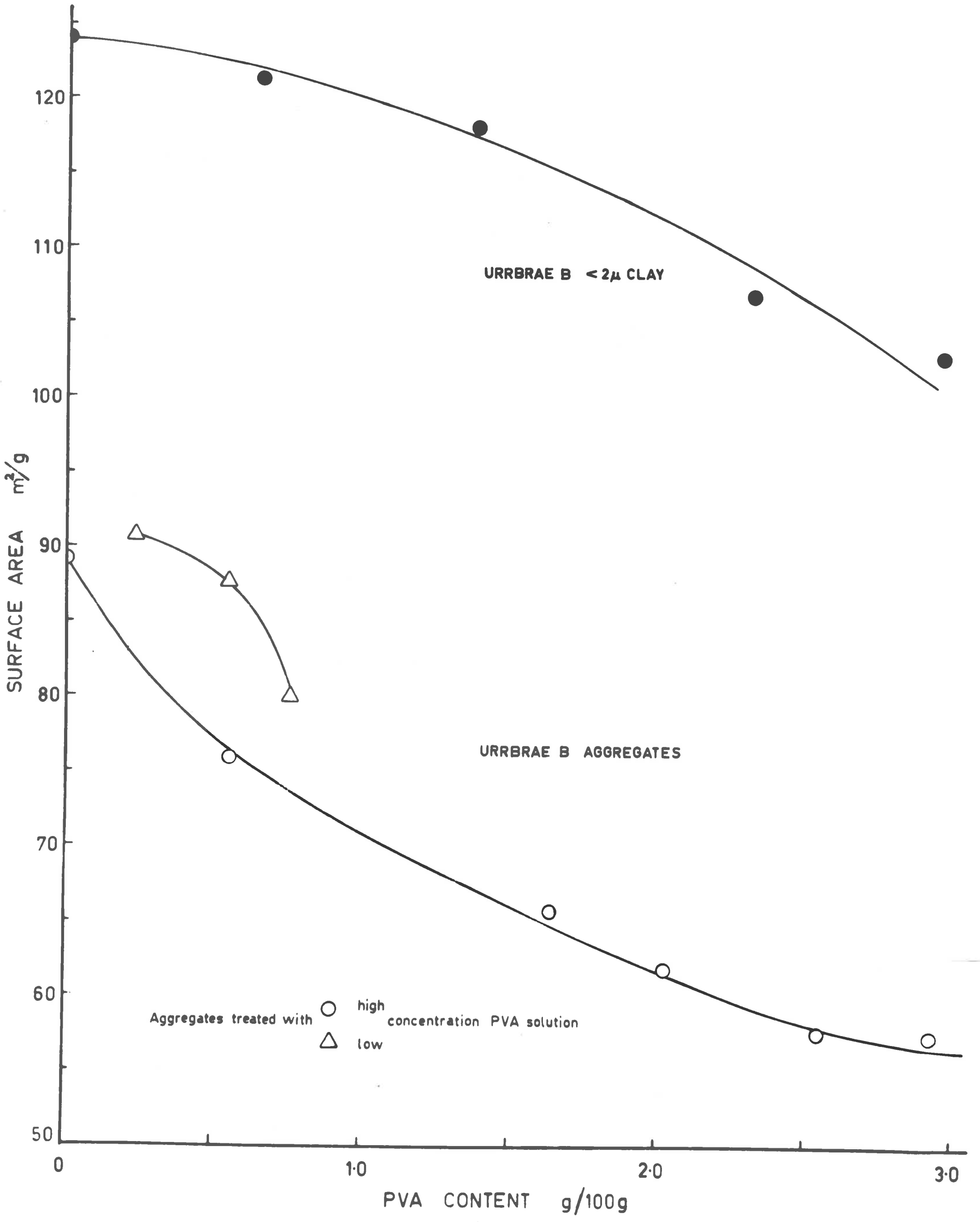


Figure 16.

obtained. Pore size distribution determinations were made on the whole aggregates with no moulding.

The samples were stored over P_2O_5 for some weeks and then outgassed to 10^{-5} mm at 70°C for at least 16 hours or until the pressure did not rise above 10^{-3} mm after isolation from the pumps for half an hour. The adsorption and desorption of liquid nitrogen was then determined in the manner described by Aylmore (1960). Equilibrium at each point of the isotherm was obtained in 10-25 minutes depending on the relative pressure.

4. Results and Discussion

4.1. Surface Area Determination

The surface areas of Urrbrae B ($\frac{1}{2}$-1) mm aggregates containing various amounts of PVA are given in Table 7 together with the surface areas of samples of the $< 2\,\mu$ fraction of Urrbrae B treated with PVA. The results are shown graphically in Figure 16.

It can be seen that -

(1) clay cores prepared from material that had previously been dispersed in water and treated with PVA, show a decrease in surface area as the amount of adsorbed PVA is increased.

(2) The addition of PVA to soil aggregates results in a decreased surface area of the aggregates.

Table 7

Nitrogen Surface Areas of Soil Treated with PVA

Sample	PVA Content (g GM-14/100 g)	Surface Area (m^2/g)
Urrbrae B (< 2 µ)	Nil	124.3
cores	0.65	121.3
	1.38	119.1
	2.32	106.8
	2.96	102.7
Urrbrae B aggregates	Nil	89.9
Short term - high	0.55	75.8
concentration treatment	1.64	65.7
	2.03	61.9
	2.55	57.6
	2.84	57.5
Urrbrae B aggregates	0.23	90.7
Long term - low concentration	0.54	87.6
tration treatment	0.75	79.9

(3) The surface area of the aggregates approaches a minimum value of approximately 55 m^2/g as the amount of adsorbed PVA is increased.

(4) The conditions of time and solution concentration in which PVA is adsorbed affect the value of surface area obtained.

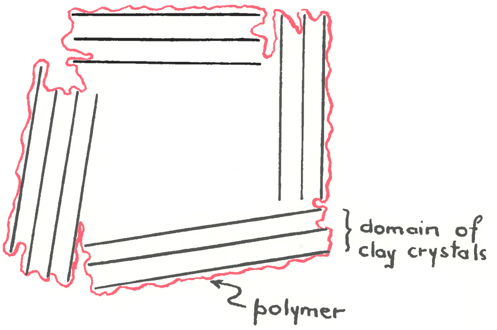
(5) The percentage reduction in surface area is greater for the aggregates than for the clay sample at equivalent amounts of adsorbed PVA.

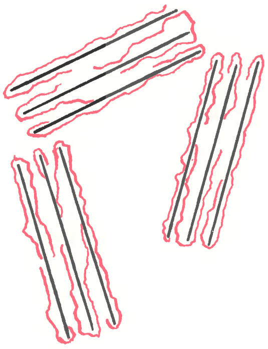
4.1.1 Surface area of clay - PVA complexes

In this experiment cores of Urrbrae B ($< 2\ \mu$) clay show a gradual decrease in surface area with increasing amounts of adsorbed PVA. That is the PVA excluded nitrogen molecules from some of the clay surfaces. Further measurements were not made with higher amounts of adsorbed polymer so the maximum reduction in surface area that could be produced in this case is not known. However Burford *et al* (1964) showed in a similar experiment that at high amounts of adsorbed PVA (20g/100g) the nitrogen surface area of calcium Wyoming bentonite was reduced from 40 m^2/g to less than 1 m^2/g.

It was suggested by Burford *et al* that on drying the adsorbed PVA formed an encapsulating film around groups or domains of clay crystals and so reduced the access of nitrogen molecules into the interior surfaces of the micro-aggregates so formed. An alternative explanation that could be considered is that PVA is adsorbed in and blocks the intercrystalline spaces of domains of clay crystals. This would also result in a decreased value of surface area without requiring the formation of micro-aggregates. The two mechanisms are shown diagramatically, below.

(a) encapsulation (b) domain occupation





The encapsulation process should result in a progressive decrease in the values of surface area with increasing amounts of adsorbed PVA, as more and more micro-aggregates are formed and as the size of the micro-aggregates increases. On the other hand domain occupation would result in a decrease in surface area to a minimum value corresponding to the sum of the external surfaces of the individual domains. This minimum value would remain relatively constant with increasing amounts of adsorbed PVA provided that no micro-aggregates were formed.

The process of encapsulation provides a satisfactory explanation for the very low surface area of Wyoming bentonite - PVA complexes obtained by Burford et al (1964) and also for the reduced surface areas of the Urrbrae B clay samples used in these experiments. It should be remembered, however, that a combination of both the encapsulation and domain occupation processes could also account for very low values of surface areas. Thus it is suggested that for dispersed clay systems this is possibly the more reasonable explanation, especially since it has been shown that PVA can penetrate partly the interlamellar spaces of calcium montmorillonite (Greenland, 1963).

4.1.2 Surface area of soil aggregate - PVA complexes

The surface area of Urrbrae B aggregates containing PVA is also considerably less than that of the untreated aggregates. In Figure 16 it can be seen that the surface area of aggregates is reduced to a minimum value which is considerably higher than that observed by Burford et al (1964) for dispersed clay suspensions. This difference is probably due to the fact that in the case of PVA adsorption on aggregates the polymer molecules enter a fixed structural environment and the particle surfaces are not as accessible for adsorption as in the case of dispersed clay systems. Thus the reduction in surface area must be viewed in terms of the existing arrangement of soil particles.

In Chapter III and Figure 12 a simple model for the structure of soil aggregates has been proposed. It is considered that PVA molecules diffuse through the larger pores of aggregates and strengthen them by forming links between the domains of clay crystals which are located along the surfaces of the large pores.

Small pores, such as occur between domains or where there are points of close approach between larger structural units, would become blocked with PVA as the extended polymer molecules in solution would have only a limited freedom of movement within such a fixed structural environment. Thus PVA adsorbed within soil aggregates probably forms a semi-continuous film along the larger pores with smaller amounts of polymer penetrating for short distances into the finer pores. This is domain occupation as shown in (b) of the previous diagram.

Further support for the mechanism of domain occupation can be obtained from considerations of the area occupied by the adsorbed PVA molecules. On the basis that PVA is adsorbed on to clay particles in a layer approximately 10Å deep (Greenland, 1963) it can be calculated that 1 mg. of PVA occupies approximately 1 m^2 of surface. Thus in the case of aggregates containing 28.4 mg PVA/g a reduction in surface area of about 28 m^2/g might be expected if the PVA was located in and blocked small pores to nitrogen adsorption. This figure is close to the observed reduction of 32 m^2/g and supports the domain occupation hypothesis.

At lower amounts of adsorbed PVA the relation between domain occupation and the reduction in surface area is not as consistent e.g. the first 0.5 g of PVA adsorbed per 100g of aggregates reduced the surface area by 12 m^2/g, while increasing the amount of PVA adsorbed from 2.0 to 2.5 g/100 g produced a further decrease in area of only 4 m^2/g. Above an amount of 2.5 g PVA/100 g there was little further reduction in area. However this is readily understood when it is considered that the first small amounts of PVA adsorbed are located on the periphery of large pores and so are able to block effectively more of the small pores, along the large pore walls, than do subsequent polymer molecules diffusing into areas already occupied by PVA. Thus the total surface area approaches a minimum value which depends on the accessibility of small pores for PVA diffusion and adsorption.

The physical state of the adsorbent also affects the reduction of the surface area e.g. when approximately 3g of GM-14 is adsorbed by 100g of dispersed clay, the surface area of the core prepared from this material was reduced from 124.3 to 102.7 m^2/g (a reduction of 17.5%) while the same amount of polymer adsorbed on to Urrbrae B aggregates reduced the area from 89 to 57 m^2/g (a reduction of 36%).

The difference can be ascribed to the accessibility of particle surfaces for adsorption of PVA. In soil aggregates the pores can become blocked with adsorbed PVA and so relatively large decreases in surface area are obtained with small amounts of polymer. In clay suspensions, however, the chance of cross-linking between particles is considerably less than within the fixed structure of aggregates. Thus with material prepared from clay suspensions there is probably a considerable proportion of the PVA collapsed on to particle surfaces (where it does not affect the value of N_2 surface area) rather than cross-linking particles into aggregates which have lower values of surface area.

The adsorption conditions used in treating soil aggregates were also found to affect the results obtained. For example the introduction of 0.54% GM-14 into aggregates from a 0.11% polymer solution over a period of 3 weeks reduced the surface area by 1.5 m^2/g while the same amount of GM-14 introduced in 1 day from a 1.1% solution reduced the area by 13.3 m^2/g. With a long term - low concentration adsorption it would be expected that PVA is distributed throughout a greater number of pores than in the short term - high concentration adsorption and this probably results in less blocking of small pores. Also on drying there would be less chance of forming a continuous film of polymer when the PVA is spread over a larger surface area and hence there would be less chance of excluding nitrogen from many of the pores.

4.2. Pore Size Distribution

To investigate the reduction in surface area further, complete adsorption-desorption isotherms for nitrogen adsorption were determined. From this it was hoped to gain information on the size of the soil pores that were rendered inaccessible to nitrogen molecules, and hence to be able to define the location of adsorbed PVA more precisely.

The isotherms for aggregates having no treatment, 0.57 g GM-14/100 g and 3.55 g GL-05/100 g are shown in Figure 17. These particular levels of polymer treatment were chosen to obtain information of the pore distribution under conditions corresponding to a rapid decrease in surface area (0.57% PVA) and the maximum decrease in surface area (3.55% PVA) as indicated in the preceding Section.

The hysteresis loops are typical of adsorbents having relatively large pores in comparison with the molecular diameter of the adsorbed molecules. The persistence of a small amount of hysteresis below a relative pressure of 0.4 has been observed by others (Brooks, 1955; Aylmore & Quirk, 1962) and although this phenomenon is not understood clearly, Brooks considers that for montmorillonite it is due to the presence of adsorbed water resulting in structural instability of the clay particles. The adsorbed water was thought

NITROGEN ADSORPTION-DESORPTION ISOTHERMS
FOR URRBRAE B AGGREGATES

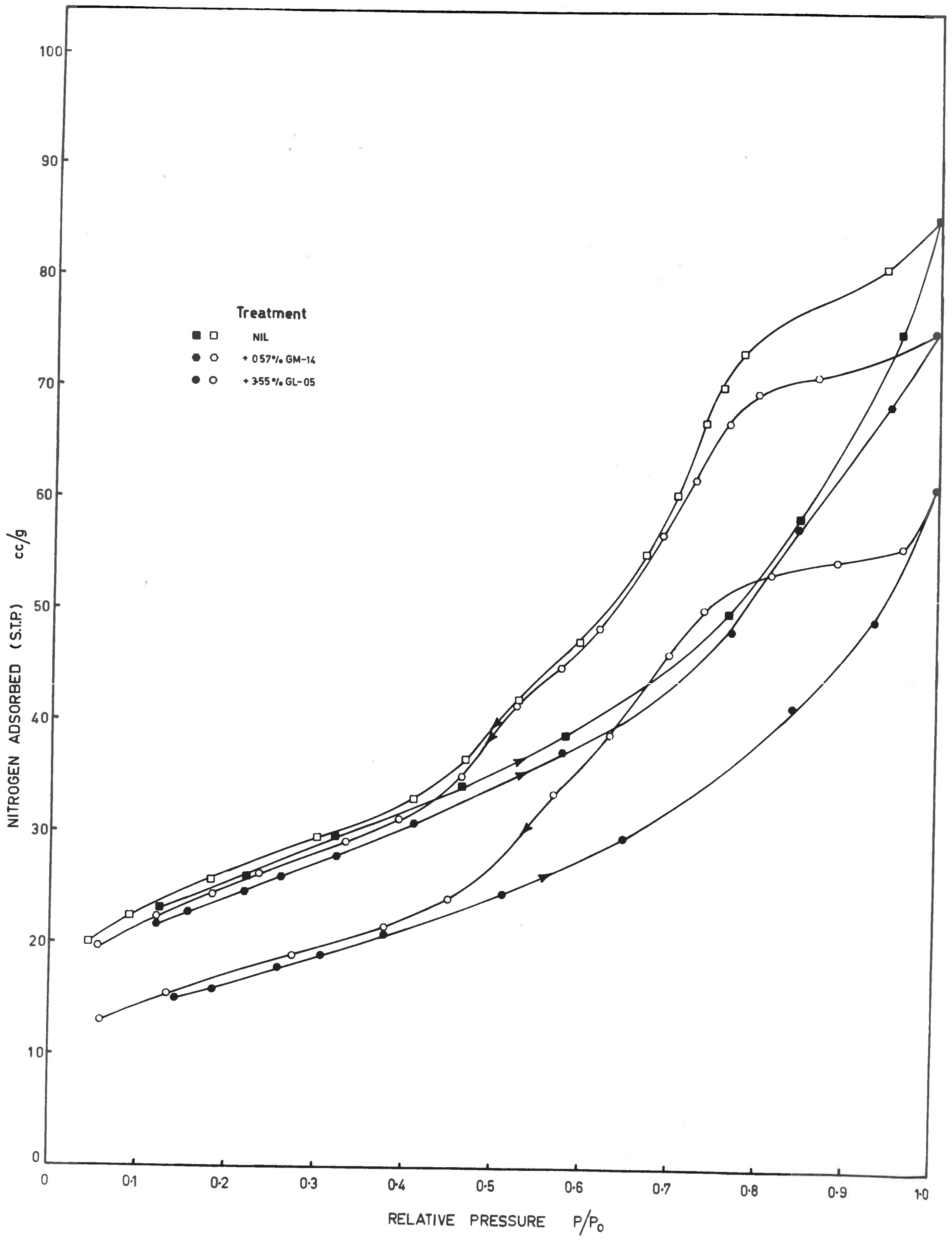


Figure 17.

THE PORE VOLUME DISTRIBUTION OF URRBRAE B AGGREGATES

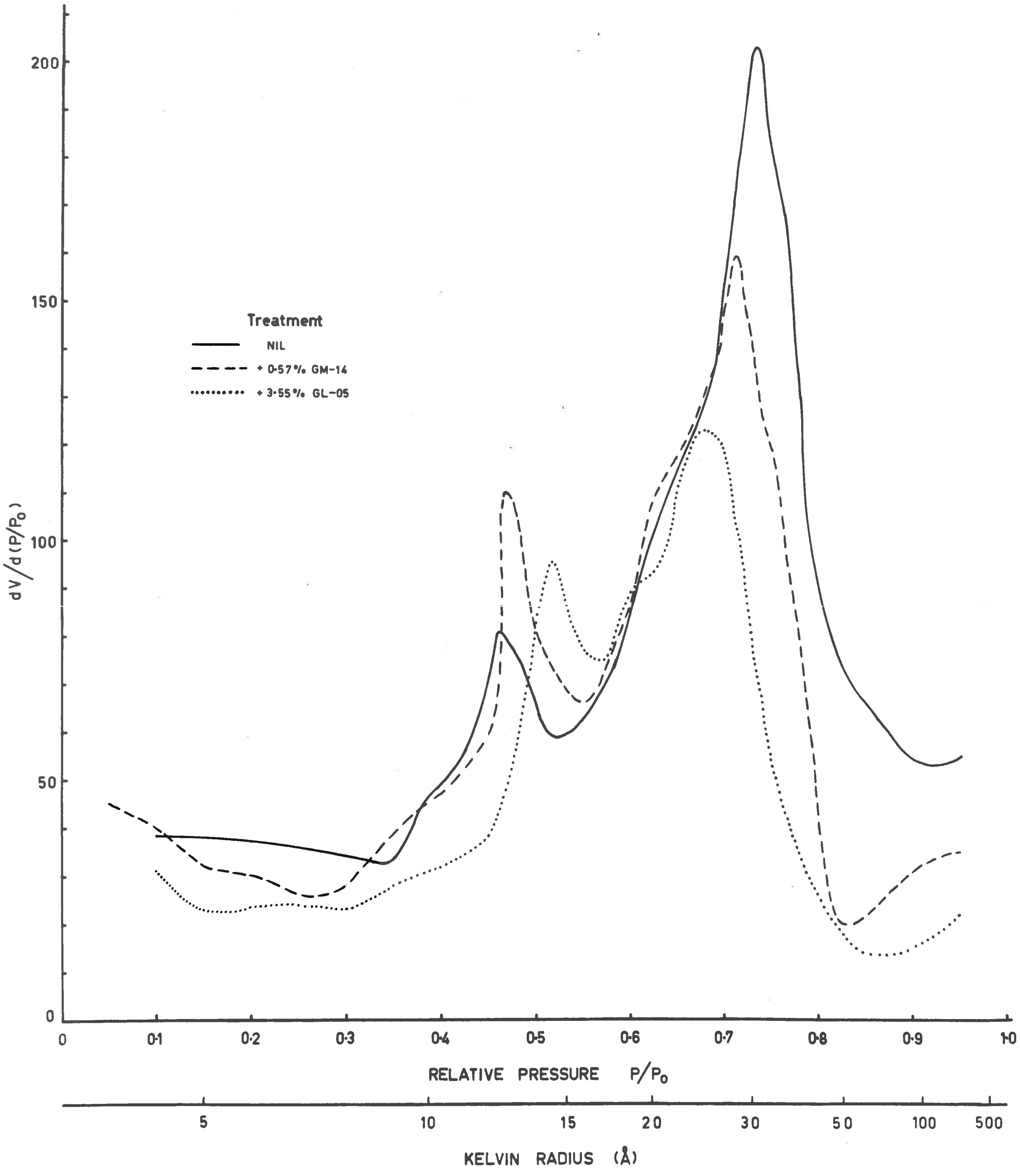


Figure 18.

to prop apart the lamellae of expanding lattice type clay minerals, or if the same reasoning can be applied in this case, prop apart individual crystals, and so augment the nitrogen adsorption capacity on the desorption branch of the isotherms.

The most striking feature of the isotherms in Figure 17 is the reduction in pore volume from 85.5 cc nitrogen (S.T.P.) per gram for the untreated aggregates to 75.3 cc/g and 61.4 cc/g for aggregates containing 0.57% GM-14 and 3.55% GL-05, respectively.

The changes in pore volume and surface area are summarised in Table 8.

Table 8

Pore Volumes and Surface Areas of PVA Treated Urrbrae B Aggregates

Treatment	Pore Volume		Surface Area m^2/g
	cc N_2(S.T.P.)/g	cc liquid N_2/g	
Nil	85.5	13.2×10^{-2}	89.9
0.57% GM-14	75.3	11.7×10^{-2}	78.5
3.55% GL-05	61.4	9.5×10^{-2}	58.4

The distribution of pores can be illustrated by using a differential plot of the volume adsorbed per gram with respect to the relative vapour pressure against relative pressure i.e. $dV/d(P/P_o)$ against P/P_o. Such plots made from the desorption branches of the isotherms are shown in Figure 18. The equivalent cylindrical radii (r) corresponding to the relative pressures were calculated from the Kelvin equation and are also shown on the absiccs. ×

The differential plots show a number of interesting features viz.

(1) the presence of adsorbed PVA reduces the volume of pores over a wide range of pore sizes.

(2) the large peak in the curves between relative pressures of 0.55 to 0.8 (plate separations of 24 and 50Å) is reduced markedly by PVA treatment.

(3) the centre of the peak is displaced to lower values of relative pressure with increasing amounts of adsorbed PVA.

(4) a second, smaller peak, occurs at approximately 0.5 relative pressure (plate separation of 22Å).

Aylmore & Quirk (1962) studied the pore size distribution of Urrbrae B aggregates and its clay components and concluded that the plate-like clay particles are stacked in an ordered manner into structural units termed domains. They also reasoned that the large peak in the pore size distribution curve for the < 2 µ clay fraction represented the intercrystalline spacings (28Å) within domains and that there were relatively few large inter-domainal pores. Thus it appears that PVA is adsorbed in the soil aggregates in such a way as to block or seal off a proportion of intercrystalline spaces. The alteration of this class of pores is summarised in Table 9 below.

Table 9

The Effect of PVA on the Pore Size Distribution of Urrbrae B Aggregates

Treatment	Values associated with the principal peak			
	P/P_o	$dV/d(P/P_o)$	Equivalent cylindrical radius (Å)	Crystal separation (Å)
Nil	0.735	204	31.5	40
0.57% GM-14	0.71	160	27.7	36
3.55% GL-05	0.685	123	25.1	33.5

The average crystal separation of 40Å is similar to that observed by Aylmore & Quirk (1962) for Urrbrae B aggregates but is somewhat higher than the 28Å spacing for the separated < 2 µ clay fraction.

The reduction in average crystal separation when PVA is adsorbed indicates that a higher proportion of pores greater than 40Å diameter, are blocked so reducing the average pore size. Inspection of the desorption isotherms shows this to be true as at relative pressures above 0.75 (crystal separation 40Å) the relative differences between the isotherms become more marked. This does not mean that adsorbed PVA is restricted entirely to pores greater than 40Å as extended PVA molecules are capable of penetrating to a limited extent the 9.8Å interlamellar spaces of Ca^{++} montmorillonite (Greenland, 1963). However in the fixed porous structure of aggregates, as compared with dispersed clay suspensions, it does seem likely that the movement of extended PVA molecules into fine pores would be restricted severely because of the greater opportunity of adsorption for extended molecules confined between closely separated adsorbent surfaces.

The second peak in the pore size distribution curves represents crystal separations of about 22Å. A well defined peak in this region was not observed by Aylmore & Quirk (1962) for Urrbrae B aggregates but this may have been due to a lack of sufficient observations in this region of relative pressure. In the present work a definite inflection can be seen in the desorption isotherms in the vicinity of a relative pressure of 0.5 but due to the few experimental determinations made at this particular part of the isotherm no significance has been attached to the relative heights and positions of the peaks obtained in the differentiated curves.

The presence of the two groups of pores indicates the presence of two highly organised particle structures. However no particular physical interpretation can be attributed to these pores from the evidence presented in this work, but they are probably associated with the domain structures described by Aylmore & Quirk (1962).

Inspection of the data in Table 8 shows that the surface areas of aggregates treated with PVA are reduced in approximately the same proportions as the reduction in pore volume, particularly with the lowest polymer treatment. This confirms the previous suggestion that PVA reduces the surface area of aggregates by simply filling small pores located in domains along the large pore walls.

Any theory of the location of the adsorbed PVA must account for the reduction in volume of not only the major group of 40Å pores but also for the general reduction of all pore sizes between 5Å and greater than 100Å, as shown in Figure 18. It has been suggested that pores of about 40Å can readily become blocked with PVA but this does not account for the reduced volume of pores of up to and greater than 100Å.

It should be remembered that the largest pore sizes that have been described by these nitrogen adsorption studies are only of the order of 100-200Å and pores of this size are small compared with those that can be demonstrated by other means e.g. Quirk & Panabokke (1962), using benzene and 1,1,2,2 - tetrachlorethane adsorptions, showed that natural Urrbrae B aggregates have at least two other major groups of pores with average Kelvin radii of approximately 300Å and 5000Å. It is probably into these large pores that PVA molecules first diffuse, and from there proceed to block smaller pores. Without information of the changes, if any, in the large pores it is not possible to place an upper limit on the size of pore that becomes blocked with PVA. All that can be said from the differentiated curves in Figure 18 is that the difference in pore volumes below a relative pressure of 0.65 (plate separation 30Å) ~~are~~ is not as great as for the pores above 30Å. This probably indicates that only relatively small amounts of PVA are able to penetrate into the regions where most of the 30Å pores are located i.e. into the regions of clay domains which are not adjacent to large pores.

It is also interesting to compare the reductions in surface area and pore volume of aggregates containing PVA with the reduced amounts of polymer adsorption observed for aggregates as compared with soil suspensions.

In Chapter II it was noted that the maximum amount of the smallest molecular weight PVA, (GL-05), adsorbed by Urrbrae B aggregates is only about 30% of that observed with suspensions of finely ground Urrbrae B soil. This is in good agreement with the percentage reductions of 35% and 28%

for the surface area and pore volume of aggregates containing 3.55 g GL-05/100 g. The comparisons further emphasise the inaccessibility of a large portion of the particle surfaces within aggregates for polymer adsorption.

5. Summary

It has been observed in the previous two sections that the presence of adsorbed PVA can reduce markedly the nitrogen surface areas and pore volumes of soil aggregates and also more finely divided clay material.

The reduction in surface area of clay-PVA complexes formed from clay suspensions has been attributed to the formation of an encapsulating film of PVA around groups of the clay particles together with occupation of the intercrystalline spaces within domains by PVA. A large proportion of the crystal surfaces are then unavailable for nitrogen adsorption. In the case of natural aggregates containing PVA it was thought unlikely that the polymer could form continuous films around groups of particles in the same manner as with the clay suspensions. The freedom of movement of extended polymer molecules in the fixed porous structure of aggregates is considerably reduced because of the greater opportunities for the polymer to come into contact with and be adsorbed by the solid particles. Thus it has been proposed that the reduced surface areas and pore volumes are a result of PVA blocking small pores associated with domains that line the walls of the large pores.

It was not possible to distinguish precisely between "large" and "small" pores but it is thought that PVA may be able to block pores with plate separations of the order of 100Å. More detailed descriptions of the pore volume distributions in the region of relative pressures of greater than 0.9 would be necessary to determine the size of the largest pores which are blocked by PVA adsorption. Use of non-polar liquids such as benzene or tetrachlorethane in conjunction with a suction plate and pressure membrane apparatus, might be satisfactory in this respect.

The volume of pores with plate separations of less than about 30Å were not reduced to the same extent as larger pores (30 - 100Å), so it was concluded that relatively little of the PVA could penetrate into regions where the bulk of pores of this size are located i.e. into domains of clay particles that are not connected directly with large pores.

It was shown that the surface areas and pore volumes of aggregates are reduced, with increasing amounts of adsorbed PVA, to values of approximately 70% of those for untreated aggregates. Amounts of adsorbed PVA above about 2.5 g/100 g did not result in further decreases in surface area, indicating that the major reduction in area is associated with the blocking of small pores, after which further amounts of PVA gradually accumulate in the larger pores where the effect on surface area is not as noticeable.

The extent to which PVA can reduce surface area values depends on the conditions in which it is adsorbed. Slow adsorption from a dilute solution apparently results in an even distribution of PVA throughout the aggregates and with less blocking of pores. The rapid adsorption of a similar amount of PVA results in more pores being blocked and hence different values of surface area may be obtained depending on the adsorption conditions.

The overall picture of PVA adsorption in aggregates obtained from this work is that the polymer molecules diffuse into the largest pores and link together the domains of clay particles that are located along the walls of the large pores. In doing so the PVA penetrates partly into the inter-domainal spaces and other pores and, depending on the sizes of the pores, it may or may not block them. On drying, the adsorbed PVA forms a layer which lines the surfaces of the large pores. The layer is probably discontinuous in those regions where the inter-particle distances are too great to be bridged by PVA molecules.

CHAPTER VI

THE MECHANICAL STRENGTH OF SOIL-PVA COMPLEXES

1. Introduction

It was pointed out in Chapter I of this thesis that some confusion has arisen in the measurements of the mechanical strength of soils treated with organic polymers. On one hand it was claimed that the tensile strength of soil-polymer complexes was considerably lower than that of the untreated soil and that organic polymers were thus useful in reducing the strength of crusts formed at the surface of soils (Jamison, 1954; Allison, 1956; Allison & Moore, 1956; Pugh, Vomocil & Nielsen, 1960). On the other hand Martinson & Olmstead (1949), Hemrighausen (1957), Williams (1959), Modina (1962) and Quirk & Panabokke (1962) found that organic materials increased the strength of both artificially prepared and natural soil aggregates. It was shown that the results of the former workers were a result of their method of sample preparation and that the interpretation of the decreased strengths of soil-polymer complexes obtained was incorrect.

The type of test applied to the soil samples is important if the results are to be interpreted in terms of the strength of soil-polymer linkages. Unconfined compression tests involve both friction and cohesive forces and hence their interpretation is not easy. Tensile strength measurements, which as the name suggests, involve the pulling apart of interparticle bonds, have a somewhat simpler interpretation, although direct tensile strength measurements, in which a sample supported at both ends is loaded to failure at the centre, involve some compaction as well as tensile forces. The test applied with the apparatus described by Richards (1953) that has been used for determining "modulus of rupture" values is an example of this type of test. The occurrence of forces of compression can be overcome by pulling the sample apart from both ends, but this is not always convenient, particularly in respect to attachment of the apparatus at the ends of the samples. Recently an indirect tensile strength method, known as the Brazilian Core Test (Carneira & Barcellos, 1953)has proved to be very satisfactory for even such weak materials as natural soils (Ingles & Frydman, 1963).

The Brazilian Test consists of a load applied radially to a cylindrical specimen until failure occurs. The dimensions and surface condition of the specimen are not critical. Failure is initiated in the centre of the core and extends to the circumference, producing a well defined cleavage. The tensile strength is then obtained by the relation,

$$6 = \frac{2P}{\pi DL}$$

where σ is the tensile strength, P is the load applied and D and L the diameter and length of the specimen.

Kirkham, De Boodt & De Leenheer (1958) used this method for comparing the tensile strengths of natural soil cores (6.9 cm diameter) taken from soils under different crop rotations. Although a high coefficient of variation was obtained they were able to show a good correlation between the tensile strength, crop yields and the bulk density of the soil, as well as certain other physical parameters.

Ingles & Frydman (1963) used artificial cores of sand of kaolin, stabilised with Portland cement. Included in their study were cores of different dimensions and containing different levels of water. They found the method to be sensitive and that variability was low when replicate but not duplicate samples were used.

Many other variables are involved in the preparation and testing of soil samples. Of particular importance are the homogeneity, the bulk density and the water content of the samples. Samples collected in the field in the form of cores suffer the disadvantage of inhomogeneity and variation of bulk density, particularly in the surface horizons. This probably is the reason for the high variability of tests obtained by Kirkham <u>et al</u>. On the other hand Williams (1959) and Quirk & Panabokke (1962) observed variations of only approximately 5% of the mean values for natural soil aggregates tested with an Atterberg balance apparatus. Quirk & Panabokke also determined the change in cohesive strength of aggregates over a range of water contents and found that the strengths decreased rapidly as the water contents increased. Aggregates from a permanent pasture remained stronger than aggregates from a continuous cultivation rotation, over the entire range of water contents used.

Artificial soil samples have the advantage that many of the variables can be controlled by use of suitable preparative methods. They are particularly useful for determining the effects of stabilising additives on the strength of soil although it must be kept in mind that the homogeneity of mixing obtained in the laboratory is usually much better than that obtained under field conditions. With the addition of organic polymers care should also be taken to use the additive in the form of a solution rather than mixing the components dry and subsequently adding water. This latter procedure appears to be the accepted method for the use of Portland cement or lime but is unlikely to produce the best results with organic materials which require a large excess of water to dissolve and to develop their solution characteristics.

2. Materials and methods of sample preparation

Finely ground Urrbrae B soil and the GL-05, GM-14, GH-20 and NM-14 polymers were used.

The cores were made by placing 7.5 g of finely ground Urrbrae B in tubes containing 20 cc of PVA solution of the required concentration. The tubes were placed on an end-over-end shaker for six days and then the soil was recovered by filtration in a Buchner funnel. The wet samples were then allowed to equilibrate at 96% R.H. in a desiccator over a saturated K_2SO_4 solution. At this stage the soil preparations had a water content of approximately 20 cc/100 g. Ten samples each equivalent to 0.500 g oven dry material, were taken from each preparation and compressed from both ends in a cylindrical mould to a constant volume, so that the cores had a final bulk density of 1.65 g/cc. The volume to which the cores were compressed was calculated to coincide with 100% saturation of the pore space with water, and some difficulties were encountered in obtaining cores of uniform properties because of differences in the equilibrium water contents (96% R.H.) of the soil - PVA preparations. Cores not conforming to the required uniform density and 100% saturation of the pore space were adjusted to the required conditions by further wetting or drying, followed by remoulding. Finally the cores were air dried, placed in an oven at 70°C overnight, and then stored over P_2O_5.

In one experiment a different method was used in that PVA was adsorbed on to 0.5 g samples in weighed adsorption tubes. The water content of the samples during drying could then be followed quite accurately by removing them at daily intervals and weighing. This method also removed the difficulty of accurately weighing out wet subsamples from a bulk preparation. However similar difficulties in obtaining the correct water content were encountered as before, because the individual samples did not all dry at the same rate in the desiccator. Unless only relatively few samples were being prepared, the method of daily weighings became tedious and time consuming. A possible solution to this problem would be to use a mould containing a porous steel base through which water from the wet sample can be forced during compression.

The cores made from Urrbrae B shrink during drying and higher bulk densities are obtained for the final samples. In spite of the difficulties of preparation discussed above the final bulk densities of the cores fell within the range of 1.99 to 2.05 g/cc as compared with their original density of 1.65 g/cc.

The PVA content of the cores was obtained by electrolytic carbon combustion as previously described.

3. <u>Testing Methods</u>

The Brazilian method for determining the indirect tensile strength (I.T.S.) was employed. A Wykeham-Farance tri-axial compression machine was used to apply the load to soil cores (Figure 19). A proving ring (maximum load of 200 lbs) with

THE TENSILE STRENGTH OF SOIL CORES

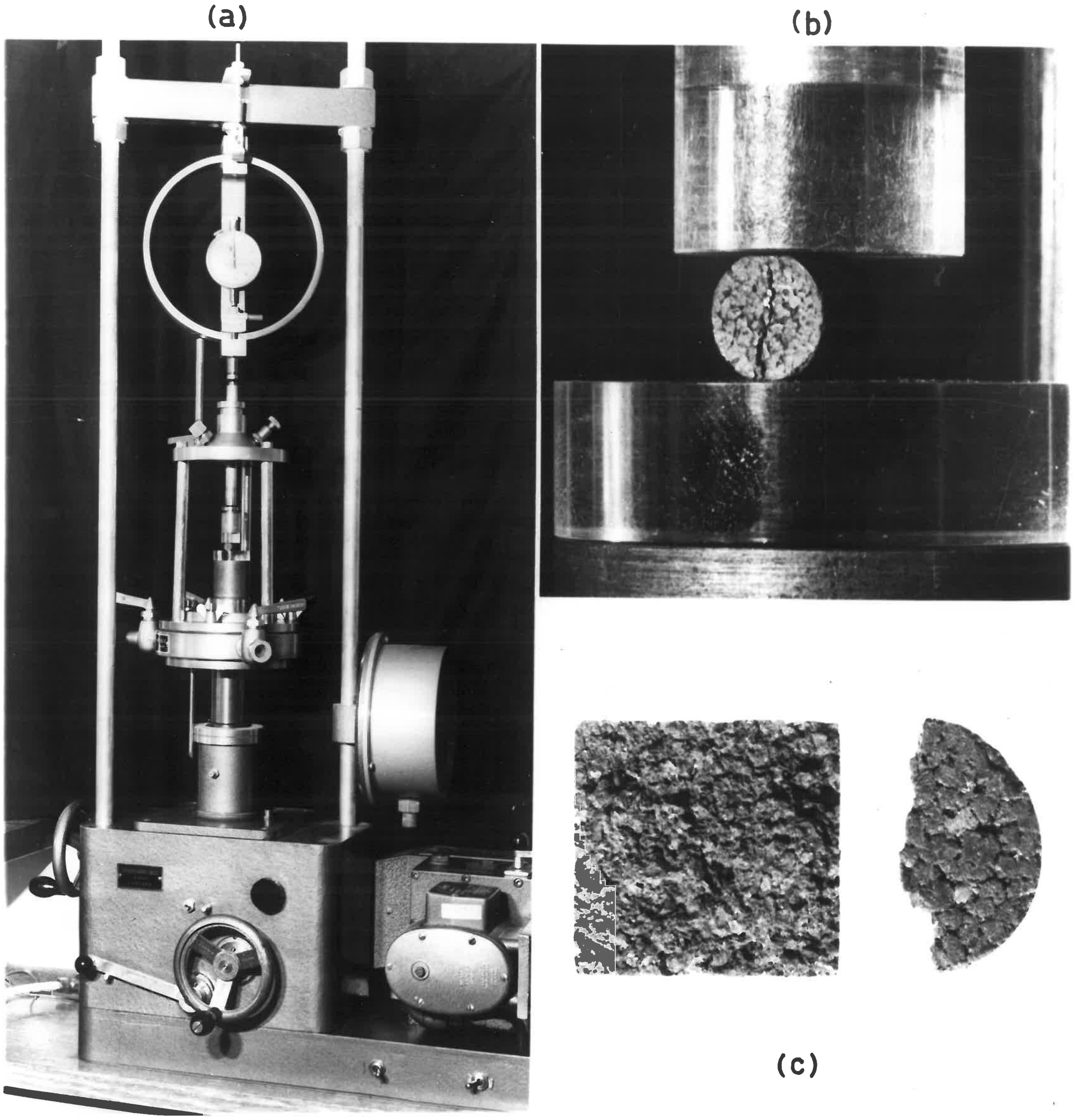
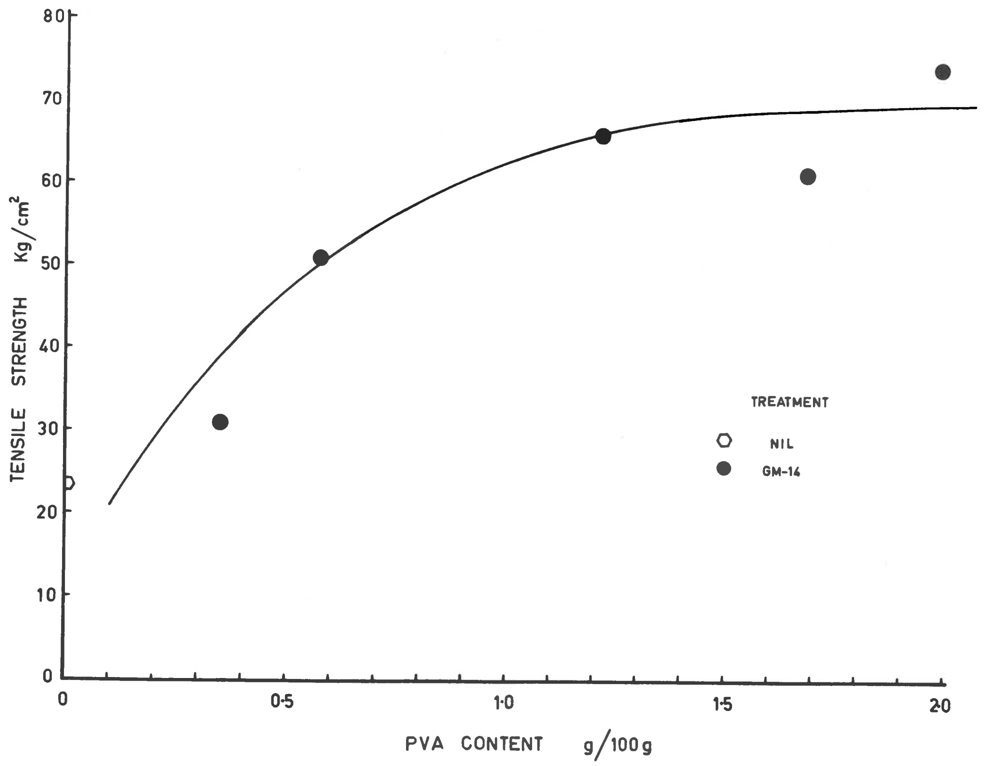


Figure 19.

THE TENSILE STRENGTH OF CORES OF URRBRAE B - PVA COMPLEXES

Figure 20.



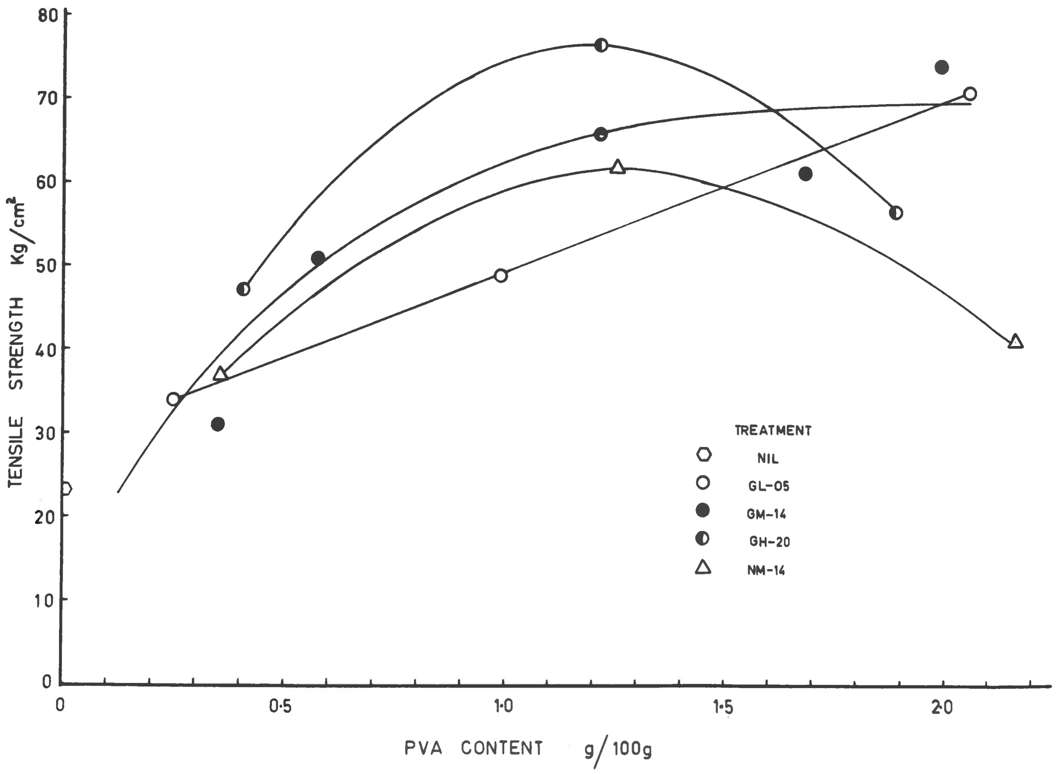


Figure 21.

a strain gauge attached was used to follow the loading to the point of failure and the strain was applied at a rate of 0.012 inches per minute.

Failure of the cores was sharp except in the experiment where the cores used were too wet to show brittle fracture, although even these commenced failure by developing a crack at the centre of the cores.

The water content of the cores was not controlled during the few minutes in which it took to test each sample. A check was made by weighing a number of the cores immediately before and after testing and it was found that the water contents rarely changed by more than 1%. The greatest change was observed with the very dry and the very wet cores, and this was not considered great enough to warrant introducing any special precautionary measures.

4. Results and Discussion

4.1. The effect of PVA on the indirect tensile strength (I.T.S.) of soil cores

In Figure 20 are shown the values of I.T.S. for cores prepared from puddled soil material and containing various amounts of GM-14. The cores had a water content of between 0 and 1% and each point is the average of ten determinations.

It can be seen that there is an increase in strength from 23 Kg/cm^2 for the untreated cores to 74 Kg/cm^2 for the cores containing 2 g GM-14/100 g of soil. There is a maximum effectiveness of PVA occurring at a level of approximately 1.5 g GM-14 per 100 g of soil.

The increase in strength is due to an increase in particle-polymer-particle linkages although a maximum level of effectiveness is reached with amounts of PVA considerably below the maximum level of adsorption observed for the fully dispersed soil. The conditions of dispersion used in this instance were not particularly severe and the finely ground soil material probably retained a high proportion of microaggregates throughout the preparation. Also it is likely that the polymer caused some clumping of fine particles. The overall result is that the surface area available for adsorption was much less than could have been achieved with complete dispersion and the available surface became saturated with PVA at a level of 1.5 to 2 g per 100 g of soil.

One important factor that should be remembered in interpreting these results is that if complete surface coverage of the soil particles were achieved then a situation could occur in which there were no polymer linkages between adjacent soil particles. This is demonstrated in the model of flocculation presented by La Mer and Healy (1963) and was discussed in detail in Chapter I. The likelihood of this occurring in practice is perhaps not very great as surface saturation with polymer molecules could still be achieved with a large number of inter-particle bonds. However it does permit the prediction of a maximum number of soil-polymer-soil linkages as evidenced by the foregoing strength measurements. Also it is possible that with larger amounts of adsorbed PVA a decline in strength could occur.

4.2. The effect of molecular weight and molecular structure of PVA on I.T.S.

The effect of various amounts of GL-05 (25,000), GM-14 (70,000), GH-20 (100,000) and NM-14 (64,000) on the I.T.S. of dry cores prepared from puddled soil material are shown in Figure 21. Each value is the average of 10 determinations.

As with the cores treated with GM-14, discussed in the previous section, the strength of cores treated with the other PVA samples increases with the amount of PVA adsorbed. In this case however there are two instances in which the maximum strength of cores is followed by a decline in strength at higher amounts of adsorbed polymer. This occurred with the high molecular weight fraction, GH-20, and the fully hydrolysed, medium molecular weight fraction, NM-14. The occurrence of such a relation was predicted in the previous section on the grounds that as complete surface coverage of the soil particles is achieved so there is less possibility of inter-particle linkages being formed. The maximum increase in strength occurs with approximately 1.25 g PVA/100 g of soil for both polymers, which once again emphasises the similarity of action of these two polymers despite their differences in molecular weight. Adsorption and water-stability experiments also showed that the fully hydrolysed NM-14 polymer, which exists in an aggregated form in solution, behaves in a similar manner to the partially acetylated PVA of higher molecular weight.

Comparing the G-series PVA's it can be seen that the low molecular weight, GL-05, is less effective than GM-14 and GH-20 with similar amounts of adsorbed polymer although the difference is less at the highest amounts used. The increases in strength obtained with GM-14 and GH-20 are somewhat similar except that the GH-20 reaches a maximum effectiveness at a lower amount of adsorbed polymer than the GM-14. The medium molecular weight PVA is able to penetrate to surfaces inaccessible to the larger GH-20 molecules and so more is required to achieve saturation of the particle surfaces. No maximum in the strength measurements with GL-05 was observed and this is probably due to its better penetration than either the GM-14 or GH-20 molecules. It appears that the maximum strength produced by GL-05 would be a little higher than that of the others, but that this would only be achieved with considerably more of the polymer.

It is not possible to draw fine distinctions between the strengths shown in Figure 21 because of the variability contained within each set of determinations as well as small differences in density between the sets of samples. These variations are summarised in Table 10. The broad differences are however quite clear and meaningful in the terms in which they have been discussed above.

Table 10

The Tensile Strengths of Urrbrae B - PVA Complexes

PVA Treatment (g/100 g)	Av. Tensile Strength (Kg/cm^2)	Standard Error (10 determinations)	Bulk Density (g/cc)
Nil	23.20	1.39	2.03
GL-05			
0.248	33.83	1.43	2.02
0.991	48.91	1.79	2.05
2.064	71.01	1.82	2.04
GM-14			
0.347	30.86	2.60	1.99
0.576	50.89	1.93	2.04
1.218	65.94	1.91	2.03
1.685	61.22	2.53	2.04
1.993	74.10	2.55	2.05
GM-20			
0.406	47.07	2.19	2.02
1.218	76.58	2.00	2.05
1.886	56.63	4.57	2.04
NM-14			
0.360	36.75	1.49	2.04
1.261	61.92	2.60	2.05
2.173	41.27	1.37	1.99

4.3 The Effect of Water Content on the I.T.S. of cores

The tensile strengths of cores containing 2 g GM-14/100 g soil were compared with untreated cores, at various water contents. Ten cores were used for each treatment and the results are shown in Figures 22 a and b, and in Table 11.

From Figure 22a it can be seen that the tensile strength of cores diminishes rapidly as the water content of the cores increases. The cores having polymer treatment retain a higher strength than the untreated cores but the difference becomes much less as the water content increases.

Some of the values for the cohesive strength of natural Urrbrae B aggregates obtained by Panabokke (1956) have been recalculated in terms of their I.T.S. values. He used an Atterberg balance to determine the cohesive strength of aggregates with dimensions of approximately 1 cm^3. His strength measurements may be converted to comparable I.T.S. values by multiplying the cohesive strength by a factor of $\frac{2}{\pi}$ and converting the units of $dynes/cm^2$ to Kg/cm^2 e.g. air-dry Urrbrae B aggregates had a cohesive strength of 9.20×10^6 $dynes/cm^2$ i.e. an I.T.S. of approximately 6.0 Kg/cm^2. They are shown in Figure 22a for comparison with the artificial cores and it can be seen that they have a lower order of strength than the artificially prepared cores. These differences would be due partly to differences in apparent density, 1.78 g/cc for the aggregates compared with

THE EFFECT OF WATER ON TENSILE STRENGTH OF URRBRAE B-PVA COMPLEXES

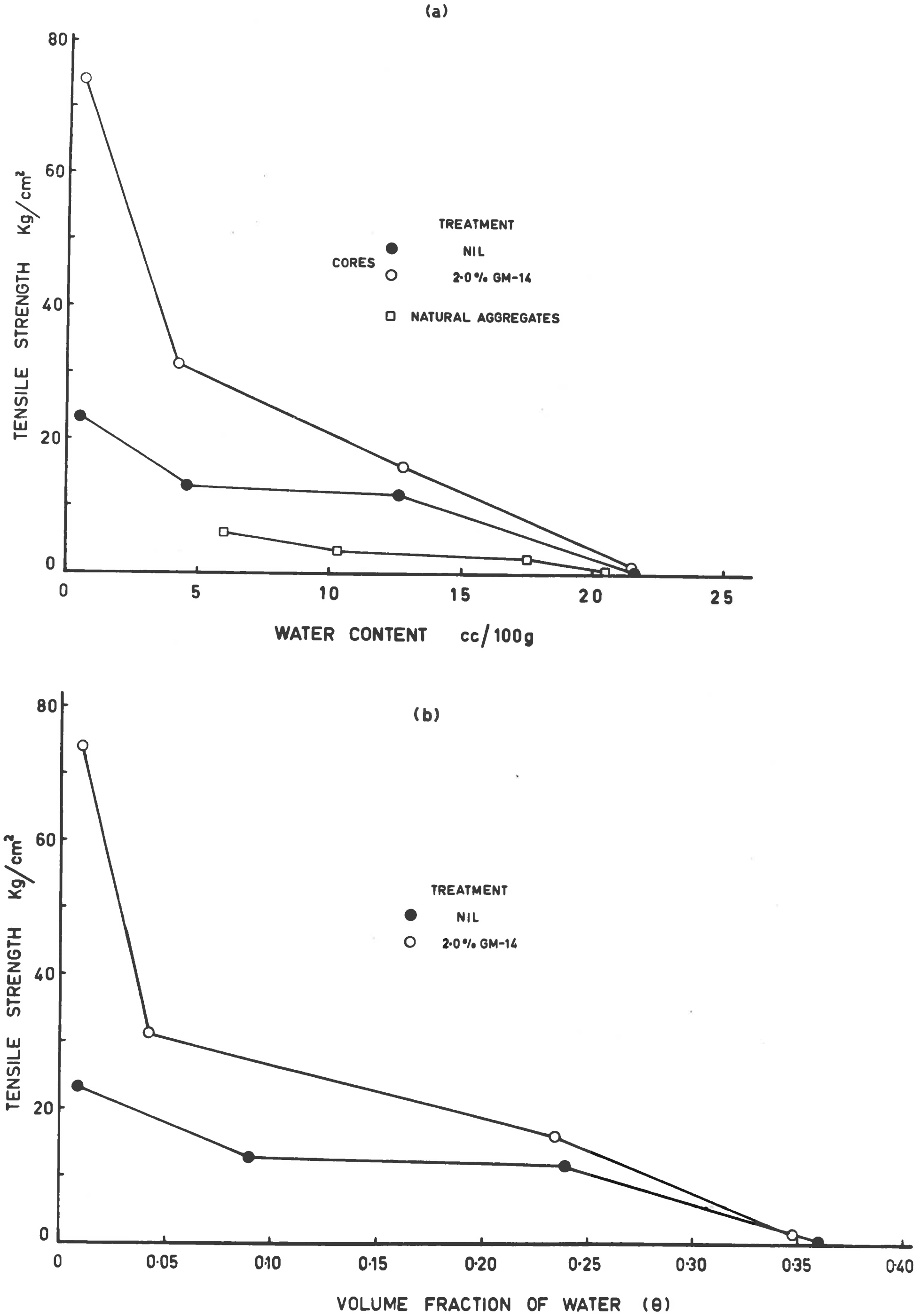


Figure 22.

2.03 g/cc for the cores, and partly to the more granular structure of the natural aggregates.

The water content in itself does not have any particular significance but rather it is the fraction of a cleavage interface occupied by water that is important. The strength measurements can then be interpreted in terms of the relative amounts of water and solid interface that resist cleavage by mechanical means.

In Figure 22b the results have been replotted to show the tensile strength as a function of Θ the percentage volume fraction of water. The values of Θ were calculated from the average volume of the wet cores and the water content. At values of Θ above about 35% it was not possible to obtain accurate readings of the point of failure. This was not due to plastic flow of the cores but rather to the insensitivity of the proving ring used.

It can be seen that increasing the value of Θ from 0 to 10 results in a decrease in tensile strength of about 50% of the dry core values, for both the treated and untreated samples. This shows that the tensile strength is very much dependent on the presence of films of water between the soil particles. The water reduces the cohesion between soil particles by causing them to swell apart and also acts as a lubricant to reduce friction.

The fact that the cores containing PVA lose their

Table 11

The Tensile Strength of Urrbrae B Cores

PVA	Water Content (cc/100 g)	Volume Fraction of H_2O (θ)	Percentage Saturation	Tensile Strength (Kg/cm^2)	Standard Error (10 determinations)
Nil	0.5	0.92	4.0	23.20	1.39
	4.57	9.01	32.9	12.93	0.92
	12.62	23.89	79.4	11.65	0.69
	21.61	35.96	92.0	0.37	0.11
2% GM-14	0.5	0.90	4.0	74.10	2.55
	4.19	8.19	31.8	31.19	1.66
	12.73	23.47	79.9	16.06	0.77
	21.47	34.73	90.4	1.31	0.09

Table 12

The pF-Water Content Relations And Apparent Densities of Urrbrae B Cores

Treatment pF	Water Content cc/100 g		Apparent Density cc/g	
	Nil	2.0% GM-14	Nil	2.0% GM-14
1.00	26.02	23.85	-	-
2.00	22.76	21.79	-	-
2.85	21.61	21.47	1.66	1.65
4.65	12.62	12.73	1.90	1.90
5.97	4.57	4.19	1.97	2.00
6.8	0.5	0.5	2.03	2.05

strength in almost the same proportions as the untreated cores with increasing water content demonstrated that the polymer films become hydrated at quite low water contents. This was also noted in the study of the swelling of Urrbrae B - PVA complexes in Chapter III.

Also shown in Table 11 are the values for the percentage saturation of the cores at the water content used. These values range up to 92% saturation and show the similarity between the two sets of cores. The pF-water content relations and apparent densities of the cores, shown in Table 12, further demonstrate the similar physical structures of the treated and untreated cores. Thus the differences in the tensile strengths of the cores can be attributed almost entirely to the presence or absence of PVA and not to structural differences of the cores.

5. Summary

These experiments were carried out in such a way that the PVA bonding between soil particles was not destroyed in the preparative stages of the samples. An indirect tensile strength (I.T.S.) measurement was used to describe the strength of soil cores, as this measurement is not complicated by other forces of compaction and shearing. The values obtained then give a good indication of the force necessary to break polymer bonds between soil particles.

It has been shown that interparticle bonding with polymer molecules can cause considerable increases in the tensile strength of a soil. The strength increases up to a maximum with increasing amounts of adsorbed polymer, after which the presence of more polymer results in a decrease in strength. This has been explained in terms of the balance between the number of interparticle linkages and the degree of coverage of the particle surfaces with adsorbed polymer.

It has been shown that at equal amounts of adsorbed polymer the PVA with the highest molecular weight is generally more effective in increasing the strength of soil cores. However there was some indication that higher values of tensile strength may be obtained with low molecular weight PVA due to its greater ability to penetrate into surfaces that are physically inaccessible to large molecules.

The medium molecular weight, fully acetylated PVA (NM-14) behaved more like the high molecular weight fraction of the partially acetylated G-series polymers rather than its medium molecular weight GM-14, counterpart. This was due to NM-14 having an aggregated form in solution and it is apparent that the polymer-polymer bonds, by which the polymer aggregates form, persist in the adsorbed state.

The large increase in strength observed with dry cores treated with PVA, rapidly diminished with increasing water contents of the cores, as also did the untreated cores. This decrease was thought to be due to the rapid hydration of adsorbed PVA molecules which then lose their rigidity although they are not desorbed from the soil particle surfaces. The results were discussed in terms of the fraction of water phase present at a plane within the soil cores and the changes in resistance to cleavage due to the presence of a water interface. Water reduces the cohesive forces between soil particles by causing them to swell apart and also aids failure of the cores by its lubricating properties.

The Brazilian core test has proved to be very satisfactory for determining the tensile strength of artificial cores of soil. It can be used with samples having a wide range of mechanical strengths and the sample dimensions are not a critical factor. It should be useful in extending the work of Kirkham _et al_ (1958) using cores of soil taken from the field and hence in obtaining information of the strength of both naturally occurring and artificial cementing agents, under field conditions.

CHAPTER VII

A GENERAL DISCUSSION OF THE INTERACTION OF PVA WITH SOIL AGGREGATES

In the preceding chapters of this thesis a number of aspects of PVA interaction with Urrbrae B aggregates have been studied. In the course of this work a model of the structure of soil aggregates has been evolved which satisfies the observations made of the adsorption of PVA by soil aggregates and its subsequent effects on the physical properties of the aggregates.

The proposed model (Figure 12) consists of a series of structural units, the smallest being groups of clay crystals or domains. These are built up into micro-aggregates which in turn form larger structural units, and so on. Looking at this model in another way an aggregate can be regarded as consisting of a series of pores of varying orders of size and strength. The relatively few large pores are regarded as being the weakest and the most likely sites for the initiation of aggregate breakdown.

This was supported by the pore size distribution data of Aylmore & Quirk (1960) and Quirk & Panabokke (1962). The model also agrees with the observation that when a dry, unstable aggregate is immersed in water it disrupts into many smaller fragments, which may themselves be broken down into smaller units by agitation. The smallest units are the most difficult to disrupt as is evidenced by the difficulties encountered in the complete dispersion of soils into primary particles.

The results of the separate investigation can now be summarised and discussed in terms of this model. PVA was chosen for this work because it is uncharged and this property was expected to aid investigations of the movement of polymers into the negatively charged pores of soil aggregates. Even so adsorption studies showed that the rate of diffusion of PVA into aggregates was very slow; the apparent diffusion coefficient, under the conditions used, being in the order of 10^{-10} cm^2/second. The overall movement of PVA into soil aggregates was found to be controlled largely by the diffusion processes within the aggregates rather than through the film of polymer solution that adheres closely to the surfaces of the aggregates. The diffusion coefficient calculated from the adsorption data can be regarded only as an apparent value because the adsorption of PVA in the soil pores is virtually irreversible and so small pores rapidly become blocked and inaccessible to other molecules in solution.

The movement of PVA into aggregates depends very much on the molecular characteristics of the polymer as well as on the conditions of adsorption. PVA of low molecular weight was able to penetrate into small pores which were inaccessible to larger molecules by virtue of their size. Also the structure of the PVA molecules was of importance as the fully hydrolysed samples (N-series) form micelles, or groups of molecules, in solution and so acted as polymers of higher molecular weight. This intermolecular interaction of the N-series polymers persisted in the adsorbed state as well as in solution.

An experiment in which PVA was introduced into a dry core of the undisturbed soil showed that forces due to the capillary suction of a dry soil can result in a much better penetration of the PVA solution into a core than is possible by diffusion processes alone. This has important practical implications in respect to polymer application in the field, particularly with negatively charged polyelectrolytes which would be expected to have an even slower rate of diffusion into soil aggregates than the uncharged PVA used in these experiments.

The stability of Urrbrae B aggregates to shaking in water was determined by a method in which 2 hours end-over-end shaking was used and the breakdown of aggregates to particles of less than 2 µ size was measured turbidmetrically. It was shown that aggregate stability increased with increasing amounts of adsorbed PVA up to a level above which further additions of PVA produced no further stabilising effect.

The molecular characteristics of the different PVA samples determined the optimum amounts of each required to produce maximum stability. The highest molecular weight PVA was the most effective and was required in the least amount. The N-series polymers produced larger increases in stability than might have been expected from considerations of their molecular weight alone, presumably because of the stronger intermolecular interactions between these polymer molecules.

The conditions of polymer adsorption also have a considerable influence on the resulting water-stability of the aggregates. A better distribution of PVA within the aggregates, and hence a greater stabilising effect, was achieved under conditions of long term adsorption from solutions of low concentration than was achieved with similar amounts of PVA introduced by short term adsorptions from solutions of high concentration.

During the water-stability experiments it was observed that the aggregates containing PVA did not breakdown into smaller particles readily when subjected to rapid wetting from an air-dry state or with shaking in water. The dispersion forces applied, resulted mainly in an abrasion of the aggregate surfaces and breakdown to particles of less than 2 µ size.

The water-stability experiments were extended to follow
the rate of this surface abrasion with time of shaking,
and the following relation was obtained -

$$\log c = \log a + b \log t \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where c is the percentage concentration of $< 2\ \mu$ particles
in suspension, t is the time of shaking and 'a' and 'b' are
constants.

From this relation the breakdown of aggregates with
shaking in water can be separated into two distinct proc-
esses. The intercept value (log a) represents the initial the
breakdown of the aggregates upon immersion in water while
subsequent rate of breakdown (dc/dt) with continued shaking
can be obtained by differentiating equation (1) with respect
to the variables c and t i.e.

$$dc/dt = abt^{(b-1)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

$$= bc/t \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

The values of 'initial state of aggregation' and 'rate
of breakdown' varied with both the amount and the type of
the PVA adsorbed by the aggregates.

The effect of the PVA was to increase the stability
of aggregates to immersion in water and also to reduce the
rate at which the aggregates were abraded. The latter effect
depends not only on PVA binding soil particles together and
making the external surfaces of the aggregates more resis-
tant to abrasion but also on the number of particles in

suspension resulting from the initial immersion of the aggregates in water.

The results of these experiments provided two pieces of information relating to the location of PVA adsorbed within the aggregates. Firstly the constant relation between the amount of breakdown and the time of shaking over periods of 10 hours indicated that PVA was not restricted to a narrow region in the periphery of the aggregates. Rather, the PVA was located in such a way as to prevent failure of the aggregates along the weakest pores that separate the larger structural units of natural aggregates. Secondly, the fact that particles of less than 2 μ size could be abraded from the surface suggested that the PVA was not able to effectively bind these units together as little PVA was able to penetrate into the pores within the domain structures.

The overall results of the water-stability experiments showed that PVA was able to diffuse through the entire aggregates via the largest pores and so strengthen the weakest sites within the aggregates. Once these sites were strengthened further amounts of adsorbed PVA produced little further increase in aggregate stability. The ability of the polymer molecules to diffuse into the smaller pores was determined by their molecular characteristics but it appeared that even the smallest PVA molecules used (M.W. 25,000), were not able to penetrate effectively into the small pores within clay domains.

To determine more precisely the location of adsorbed PVA the surface areas and pore size distributions of aggregates containing PVA were determined, using the method of low temperature nitrogen adsorption. PVA caused a reduction in surface area and pore volume of aggregates to values of between 60 to 70% of those for the untreated aggregates. The first small amounts of PVA adsorbed produced relatively large effects indicating that PVA diffusing into the largest pores was adsorbed there? in, and blocked the entrances of small pores that are associated with clay domains and other small structural units located along the walls of larger pores.

The greatest changes in the pore size distributions occurred with pores of greater than 30-40Å size showing that little PVA penetrated into the domain structures. It appeared that pores in excess of 100-200Å size may also become blocked with PVA due to the markedly reduced freedom of movement of polymer molecules within the fixed porous structure of aggregates as compared with the conditions encountered with dispersed clay suspensions.

Surface area determinations of clay-polymer complexes produced from dispersed Urrbrae B ($< 2\ \mu$) clay suspensions indicated that adsorbed PVA when dried probably forms an encapsulating film around groups of the clay particles. The film is impervious to nitrogen molecules and hence the reduction in surface area could be explained by the unavailability of some surfaces, within the groups of particles, for nitrogen adsorption. However it is thought unlikely that the same type of encapsulation process occurs to any great extent within soil aggregates, but rather that the reduction in surface area is due to PVA filling and blocking small pores i.e. domain occupation. This agrees with the water-stability experiments in which it was thought that PVA probably increases the strength of soil aggregates by forming a polymer lining along the walls of the largest pores.

One important aspect, relating to aggregate stability, that arose out of the nitrogen adsorption studies was the indication of the development of PVA layers that are impermeable to nitrogen molecules. It was thought that such layers may also reduce the access of water to clay surfaces and hence reduce the disruption forces of rapid water entry into aggregates. However the total swelling and also the rate of water vapour adsorption by cores of Urrbrae B ($< 2 \mu$) clay, were relatively unaffected by the presence of PVA. Thus it was concluded that PVA adsorbed on clay surfaces hydrates quite rapidly and so does not affect appreciably the access of water to the clay surfaces within soil aggregates.

Some indication of the strength of the inter-particle bonds was obtained by determining the tensile strength of cores of Urrbrae B - PVA complexes. Dry cores containing PVA showed increases in tensile strength of up to three times that of the untreated cores. The increases in strength varied with the amount as well as the molecular characterisation of the polymer. Introduction of small amounts of water (4 cc/100 g) into the cores resulted in a decrease in the mechanical strength of approximately 50%, and the strength decreased even more at higher water contents. This could not be attributed to desorption of the polymer molecules from the clay surfaces. It appeared that in the dry state PVA could form quite strong bonds, but on hydration the polymer molecules stretch and were disrupted by forces of the order of 1 kg/cm^2.

The overall results of these experiments indicate that when Urrbrae B aggregates are treated with PVA solutions the polymer diffuses most rapidly into the few relatively large pores. From there it is able to diffuse into some of the smaller adjoining pores and, depending on their size, they may or may not become blocked with polymer. For small aggregates, such as the (½-1) mm. size used in these experiments, the polymer can be considered to be distributed throughout the entire aggregate, but for larger cores of soil it is likely that PVA can penetrate only very small distances (less than 2 mm) by diffusion processes alone.

On drying, the polymer forms semi-continuous films along the walls of the larger pores so strengthening them by interparticle bonding. However in the presence of water the polymer is rapidly hydrated and loses tensile strength. The strengthening of the large pores is considered to be of prime importance in the stability of soil aggregates and it appears that PVA adsorbed in these sites can buffer the disruptive forces of rapid water entry and agitation in water. The results confirm the earlier hypothesis and experiments of Quirk & Panabokke (1962) and Williams (1959) in which it was postulated that it is not only the inter-particle bonds formed by organic materials that is important in aggregate stability, but also the disposition of the organic molecules within the aggregates. Thus quite small amounts of organic stabilising compounds, if placed at strategic sites within soil aggregates, can impart considerable stability to the aggregates as a whole.

Future Work

The work described in this thesis has been directed towards gaining an understanding of the movement and action of large organic molecules within the porous structure of soil aggregates. It is thought that more conclusive evidence of the proposed inter-relationship between the stabilising action and the location of organic materials within aggregates could be gained by the use of both uncharged and charged polymers, in the following ways.

(1) Extending the pore size distribution work to characterise the changes in both large and

small pores upon the introduction of synthetic polymers.

(2) Similar pore size distribution work with aggregates containing natural organic matter, especially by,

  (a) the use of a single soil type having different crop rotation histories

  (b) selectively removing components of the organic fraction, or other stabilising agents without disrupting the original aggregate structure.

(3) Use could be made of labelled organic compounds to assist investigations of the movement of organic polymers within aggregates and within soil profiles in the field.

The pore size distribution work should be coupled with aggregate stability changes.

The methods used to determine aggregate stability warrant further investigation e.g.

(1) The abrasion processes involved in end-over-end shaking could be clarified by,

  (a) Use of larger samples and complete particle size analyses at various periods of shaking.

(b) Use of non-polar liquids in the shaking cylinders to permit a clearer separation of effects due to initial breakdown and those due to abrasion.

(2) The work of Kirkham *et al* (1958), using the Brazilian core test should be pursued with field samples in an attempt to reduce the variability of the results.

SUMMARY

The entry of a non-charged organic polymer, poly (vinyl alcohol), into natural aggregates of Urrbrae soil, and the subsequent effect of the polymer on the physical properties of the aggregates has been studied.

The approach used was to study first the factors affecting the adsorption of PVA by soil aggregates. In particular, the amount and rate of adsorption, the molecular weight and configuration of the organic molecules in solution, the solution concentration, the size of the aggregates, the presence of other organic material already adsorbed at the clay surfaces and agitation of the reaction mixture, were investigated. Cores of soil taken from the field were used to demonstrate the influence of the initial soil water energy status on the movement of PVA into soil.

The water-stability of aggregates containing PVA was measured by the method of end-over-end shaking in water. The breakdown of aggregates to particles of less than 2 μ diameter was determined with a turbidimetric method, devised to suit the particular experimental conditions. Similarly the rate of breakdown of aggregates with shaking in water was investigated and information was obtained concerning the factors involved in this commonly used method for determining the water-stability of soil aggregates.

The tensile strength of Urrbrae B - PVA complexes, in

the form of small cores (approximate dimensions of 0.74 cm diameter, 0.65 cm length) were determined by the Brazilian Core method. The strength of the PVA-soil particle bonds was investigated in relation to the hydration and molecular characteristics of the polymer.

The marked changes in the physical properties of soil aggregates containing PVA were related to both the disposition and the properties of the adsorbed polymer. Low temperature, nitrogen adsorption by Urrbrae B - PVA complexes was used to determine the location and physical state of the adsorbed polymer, while swelling studies were used to measure the effect that this treatment had on the rate and total water uptake by Urrbrae B clay.

It was regarded as a matter of prime importance that the physical state of the system being studied should be defined as clearly as possible. Thus a model for the structure of soil aggregates was proposed in which an aggregate is considered to be built up of structural units of various sizes. The smallest units correspond with domains of clay crystals and these are grouped together to form microaggregates. The micro-aggregates are in turn grouped to form larger structural units, and so on, until aggregates of the size commonly observed in the field are obtained. This model was found to account satisfactorily for the observations made of the adsorption of PVA and its effect on the pore structure, water-stability, mechanical stability and swelling properties of Urrbrae B aggregates.

Where possible, emphasis has been placed on the interaction of PVA with aggregates having a natural field structure rather than using puddled soil material or artificial aggregates. In this way it has been possible to relate more closely the stabilising action of the synthetic polymer to possible modes of action of the stabilising fraction of natural organic matter.

The techniques described for treating and testing aggregates have been designed to allow interpretation of the results in terms of the state and disposition of the adsorbed polymer. They provide a basis for extending the work to the more difficult problem of the movement and action of charged organic polymers in soil aggregates. This latter problem will be an important consideration in the final understanding of the dynamics and action of naturally occurring organic matter in agricultural soils.

APPENDIX I

1. The Turbidimetric Determination of The Concentration of Urrbrae B Clay Suspensions

West (1949) has reviewed the theory of light scattering by inhomogenous solutions in the following terms.

$$I = I_o e^{-tx} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where I_o = the initial intensity of the light beam
I = the final intensity of the light beam
x = the path length
t = turbidity

$$t = \frac{8\pi}{3} \left(\frac{2\pi}{\lambda} \right)^4 n\alpha^2 \quad \ldots\ldots\ldots \quad (2)$$

where λ = the wavelength of the primary light
n = the number of light scattering particles per cc of solution
α = the polarizability of the particles

This equation can be modified to take into account the size, shape and refractive index of the solute particles, solute-solute interactions and solute-solvent interactions. In this work however equation (2) has been simplified by assuming that all of these factors remain constant and are independent of the concentration of suspended particles. These assumptions appear appropriate for dilute suspensions of clay particles with diameters of less than 2 microns.

Equation (2) is then written as

$$t = kc \quad .... (3)$$

where c is the concentration of less than 2μ particles in suspension.

Rearranging equation (1) and taking the ratio of the transmitted light intensities of two different suspensions, yields -

$$I_2/I_1 = e^{x(t_1 - t_2)} \quad .... (4)$$

where I_1, t_1 and I_2, t_2 are the final light intensities and the turbidities of the two suspensions.

Then, $\ln (I_2/I_1) = x (t_1 - t_2)$ ..... (5)

and substituting t from equation (3) and keeping the path length (x) constant,

$$\log (I_2/I_1) = k (c_1 - c_2) \quad ...... (6)$$

where k is a constant.

Finally, T (the percentage light transmission) is equal to $(I/I_o)100$, by definition, so equation (6) can be written as

$$\log (T_2/T_1) = K(c_1 - c_2) \quad .... (7)$$

This is a straight line relationship provided that the constant in equation (3) does not vary due to any of the factors referred to above.

The derived relationship was tested by determining the percentage light transmission through a number of suspensions

THE TURBIDIMETRIC DETERMINATION OF THE
CONCENTRATION OF URRBRAE B CLAY SUSPENSIONS

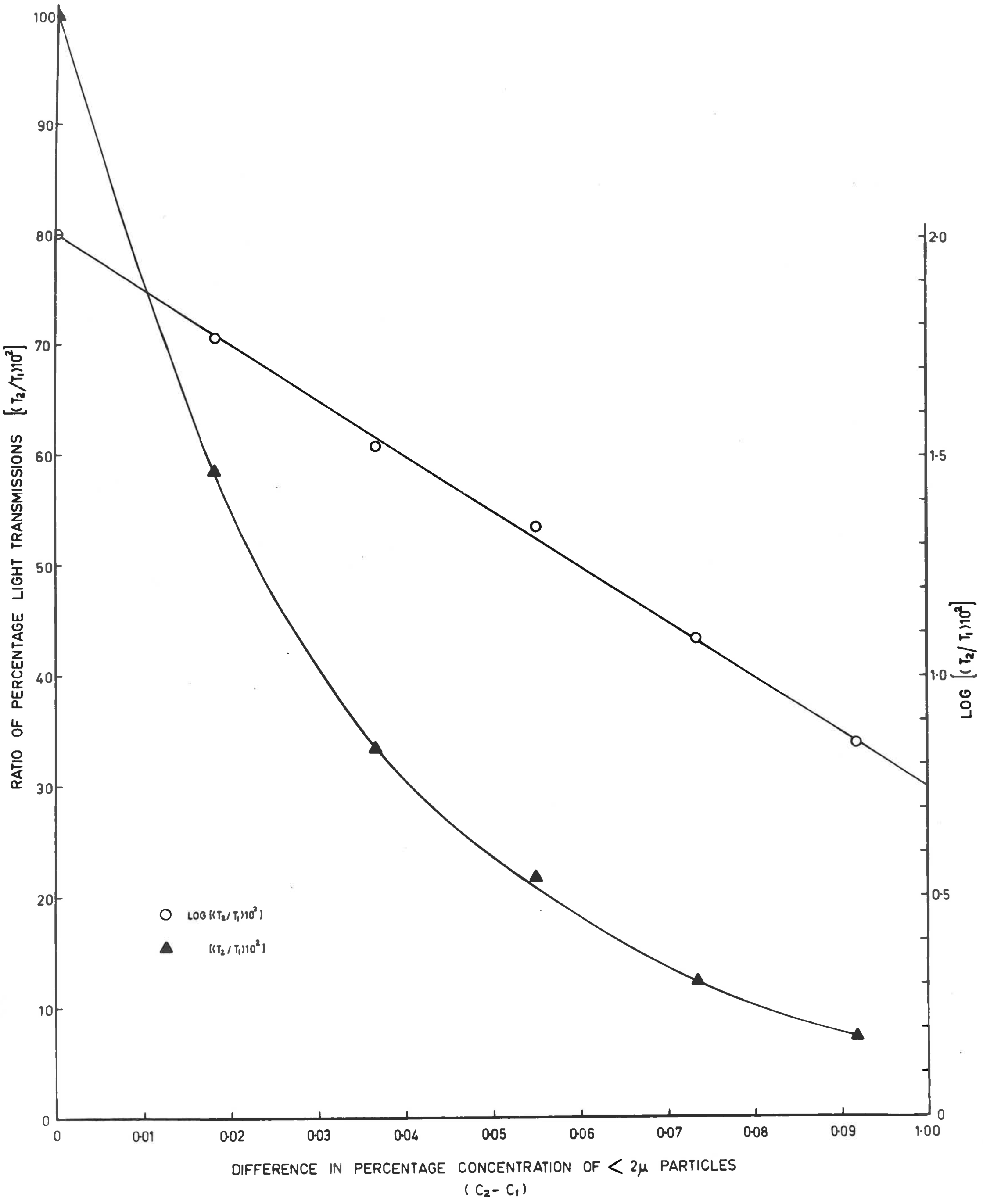


Figure 23.

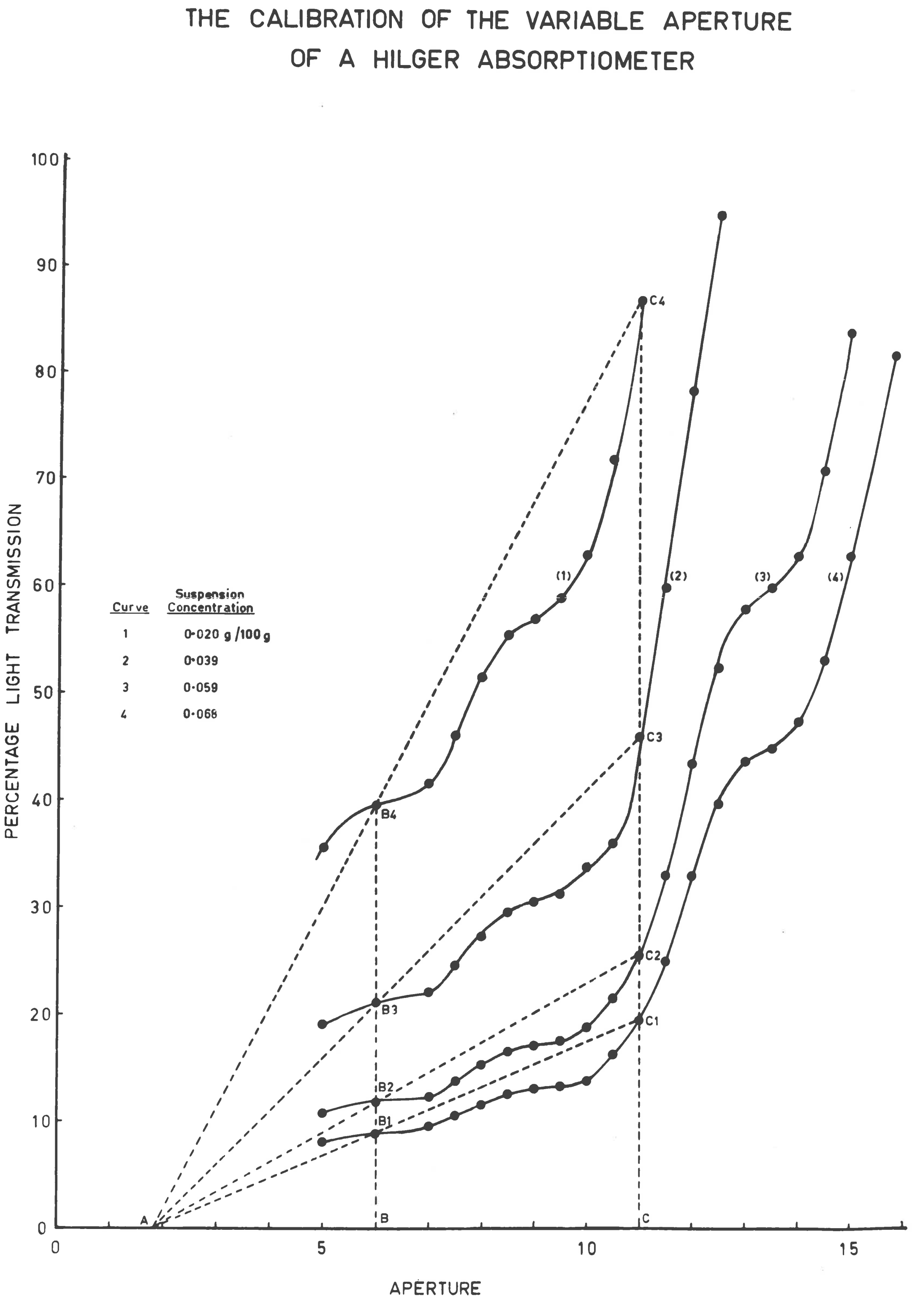

THE CALIBRATION OF THE VARIABLE APERTURE OF A HILGER ABSORPTIOMETER

Figure 24.

of the less than 2 µ fraction of Urrbrae B, using a Hilger Biochemical Adsorptiometer. The results are shown in Figure 23, using both linear and logarithmic values of the ratio of light transmissions as functions of the difference in concentration between two clay suspensions. The agreement of the experimental results with the predictions embodied in equation (7) can be seen to be very good and the assumptions made in respect to the constant in equation (3) are justified in this particular case.

If one of the suspensions is chosen to have zero concentration then the concentration of a suspension of unknown concentration can be obtained either from the curvilinear relationship shown in Figure 25 or it may be calculated from the equation of the straight line relationship. It should be emphasised that use of equation (7) implies the use of the same amount of incident light (I_o) for both the blank and the unknown suspensions unless appropriate corrections are made.

The calibration and use of the variable light source supplied with the adsorptiometer used, is discussed in Appendix 1.2.

2. The Calibration of The Variable Aperture of a Hilger Biochemical Adsorptiometer.

In Appendix I.1 it was shown that a simple relation exists between the concentration of a clay suspension and the percentage light transmission through the suspension provided a constant light source is used. The use of a light source of constant intensity limits the range of suspension concentrations that can be measured unless the suspensions are diluted. For experiments in which the rate of breakdown of aggregates was being followed it was not possible to make dilutions of the suspensions at each period of shaking, so the relation between the percentage light transmission and the light intensity was investigated.

A variable aperture is provided with the adsorptiometer but this does not have a graduated scale, so the knurled control knob was marked in linear divisions of 0.05 units from values of 0 to 15.85. Then the percentage light transmission of a number of Urrbrae B (< 2 μ) clay suspensions were determined at different apertures. The irregular relation obtained is shown in Figure 24 for suspensions of from 0.018 to 0.074 g clay per 100 cc of water.

The light scattering theory discussed in Appendix I.1. predicts that the ratio of percentage light transmission of two suspensions remains constant regardless of the aperture used. This is verified by the data in Figure 24 where the ratios at apertures 6 and 11 are shown geometrically. It can be seen that the two parallel lines BB4 and CC4 divide the lines AC4, AC3, AC2, AC1 and AC proportionally and hence BB3/BB4 = CC3/CC4, etc.

It was found, however, that the maximum aperture that could be used at zero concentration was 8.00 and for suspension concentrations of greater than 0.075 g clay per 100 cc the percentage light transmission at this aperture was difficult to obtain with the accuracy required. Hence it was necessary to determine the percentage light transmission through water at all apertures above 8.00 so that the concentration of suspensions greater than 0.075 g/100c could be calculated. This was done by making use of the constancy of the light transmission ratios as shown in the following calculation.

RESULTS

Clay concentration g/100 cc	Aperture	% Light Transmission
0	7.5	86
	12.0	x
	15.85	y
0.068	7.5	10.5
	12.0	33
	15.85	82
0.098	12.0	14
	15.85	35

Making use of the percentage light transmissions at apertures 7.5 and 12.,

$$x = 86 \times \frac{33}{10.5}$$

then using apertures 12.0 and 18.5,

$$y = \frac{35x}{14} = 675.7$$

i.e. the percentage light transmission for water at the maximum aperture of 15.85 would be 675.7 if it were possible to measure it with this instrument. A number of such values may be calculated readily from the data obtained with suspensions of known concentration, and the concentration of an unknown suspension is then calculated from the relation

$$\log (T_x/T_{H_2O}) = K.C_x$$

This procedure may be varied by using suspensions of known concentration as standards rather than water but the latter is preferable in that there is no difficulty in its preparation and there is no likelihood of physical or chemical changes occurring over a period of time. The calibration of the variable aperture made it possible to measure quite accurately the concentration of Urrbrae B clay suspensions of up to 0.15 g/100 cc as compared with concentration of 0.075 g/100 cc when an aperture of 8.0 was used.

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BIBLIOGRAPHY

	Vol.	Page	Year
Allison, L.E. Soil Sci. Soc. Am. Proc.	20	147	1956a
Allison, L.E. Soil Sci. Soc. Am. Proc.	20	314	1956b
Allison, L.E. and Moore, D.C. Soil Sci. Soc. Am. Proc.	20	143	1956
Archibald, J.A. and Erickson, A.E. Soil Sci. Soc. Am. Proc.	19	444	1955
Aylmore, L.A.G. and Quirk, J.P. Nature	187	1046	1960
Aylmore, L.A.G. Thesis for Degree of Ph.D. Univ. of Adelaide			1960
Aylmore, L.A.G. and Quirk, J.P. Clays and Clay Min.	9	104	1962
Barret, H.M., Birnie, A.W. and Cohen, M. J. Am. Chem. Soc.	62	2839	1940
Baver, L.D. & Rhoades, H.F. J. Am. Soc. Agron.	16	55	1932
Beresniewicz, A. J. Polymer Sci.	39	63	1959
Beutelspacher, H. Z. Pflanz. Dung. Bodenk.	69	108	1955
Beutelspacher, H. Proc. Natl. Acad. Sci. India	24A	132	1957
Bobchenko, V.I. Pochvovedenie	No. 10	70	1961
Bodman, G.B. and Hag~~i~~an, R.M. "Californian Agriculture" Univ. California Coll. Agric.	6	6	1952

	Vol.	Page	Year
Bouyoucos, G.J. Soil Sci.	23	343	1927
Bradfield, R. Am. Soil Survey Assn. Bull.	17	31	1936
Bradfield, R. and Jamieson, V.C. Soil Sci. Soc. Am. Proc.	3	70	1938
Brockman, F.J. and Allenby, O.C.W. Can. J. Agr. Sci.	33	623	1953
Brockman, F.J. and Allenby, O.C.W. Can. J. Agr. Sci.	35	27	1955
Brooks, C.S. Soil Sci.	79	331	1955
Brunauer, S. "The Adsorption of Gases and Vapours" Princeton University Press			1943
Brunauer, S. Advances in Chemistry Series "Solid Surfaces and the Gas-Solid Interface"		2	1961
Bunn, C.A. Nature	161	989	1948
Burford, J., Deshpande, T.L., Greenland, D.G. and Quirk, J.P.		(in press)	1964
Carneiro, F.L.L.B. and Barcellos, A. R.I.L.E.M. Bull.	13	97	1953
Chepil, W.S. Soil Sci. Soc. Am. Proc.	26	4	1962
Childs, E.C. Soil Sci.	50	239	1940
Childs, E.C. Soil Sci.	53	79	1942

	Vol.	Page	Year
Childs, E.C. & Poulovassilis, A. Soil Sci.	90	326	1960
Clampitt, B.H. and German, D.E. J. Phys. Chem.	62	438	1958
Clare, K.E. Nature	160	828	1947
Croney, D. and Coleman, J.D. J. Soil Sci.	5	75	1954
Culver, R.V. and Heath, N.S. Trans. Faraday Soc.	51	1569	1955
Damkohler, G. J. Phys. Chem.	A174	222	1935
Davidson, J.M. and Evans, D.D. Soil Sci. Soc. Am. Proc.	24	75	1960
Dettman, M.G. and Emerson, W.W. J. Soil Sci.	10	215	1959
Dhawan, C.L., Lal Malhotra, M.M. and Singh, J. Proc. Natl. Acad. Sci. India Section A	27	225	1958
Dialer, K., Vogler, K. and Patat, F. Helv. Chim. Acta.	35	869	1952
Dieu, H.A. Industrie chim. belge.	2	355	1959
Edwards, D.G. and Quirk, J.P. J. Coll. Sci.	17	872	1962
Ellerstein, S. and Ullman, R. J. Polymer Sci.	55	123	1961
Emerson, W.W. J. Agric. Sci.	47	117	1956
Emerson, W.W. Nature	186	573	1960

	Vol.	Page	Year
Emerson, W.W. J. Soil Sci.	14	52	1963
Emerson, W.W. and Raupach, M. Aust. J. Soil Res.	2	46	1964
Ensminger, L.E. and Giesking, J.E. Soil Sci.	48	467	1939
Fiedler, H.J. and Bergmann, W. Die Deutsche Landwirtschaft	5	313	1954
Fiedler, H.J. Kg. Lantbruks-Hogskol. Ann.	23	367	1957
Fiedler, H.J. and Torstensonn, G. Kgl. Lantbruks-Hogskol. Ann.	23	342	1957
Fontana, B.J. and Thomas, J.R. J. Phys. Chem.	65	480	1961
Forsyth, W.G.C. Biochem. J.	41	176	1947
Foster, A.G. Trans. Faraday Soc.	28	645	1932
French, R.O., Wadsworth, M.E., Cook, M.A. and Cutler, I.B. J. Phys. Chem.	58	805	1954
Fuller, W.H. and Gairaud, C. Soil Sci. Soc. Am. Proc.	18	35	1954
Giles, C.H., MacEwan, T.H., Nakhwa, S.N. and Smith, D. J. Chem. Soc.	Part 3	3973	1960
Goring, C.A.I. and Bartholomew, W.V. Soil Sci.	74	149	1952
Graveland, D.N. and Lynch, D.L. Soil Sci.	91	162	1961

	Vol.	Page	Year
Greathouse, G.A., Wessel, C.J. and Shirk, H.G. Ann. Rev. Microbiol.	5	333	1951
Greenland, D.J. J. Coll. Sci.	18	647	1963
Greenland, D.J., Lindstrom, G.R. and Quirk, J.P. Soil Sci. Soc. Am. Proc.	26	366	1962
Gussak, V.B. Pochvovedenie	No. 8	42	1961
Hagin, J. and Bodman, G.B. Soil Sci.	78	367	1954
Haise, H.R., Jensen, L.R. and Alessi. J. Soil Sci. Soc. Am. Proc.	19	17	1955
Hanotiaux, G. and Mani, G. Bull de L'Inst. Agron. Stat. Rech. Gemblous	20	66	1952
Healy, T.W. J. Coll. Sci.	16	609	1961
Healy, T.W. and La Mer, V.K. J. Coll. Sci.	19	323	1964
Hedrick, R.M. and Mowry, D.T. Soil Sci.	73	427	1952
Hedrick, R.M. J. Agr. Food Chem.	2	182	1954
Helfferich, F.G. "Ion Exchange" N.Y. McGraw-Hill			1962
Hendricks, S.B. J. Phys. Chem.	45	65	1941
Holmes, J.W. J. Soil Sci.	6	200	1955
Holmes, R.M. and Toth, S.J. Soil Sci.	84	479	1957a

	Vol.	Page.	Year
Holmes, R.M. and Toth, S.J. Can. J. Soil Sci.	37	102	1957b
Homrighausen, E. Z. Pflanz. Dung. Bodenk.	78	38	1957
Hoover, J.M. and Davidson, D.T. Natl. Acad. Sci. Natl. Res. Council Publ.	No. 418	10	1956
Hosono, M. and Sakurada, I. Chem. High Polymers	9	64	1952
Ingles, O.G. Proc. 1st Conf. Aust. Road Res. Board	1	1014	1962
Ingles, O.G. and Frydman, S. 4th Aust-New Zealand Conf. Soil Mechanics and Found. Eng.		213	1963
Jackson, M.L. Soil Chemical Analysis Prentice-Hall Inc., N.J.		208	1958
Jamison, V.C. Soil Sci. Soc. Am. Proc.	18	391	1954
Jones, M.B. and Martin, W.E. Soil Sci.	83	475	1957
Kirkham, D., De Boodt, M. and De Leenheer, L. Proc. Int. Symp. Soil Structure (Ghent).		369	1958
Koral, J., Ullman, R. and Eirich, F.R. J. Phys. Chem.	57	584	1953
Kurosaki, S. Bull. Chem. Soc. Japan.	75	376	1954
Leamer, R.W. and Lutz, J.F. Soil Sci.	49	347	1940

	Vol.	Page	Year
de Leenheer, L. and de Boodt, M. Mededel. Landboucohogeschool en Opzoekingsstas. Staat. Gent.	24	89	1959
Lynch, D.L., Wright, L.M. and Cotnoir, L.J. Soil Sci. Soc. Am. Proc.	20	6	1956
Lynch, D.L., Wright, L.M. and Cotnoir, L.J. Soil Sci.	84	113	1957
Lynch, D.L., Olney, H.O. and Wright, L.M. J. Sci. Food Agr.	9	56	1958
McBain, J.W. Z. Phys. Chem.	68	471	1909
McCalla, T.M. Trans. Kansas Acad. Sci.	62	53	1959
MacEwan, D.M.C. Nature	162	935	1948
Martin, J.P. Soil Sci.	61	157	1946
Martin, J.P. and Aldrich, D.G. Soil Sci. Soc. Am. Proc.	19	50	1955
Maslenkova, G.L. Pochvovedenie	No. 11	31	1961
Mehta, N.C., Streuli, H., Muller, M. and Deuel, H. J. Sci. Food Agr.	11	40	1960
La Mer, V.K. and Healy, T.W. Rev. Pure and Appl. Chem. (Aust.)	13	112	1963
Michaels, A.S. Ind. Eng. Chem.	46	1485	1954
Michaels, A.S. and Morelos, O. Ind. Eng. Chem.	47	1801	1955
Miller, I.R. Trans. Faraday Soc.	57	301	1961

	Vol.	Page	Year
Modina, S.A. Pochvovedenie	No. 3	62	1962
Mortensen, J.L. and Martin, W.P. Soil Sci. Soc. Am. Proc.	18	395	1954
Mortensen, J.L. and Martin, W.P. Soil Sci.	81	33	1956
Mortensen, J.L. Soil Sci. Soc. Am. Proc.	21	385	1957
Mortensen, J.L. Soil Sci. Soc. Am. Proc.	23	199	1959
Moss, G.R., Browning, H.A. and Southon, T.F. New Zealand J. Agr.	88	67	1954
Nath, T. and Nagar, B.R. Current Sci. (India)	28	193	1959
Nath, T. and Nagar, B.R. J. Indian Soc. Soil Sci.	8	45	1960
Norrish, K. and Quirk, J.P. Nature	173	225	1954
Norrish, K. Disc. Faraday Soc.	18	120	1954
Novak, L.J., Witt, E.E. and Hiler, M.J. J. Agr. Food Chem.	3	1028	1955
Packter, A. Soil Sci.	83	335	1957
Panabokke, C.R. Thesis for Degree of Ph.D. Univ. of Adelaide			1956
Panabokke, C.R. and Quirk, J.P. Soil Sci.	83	185	1957
Patrick, W.A. and Cohan, L.H. J. Phys. Chem.	41	437	1937

	Vol.	Page	Year
Pavlov, G.I. Proc. 22nd Int. Cong. Soil Sci.	1	82	1932
Piper, C.S. Trans. Roy. Soc. S. Australia	62	53	1938
Posner, P. and Quirk, J.P.	in press		1964
Pugh, A.L., Vomocil, J.A. and Nielsen, T.R. Agron. J.	52	399	1960
Puri, A.N. and Keen, B.A. J. Agr. Sci.	15	147	1925
Quartaroli, A. Ann. Univ. Pise, Fac. agrar.	15	25	1954
Quastel, J.H. and Webley, D.M. J. Agr. Sci.	37	257	1947
Quastel, J.H. Ann. Rev. Plant Physiology	5	75	1954
Quirk, J.P. Aust. J. Agric. Res.	1	276	1950
Quirk, J.P. Nature	188	253	1960
Quirk, J.P. and Panabokke, C.R. J. Soil Sci.	13	60	1962a
Quirk, J.P. and Panabokke, C.R. J. Soil Sci.	13	71	1962b
Rennie, D.A., Truog, E. and Allen, O.N. Soil Sci. Soc. Am. Proc.	18	399	1954
Richards, L.A. Soil Sci. Soc. Am. Proc.	17	321	1953
Ruehrwein, R.A. and Ward, D.W. Soil Sci.	73	485	1952
Russell, E.W. Imp. Bur. Soil Sci. Tech. Comm.	No. 37		1938

	Vol.	Page	Year
Russell, M.B. and Feng, C.L. Soil Sci.	63	299	1947
Schofield, R.K. Trans. Faraday Soc.	42B	219	1946
Schofield, R.K. and Samson, H.R. Clay Min. Bull.	2	45	1953
Schwartz, S.M., Freeman, P.G., and Russell, C.R. Soil Sci. Soc. Am. Proc.	22	409	1958
Silberberg, A. J. Phys. Chem.	66	1872	1962a
Silberberg, A. J. Phys. Chem.	66	1884	1962b
Sillanpaa, M. and Webber, L.R. Can. J. Soil Sci.	41	182	1961
Simha, R, Frisch, H.L. and Eirich, F.R. J. Phys. Chem.	57	584	1953
Simpson, K. and Hayes, S.F. J. Sci. Food Agr.	9	163	1958
Smellie, Jr., R.H. and La Mer, V.K. J. Coll. Sci.	13	589	1958
Smith, H.E., Schwartz, S.M., Gugliemelli, L.A., Freeman, P.G. and Russell, C.R. Soil Sci. Soc. Am. Proc.	22	405	1958
Swaby, R.J. J. Gen. Microbiol.	3	236	1949
Tamhane, R.V. and Chibber, R.K. J. Indian Soc. Soil Sci.	3	91	1955
Taylor, G.S. and Baldridge, P.E. Soil Sci. Soc. Am. Proc.	18	382	1954
Theng, B.K.G. Thesis for Degree of Ph.D. Univ. of Adelaide			1964

	Vol.	Page	Year
Tiulin, A.F. Trans. Sov. Sect. Int. Soc. Soil Sci.	2	28	1936
Toth, S.J. J. Assoc. Offic. Agr. Chemists	38	252	1955
Vermeulen, T. Ind. Eng. Chem.	45	1664	1953
Wahhab, A., Khabir, A., Azim, M.N., and Uddin, F.	81	139	1956
Warkentin, B.P. and Miller, R.D. Soil Sci.	85	14	1958
West, W. Physical Methods of Organic Chemistry. Ed. 2. Part II		1450	1959
Wester, R.E. Agr. Chemicals	10	44	1955
Whistler, R.L. and Kirby, K.W. J. Am. Chem. Soc.	78	1755	1956
Williams, B.G. Thesis for Honours Degree of B.Ag.Sc. Univ. of Adelaide			1959
Williams, B.G., Lindstrom, G.R., Greenland, D.G. and Quirk, J.P.		in press	1964
Woodruff, C.M. Soil Sci. Soc. Am. Proc.	4	13	1939
Yoder, R.E. J. Am. Soc. Agron.	28	337	1936
Young, J.L. and Lindbeck, M.R. Soil Sci. Soc. Am. Proc.	28	377	1964