SURFACE CHEMISTRY OF TALC FLOTATION

by

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A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfilment of the requirements for the degree of Master of Science in Metallurgical Engineering.

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October 1972

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ACKNOWLEDGEMENTS

I would like to thank Dr. T. Salman, without whom this research would have been impossible. Gratitude is extended to the Department of Energy, Mines and Resources for their financial support (1970-72). My appreciation is also offered to fellow graduate students for their aid and co-operation. I laud my wife for her patience in typing this manuscript.

ABSTRACT

The hydrophobic-hydrophilic nature of talc surfaces is discussed and investigated using aqueous solutions of 2 phenyl 2 propanol. Isotherms at natural pH of 6.9 exhibit S-L multi-layer characteristics, indicating initial adsorption occurs at the edges of the broken talc sheets. Adsorption is increased in more alkaline media and by the presence of excess calcium ions. Basic isotherms are L type. Infra-red spectra indicate physical adsorption through hydroxy group of alcohol. Natural flotation of talc is dependent on pH and particle mesh size. Flotation recovery can be correlated with equilibrium solute concentration, suggesting that the aromatic alcohol possesses collector power. Apparent liquid specific surface values for talc are reported.

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SECTION I

INTRODUCTION

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AIM OF RESEARCH

LITERATURE REVIEW

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INTRODUCTION

Nonmetallic mineral flotation has become increasingly more important in recent years⁽¹⁻³⁾. Selective nonmetallic flotation is hampered by the difficulty in choosing appropriate chemicals from the wide array of available modifying agents, and by the nature of the interactions between these reagents and the oxides or salt minerals. Although metallic flotation is generally characterized by strong chemical adsorptive bonds between the mineral and sulfhydral collector, the forces of adsorption in nonmetallic mineral systems are predominantly physical and thus much weaker. Collector adsorption on oxide minerals results primarily from electrostatic attraction and Van der Waals attraction between hydrocarbon chains. Salttype nonmetallic minerals can exhibit both physical and chemical adsorption.

The silicates are an important class of nonmetallic minerals. All silicate minerals are comprised of silica tetrahedra in which a silicon atom sits in the center of four tetrahedrally co-ordinating oxygen atoms. The properties of the various silicates are dependent on the method by which these silica tetrahedra are linked together through the sharing of the oxygen atoms. Azaroff⁽⁴⁾ classifies the types of silicates according to the number of shared oxygen atoms. When there are no shared oxygen, as in zircon, the negative charge on the individual tetrahedra is compensated by inter-

stitial cations. One shared oxygen results in pairs of silica tetrahedra bound ionically with cations, as in hemimorphite. Two shared oxygen result in infinite chaims of silica tetrahedra with cations linking the chains together ionically as in wollastonite. Two and a half shared oxygen give rise to a double chain structure characteristic of amphiboles. Four oxygen shared between tetrahedra give an infinite three dimensional structure, exemplified by quartz.

Of particular interest here is the two dimensional sheet structure that arises from the sharing of three oxygen atoms. These minerals are made up of layers of silica tetrahedra condensed with gibbsite, or brucite, in a variety of ways. Talc is formed when silica tetrahedra condense with brucite. Talc differs from the majority of sheet silicates in that its silicon oxygen sheets are electrically balanced. The bonding between the sheets of talc molecules results from weak residual oxygen-oxygen bonds.

Talc is the main component of soapstone and steatite. Although grinding the mineral to -200 mesh or less has been often the only mill treatment given the mineral⁽⁵⁾, the use of flotation has become widespread because of the need for higher purity talc. Such talc finds use as a lubricant, in fillers, and in the production of papers, rubber, and paints. Further purification enables talc to be used in the cosmetic industry in soaps, cosmetics, and other toiletries. Talc's electrical and insulating characteristics result in its

application in ceramics⁽⁶⁾.

Apart from its commercial value, talc possesses a "nuisance" value in that talc slimes, like clay slimes, can destroy flotation selectivity. The magnesium content of talc is corrosive to smelting operations and must be kept to a minimum in concentrate grades. Talc slimes are generally removed prior to flotation processing of a nonmetallic ore, or are depressed by the use of such reagents as starch, dextrin, glue, and alum.

AIM OF RESEARCH

Booth and Freyberger (7), among others (1)(2), have noted that there has not been a great deal of research into the possible interaction of alcohols and mineral surfaces. Although talc is commonly floated in North American mills by means of frothers such as alcohols, the collective power of such species does not appear to have been investigated. Thus, one aim of the present work was to investigate the interactions of the surfaces of talc particles, and the subsequent flotation of said particles in an aqueous medium, with or without the aromatic alcohol, 2 phenyl 2 propanol. Also, it was expected that information about the adsorption mechanisms and factors that affect the adsorption of 2 phenyl 2 propanol might yield concepts to help explain the adsorption interactions of talc surfaces and organic depressants which adsorb through their hydroxyl (-OH) group, such as starch and dextrin. Finally, the extent to which talc surfaces appear to interact with the surrounding aqueous medium, namely the apparent active liquid surface areas of talc particles of different mesh sizes, was to be investigated.

LITERATURE REVIEW

The literature review is divided into crystal, contact angle, and electrokinetic phenomena, with an added discussion of the latter. Each of these concepts is later co-ordinated with the discussions of the experimental adsorption, flotation, and infrared data.

Talc is an easily flotable mineral. It is suspected that the mineral's innate flotability is related to its crystal structure $^{(1)}(8)$. Thus, the first step towards understanding talc's surface chemistry should involve a discussion of the crystal structure literature about talc.

A. Crystal Structure

The structural formula was first suggested by Pauling⁽⁹⁾ and determined from X-ray powder diffraction studies by Gruner⁽¹⁰⁾. Hendricks⁽¹¹⁾ substantiated Gruner's work in principle by means of single crystal work. He indicated that talc is a layer lattice mineral with irregular shifts in the stacking of the layers. The elements within a layer of talc molecules were held together primarily by ionic bonds. The layers of talc molecules were in turn held together by residual or Van der Waals forces. The unit cell dimensions, according to Hendricks are: $a=5.27 \stackrel{+}{=} 0.02 \text{ a.u.}$, $b=9.13 \stackrel{+}{=} 0.03 \text{ a.u.}$, $c=18.88 \stackrel{+}{=} 0.05 \text{ a.u.}$, $\beta =100^{\circ}15^{\circ} \stackrel{+}{=} 15^{\circ}$. Thus, talc is considered to crystallize in the monoclinic system with two structural layers of two molecules each per unit cell.

Brown⁽¹²⁾ and Rayner and Brown⁽¹³⁾ have reexamined a Maryland talc sample from Hendricks and reported that their reflexions fit a primitive triclinic unit cell with a=5.29A°, b=5.3A°, c=9.47A°, α =86.1°, β =98.9°, γ =120.0°. The c dimension is such that the unit cell can contain only one silicate layer.

Ross and Ashton⁽¹⁴⁾ examined talc crystals from the Gouverneur mining district, N.Y., and concluded that the talc is triclinic with space group CI or Cl. The structure type is one-layer triclinic (1Tc), with cell dimensions $a=5.25^{5}A$, $b=9.13_{7}$, $c=9.44_{8}A^{\circ}$, $\alpha=90.46^{\circ}$, $\beta=98^{\circ}55^{\circ}$, $\gamma=90^{\circ}$.

Pask and Warner⁽¹⁵⁾ report X-ray diffractometer patterns of talc which agree with the monoclinic data. Their differential thermal analysis suggests that changes of shape and position of the endothermic peak of talc at a temperature of 950°C might be the result of mixed-layer sequences in the crystal structure. Stemple and Brindley⁽¹⁶⁾ examined forty different talc specimens by X-ray diffraction technique and concluded that variations in the degree of crystallinity may occur, but that there is no evidence for polymorphic structural varieties of talc, and little evidence for talc's containing mixed-layer sequences. Their single-crystal data indicate the two layer monoclinic cell with a=5.28₇, b=9.15₈, c=18.95, β =99°30'. However, they noted that direct evidence for a 2 layer cell was lacking because all their 1 indices using the 2 layer cell were even numbers (17).

Thus, the exact nature of talc crystals, whether they be one layer triclinic or two layer monoclinic, has yet to be definitely determined. However, the surface chemistry of talc in either system should be the same in that the structure of the individual layers is identical.

The accepted formula for the mineral talc is $(OH)_2 Mg_3 (Si_2 O_5)_2$ or 3Mg0'4SiO, H,O⁽⁶⁾. The other ratios of MgO to SiO, that have been reported are generally considered to be the result of the selection of impure or modified samples. There appears to be little variation in the chemical composition of talc, although sometimes small amounts of aluminum or titanium substitute for silicon and small amounts of iron, manganese, or aluminum may replace the magnesium. Ashton and Ross (14) suggest that talc derived from metamorphosed sedimentary rocks contains appreciable fluorine, from 0.11 to 0.48 weight percent, whereas talc derived from ultramafic rocks contains less fluorine. Their chemical analysis gives the composition of talc from the Arnold pit, N.Y., as $Mg_{3.04}Si_{3.96}O_{10}F_{0.1}(OH)_{1.9}$. The fluorine, if it is indeed an integral part of talc, might be expected to substitute for the comparably sized hydroxyl groups, thus not affecting the crystal structure (18).

The layer structure of talc is illustrated in figure 1.

FIGURE 1

- a) Edge view of talc crystaline structure. Talc $(OH)_2Mg_3(Si_2O_5)_2$ or $(OH)_8Mg_{12}Si_{16}O_{40}$ (unit cell).
- b) Hexagonal array of atoms in a talc single layer unit cell.
 - Only half of silicon and oxygen ions are shown.

1a) Edge View of Talc

16)



Array of one half of Talc Sheet C_{2} C_{2} C_{2} C_{2} C_{2} C_{2} C_{2} C_{3} C_{4} C_{2} C_{4} C_{5} C_{5} C_{5} C_{6} C_{6} C_{6} C_{7} $C_{$

0 Outer Oxygen • Silicon 0 Hydroxyl • Magnesium {} Inner Oxygen

Ь

Talc is distinct from other layer silicates in that forces between layers of talc molecules are of a weak Van der Waals nature. The ions within the layers are bound together by ionicelectrostatic forces. The three magnesium ions have only two hydroxyl ions, thus the "brucite" layer with a charge of +4 is balanced by two $(Si_2O_5)^{2-}$ units on each side. With no ne: charge on the sheets, there is no need for alkaline cations to lie between the layers as is found in micas such as muscovite and lepidolite.

The weak bonding between the layers, plus the fact that the layers extend indefinitely in all directions in a plane perpendicular to figure la, is responsible for the physical properties of talc, namely talc's greasy feeling, softness, and its normal platy structure.

The separation of crystallographic planes and crystal breakage is dependent on the amount of stress normal to the planes, on the degree of intermolecular separation between the planes, and on the nature of the intermolecular forces in the crystals. Cleavage of crystals is said to occur along welldefined planes so that the two values of the fractured crystal are bound by flat faces. The (100) planes in NaCl and a Fe⁽¹⁹⁾ are the cleavage planes of these crystals because of their large intermolecular spacings. In general, any crystalline solid will tend to cleave preferentially along such crystal faces which require the least amount of energy to create a new surface.

If a crystal contains chemical bonds of different types and strengths, breakage will occur along the crystal faces where the weakest bonds reside. Quartz, which has only one type of bond, cleaves along the planes where bond density is a minimum.

Crystals which have layered structures cleave along planes parallel to the layers because the forces between layers are frequently weaker than those within a layer. Thus, because the ionic/electrostatic forces binding the magnesium,hydroxyl, silica, and oxygen atoms within a talc molecule, are much stronger than the weak residual bonding between the uncharged oxygen layers of talc molecules, cleavage is expected to occur predominantly between the uncharged sheets, namely along the (001) plane⁽²⁰⁾. Talc particles, being essentially crystal aggregates, should exhibit inter-mixed surfaces of neutral silicon oxygen sheets and more complexly charged oxygen-silicon-magnesium-hydroxylsilicon-oxygen surfaces. The area of the uncharged planes would be expected to predominate even as the talc is ground to extremely fine particle sizes. The hexagonal array of uncharged silicon oxygen atoms is illustrated in figure 1 b.

B. Contact Angle Phenomena

Contact angle studies have been used to investigate the hydrophobic nature of talc surfaces.

When a liquid is placed on a mineral surface, in most cases, it remains as a drop with a definite angle of contact, \odot , between the liquid and solid phases. At equilibrium, the surface tension of the liquid-vapour, δ_{LW} , solid-vapour,

 δ_{SV} , and solid-liquid. δ_{SL} are related to the contact angle by the Young-Dupre equation (21-23).

 $\delta_{LV} \cos \Theta = \delta_{SV} - \delta_{SL}$ Furthermore, the work of adhesion, W_{SLV} , between phases at equilibrium can be expressed as

$$W_{SLV} = \delta_{LV} (1 + \cos \theta) \qquad 2$$

Of interest here is the use of contact angle for the investigation of the wettability of a mineral surface. For practical purposes, if the contact angle is greater than 90°, the liquid is said not to wet the solid (24). Thus, drops of the liquid tend to move about easily on the surface and not to enter capillary pores.

Bartell and Zuidema⁽²⁵⁾ investigated freshly cleaved talc surfaces by means of contact angle measurements using the sessile drop method. They report a contact angle for talcwater-air of 86°. The contact angle in other pure organic liquids is less, for methylene iodide $\textcircled{B}=53^\circ$, benyl alcohol

 \bigcirc =32°, benzene \bigotimes =0°. However, they observe that a drop of any of the organic liquids readily displaced water from a talc surface to give interfacial contact angles which all

exceed 100°. They conclude that talc is neither strongly hydrophilic nor strongly organophilic.

More recently, Strel'tsyn⁽²⁷⁾ investigated the intermolecular forces of several systems, including talc-tetrabromomethane-air, talc-mercury-air, and talc-water-air. He reports that the respective contact angles are $32^{\pm}1^{\circ}$, $137^{\pm}1^{\circ}$, and 90°. He concludes that interactions of the siliconoxygen-silicon uncharged surfaces of talc with the aforementioned systems is mainly dependent on the system's dispersive forces, rather than hydrogen-bond forces. He determines the dispersion surface tension of talc to be $\delta_{talc} = 42.3^{\pm}1^{erg}/cm^2$.

The contact angle data indicate that talc presents a predominantly hydrophobic and low energy surface to an aqueous

medium. However, the literature does not report any studies of the possible changes of contact angle, surface energies, and hydrophobicity of talc in alkaline or acid aqueous systems.

C. Electrical Phenomenon

i) Literature

An important aspect of oxide interfaces is the concept of the electrical double layer. For talc, an understanding of electrical effects will be an important part in describing the adsorption and flotation characteristics of the mineral. Thus, a review of the concepts associated with electrical phenomena and a presentation of the literature zeta potential curves for talc now follows.

The double layer of charge refers to the localization of one charge on the surface of a mineral, and the development of the other charge in a diffuse region extending into the solution. Two basic types of electrochemical double layer can be characterized and depend on the mechanisms by which free charges are distributed across a solid/solution interface (28). The reversible double layer is the result of transfer of potential determining ions across the phase boundary which includes the ionic double layer around Oxide hydroxides or soluble salts in aqueous environment. A completely polarizable double layer is established by imposing a potential

difference so that any charges carried to it have meaningful concentrations only in either of the phases. The two types of electrical double layer display similar structure and magnitude at equilibrium.

The Helmholtz model of electrical double layer presumes the rigid arrays of opposite charges in a molecular distance and is equivalent to a simple parallel capacitor. However, the thermal motion of the liquid molecules and the electrostatic repulsion between charged particles do not permit the formation of the molecular capacitor.

The mathematics of the electrical double layer have been studied by Gouy⁽²⁹⁾, Chapman⁽³⁰⁾, Debye and Huckel⁽³¹⁾, and been summarized by Vernwey and Overbeek⁽¹³⁰⁾ and by Kruyt⁽²⁸⁾. Gouy and Chapman considered the electrical double layer to consist of excess ions present in the solid phase and an equivalent amount of ionic charges of opposite sign distributed in the solution phase near the interface. However, for situations where the surface potential Ψ is large, the Gouy Chapman theory can run into difficulties because of the theory's inherent assumption of point charges and the consequent neglect of ionic diameters.

Stern⁽³²⁾ has suggested that the region near the surface be divided into two parts, the first consisting of a layer of ions adsorbed at the surface forming an inner compact double layer and the second consisting of a diffuse Gouy layer (figure 2). Stern thus has divided both the surface region and the bulk solution region into occupiable sites, assuming

FIGURE 2

Model of Stern Layer.

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that the fraction of sites in each region that are occupied by ions, are related by a Boltzmann expression. Stern's treatment is mainly concerned with the estimation of the extent to which ions enter the compact layer and the degree by which the potential, Ψ , is reduced by a factor, namely $\psi_{\delta} \cdot \psi_{\delta}$ represents the potential at the boundary between the compact and diffuse layers. The diffuse Gouy layer follows the compact layer with Ψ_0 replaced by ψ_{δ} . Further subdivisions can be postulated⁽³³⁾. Thus, the Stern layer may be preceded by an inner layer of desolvated, chemically adsorbed, and potential determining ions, as in the case of gold sol in a mixed electrolyte solution⁽³⁴⁾.

It can be expected that the ions and surrounding medium in the Stern layer would be rather rigidly held and that the Stern layer itself would also be immobile in the sense of resisting shear. However, since this type of immobility refers to the medium as a whole, and hence, primarily to the solvent, there is no reason why the shear plane should coincide exactly with the Stern layer boundary at Ψ_{δ} , but in certain situations may well be located somewhat further out in the Gouy region⁽²⁴⁾. The potential at the shear layer is defined as the zeta (ρ) potential.

The zeta potential is not strictly a phase boundary potential because it is developed wholly within the fluid region. Curves of the changing zeta potential with varying solute concentration and/or pH can be determined by the

FIGURE 3

3 a) Zeta Potential of Talc in Distilled Water pH 2 - 12 $\rho = 14.1 \frac{V}{E}$ (ref 35)

3 b) Mobility of Talc Particles versus pH with KCl 10⁻²N

$$v = \frac{p}{12.9} \qquad (ref 36)$$

18





techniques of electroosmosis, streaming potential, electrophoresis, and sedimentation potential. Brien and Kar⁽³⁵⁾ and Lafaye and Jacouelin⁽³⁶⁾ have independently determined zeta potential and particle mobility curves for talc with changing pH (figure 3). The technique of electrophoresis was used, the zeta potential, $\hat{\rho}$, being determined from the expression

$$\rho = \frac{4\pi\mu}{D} \frac{V}{E} \equiv \frac{4\pi\mu}{D} v$$

where μ is the viscoscity of the liquid, D is the liquid dielectric constant, V is the velocity of the particles relative to the liquid, and E is the applied potential per unit length. The dotted lines represent extrapolations of the curves by this writer, to determine in what range, if any, a zero point of charge (Z.P.C.) may be expected. The literature has not fully described various aspects of the electrokinetic phenomena for talc particles, such as calculation of expected Z.P.C. or hydration mechanisms for talc surfaces. The following discussion is intended to present a more complete picture of the nature of talc surfaces, thus laying the groundwork for the discussion of experimental results.

ii) Discussion

It has been suggested that H^+ and OH^- ions are potential determining ions for oxide systems (37)(38). However, other

independent mechanisms for charge development such as foreign ion inclusion into solid⁽³⁹⁾ and proton diffusion into and out of the hydroxylated surface of an oxide⁽⁴⁰⁾, can make the charging mechanisms more complex.

A hydroxylated surface should be expected on all oxidic materials which have had a chance to come to equilibrium with an aqueous environment. The hydration of an anhydrous oxide can proceed in several ways (37)(41)(42). Physical adsorption of water molecules, including hydrogen bonding to surface oxygen ions, but not dissociation, can occur. Chemisorption of water, which dissociates resulting in surface MOH groups, as well as reactions resulting in conversion to an oxyhydroxide, are other mechanisms.

Nondissociative or physical adsorption involves no dissociation of surface MOH groups and can be represented as follows:

where the underlined symbols refer to species forming part of the surface.

Parks⁽⁴³⁾ has suggested various expressions to describe the amphoteric dissociation of surface hydroxide groups to develop a surface charge. Acid dissociation produces negative surface sites:

20

Basic dissociation is illustrated by:

$$\underline{MOH} = \underline{M}^{+} + OH i aq$$

$$\underline{M}^{+} + H_2 O = \underline{M} O H_2^{+}$$
 7

Reactions (6) and (7) may be combined because the probability of the existence of bare M^+ is small, thus:

$$\underline{MOH} + H^{\dagger} = \underline{MOH}_{2}^{\dagger}$$

The adsorption of charged hydroxo complexes derived from the solid would be the chief competitor of the mechanism (8).

If one considers the close analogy between dissociation reactions of surface hydroxide groups and of mononuclear hydroxyl complexes, namely:

$$M^{Z^+}(OH_2(aq) \iff MOH_{Z-1}^+(aq) + OH i aq) \qquad 9$$

$$\underline{MOH} + H_2 O = \underline{M(OH)}^+ + OH \, \overline{iaq_3}$$
 10

then, the equilibrium between positive and negative surface sites may be assumed to occur as follows:

$$MO^- + 2Htag = MOH_2^+$$
 11

If hydroxo complexes rather than H^{*} are the potential determining ions, the equilibrium reactions are:

$$M^{Z^{+}}(OH)_{Z^{+}}[aq_{1}+2Haq_{2}-M^{Z^{+}}(OH)_{Z^{-}1}^{+}+2H_{2}O$$
 12

$$M^{2+}(OM)_{Z-1}^{-}(aq) = M^{2+}(OH)_{Z+1}^{-}$$
 13

$$M^{Z^+}(OH)^+_{Z^-}(aa) = M^{Z^+}(OH)^+_{Z^-1}$$
 14

For equations (12) - (14) the assumptions are that no hydroxo complexes other than the two monovalent species play a significant potential determining role and that the equilibrium constants for the two adsorption reactions are identical.

Finally, reactions resulting in conversion to an oxyhydroxide or hydroxide are exemplified by $MgO - Mg(OH)_2^{(44)}$. Many anhydrous oxides do not hydrate completely to produce the hydroxide, either because of unstable nature of the oxide or slowness of reaction rate.

Talc, and other clay minerals, may be described as complex oxides of the formula $A_x B_y O_n^{(45-47)}$. The talc sheet structure has broken bonds only on the edges of sheets. The broken bonds hydroxylate; they can dissociate to produce a pH dependent charge in the same way as described for the surfaces of simpler oxides (reactions $2^{\circ} - 1^{4}$). Charge from this source may be referred to as originating in the hydroxylated surface. The net charge on the solid is not confined to the surface but is distributed as a space charge.

The zero point of charge (Z.P.C.) is defined (37) as the concentration of potential determining ionic species at which the solid surface charge from all sources is zero. The location of the Z.P.C. is dependent on any and all of the charge mechanisms for a solid surface. The Z.P.C. for complex oxides, containing two types of oxide charge sites A and B, occurs at the pH at which positive hydrogen ion adsorption on one site type exactly balances negative hydrogen ion ad-sorption at the other.

The attempted extrapolations of the zeta curves of figure 3 indicate that if a Z.P.C. for talc particles can occur, it will occur at a pH less than one. In the pH range

1 to 12, the particles exhibit an increasing negativity. The mineral talc can be compared with serpentine minerals of the formula $Mg_3Si_2O_5(OH)_8$ in that both can be considered, as a first approximation, to contain two types of charge sites, namely silicon-oxygen and magnesium-oxygen - hydroxyl species. The Z.P.C. of the minerals might be expected to lie intermediate between the Z.P.C.'s or more rigorously the I.E.P. (isoelectric points when only H^+ or OH^- potential determining ions are involved) of the two species. Furthermore, the total particle charge attributable to each site group will depend upon the relative number of each type of site, namely on the composition of the mineral as reflected in the fraction of the total surface area occupied by each type of site. A formula⁽⁴³⁾ to predict the Z.P.C. of a complex oxide can be written as follows:

 $ZPC. = -A + \sum_{j} f_{j}(IEP_{(S)j})$ 15 where I.E.P_(S) are the isoelectric points of the component oxide sites and f_{i} accounts for the atomic fraction of each type of surface hydroxylated site. The term A takes into account the presence of an intrinsic surface charge δ_{j} divided by an undetermined proportionality constant K. δ_{j} is particularly important for clay minerals containing interstitial cations between the sheets, such as montmorillonite⁽⁴⁸⁾ or micas. Such cations are not present for serpentine or talc structures.

There are a minimum of five assumptions (43) related to the use of equation (15) all of which emphasize the ideal and oversimplified characteristics of the expression.

The I.E.P. of silica (SiO₂) has been reported to occur at several pH values, in the range 1.8 to $3.7^{(38)(49)}$, depending on the amorphous or crystalline nature of the silica. An I.E.P. of 2.1^{\pm} 0.3 pH units has been assigned to silica⁽⁴³⁾, a value of 1.8 for hydrous I.E.P. and 2.4 to an anhydrous I.E.P. For magnesia (MgO) or brucite (Mg(OH)), the I.E.P. occurs at pH range of 10.4 (anhydrous) to 12.5 (hydrous)⁽⁵⁰⁾. If equation (15) is applied to serpentine minerals, assuming that their composition is that of their molecular formula and that the term -A is negligible, then the Z.P.C. is calculated to be in the range 8.9 (hydrous) to 7.2 (anhydrous) (43). Furthermore, if the MgOH surface predominates, the Z.P.C. should be less than or equal to 12.5. Martinez et al⁽⁵¹⁾ have reported that chrysotile, a fibrous serpentine mineral, exhibits a Z.P.C. at pH 11.8. On grinding chrysotile tends to roll up such that the MgOH surface predominates, and the Z.P.C. value approximates that of brucite. On the other hand, the more platy habit of the serpentine mineral, lizardite, results in a more acidic Z.P.C. at pH 9.6, thus indicating a surface area containing more exposed SiOH sites. For both serpentine minerals the zeta potential remains positive on the acid side of the Z.P.C., although as pH 2 is approached a decrease in the positive zeta potential occurs, reflecting the dissolution of MgOH species and the

appearance of more SiOH sites.

To calculate the expected Z.P.C. for talc, use has been made of an experimental three dimensional model which was constructed according to specifications for the monoclinic unit crystal cell of talc, discussed previously. The model is composed of approximately two complete monoclinic cells. From this model, one layer of talc molecules has the composition (OH) 10 Mg 20 Si 30 O 86 (approximately 7 talc molecules). The species exposed on the edges of the sheet and on the uncharged sheet itself consist of $Si_{30}O_{56}$ (of which 22 oxygens are in the form of O), eight magnesium and 2 hydroxyl ions. The remaining species lie within the interior of the molecules. The exposed $Si_{30}O_{56}$ are equal to 92/146=.63fraction of the 146 atoms present. The magnesium and hydroxyl ions represent $10/146 = .068^5$ of the atoms present. Using these values in equation (15), with the term (-A) assumed negligible, the hydrous Z.P.C. is:

 $Z.P.C. = .63(1.8) + (.0685)(12.5) = 1.9^9$ and the anhydrous Z.P.C. is:

Z.P.C. = $.63(2.4) + (.0685)(10.4) = 2.2^2$

Experimental Z.P.C.'s determined by electrophoresis integrate charge contributions from all sources. The intrinsic structural charge on the clay minerals is negative and finite $\binom{(45)}{2}$ Thus, one expects that effective Z.F.C.'s observed to be quite variable and more acid than predicted. For talc, the presence of a small finite intrinsic negative charge, as reflected in the term (-A), would shift the Z.P.C. to more
acid values. The exact value of A cannot be determined since the proportionality constant (K) is unknown ⁽⁴³⁾, and for a known $\delta_{\vec{l}}$, the term (-A) indicates the direction (acid or basic) necessary to correct the calculation.

The inability to achieve positive charge on suspended talc particles is comparable to the observations with other clay minerals (43)(45). The acid resistance of talc surfaces and the complex nature of the uncharged sheets and charged ions on the edges of the sheet must inhibit the establishment of the equilibrium between adsorption and desorption of H⁺ ions. The exact role of silica in different clay structures has yet to be fully determined. Pauling has predicted (52)significant differences in acidity, reflecting the degree of oxygen sharing by SiO₄ tetrahedra in clays.

Further consideration of the aqueous chemistry of talc particles, including possible hydration mechanisms, are included in the discussion of the adsorption and I.R. results.

SECTION II

ADSORPTION AND INFRARED RESULTS

DISCUSSION

ADSORPTION THEORY

i) Introduction

Adsorption is said to occur when the concentration of one of two immiscible phases, at the interface between these phases, is greater than its concentration in the bulk. Adsorption from solution is a relatively complex phenomenon. It depends on the nature of solute-solvent interactions in the solution phase and in the interfacial region, as well as on their interactions with the absorbent.

The adsorption of nonelectrolytes at the solid-solution interface may be viewed in terms of two different physical pictures (24). One implies that the adsorption is confined to a monolayer next to the surface and that succeeding layers are virtually normal bulk solution. Thus solute-solvent interactions decay very rapidly with distance. The other concept is that of an interfacial layer or region, multimolecular in depth, over which a more slowly decaying interaction potential with the solid is present. Adsorption thus corresponds to a partition between a bulk and an interfacial phase. The monolayer concept is more widely used.

Some portion of a crystal surface, no matter where it is defined, must exhibit broken bonds. Whereas all the internal atoms are completely surrounded by other atoms in a

symmetrical way such that all attractive forces between the atoms are cancelled out, the surface atoms are subject to an asymmetric distribution of forces and do not exist in a state of maximum entropy. Adsorption of foreign molecules onto the surface, partially relieves the state of unsaturation or strain at the crystal surface⁽⁵³⁾.

Adsorption is accompanied by a decrease in Gibb's free energy, $\triangle G$. There is generally a decrease in entropy $\triangle S$, caused by the lost degrees of freedom when the adsorbed molecule is constrained to two dimensional motion. From the following equation:

$$AG = AH - TAS$$
 16

where T is the absolute temperature, it is seen that the enthalpy ΔM_{γ} is nearly always negative, and its decrease is called the heat of adsorption⁽⁵⁴⁾.

The mechanisms of adsorption may be either physical or chemical. Van der Waals forces are considered to be responsible for physical adsorption and thus, this type of adsorption is characterized by the absence of true bond formation and by a low heat of adsorption, usually of the order of 2 - 5 cal./mole. Electron transfers do not take place between the adsorbate and the adsorbent. Physical adsorption is nonselective in nature, is reversible and occurs rapidly forming multimolecular layers.

In contrast, chemisorption or chemical adsorption is irreversible or reversible with great difficulty. It is completed by monolayer formation, although physical multimolecular adsorption may occur over a chemisorbed film. Chemisorption always involves chemical bond formation between the adsorbent and adsorbate by means of the partial or complete transfer of an electron overlap. A high heat of adsorption, generally greater than 15 kcal./mole accompanies chemisorption. Appreciable activation energies may be involved, thus requiring a certain minimum temperature below which the reaction will not proceed. Chemisorption may thus be dissociative, nondissociative or reactive in nature.

ii) Adsorption Isotherms

Langmuir, Bruneauer, and Freundlich have each proposed adsorption theories to explain adsorption isotherms.

Langmuir⁽⁵⁵⁾ envisages a dynamic model in which the rate of adsorption is equal to the rate of desorption, and adsorption occurs as a monomolecular film. For gas phase adsorption, one has

$$V = V_m \frac{bp}{1+bp}$$
 17

where V is the volume of adsorbed gas, V_M is the volume for monolayer coverage, p is the equilibrium pressure of the adsorbing gas, and b a constant which can be related to the heat of adsorption.

For the adsorption of liquid on solids, Langmuir's equation takes the following linear form:

$$\hat{\xi} = \frac{1}{ab} + \frac{c}{a}$$
 18

where X is the amount of adsorbate per gram solid, C is the equilibrium concentration of the solid, and a and b are constants related to monolayer coverage and heat of adsorption, respectively.

An explanation for multimolecular gas adsorption is offered by Brunauer, Emmett and Teller⁽⁵⁶⁾ and modified by Bartell and his co-workers⁽⁵⁷⁻⁵⁹⁾, for liquid phase adsorption. Brunauer's theory is based on the same dynamic model of the Langmuir's unimolecular adsorption, but with the added assumption that the evaporation-condensation properties of the second and higher adsorbed layers are the same as those in the liquid state. The form of the isotherm equation to describe an infinitely thick layer of condensate, when gas pressure equals vapour pressure of the adsorbate, is:

$$V = \frac{V_{m}C_{p}}{(p_{0}-p)(1+(C-1))P_{p_{0}}}$$
19

In linear form, the equation becomes:

$$\frac{p}{V(p-p)} = \frac{1}{V_{m}C} + \frac{C-1}{V_{m}C} \frac{p}{P_{0}} 20$$

where V is the volume of the adsorbed gas at an equilibrium pressure p, V_M is the volume of gas satisfying the monolayer

capacity of an adsorbent, p_0 is the saturation pressure of the gas, and c is a constant.

For multilayer adsorption limited to n layers, the B.E.T. equation can be written as:

$$V = \frac{V_{m}CX}{(1-X)} \left[\frac{1+(n+1)X^{n} + nX^{n}}{1+(C-1)X - CX^{n+1}} \right] 21$$

where X is equal p/p_0 . For the limiting case of n=1, the equation reduces to the Langmuir adsorption isotherm.

Liquid phase adsorption may be expressed by the modified linear isotherm equation of Bartell⁽⁵⁹⁾

$$\frac{C}{X(C_0C)} = \frac{1}{X_mk} + \left(\frac{k-1}{X_mk} \times \frac{C}{C_0}\right) \qquad 22$$

where X equals the amount of solute adsorbed per gram of adsorbent at the equilibrium concentration C, X_m is the value of X at the monolayer point, C_0 refers to the solubility of the solute, and k is a constant.

Freundlich⁽⁶⁰⁾ describes an empirical equation for gaseous adsorption which has the form

$$V = k p^{1/m}$$
 23

where V and p are the same as before, k and n are constants related to adsorption density.

Liquid phase adsorption changes the form of the equation to

$$\frac{X}{m} = d C_0^{1/m}$$
 24

or its linear equivalent:

$$\log\left(\frac{X}{m}\right) = \log d + \frac{1}{n}\log C_0 \qquad 25$$

where x/m is the amount of solute adsorbed on a surface, C_0 is the equilibrium solute concentration, and d and n are constants. The Freundlich equation is not valid at very low or high concentrations but otherwise often compares with the Langmuir equation at moderate concentrations. No theoretical basis for the Freundlich equation has been developed, and its usefulness is limited to its ability to fit data.

iii) Isotherm Shapes

The shapes of the isotherm curves may provide additional information about the adsorption mechanisms.

Brunauer $^{(61)}$ classifies the shapes of adsorption isotherms for vapours on solids into five main types. Giles et al $^{(62)}$ modifies these classifications and considers that the isotherms for the adsorption of organic solutes are divided into four main classes according to the nature of the slope of the initial portion of the curve and thereafter into sub-groups.

S curves indicate vertical orientation of adsorbed molecules at the surface. L curves or "Langmuir" isotherms usually result when molecules are adsorbed flat on a surface or when vertically oriented adsorbed ions have particularly strong intermolecular attraction. H curves commence at some positive value on the adsorption density axis and are

indicative of solutes adsorbed as ionic micelles or by high affinity ions exchanging with low affinity ions. C curves, or constant partition or linear curves, are observed when the solute penetrates more easily into the solid than does the solvent.

The shape of the curves farther from the origin can result in further sub-classes of the four main isotherm types. Thus, a curve with a long plateau may indicate that the adsorbed solute molecules in the monolayer are so oriented that the new surface they present to the solution has a low attraction for solute molecules. However, if they are oriented so that the new surface has a high attraction for more solute, the curve rises steadily and has no plateau. A long flat plateau may also indicate adsorption of micelles.

EXPERIMENTAL

i) Talc Sample Preparation

The talc samples were obtained through the courtesy of Baker Talc Limited, from the Company's mine at Mansonville in the Eastern Townships of Quebec. Experimental samples were hand-picked and ground with mortar and pestle to -10

mesh. The talc particles were then dry ground with 1/2 inch stainless steel balls in an Abbé Ball mill (diameter 25"). The mill discharge was divided into aliquots of -28 +65, -65 +100, -100 +150, -150 +200, -200 +325, and -325 mesh sizes. The +28 mesh was returned to the mill. In the experimental work, a mixed sample containing 60% -65 +150 mesh and 40% -150 +325 mesh was used as well as separate aliquots of -100 +150, -150 +200, and -200 +325 mesh sizes.

The specific gravity of the talc was determined to be 2.78, which is in agreement with the literature values (20)(62). The ignition loss at 910°C was $4.9^{\circ} \stackrel{+}{=} 0.08$ % water, about 1% higher than the theoretically expected value. The X-ray diffraction patterns (Appendix B) confirmed the high purity of the talc. Treatment of the talc with boiling nitric and hydrochloric acids indicated that the talc contained $2.8\stackrel{+}{=}0.2$ % soluble impurity, namely magnesite and dolomite.

The high purity handpicked samples were used with no purification, in the experiments.

ii) Alcohol

The aromatic alcohol, 2 phenyl 2 propanol, or $a_{,a}$ - dimethyl benzyl alcohol, has the formula⁽⁶⁴⁾:



Bishop et al⁽⁶⁵⁾ recommend the use of the alcohol for the flotation of lead, zinc, and copper ores at concentrations of 0.005 - 5.0 lb. alcohol/ton ore. They report that the reagent is not only a good frother, producing a brittle, stable froth, but may also have collector ability. The use of the alcohol in nonmetallic mineral flotation does not appear to be documented in the literature.

2 phenyl 2 propanol solidifies to hexagonal prisms below 33°C and the liquid boils at 202°C. The formula weight is 136 gm./mole and the density 0.9724 gm./ml.⁽⁶⁶⁾. Although the alcohol is readily soluble in ethanol, ether, benzene, etc., it is only moderately soluble in water up to 0.1%. Indeed, water is soluble in the alcohol up to 4 - 5 (⁶⁷⁾.

The concentration of the alcohol in aqueous solution may be measured by means of ultra-violet spectrophotometry. The reagent exhibits three peaks at 261, 256, and 250 $m\mu$ arising from benzene ring vibrations. All three peaks appear to follow Beer's Law at least up to concentration of 600 mg./l. The experimental data is based on the changing magnitude of the peak at 261 $m\mu$ the calibration curve for which is given in figure 4.

Models of 2 phenyl 2 propanol have been constructed using Godfrey stereomodels and molecular models, the molecular dimensions of which are derived from the literature (68-70). If the molecule is adsorbed end-on through the hydroxy

Calibration Curve for 2 Phenyl 2 Propanol



group, then the two methyl groups and the benzene ring are distributed tetrahedrally about the carbon-hydroxy bond, and the molecule occupies a roughly spherical area with radius $3.5A^{\circ}$ and area $38.5A^{\circ 2}$. If the molecule is adsorbed flat onto the surface, it sweeps out a roughly rectangular area with dimensions $9.6^{3} \times 6.9^{2}A^{\circ}$, namely $66.5A^{\circ 2}$.

iii) Experimental Technique and Reagents

One gram samples of the appropriate talc particle size were accurately weighed and transferred to dry 50 ml. vials. The exact volume of the vials was determined by measuring their water capacity at 20°C. Solutions of the 2 phenyl 2 propanol were added to the vials, air bubbles trapped within the talc particles were removed, and the vials were tightly stoppered. The talc was mixed with the solutions by rotating the vials on an apparatus designed by Yoon⁽⁴²⁾. After equilibration time was attained, the vials were centrifuged at 3200 r.p.m.for five minutes, so that a clear portion of aqueous solution could be made available for analysis.

The clear solutions were analyzed in U.V. Spectrosil cells by means of the Perkin Elmer Hitachi ultraviolet visible spectrometer model 124D with a digital readout accurate to three decimal places. The adsorbance values for the alcohol peak at 261 mm were used.

Apart from the 2 phenyl 2 propanol, stock solutions of analytical grade hydrochloric acid (Fisher Co.), sodium hydroxide pellets (Mallincroft Co.), and calcium chloride (Fisher Co.) were prepared separately and used where required.

ADSORPTION RESULTS

The adsorption of the alcohol on talc surfaces appears to be complete within four to six hours in solutions of natural pH and alkaline pH, respectively (Figure 5).

The variation of 2 phenyl 2 propanol adsorption with pH is described by the curves of figures 6 and 7. Figure 6 was determined at an alcohol concentration of 486 mg./l. on one gram talc samples, while figure 4 was obtained at 97 mg./l. 2 phenyl 2 propanol on two gram talc samples. It is noted that the presence of excess hydroxyl ions significantly increases the alcohol adsorption, but excess hydronium ions have little effect.

The effect of calcium ions on the adsorption of the alcohol is illustrated in figure 8 for -150 +200 mesh talc. Excess calcium ions apparently enhance the alcohol's adsorption, especially at pH greater than 8, but the basic shape of the curve is essentially the same as that without calcium ions.

The adsorption isotherms at pH 6.9 for -100 + 150 mesh, mixed mesh (60% -65 +150, 40% -150 +325), and -200 +325 mesh talc are described in figure 9. The three isotherms all exhibit

Adsorption of Alcohol vs

Time (Hours)

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Initial Concentration 486 mg./1 $_{\odot}$ 2 phenyl 2 propanol

l gm. mixed mesh talc



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Adsorption vs pH

486 mg./l. 2 phenyl 2 propanol = Initial Concentration

1 gm. mixed mesh



Adsorption vs pH

Initial Concentration 97 mg./l. 2 phenyl 2 propanol

2 gm. mixed mesh talc



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Adsorption vs pH 1 gm. -150 +200 mesh talc A • C_{init}. = 485 mg./1. 2 phenyl 2 propanol B © C_{init}. = 486 mg./1. 2 phenyl 2 propanol and 74.4 mg./1. Ca⁺⁺



Adsorption Isotherm pH 6.9

▲ -100 +150 mesh

◎ (60% ~65 +150 40% -150 +325) mesh

•

-200 +325 mesh
l gm. talc

- 1



•

Adsorption Isotherm pH 6.9

-200 +325 mesh talc
 l gm. talc



Freundlich Isotherm

pH 6.9

▲ -100 +150 mesh

0 -200 +325 mesh

l gm. talc

`}



two plateau regions over the equilibrium concentration ranges of .050 to .400 millimoles/litre and .600 to 1.000 millimoles/litre. The -200 +325 mesh talc isotherm exhibits another plateau at the equilibrium concentration range of 1.700 to 1.900 millimoles/litre (figure 10). An interesting feature of the isotherms is the difference in the magnitude of the amount of alcohol adsorbed to form the first plateau and second plateau regions. The amount adsorbed is three to four times that of the first plateau. However, the amount adsorbed for the third plateau of the -200 +325 mesh talc is only roughly double that of the second plateau. Desorption experiments indicate that the alcohol is removed from the talc surface.

The data has been best fitted to the Freundlich equation, figure 11. The constants associated with the equation and the equilibrium concentration over which they appear to be valid are listed in Table I. Plateaus occur for -100 +150 mesh at 0.28 and 1.5 micromoles/gm. talc; for mixed mesh talc at 0.78 and 2.5 micromoles/gm talc; and for -200 +325 mesh talc at 1.1, 4.1 and 7.5 micromoles alcohol/gm, talc.

The adsorption isotherms of -100 +150 mesh and -200 +325 mesh talc at pH 11.0 are described in figure 12. The shape of the curves is quite different from that observed at pH 6.9. Only one plateau region is observed in either curve over the equilibrium concentration range up to 1.000 millimoles/1. of 2 phenyl 2 propanol. The corresponding Freundlich plots

a7

(figure 13) and equations (Table II) indicate that a plateau occurs at 2.1 micromoles/gm. for -100 +150 mesh talc and 5.0 micromoles/gm. for -200 +325 mesh talc.

TABLE I

Freundlich Equations pH 6.9

Equation -100 +150 mesh	Concentration Range moles/1.			
$x/m=(.017 \times 10^{-6}) C_0^{.0069}$	1×10^{-6} -34 × 10 ⁻⁶			
$x/m=.28 \times 10^{-6}$	$75 \times 10^{-6} - 350 \times 10^{-6}$			
$x/m=(.0033 \times 10^{-6}) C_0^{.0042}$	500 " -720×10^{-6}			
$x/m=1.65 \times 10^{-6}$	920 " -1200 x 10 ⁻⁶			
mixed mesh				
$x/m=(.14 \times 10^{-6}) C_0^{.0552}$	1 " -6.8 x 10^{-6}			
$x/m=0.78 \times 10^{-6}$	23 " -310×10^{-6}			
$x/m=(.0185 \times 10^{-6}) C_0^{.00173}$	$480 " -670 \times 10^{-6}$			
$x/m=2.5 \times 10^{-6}$	810 " -C x 10 ⁻⁶			
-200 +325 mesh				
$x/m=(.28 \times 10^{-6}) C_0^{.0143}$	1 "-3.8 x 10^{-6}			
x/m=1.1 x 10 ⁻⁶	18 " -290×10^{-6}			
$x/m=(.036 \times 10^{-6}) C_0^{.0176}$	410 " -580×10^{-6}			
x/m=4.10 x 10 ⁻⁶	890 " -1005×10^{-6}			
x/m=(.044 x 10 ⁻⁶) C _o .01	$1200 \times 10^{-6} - 1400 \times 10^{-6}$			

Adsorption Isotherm

pH 11.0 l gm. talc

▲-100 +150 mesh

⊘ -200 +325 mesh



 $E_{\rm sub}$

Freundlich Isotherm pH 11.0 lgm.talc A-100 + 150 mesh talc

-200 +325 mesh talc



Equation -100 +150	Concentration Range moles/litre			
$x/m=(.0315 \times 10^{-6}) C_0^{.0152}$	$1 - 58 \times 10^{-6}$			
$x/m=2.1 \times 10^{-6}$	$510 - 790 \times 10^{-6}$			
-200 +325				
$x/m=(.35 \times 10^{-6}) C_0^{.032}$	$1 - 68 \times 10^{-6}$			
x/m=5.0 x 10 ⁻⁶	$680 - 990 \times 10^{-6}$			

TABLE II				
Freundlich	Equa	ations	Ha	11.0

INFRARED

i) Introduction to I.R.

Infrared spectroscopy has become a useful tool for the analysis of surface reactions⁽⁵³⁾. Infrared spectra arise as a result of the vibrations of the atoms within a molecule. The number and frequency of the vibrations is dependent on the symmetry and bond strengths of the molecule. When a molecule is adsorbed, the symmetry of the molecule is altered, however slightly, by the "one sided" surface forces. The nature of the adsorption can be related to any quantitative measure of the symmetry change. In physical adsorption, the
absorbate is subjected only to weak intermolecular forces of the Van der Waals type and thus its symmetry is only slightly altered, and small frequency shifts, usually less than 1% are observed. Leftin and Hobson⁽⁷¹⁾ define physical adsorption as "adsorption which leads to perturbation of the electronic or stereochemical states of the molecule but otherwise leaves the molecule and its entire electron complement intact".

Chemisorption causes a completely new symmetry for the adsorbed species from that observed in the gas phase. Since the surface bond is very strong and the adsorption may be dissociative in nature, a completely new infrared spectrum is observed and bond shifts and intensities are far removed from those of the gaseous adsorbate. Thus, the literature⁽⁷²⁾ defines chemisorption as "adsorption which produces a new chemical species by fragmentation of the molecule or of its electron component".

ii) Experimental I.R.

The potassium bromide disks of talc were prepared by methods indicated in the literature (72-74). A modification was introduced by mixing the talc particles, which were less than 30 microns in size, with the spectral pure potassium bromide in the ratio 1 mg. talc per 220 mg. KBr. The

2 phenyl 2 propanol spectrum was determined in carbon tetrachloride and carbon disulphide, the solution concentration being approximately 10% alcohol by weight.

A spectrum of the 2 phenyl 2 propanol on talc surface was more difficult to obtain, presumably because of the weak interaction between the talc and the alcohol, and the small amounts of adsorbed alcohol. Only by mixing the talc with saturated aqueous solution of the alcohol and allowing the sample to completely dry at room temperature before mixing with potassium bromide could a suitable spectrum be observed. It is noted that the broad band for adsorbed water in the potassium bromide disks (approximately 3400 cm.⁻¹) could thus not be avoided.

The spectra were determined on the Perkin Elmer Infrared Scanner, model 457 and the spectra peaks were standardized against a calibration spectrum of polystyrene.

Table III lists the experimental wave lengths of the three spectra with the peak assignments.

Talc Spectrum				
Peak (cm. ⁻¹)	Assignment			
3670	OH str.			
3650	OH str.			
1045	Si-O v _l str.			
1015	Si-O v ₃ str.			
690	Si-O v ₂ str.			
670	Si-O v ₄ bend			
530	Mg-O \perp vib.			
467	Mg-OH in plane vib.			
445	Mg-OH in plane vib.			
426	Si-O v ₅ bend			
380	OH bend			
2 Phenyl 2 Propanol				
3600	OH str.			
3080				
3060	C - H str. in benzene ring			
3020				
2970				
2920	C - H str. of methyl groups			
2870				

TABLE III

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TABLE III (cont'd	<u>)</u>
Peak (cm. ⁻¹)	Assignment
200 - 1600	char. of monosubst. benzene
1490	
1445	C - C str. benzene ring
1460	
1380	C - CH ₃ bend
1364	0 - H bend
1255	C - O str.
1175	
1105	characteristic complex bend of
1070	monosubst. benzene rings
1030	CH ₃
950	-c - bending vib.
860	CH ₃
765	C - H bend of 5 adj.
700	H on benzene ring
Talc with Adsor	bed 2 Phenyl 2 Propanol
Peak $(v^{-1} cm^{-1})$	AV Assignment
3670	
3650	OH str. (talc)
3530	70 OH str. alcohol

TABLE III (cont'	<u>d)</u>	1
Peak (cm. ⁻¹)	sv-1	Assignment
3080	·	
3060	—	C - H str. in benzene ring
3020	-	
2970		
2920	-	C - H str. of methyl groups
2860	10	
1490	-	
1445	5	C - C Str. Denzene ring
1460		$C = C^{\mu}$ bond
1380	-	c - ch ₃ bena
1359	5	0 - H bend (Alcohol)
1255	-	C - 0 str.
1173	2	
1100	5	characteristics of complex bend
1070	—	OI MONOSUDST. Denzene
1045	-	Si - O v, str.
1015	-	v ₃ str.
950	—	-c here is a set
860	-	CH ₃ Dend Vib.
765	-	C - H bend of 5 adi.
700		H on benzene ring
690		$Si - 0$ v_2 str.
670		v ₄ bend

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TABLE III (cont'd	<u>)</u>	
Peak (cm. ⁻¹)	av ⁻¹	Assignment
530		Mg-O vib.
467	—	
445	—	MgOH in plane vib.
426		Si-O v ₅ bend
380	-	OH bend (talc)

INFRARED SPECTRA

i) Talc

Hunt⁽⁷²⁾ et al, and Farmer⁽⁷³⁾ have reported talc spectra. Hunt spread talc particles of size less than five microns as a thin film over a sodium chloride window. Farmer used potassium bromide pressed disk technique, as well as evaporating suspensions of talc particles on potassium bromide plate. The experimental spectrum (figure 14) exhibits the basic features of those in the literature.

If the unit cell of talc is considered to contain two units of empirical formuls $Mg_3Si_4O_{10}(OH)_2$ from separate sheets, then one can expect 123 normal vibrations, about half of which can be infrared active, the remainder being Ramanactive ⁽⁷³⁾. The infrared active vibrations fall into two classes of symmetry; namely, A_u in which the change in dipole moment is along the b axis which lies in the plane of the sheets, and B_u in which the dipole moment changes perpendicular ularly to this axis, so that none need be perpendicular to the plane of the sheets. However, the simplicity of the experimental spectrum and the presence of perpendicularly polarized bands⁽⁷¹⁾ suggest that the spectrum can be interpreted in terms of the pseudo-hexagonal symmetry of talc, arising from the hexagonal symmetry of the silicon oxygen framework (figure 1b).

A magnesium-silicate sheet can be assigned a symmetry C_{2h} . The silicate layers which sandwich the magnesium ions are symmetrically related by twofold axes passing through the magnesium ions.

The vibrations of the silicon-oxygen layers are now treated separately from the magnesium vibrations. The higher frequency vibrations are expected to involve silicon-oxygen ions rather than magnesium ions. Launer⁽⁷⁴⁾ observed that all silicates show strong adsorption near 1000 cm.⁻¹ arising from Si-O stretching frequencies.

Isolated units of the silicon-oxygen layers have hexagonal symmetry, C_{6v} , with hexagonal axes perpendicular to the sheets. Mathieu⁽⁷⁵⁾ suggested that such a structure has five infrared active vibrations, two polarized perpendicularly to the sheets (v_1 and v_2 ; class A_1), and three degenerate vibrations in the plane of the sheets (v_3 , v_4 , and v_5 ; class E_1). There is also an inactive vibration of class B, three

FIGURE 14

Infrared Spectra of Talc



of class B_2 and three degenerate Raman-active vibrations of class E_2 . An integration of this system into a crystal of symmetry of C_{2h} causes the degenerate vibrations to split, the inactive vibrations to absorb radiation, and the form of the vibrations to become altered. In talc, the fact that the magnesium ions are bonded to the silicon-oxygen layers only through the inner layer of oxygen atoms causes the symmetry of the force field to be preserved and little environmental perturbation of the Si-O vibration occurs.

The single silicon-oxygen tetrahedron thus has five infrared active vibrations arising from C_{6v} symmetry. The pure stretching frequency, v_1 , is correlated with the highest frequency perpendicular vibration which occurs as a shoulder band at 1045 cm.⁻¹. The parallel stretching frequency, v_3 , is assigned to the slightly lower frequency at 1015 cm.⁻¹ because v_3 includes a small bending component. The shoulder at 690 cm.⁻¹ and the band at 670 cm.⁻¹ are the v_2 and v_4 stretching and bending frequencies, respectively. The complex band centered at 445 cm.⁻¹ results at least in part from the largely bending vibration v_5 .

If the magnesium ions all move in phase, with their motions restricted to being either perpendicular or parallel the sheets, they can couple with the silicon-oxygen vibrations without perturbing the Si-O form and splitting the degeneracy of the E_1 vibrations. Thus, the perpendicular magnesium

vibration is assigned to the shoulder 530 cm.⁻¹, somewhat lower than the comparable band observed for brucite by Beutelspacher⁽⁷⁶⁾. The bands at 467 and 445 cm.⁻¹ are taken to correspond to in-plane vibration of the brucite layer with its degeneracy lifted. This vibration should couple strongly with the v_5 vibration of the silicate layer now considered to occur at 426 cm.⁻¹.

The magnesium ions in talc are not all symmetrically related, one in each unit cell at a site of symmetry C_{2h} , the other two having symmetry C_2 . If three of the resulting six degrees of freedom of the infrared active vibrations of talc are correctly identified above, the remaining three are expected to couple only with the inactive vibrations of the silicon-oxygen sheets, alternate oxygens of the inner layer being 180° out of phase.

A complete analysis of the vibrations of the magnesium and the hydroxyl ions remains tentative. The sharp peak at 3670 and its shoulder at 3650 cm.⁻¹ can be assigned to hydroxyl stretching frequency (77). The broad peak at 3413 represents adsorbed water on the talc and/or potassium bromide disk. Nauman et al, by means of infrared and neutron diffraction studies, concluded that a significant correlation between low frequency hydroxyl vibrations in clay minerals and the corresponding hydroxide was doubtful. Thus, a comparison of hydroxyl motions in the brucite layer of talc with those

in magnesium hydroxide is restricted. The rocking frequency of the structural hydroxyl groups, and the bands arising from vibrations of the hydroxyl groups as a whole, out of phase with the other oxygen atoms of the inner layer in which they lie, remain unidentified, although these vibrations may be expected to lie below 1000 cm.⁻¹ (78). Indeed, the band at 380 cm.⁻¹ may be the result of the bending frequency of the hydroxyl groups, as suggested by Hexter et al⁽⁷⁹⁾.

Two other factors might be noted at this point. Farmer (73) has observed that the talc structure persists despite severe grinding in that hydroxyl stretching and silicon-oxygen bending frequencies, although somewhat broadened, are still observed. Also, Nauman et al (77) concluded from their work that the silicate layer in talc is fully extended and undistorted, and the hydroxyl groups exhibit only weak, if indeed any, hydrogen bonding with its neighbours within the talc structure.

ii) I.R. of Alcohol

The infrared spectrum of 2 phenyl 2 propanol, exhibited in figure 15, is a composite spectrum obtained in two solvents, carbontetrachloride and carbon disulphide, with the solvent peaks removed to obtain complete spectrum of the alcohol. The spectrum agrees with those observed in the literature⁽⁸⁰⁾.

FIGURE 15

Infrared Spectra of 2 Phenyl 2 Propanol



The assignment of the bands results from inspection of various sources in the literature (81-83). The band at 3600 cm.⁻¹ represents hydroxyl stretching vibration. The frequencies at 3080, 3060, 3020 cm.⁻¹ are characteristic of benzene rings and are indicative of carbon-hydrogen stretches on the aromatic ring. The three peaks at 2970, 2920, and 2870 cm.^{-1} result from the alkane portion of the molecule, namely carbon-hydrogen stretches of the methyl groups. The fine structure in the region 2000 to 1670 cm.⁻¹ is characteristic of monosubstituted benzene and the peaks at 1490 and 1445 cm.⁻¹ result from carbon-carbon stretches in the benzene ring. The shoulders at 1460 and 1380 cm.⁻¹ are indicative of carbon-methyl hydrogen bending frequencies. The band at 1364 can be assigned to the O-H bending vibrations and the band at 1255 cm.⁻¹ to the carbon-oxygen stretching frequency. The bands at 1175, 1105, and 1070 cm.⁻¹ are characteristic of complex bending frequencies of monosubstituted benzene rings and the bands at 1030, 950, and 860 cm. $^{-1}$ result from bending vibrations of the propyl group. The peaks at 765 and 700 cm.⁻¹ represent the carbon-hydrogen bending frequencies of the five adjacent hydrogen atoms on the benzene ring.

iii) I.R. Spectra of Alcohol and Talc

The infrared spectrum of the 2 phenyl 2 propanol present on a talc surface (figure 16) would appear to exhibit features indicative of physical adsorption. The bands previously described for talc particles remain unperturbed by the presence of the alcohol. The 2 phenyl 2 propanol peaks occur, for the most part, at the previously designated frequencies, although the propyl peak at 1030 cm.⁻¹ is blocked out by the combined silicon-oxygen stretches at 1045 and 1015 cm.⁻¹.

Of particular interest, are the changes in frequencies of the hydroxyl stretching and bending vibrations. The O-H stretching vibration is shifted to 3530 cm.⁻¹ and is almost masked by the broad band about 3400 cm.⁻¹ of adsorbed water. Similarly, O-H bending frequency at 1364 cm.⁻¹ has been shifted to 1359 cm.⁻¹. The change in the stretching frequency, $\Delta \overline{V}_{p}$ of approximately 70 cm.⁻¹ exceeds the 1% variation expected for physically adsorbed species ⁽⁵³⁾, but the less perturbed bending frequency, whose $\Delta \overline{V}_{p}$ is 5 cm.⁻¹, lies within the expected range.

Other perturbations occur in the carbon-hydrogen and carbon-carbon stretching frequencies, as well as the complex bending frequencies, associated with the monosubstituted

FIGURE 16

Infrared Spectrum of Talc with Adsorbed

2 Phenyl 2 Propanol

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carbon-hydrogen system of the benzene ring. Thus, the carbonhydrogen stretches of the benzene ring, previously at 3080, 3060 and 3020 cm.⁻¹, almost completely disappear when adsorbed on a talc surface. An aromatic carbon-carbon stretch previously assigned to a band at 1445, now occurs at 1440 cm.⁻¹. Two of the bands associated with monosubstituted benzene rings appear at 1173 and 1100 cm.⁻¹ slightly shifted from their previous values of 1175 and 1105 cm.⁻¹. Only one of the alkane carbon-methyl stretches undergoes perturbation and is shifted from its initial value of 2870 cm.⁻¹ to 2860 cm.⁻¹. All of the aforementioned frequency changes lie within the l% range expected for physical adsorption perturbations.

It is noted that subsequent washing of the talc surfaces with distilled water or alkaline solution, or heating at 100°F in an oven removes all the peaks associated with the aromatic alcohol leaving a spectrum identical with that of talc in figure 12. This is strong indication of physical adsorption.

The perturbation of the hydroxyl free stretch of the alcohol is indicative of a single hydrogen bond being formed with the talc surface⁽⁸¹⁾. It is expected that the hydroxyl bending frequency might be affected to a lesser extent than the stretching frequency. The other small perturbations of the 2 phenyl 2 pmopanol bands must also be the result of the hydrogen bond attraction between the hydroxyl group of the

alcohol and the talc surface. The adsorbed molecules apparently inhibit the carbon-hydrogen and carbon-carbon stretching frequencies of their adsorbed neighbouring molecules. Similarly the carbon-methyl stretching frequency might be expected to undergo perturbation because of its proximity to the talc surface.

In conclusion, the infrared spectra indicate that the adsorption of the 2 phenyl 2 propanol on the talc surface occurs by means of a hydrogen bond formation between the aromatic hydroxyl group and the talc.

DISCUSSION

From the presentation of crystal, electrokinetic and contact angle aspects related to talc, it is suggested that talc particles should exhibit two distinct types of surfaces in an aqueous medium; namely, i) an uncharged hexagonal array of silicon-oxygen atoms, with a hydroxyl group at the center, recessed from the oxygen plane, and ii) a complexly charged surface of silicon, oxygen, hydroxyl, and magnesium ions formed by cleavage across the uncharged sheets. It is not expected that the uncharged surface can interact strongly with a neutral aqueous medium. Physical adsorption of water

on the uncharged and unreactive talc surface may be represented as follows:



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Furthermore, penetration of the hexagonal rings by water molecules, resulting in a weak physical interaction between the hydrogen of the interior hydroxyl group and the oxygen of the water molecule should not be overlooked. This phenomena would be time dependent, and might explain an experimental observation that the natural flotation of talc particles varies slightly with the time of aqueous conditioning.

The interactions of the broken bonds at the edges of the sheets are difficult to analyze. It might be expected that the outer Si-O⁻, at either side of the edge of a talc sheet, might interact in a manner comparable to quartz (SiO_2) . Thus, these broken bonds at the surface would react with water molecules to form a surface silicic acid⁽³⁾⁽⁴⁹⁾. The ionization of this surface silicic acid would give rise to charge on the sheet edges as follows:

 $\sim Si - M = \sim Si + H^+ 27$

The potential determining ions for such interaction would be H^+ and OH^- .

The inner magnesium, oxygen and hydroxyl ions of talc exhibit multiple co-ordinate type bonding. The magnesium ions exhibit 6-fold co-ordination, the oxygen and hydroxyl, 3-fold co-ordination. On cleavage, unlike the SiO⁻ sites which would exhibit a full negative charge, the inner core ions might exhibit partially positive and/or negative charge sites dependent on the degree of redistribution of electron densities with the unbroken co-ordinate bonds. A hydration mechanism for these inner core charge sites might be: i)





or ii)



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 $\mathbf{28}$

An overall ionization and hydration mechanism for the talc edge might be ideally represented by:



The infrared data suggest that the single polar hydroxy (OH) group of 2 phenyl 2 propanol can orient towards the talc surface. It is not expected that the hydroxy group can form strong stable bonds at the mineral surface⁽⁷⁾. However, 2 phenyl 2 propanol might be expected to exhibit somewhat stronger bond interactions with the talc surface than comparable saturated straight chain or cyclic organic alcohols. This phenomenon results from the ability of the benzene ring to delocalize and stabilize electron perturbations, (84) (85) originating from the interaction of the hydroxy group and oxide surface. Thus, several interesting phenomena

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associated with the adsorption behaviour of the alcohol are not totally unexpected and warrant further discussion.

It is apparent that the adsorption isotherms at pH 6.9 and pH 11.0 display different characteristics which would indicate that different mechanisms of adsorption are predominating. The curves at pH 6.9 exhibit features of both L (Langmuir) and S type isotherms, according to the classification of Giles et al⁽⁸⁶⁾. The L characteristics are observed in the initial portion of the curves, as indicated by the Freundlich plots, and by the well defined plateau regions. The S features result from the difference in magnitude of the adsorption densities of the first and second plateau regions. A S type isotherm of multi-layer adsorption is such that the adsorption density at the first inflection point is several times less than that of the second plateau region. This indicates that the more solute there is already adsorbed, the easier it is for additional amounts to become fixed, implying a side by side association between adsorbed molecules, helping to hold them to the surface. A third plateau in an S type isotherm occurs at an adsorption density roughly double that of the second plateau. Thus, it would appear that the -100 +150 mesh and mixed mesh talc exhibit a modified S3 isotherm, and the -200 +325 mesh talc with its three plateau regions, displays a modified S(5) type isotherm.

The appearance of S curves is dependent on three conditions: the solute molecule is monofunctional, has moderate intermolecular attraction, causing it to pack vertically in a regular array in the adsorbed layer, and meets strong competition for substrate sites from molecules of the solvent. It is apparent that 2 phenyl 2 propanol is monofunctional in that its attraction towards a polar substrate arises from its hydroxy group. Apart from this marked localization of the forces of attraction for the substrate, the remaining portion of the molecule is hydrophobic and the molecule may be expected to adsorb as a single unit, not a micelle. Finally, it is expected that 2 phenyl 2 propanol would have to compete with the water molecules for adsorption sites.

It has been reported that benzyl $alcohol^{(87)}$ can display an S isotherm, as can monohydric phenol when adsorbed on the polar substrate, alumina, from polar solvents such as water and ethanol⁽⁸⁸⁾. However, phenol gives L (Langmuir) type curves when adsorbed from water on a non-polar substrate such as graphite⁽⁸⁹⁻⁹⁰⁾. The two distinct polar and non-polar surfaces of talc particles may be the important factor in causing the 2 phenyl 2 propanol to exhibit S-L type isotherms at pH 6.9.

Thus, at low concentrations of $\operatorname{alcohol}_{\varphi}$.06-.1 millimoles per litre, the solute molecules will tend to cluster at the charged sites along the edges of the talc sheets. There, they might be expected to hydrogen-bond with negative oxygen sites, $O^{-\cdots}$ HOR. A more complete reaction is illustrated by:



At such low equilibrium concentrations of alcohol, the water molecules will compete more successfully for adsorption sites. Thus, the initial plateau corresponds to a mixed array of solvent water and solute 2 phenyl 2 propanol molecules. As the concentration of solute increases, the alcohol molecules may compete more effectively with the solvent for adsorption sites, and hence the second plateau region would indicate a more dense array of vertically oriented 2 phenyl 2 propanol molecules on the talc surface. From Appendix A., the liquid phase surface areas of -100 +150 and -200 +325 mesh talc at pH 6.9 are calculated to be 0.506 and 0.93 $m^2/gm.$, respectively. These values, when compared with the adsorption density of the second plateau regions of the isotherms, indicate a surface area for the alcohol of between 50.6 and 37.8 A^2 /molecule, or an average value of 44.2A°². This value agrees roughly with the molecular model value of 38.5A°² determined for end-on adsorption. The variation of area values with the mesh size of the talc particles suggests that surface irregularities (i.e. stepped edges) and crystal defects of the talc particles permit closer or looser packing of the solute on the surface.

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For the -100 +150 mesh talc, there may be one water molecule (approximately $10A^{\circ 2}$) ⁽⁸⁶⁾⁽⁹¹⁾ between the adsorbed solute molecules, causing the substantially larger surface area value/molecule.

The adsorption densities of the first plateau regions do not suggest flat-on adsorption of the alcohol since the corresponding surface area values are greater than $100A^{\circ^2}$ per molecule. The initial plateau region adsorption densities are 17, 25.6, and 31 per cent of the second plateau densities for -100 +150, -200 +325, and mixed mesh talc, suggesting that at pH 6.9, about 74% of talc surface is uncharged and potentially hydrophobic.

The third inflection point observed for -200 + 325 mesh talc particles should correspond to a second layer of solute molecules over the surface coverage corresponding to the second plateau region of the isotherm. The interaction between the hydroxy group of the alcohol and the adsorption sites on the talc surface is expected to produce an electron shift in the benzene ring which is para-directing (84-85). In other words, the electron shift would cause the apex of the benzene ring directly opposite the isopropyl group to become somewhat active, thus causing a weak attraction for more solute molecules resulting in a second layer. The orientation of solute molecules in this second layer may be mixed such that some molecules have their hydroxy groups oriented towards the talc

surface, while others have theirs oriented into the solvent. This would create a surface exhibiting solute affinity and would explain the increasing adsorption after the third plateau. Comparable phenomena have been observed for paranitro phenol on alumina⁽⁸⁶⁾.

The marked increase in alcohol adsorption above pH 9 can be correlated to the increasing negative zeta potential of talc particles above the aforementioned pH. This would suggest that at larger OH⁻ ion concentrations, the 2 phenyl 2 propanol may be co-adsorbed with the OH⁻ ions into the electrical double layer about the talc particles. As pH increases, the OH⁻ ions may be expected to penetrate the uncharged hexagonal rings of the talc surface and impart a more negative surface charge to the talc particles.

The isotherms at pH 11 reflect the changing adsorption criteria, and, unlike those at pH 6.9, exhibit L3 characteristics. The initial slopes of the curves indicate that as more solute molecules are taken up, it becomes increasingly difficult for more alcohol molecules to find suitable adsorption sites. The plateau region of the isotherms occur at adsorption densities about 25% larger than the second plateau region at pH 6.9 for -200 +325 mesh talc and about 36% greater for -100 +150 mesh talc. The increased adsorption is attributed to the spreading of charge on the previously uncharged siliconoxygen sheets and the subsequent co-adsorption of vertically oriented 2 phenyl 2 propanol with OH^{-} ions, as follows:



It is unlikely that all the adsorbed OH⁻ ions will co-ordinate with the hydroxy group of the alcohol, because the alcohol is not that strongly polar, and hence the plateau region of the isotherm may be expected to correlate to surface coverage of a mixture of hydrated adsorbed OH⁻ ions and adsorbed alcohol molecules.

It has been reported that the adsorption of starch molecules may be enhanced by the presence of calcium ions $(^{35})$. Greenberg $(^{92})$ has described the adsorption of calcium hydroxide on silica (Sio^-) surfaces. The effect of excess Ca^{++} ions on 2 phenyl 2 propanol was briefly investigated for two reasons: i) because talc is often floated in circuits made alkaline by lime additions, and ii) to determine if the adsorption characteristics of the alcohol might be comparable to starch. A detailed investigation was not attempted because of the presence of small amounts of soluble calcium impurities in the talc samples, making quantitative assessments of calcium adsorption densities impossible. However, the experimental data does indicate that excess Ca^{++} ions increase the

adsorption density of 2 phenyl 2 propanol, especially in alkaline conditions. The increased adsorption density at higher pH may result from co-ordination of 2 phenyl 2 propanol molecules with the calcium ions, as follows:

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In other words, the electron rich benzene ring may co-ordinate with electropositive calcium ion, in a manner comparable to transition metal complexes (93). This reaction might enable the alcohol to adsorb at more -OH⁻ sites on the talc surface than observed for the isotherms at pH 11, and the perturbed benzene ring would attract other solute molecules to it. Another mechanism has been postulated for starch adsorption through its hydroxy groups (35) with excess Ca⁺⁺ ions, and this mechanism, somewhat modified for alcohol adsorption, is:



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It is seen that this mechanism involves displacement of a hydrogen ion by calcium ion resulting in a positive charge site which might attract an electron rich benzene ring. Such a reaction would be accompanied by a decrease in pH, but significant pH changes were not observed. It is apparent that, in either mechanism, the polar aqueous solvent would compete for the adsorption sites.

SECTION III

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TALC FLOTATION LITERATURE

TALC FLOTATION RESULTS

DISCUSSION

TALC FLOTATION LITERATURE

Sutherland and Wark⁽²⁾ consider that, although talc is usually stated to be a natural "floater", conclusive evidence is lacking. They point to the correlation between per cent recovery of talc and abstraction of isovaleric acid and isoamyl alcohol observed by Volkova et al⁽⁹⁴⁾. Similarly, although Clemmer and Cooke⁽⁹⁵⁾ separated talc from magnesite using frothers such as pine oil, alcohol or cresol, the use of kerosene was beneficial and the collective power of the frothers was not considered.

Norman, et al⁽⁹⁶⁾ report that foliated talcs seem to require only frother, but fibrous talcs require collectors. They observed that amines of any chain length were suitable collectors working best in alkaline circuits, although triamylamine was best in acid circuit.

Gaudin⁽¹⁾ reported talc to be a self-floater. He stated that a frother was sufficient, with kerosene helping to keep the froth under control, although it may spread on the mineral increasing its water repellency.

Berkelhamer⁽⁹⁷⁾ noted that talc may be contaminated by attached or included impurities, which may thus affect its floatability. Buckenham et al⁽⁹⁸⁾ reported floating talc from magnesite using Duponel 80, Armeen 100, and terpineol. The talc (69% - 200 mesh) was best floated at pH 8.2 with

0.1 lb. reagent/ton ore. Baranovskii⁽⁹⁹⁾ observed that talc may be floated from magnesite by the use of 90 - 120 mg./kg. flotation oil and up to 500 mg./kg. kerosene. Optimum grind was 65% minus .075 mm.

Manser⁽¹⁰⁰⁾ observed a remarkable similarity between the anionic sodium oleate and cationic dodecylamine flotation areas for talc. Using the technique of vacuum flotation, he floated -100 +100 mesh talc over the pH range 2 - 12, against increasing collector concentration. The addition of fluoride, in the form of CaF_2 , to either the cationic or anionic flotation systems activated and increased the flotation area of talc in a comparable manner.

Bain et al⁽¹⁰¹⁾ reported the successful flotation of talc from magnesite using no reagents in the rougher and only small amounts of pine oil in the scavenger. Yet Mercade⁽¹⁰²⁾ described the flotation of talc at pH 9 - 11 from alkali earth metal carbonate gangue by using small amounts of alkaline dispersing agents and a non-ionic water-dispersible fatty acid, alkanolamide, with an optional frothing agent such as anionic sodium alkylaryl sulphonate.

Thus, the flotation of talc appears very much dependent on the nature of the minerals associated with it. North American mills generally find the use of frothers (alcohols or Dowfroth 250) sufficient whether the talc is floated as a product or is floated off and discarded prior to the flotation of more valuable minerals.

Despite the common use of oils, or frothers in talc flotation, an investigation to observe the correlation between alcohol adsorption and talc flotation has not been recently reported in the literature. This section describes the effects of mesh size and pH changes on talc native floatability as well as describing the flotation behaviour of talc particles with changing equilibrium concentration of 2 phenyl 2 propanol.

EXPERIMENTAL

i) Experimental Technique

The flotation characteristics of the talc particles were determined in a Hallimond flotation apparatus. One gram samples of talc, after equilibrium adsorption with the 2 phenyl 2 propanol, were transferred quantitatively to the flotation tube. A magnetic stirrer kept the talc particles mixed at the bottom of the tube. Compressed air was introduced through the sintered glass at a gentle rate of 25 - 30 cc. air/minute. Flotation was continued till the accumulation of talc particles in the collector arm of the tube appeared complete (12 minutes). Natural flotation tests of the alcohol were determined in an analogous manner, after conditioning in acid, neutral, or basic aqueous medium. Conditioning times of at least one hour were necessary to observe natural

flotation values of the talc equal to those observed for the equilibrium adsorption times. All reagents used were of the same purity and type as those for the adsorption tests.

ii) Results

The variation of the flotation recovery, in the absence of 2 phenyl 2 propanol, for mixed mesh talc particles (60% -65 +150 mesh, 40% -150 +325 mesh) in aqueous solutions of hydrochloric acid or sodium hydroxide is illustrated in figure 17. The easy and apparently inherent floatability of talc particles is noted. Above pH 10, the per cent recovery decreases approximately 20% to a value of 65% at pH 13. Below pH 4, a less rapid decrease in flotation recovery is observed, the maximum decrease being in the range 5 - 10%, namely a value of 77% at pH 1. Sulphuric and nitric acids, when used as modifiers, produced quite comparable results as those observed with hydrochloric acid. The maximum natural flotation recovery of the talc occurs in the pH range 5.2 to 7.3, at a value of 85%. It was observed that the flotation values were dependent on the length of conditioning time. Thus, a one hour conditioning of talc in water resulted in a natural flotation recovery of 90% at pH 6.9, whereas
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Natural Flotation of Talc vs pH

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l gm. (60% -65 +150, 40% -150 +325) mesh talc



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Natural Flotation of Talc vs Mesh Size

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▲ рн 11.0● рн 6.9

l gm. taic

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Flotation Recovery vs Equilibrium Concentration

6.9 рH

▲ -100 +150 mesh talc

l gm. talc



Flotation Recovery vs Equilibrium Concentration

pH 11.0

▲ -100 +150 mesh talc

0 -200 +325 mesh talc

l gm. talc



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conditioning for the four to six hour equilibrium time periods used for adsorption work produced the slightly lower values of figure 15.

The effect of the size of the talc particles on the flotation recovery, again in the absence of 2 phenyl 2 propanol, is indicated in figure 18. At pH 6.9, the maximum flotation recovery of 85% is observed for particles less than 80 microns in diameter or less than 200 mesh. Coarse talc particles, between 65 and 100 mesh have an apparent natural floatability of 70%. At pH 11.5, the different sizes of talc particles all decrease in flotation recovery but by differing amounts. Thus, -200 +325 mesh talc decreases approximately 5%, while coarser particles (-65 +100, -100 +150 mesh talc) decrease five to ten per cent from their values at neutral pH.

Figures 19 and 20 illustrate the flotation recovery dependence of talc on the equilibrium concentration of 2 phenyl 2 propanol. It is seen that at pH 6.9, the -100 +150 mesh talc achieves 100% recovery at equilibrium concentration of alcohol of .140 millimoles / litre. Monolayer coverage at equilibrium concentration of .075 millimoles / litre (figure 7) occurs approximately midway in the increasing flotation recovery. In contrast, for the -200 +325 mesh talc, the monolayer coverage at .023 millimoles / litre (figure 9, 10) marks the beginning of the increase in talc flotation recovery, which achieves 100% at equilibrium concentration of.100 millimoles / litre.

At pH 11.0, the 100% flotation of -100 +150 and -200 +325 mesh talc occurs at equilibrium alcohol concentrations of .200 and .140 millimoles / litre, respectively. Monolayer coverage for the -100 +150 mesh and -200 +325 mesh talc appears to occur at .510 and .680 millimoles / litre, respectively (figure 12). However, the amounts of aromatic alcohol adsorbed at the equilibrium concentrations necessary for the 100% flotation are 1.7^5 and 3.3 micromoles / gram talc (figure 10) for the -100 +150 and -200 +325 mesh talc respec tively. These values greatly exceed the corresponding adsorption values necessary for 100% flotation at pH 6.9.

2 phenyl 2 propanol was not observed to form a significant froth below concentrations of .050 millimoles / litre, and excessive frothing was observed only above concentrations of .500 millimoles / litre.

DISCUSSION

It is apparent that talc particles possess a high native floatability. The use of flotation data is thus not strictly traditional in the sense of taking a mineral with negligible floatability and achieving 100% recovery with the addition of reagents; rather, these flotation results serve to illustrate various aspects of the surface chemistry of the mineral talc.

The process of flotation involves bringing a mineral particle into contact with a bubble surface, such that the intervening film of water surfactants is ruptured so that a finite contact angle between bubble and mineral can be established. Generally, some portion of the mineral surface is coated with a collector species thus making its surface more hydrophobic and ammenable for bubble attachment.

Two main theories of bubble-particle contact have been postulated $^{(1)}(103-105)$. One suggests that gas precipitates on a particle surface, forming a bubble that grows and finally lifts the particle to the surface; this mechanism is generally called "gas precipitation". Advocates of this mechanism often cite the success of vacuum flotation as verification of the concept. The use of vacuum flotation on talc by Manser $^{(100)}$ has been described and tends to confirm the mineral's high native floatability. However, recent theoretical work $^{(106)}$ indicates that vacuum flotation is but a special case of the other, and more commonly accepted theory of bubble attachment; namely, "bubble-particle collision". This mechanism postulates that the bubble, as it rises through the pulp, hits particles and makes contact if the intervening film is ruptured.

To 'study the rupture of the layer of water that separates the air in a bubble from the hydrophobic surface of a mineral

is very difficult because bubble attachment in a flotation system is a dynamic process which cannot be fully evaluated by static, equilibrium study. Several researchers ⁽¹⁰⁷⁻¹⁰⁹⁾ have studied the induction time of a quiescent bubble pressed against a mineral surface and have observed that, for readily flotable minerals, the time varied from fractions of a second to hours. The time available for attachment during flotation is milliseconds or fractions of milliseconds. Thus, it is apparent that the previously described contact angle literature for talc can give only qualitative descriptions of talcwater-air interactions. Yet, it is noted that the experimental flotation results tend to confirm the high native flotability expected for a poorly wettable, low energy talc surface at neutral pH, as postulated from contact angle sources.

The variation of the natural flotability of mixed mesh talc with changing pH would indicate that hydroxyl ions are more successful at wetting the hydrophobic talc surfaces than H^+ ions. At acid pH, protonation of the uncharged oxygen on the talc surface might occur to a limited extent, but the flotation results are consistent with the observation that talc particles are resistant to all strong acids except hydrofluoric ⁽¹¹⁰⁻¹¹¹⁾. It would appear that at neutral pH, the bulk of talc surfaces have no strong affinity for water molecules and air bubbles readily displace

any weakly adsorbed water on the uncharged surface. At higher pH, the OH⁻ ions must penetrate the uncharged oxygen rings. Water molecules would hydrate these negatively charged sites and the talc surface would be more hydrophilic. It is noted that the increasing negativity of the zeta potential for talc particles roughly correlates with the decreasing natural flotability of the mineral. The role of H^+ and OH⁻ ions as potential determining ions at the talc water interface is consistent with the studies of other silicates ⁽¹¹²⁻¹¹³⁾. The role of the electrical double layer in particle-bubble attachment is increasingly important as the particle size decreases, especially for slimes containing particles less than 10 microns ⁽¹⁰⁶⁾.

The dependence of talc's native flotability with particle size is consistent with the previously discussed cleavage aspects of the mineral. The mineral is expected to cleave predominantly between the uncharged sheets. Thus, as the mineral particles decrease in size down to 325 mesh, more and more hydrophobic surface is exposed relative to the charged edges: the increasing natural flotability is not unexpected. Furthermore, the decreasing radius of the particles will be a stabilizing factor in bubble attachment⁽²⁴⁾. The restoring force stabilizing the particle at the liquid-air interface varies approximately with particle radius; for the particle to remain floating the restoring force must be equal to or

exceed that of gravity. It can be expected that the coarser mesh talc particles in the turbulence of the flotation cell, can more easily displace one another from the rising bubbles, through collision of particle laden bubbles. The high natural flotability of mixed mesh talc can result in part from the changing particle density as the more readily flotable particles are removed enabling the coarser mesh sizes to follow more easily.

There would appear to be some correlation between the flotation recovery of talc particles and the adsorption of 2 phenyl 2 propanol on the mineral surface, indicating that the alcohol exhibits some collecting power. At pH 6.9, the onset of the first inflection of the adsorption isotherm coincides with increasing flotation recovery. One hundred per cent recovery is achieved at equilibrium concentration values within the first plateau region of the isotherm (figure 9). Complete flotation recovery of -100 +150 and -200 +325 mesh particles occurs at adsorption densities of .28/1.65 = 17% and 1.05/4.05 = 25.6% of the second plateau region densities, which have been assumed to represent a more complete coverage of the talc surface. These results tend to be consistent with the concept that the 2 phenyl 2 propanol molecules are initially attracted to the charged broken edges of the talc sheets, thus reducing the hydrophilic nature of these adsorption sites. If flotation is considered to result from the collision of particle and bubble, it is

not unexpected that, by converting the small charged hydrophilic areas of the talc particles to a more hydrophobic character, the probability of successful bubble-particle attachment after collision is enhanced. Improved flotation would result.

At pH 11.0, the flotation recovery improves with increasing solute adsorption. One hundred per cent flotation of -100 +150 and -200 +325 mesh talc occurs at 1.6/2.2=72.8% and $3\pi 3/5.0=66.2$ % adsorption densities respectively of the densities for the corresponding base isotherm plateau regions (figure 12).

Complete flotation recovery with less than 100% surface coverage has been reported in several systems ⁽¹¹⁴⁻¹¹⁵⁾. It has been suggested ⁽¹¹⁶⁻¹¹⁷⁾ that frothing agents, apart from frothing ability, may play a role in stabilizing the attachment of the particle to the bubble. Thus, in a system containing collector and frothing agent, when the bubble and particle interfaces merge, penetration of the collector film by that of the frother occurs, with consequent great stabilization of the solid-liquid-air contact.

In the experimental flotation system, it is expected that 2 phenyl 2 propanol, because of its frothing capability, will collect at the liquid-air interface of the bubbles, with the hydroxy group oriented into the liquid. From the adsorption discussion, it has been postulated that the adsorbed molecules on the talc surface are intermixed with

the competing solvent molecules. Thus, it is possible that with particle-bubble collision, the 2 phenyl 2 propanol molecules on the bubble surface may intermix with adsorbed solute molecules to form a more complete and more stable contact with the hydroxylated talc surface. At pH 6.9, a similar interaction could occur at the charged edges of the talc sheet, containing a mixture of adsorbed solute and solvent. Penetration by the 2 phenyl 2 propanol of the solvent-solute film about the hydrophobic and hydrophilic portions of talc surfaces should have the immediate effect of lowering the solid vapour surface tension, δ_{SW} , without necessarily δSL affecting the solid-liquid surface tension, Such an effect can increase the contact angle value because, from the Young Equation (reaction number 1) the increasing negativity of $(\delta_{SV} - \delta_{SL})$ corresponds to larger values of Θ (23-24) Stronger bubble-particle attachment and improving flotation recovery would result.

ORIGINALITY AND SUGGESTIONS FOR FUTURE WORK

a) 2 phenyl 2 propanol does not appear to have been previously used for non-metallic mineral flotation. It is felt that the use of an aromatic alcohol, with a potential mild collector power, to investigate the hydrophobic-hydrophilic nature of talc particles is a new concept. Indeed, the collector power of the alcohol in talc flotation has not been previously investigated in this manner. Specific liquid phase values for talc have not been reported prior to this work.

b) Future work could be concerned with the effect of adsorbed solutes on zeta potential of talc particles. Indeed, the effect of talc mesh size on its zeta potential may prove a worthwhile investigation to determine if talc zeta potential can be fitted to calculated curves. Mechanisms of depressants and the enhancement of the effect of depressants on talc surfaces remain not only open fields but perhaps the most important research areas for talc. APPENDIX A

Surface Area Determination

i) Introduction

Several techniques for the surface area determination of powder samples are proposed in the literature (118); for example, microscopic examination, X-ray diffraction, permeability, heat of wetting, gas and liquid phase adsorption, and the negative adsorption. The B.E.T. gas adsorption method finds widespread acceptance. The adsorbed gas molecules are considered to form close-packing array at least in the first adsorbed layer, if the vapour pressure of the adsorption system is high enough. Furthermore, the adsorption of inert gas molecules is not restricted on any particular active surface, but spreads all over the surface (119).

Kini et al⁽¹²⁰⁾ have reported surface areas for -100 +150 mesh talc by means of the B.E.T. method. Xenon at -78°C, nitrogen at -196°C, and argon at -196°C were used and resulted in the surface areas of 0.73, 0.42, and 0.37 m^2/gm . talc, respectively. The larger surface area value, obtained with Xenon, was attributed to the penetration of xenon between the sheet layers of the mineral, due to the higher operating temperature of xenon as compared with nitrogen or argon.

The adsorption of various ionic species might be expected to involve different mechanism from those operating in the adsorption of gas phase molecules. Van der Hall and Lykema⁽¹²¹⁾

recommend the use of the negative adsorption method, employing the Gouy-Chapman approximation of the double layer theories, to obtain good correlation with experiments investigating double layer properties.

The adsorption of solute from solution is also becoming a more widespread technique, although Adamson⁽²⁴⁾ warns that the results need not be extremely reliable and may be more useful for relative areas. Smith and Hurley⁽¹²²⁾ suggested the use of fatty acids. More recently, Giles et al⁽¹²³⁾ have proposed the use of dyestuffs, including p-nitrophenol. Greenland et al⁽¹²⁴⁾ have reported the use of n-decyl pyridinium salts for the surface area determination of montmorillonite. For the present work, 1-hexadecyl pyridinium bromide (1-HPB) has been chosen because of the use of similar salts in the adsorption studies on oxide surfaces⁽¹²⁵⁻¹²⁶⁾⁽⁴²⁾.

ii) Technique and Reagents

The adsorption tests were carried out in an identical manner as for the adsorption of 2 phenyl 2 propanol. The structure of 1-hexadecyl pyridinium is outlined below: ⁽⁶⁴⁾

((CH2) 25 CH3) + Br

The formula weight is 384.6 gm./mole. The solutions were analyzed using the Perkin Elmer UV spectrophotometer model 124D with a digital readout. The calibration curve (figure 21) was obtained by measuring the peak at 258 MMU.

Stock solutions of solium hydroxide (analytical grade) were used as modifier.

iii) Results

Equilibrium tests were carried out at an initial concentration of 20 mg./l. Equilibrium was attained within four hours (figure 22). Subsequent tests were run for six hour periods. Figure 23 illustrates the increasing adsorption of the dye, with increasing pH at an initial concentration of 40 mg./l.

The adsorption isotherms for -100 + 150 and -200 + 325 mesh talc at pH 6.9 are illustrated in figure 24, while the isotherms at pH 6.9, 10.3, and 11.0 for -100 + 150 mesh talc are described in figure 25. The isotherms appear to follow L type curves of Giles⁽⁶²⁾. It is noted that the isotherms display a rapid initial adsorption and then a more gradual adsorption as the distinct plateau regions are attained. As monolayer coverage is approached, it would appear that the solute molecules find it more difficult to adsorb on vacant sites on the talc surface. This can be an indication

Calibration Curve 1 Hexadecyl Pyridinium Bromide



goned to 2d A

Adsorption vs Time (Hours)

l gm. -100 +150 mesh talc Initial Concentration 20 mg./l. l HPB . 1



Adsorption vs pH

Initial Concentration 40 mg./l. |•HPB l gm. -100 +150 mesh talc



Adsorption Isotherm pH 6.9

▲ -100 +150 mesh talc (1 gm.)
Ø -200 +325 mesh talc (1 gm.)



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Adsorption Isotherm

l gm. -100 +150 mesh talc ▲ pH 6.9 ● pH 10.3 × pH 11.0



Isotherms Using Bartell Equation

l gm. talc © -200 +325 mesh pH 6.9 △ -100 +150 mesh pH 6.9 ◎ -100 +150 mesh pH 10.3 × -100 +150 mesh pH 11.0



·]. that the dye molecule is being adsorbed flat onto the mineral surface. A cross-sectional area of $54A^{\circ^2}$ per molecule has been determined for a molecule of 1 hexadecyl pyridinium bromide with the benzene ring adsorbed flat and the alkane chain perpendicular to the mineral surface ⁽⁴²⁾.

The data has been fitted to the modified B.E.T. equation of Bartell et al⁽¹²⁷⁾ (figure 26), where the saturation concentration of 1 hexadecyl pyridinium bromide was taken to be the critical micelle concentration of the salt, namely, 7.0 x 10^{-4} moles/1. at $25 \circ C^{(128)}$. The adsorption necessary for monolayer coverage is taken to be 1.56 and 2.86 micromoles/gm. talc for -100 +150 and -200 +325 mesh talc, respectively. At pH 10.3 and 11.0, the monolayer values are 2.34 and 3.12 micromoles/gm. talc for -100 +150 mesh talc, respectively. The apparent specific surface areas are determined to be, for -100 +150 mesh talc, 0.506 m²/gm. at pH 6.9, 0.76 m²/gm. at pH 10.3, and 1.015 m²/gm. at pH 11. The surface area for -200 +325 mesh talc at pH 6.9 is calculated to be 0.93 m²/gm.

Greenland et al⁽¹²⁹⁾ had previously found good agreement between the surface area for montmorillonite determined by 1 HPB adsorption and gas phase adsorption. In the present work, the surface area of -100 +150 mesh talc at pH 6.9 lies within the range of values determined by xenon, nitrogen, and argon gaseous adsorption of Kini et al⁽¹²⁰⁾.

APPENDIX B

X-Ray Data

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TABLE IV

X-RAY DATA*

Mesh						
-65	-100	-200	Average	Plane	Lit.	d _{lit}
+100	+150	+325	a	b le 1	J * *	
đ	đ	d	u	IIKI	a	average
9 313	9 112	0 370	0.000.#	100		
A 697	J.412	9.370	9.398 S"	100	9.35	+.05
4.007 2 AFA	4./44	4.8/3	4./68 S	004	4.67	+.09
3.454	3.466	3.536	3.485 mw	114	3.52	04
3.121	3.154	3.187	3.154 s	006	3.12 -	+.034
2.629	2.626	2.645	2.633 wb	130	2.635	002
2.488	2.495	2.536	2.506 wb	133	2.496	+.01
2.338	2.350	2.380	2.356 wd	133	2.360	004
2.227	2.227	-	2.227 m	22 3	2.234	007
2.099	2.099	2.122	2.103 wđ	136	2.104	001
1.870	1.877	1.895	1.881 wb	208	1.870	+.011
1.689	1.701	1.714	1.701 s	153	1.692	+.008
1.656	1.658	1.657	1.657 md	-	1.654	+.003
1.559	1.563	1.573	1.565 md	317	1.558	+.007
1.530	1.539	1.544	1.538 s	060	1.529	+.009
1.480	1.482	1.491	1.484 wb	334	1.503	019
1.419	1.421	1.437	1.426 wb	-	1.411	+.015
1.388	1.391	1.417	1.399 mb	-	1.386	+.013
1.337	1.339	1.339	1.338 md	335	1.336	+.002
-	-	1.301	1.301 s	405	1.300	+.001
-	1.171	-	1.171 m	0016	1.169	002
- other peaks -						
2.902	-	-	2.902 wb		2.886	Dolomite
2.746	2.755	_	2.751 wb		2.742	Magnesite
Øs - strong m - medium w - weak b - broad d - distorted						

).
- * Philips X-ray Diffractometer
 40 kV x 20 ma; 1 x 10³ cps; 1°/min. chart speed
 Cu(Ka); Nickel Filter; chart read-out standardized
 against mica standard.
 Samples were spread on glass slides with balsam glue.
- ** The literature d values are from card number 19-770, and 19-770A in the X-ray Diffraction files. Not all literature d values were observed. Data best fits monoclinic unit cell, although such powder data is inconclusive.

APPENDIX C

Experimental Data

- 2 phenyl 2 propanol
- 1 hexadecyl pyridinium bromide

- talc

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TABLE V

Calibrati	ion 2	Phenyl	2	Propanol
	the second se	and the second se		

Abs.	Conc. gm./1.
.004	.005
.010	.0097
.020	.019
.056	.0486
.084	.073
.119	.097
.176	.146
.294	.243
.606	.486

TABLE VI

Adsorption vs Time

C_{init} = 486 mg./l.; mixed mesh talc

Sample Vol Wt.gm. l.	. Abs.	C equil. gm/1.	∆C gm/l.	Time Hrs.	Ads. Density micromoles/gm.
0.98 .05 0.98 .05 0.98 .05 0.98 .05 0.99 .05 0.99 .05 0.99 .05	11 .592 31 .589 42 .582 13 .582 28 .580 22 .582 14 .583	.4768 .4738 .4688 .4688 .4673 .4688 .4688	.0092 .0122 .0172 .0172 .0172 .0187 .0172 .0175	0.76 1.18 3.33 4.75 5.95 7.0 7.75	3.55 4.89 7.05 6.65 7.25 7.0 7.1

TABLE VII

Adsorption vs pH Mixed mesh 1 gm.; 486 mg./1. Alcohol

	Talc	Vol.	Abs.	Cequil	∆ c	. p	H	Adsorption
	gm.	1.		gm/l.	gm/1.	init	final	Density Micromoles/
_								gm.
	0.96	.0513	.583	.468	.018	2.8	3.0	6.55
	0.97	.0531	.586	.4675	.0185	5.6	5.65	7.45
	0.98	.0508	.584	.688	.0172	7.0	7.0	7.0
	0.96	.051	.578	.4642	÷0218	7.9	7.95	7.85
	0.96	.0525	.575	.461	.025	9.2	9.1	9.25
	0.97	.0513	.565	.453	.029	9.9	9.85	11.3
	0.96	.0514	.566	.454	.028	10.1	10.0	10.05
	0.97	.0527	.565	.473	.029	10.6	10.55	11.6
	0.97	.0513	.564	.453	.033	11.2	11.0	12.85
	0.97	.0527	.563	.456	.03	11.7	11.6	11.95
	0.97	.0531	.561	.451	.035	12.3	12.1	14.15
	0.96	.0522	.552	.447	.0414	13.4	13.0	15.25
			•		8			
	M	lixed mes	h 2 gm.	; 97 mg./	1. Alcoho	1		
		1			8	n İ		1
	1.95	.0531	.118	.09653	.00047	2.6	2.8	0.36
	1.96	.0508	.117	.09651	.00049	4.0	4.2	0.36
	1.95	.0514	.116	.09648	.00052	4.6	5.0	0.38
	1.95	.0532	.117	.09651	.00049	5.8	6.0	0.37
	1.95	.0510	.116	.09645	.00055	6.8	7.0	0.40
	1.95	.0532	.117	.09653	.00047	7.1	7.25	0.36
	1.96	.0525	.115	.09619	.00081	9.1	8.95	0.61
	1.95	.0517	.115	.09616	.00084	9.6	9.45	0.62
	1.95	.0511	.114	.0948	.0022	10.2	10.0	1.62
	1.95	.054	.114	.09485	.00215	10.5	10.3	1.66
	1.95	.0513	.113	.0940	.003	12.2	12.0	2.2
	· · · · · · · · · · · · · · · · · · ·	8	N	A	a	1 8		

TABLE VIII

Adsorption vs pH

Curve A: C_{init} = 486 mg./l. -150 +200 mesh

Talc gm.	Vol. 1.	Abs.	C equil. gm/1.	∆C gm/l.	<i>pH</i> init	final	Adsorption Density Micromoles/ gm.
0.95	.0514	.584	.469 7 .4698	.0163	3.6 6.8	4.0 7.0	5.85 6.05
0.95	.0517	.581	.4676	.0184	9.0	8.9	6.65
0.96	.0513	.580	.467	.019	10.3	10.2	7.65
0.95	.0514	.575	.462	.024	11.65	11.5	8.75
0.96	.0522	.577	.464	.022	12.4	12.2	9.1
0.96	.0532	.471	.458	.028	12.8	12.6	12.1
0.95	.0525	.561	.453	.033	13.3	13.0	12.55
Curve	B: C _{ini}	.t = 485] mg./l.	alcohol;	74 mg.,	/1. Ca ^{+.}	6 + 1
0.96	.0511	.579	.4656	.0194	3.6	4.0	7.0
0.96	.0531	.578	.4653	.0197	6.8	7.0	7.4
0.96	.0513	.576	.463	.022	9.0	8.9	7.9
0.96	.0528	.573	.461	.024	10.3	10.2	9.9
0.96	.0532	.568	.457	.028	11.4	11.3	10.5
0.96	.0514	.568	. 457	.028	12.2	12.1	11.35
0.96	。0532	.560	.45	.036	12.9	12.6	15.6
0.96	.0511	.549	.4413	.0437	13.3	13.0	15.75

TABLE IX

Adsorption Isotherm pH 6.9

Talc gm.	Vol. 1.	Abs. Sample	C _{init} gm/1.	C equil. gm/l.	▲ C gm/l.	C equil. milli- moles/1	Ads. Dens. micro-
M1xec .95 .95 .95 .95 .96 .95 .95 .95 .95	mesh .0532 .0517 .0511 .0531 .0514 .0532 .051 .0532 .0525	.004 .008 .018 .023 .039 .054 .067 .084 .111	.005 .0055 .0130 .025 .035 .0467 .0582 .0729 .0973 123	.0045 .0039 .0110 .0232 .033 .0465 .0564 .070 .0915 .1171	.00053 .002 .002 .0018 .002 .0022 .0018 .0029 .0058	0.014 0.039 0.092 0.165 0.254 0.342 0.415 0.515 0.673	0.21 0.83 0.80 0.71 0.82 0.84 0.75 1.15 2.38
.95 .95 .95 -100	.0517 .0531 .0525 +150 mes	.172 .224 .275	.145 .186 .2305	.1391 .182 .223	.0059 .0059 .0066 .00745	0.858 1.022 1.34 1.64	2.51 2.39 2.58 2.76
.95 .95 .95 .95	.0512 .0527 .0521 .0513	.0023 .005 .0180 .03 .04	.00243 .00486 .0146 .0243 .034	.00225 .00427 .014 .0236 .0333	.00018 .00059 .0006 .0007 .0007	0.016 0.031 0.103 0.173 0.245	0.074 0.24 0.24 0.28 0.28
.95 .95 .95 .95 .95	.053 .053 .053 .0511 .0514	.059 .09 .118 .147 .205	.0486 .073 .0972 .123 .1715	.048 .072 .094 .119 .167	.0006 .001 .0032 .0046 .0045	0.353 0.529 0.691 0.875 1.225	0.25 0.41 1.31 1.65 1.58
.95 .95 -200 .95 .95	.0525 .053 +325 mes .0511 .0531	.245 .275 sh .0005	.203 .2275 .00097	.198 .222 .00047	.0049 .0055 .0005	1.46 1.64 0.036	1.83 2.05 0.19
.99 .95 .96 .95	.0514 .0508 .0541 .0528	.002 .008 .018 .054	.0049 .0097 .0194 .0486	.002 .008 .017 .0467	.0018 .0032 .0017 .0024 .0019	0.001 0.012 0.059 0.125 0.343	1.10 1.06 1.0 1.06
.96 .96 .95 .95	.051 .0532 .0525 .0525 .0514	.107 .167 .236 .278 .335	.0972 .146 .2053 .243 .292	.0875 .0361 .1915 .2349 .271	.0097 .0099 .0138 .0181 .021	0.643 1.00 1.41 1.654 1.993	3.9 4.1 5.12 7.46 8.42
.96	.0532	.492	.4296 ' .586	.396 .549 ·	.0336 .0372	2.90 3.301	12.6 15.4

TABLE X

Talc Gm.	Vol. 1.	Abs. Sample	C _{init} gm/l.	Cequil. gm/l.	∆C gm/l.	C _{equil.} milli- moles/1	Ads. Dens. micro- moles/gm
-100	+150 me	sh					
.95	.0531	.004	.00486	.00408	.00078	0.024	0.67
.96	.0513	.015	.0145	.012	.0025	0.088	0.97
.95	.0528	.025	.0243	.0202	.0041	0.149	1.65
.96	.0522	.053	.0486	.0432	.0054	0.318	2.08
.95	.0514	.084	.0729	.067	.0059	0.493	2.21
.95	.0523	.110	.0903	.085	.0053	0.625	2.0
.96	.091	.162	.1316	.125	.0066	0.92	2.35
.96	.0532	.208	.1681	.159	.0091	1.17	3.4
.96	.0525	.237	.1917	.182	.0097	1.34	3.6
.95	.0532	.281	.2274	.217	.0104	1.60	3.9
-200	+325 me	esh		i		n	•
.95	.0531	.002	.00486	.0016	.0027	0.012	1.32
.95	.0513	.012	.0146	.009	.0056	0.066	2.3
.96	.0513	.02	.0243	.0153	.009	0.113	2.57
.95	.0528	.033	.034	.0257	.0083	0.189	3.40
.96	.051	.072	.0581	.0461	.0121	0.34	4.55
.96	.0532	.075	.0604	.058	.0124	0.50	4.65
.95	.0514	.108	.097	.085	.0125	0.625	4.9
.91	.0514	.172	.146	.135	.011	0.993	5.0
.95	.0525	.22	.178	.163	.0150	1.20	5.55
.95	.0532	275	.243	.223	.020	1.64	8.13
		-	-				-

Adsorption Isotherm pH 11.0

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TABLE XI

Talc Wt. Conc.	Talc Wt. Tails	pH Final	% Talc Rec.	% Talc Tails
.715	.19	1.9	79.0	21.0
.800	.205	2.5	79.5	20.5
.936	.164	5.0	85.0	15.0
.909	.071	7.0	84.0	16.0
.91	.06	8.3	84.5	15.5
.831	.184	10.0	82.0	18.0
.72	.234	11.6	75.5	24.5
.49	.295	12.0	62.5	37.5
. 52	.28	13.5	65.0	35.0
	1	1		

Natı	ıral	Flo	tati	.on	VS	pН

TABLE XII

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Natural Flotation vs Mesh Size

		Mesh	Talc Wt. Conc.	· Talc Wt. Tails	% Talc Rec.	% Talc Tails
рН	6.9					
		-65+100	0.69	0.295	70.0	30.0
		-100+150	0.79	0.207	79.3	21.7
		-100+200	0.91	0.16	84.7	15.3
		-200+325	0.92	0.16	85.0	15.0
рн	11.0					
		-65+100	0.55	0.368	60.0	40.0
		-100+150	0.63	0.304	67.5	32.5
		-150+200	0.75	0.235	76.3	23.7
		-200+325	0.80	0.205	79.5	20.5

-

TABLE XIII and XIV

Flotation vs Equil. Conc.

Talc Wt. Conc.	Talc Wt. Tails	C _{equil.} millimoles / l.	t Talc Comc.	% Talc Tails
	рН 6.	9		
-100+150 mosh				
0.734	0 201	0 016	7 0 F	23 F
0.846	0.20	0.0314	70.5 80 5	21.5
0.86	0.145	0.0715	85.3	
0.91	0.07	0.103	92.7	7.3
0.98	-	0.179	100.0	-
-200+325 mesh				
0.85	0.18	0.012	82.2	17.8
0.908	0.092	0.049	89.5	10.5
0.91	0.075	0.049	92.5	7.5
0.98	0.012	0.081	99.0	1.0
0.98	0.018	0.09/5	98.3	1.7
0.947		0.125	100.0	-
	pH 11.	. 0		
-100+150 mesh)		
0.544	0.388	0.009	59 A	A7 C
0.727	0.180	0.025	80.0	20 0
0.85	0.125	0.056	87.2	12 8
0.90	0.044	0.090	94.7	5.3
0.921	0.034	0.149	96.4	3.6
0.98	0.004	0.182	99.5	0.5
0.96	-	0.23	100.0	-
1.05	-	0.304	100.0	-
-200+325 mesn	0.17			
0.048	0.1/	0.004	79.2	20.8
0.731	0.142	0.006	83.9	16.1
0.752	0.094	0.019	04.0	
0.838	0.046	0.067	94 9	1 77.7
0.95	0.01	0.112	99.0	
0.967	-	0.130	100.0	
0.812	0.008	0.16	99.0	1.0
0.96	-	0.32	100.0	

— <u>]</u>.

TABLE XV

Calibration of 1-HPB

Conc. gm./l.	Abs.
.01	.115
.015	.175
.02	.225
.025	.275
.03	.335
.035	.385
.04	.435
.05	.545
.06	.645

TABLE XVI

Adsorption vs Time .02 gm./l. 1 HPB

Talc Gm.	Vol. 1.	Abs.	C equil gm/l.	▲ C gm/l.	Time Hours	Ads. Dens. mg./gm.
.98	.0514	.155	.0143	.0057	0.5	.3
.95	.0511	.115	.0112	.0088	1.0	.47
.96	.0508	.101	.0093	.0107	2.1	.565
.95	.0531	.105	.0102	.0098	2.75	.54
.96	.0510	.1	.0091	.0109	3.5	.58
.96	.0517	.101	.0093	.0107	5.0	.58
.95	.0513	.093	.0093	.0107	5.85	.58
.95	.0528	.095	.0094	.0106	6.0	.585

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Adsorption vs pH 40 mg./l. 1 HPB -100 +150

Talc	Vol.	Abs.	Cequil	∆C	pH	Ads. Dens.
Wt.	l.		gm/l.	gm/l.	final	mg./gm.
.96	.0514	.257	.0288	.0112	6.90	0.6
.95	.0508	.25	.0274	.0126	8.47	0.675
.96	.0514	.238	.0255	.0145	9.0	0.77
.96	.0532	.235	.0246	.0154	9.63	0.855
.95	.051	.218	.0215	.0815	10.3	0.99
.95	.0532	.21	.0203	.0197	10.73	1.105
.95	.0525	.21	.018	.022	11.0	1.20

7.

TABLE XVIII

Adsorption Isotherms

Talc Wt.	Vol. 1.	Abs.	C _{init.} gm/1.	C _{final}	ΔC gm/l.	C mg/l.	Ads. Dens. mg/gm.
			рН 6.9				T the second
			-100 +150				
.96	.0522	.003	.005	.0003	.0047	00.030	0.25
.95	.051	.007	.007	.00095	.00615	00.095	0.33
.95	.0514	.029	.UL 015	.0028	.0072	2.8	0.39
.95	.0514	.161	-025	.008	.009	6.0	0.49
.95	.0525	.191	.027	.0165	.0105	16.5	0.575
.95	.0527	.30	.04	.029	.011	29.0	0.605
.96	.0517	.415	.0515	.0399	.0116	39.9	0.625
.94	.0525	003		00075	0007		
.94	.0513	.005	.0105	.00075	.0097	00.75	0.53
.94	.0528	.036	.02	.0035	.0167	3.4	0.76
.94	.051	.047	.025	.0045	.0205	4.5	1.1
.94	.0522	.054	.025	.0052	.0198	5.2	1.1
.95	.0527	.082	.026	.0075	.0195	7.5	1.08
.94	.0525	.110	.03	.0113	.0187		1.07
.94	.0532	.165	.035	.0155	.0195	15.5	1.09
.94	.051	.270	04	.0205	.0195	20.5	1.16
.95	.0532	.249	.046	.0274	.196	27.4	1.10
.95	.0522	.363	.055	.0332	.0218	33.2	1.20
.,,	.0525	•410	.062	.040	.022	40.0	1.22
			pH 10.	3			
06	0511		-100 +150				
.90	.0511	.012	.009	.0011	.0079	1.10	0.42
.95	.0541	.086	.0108	.00125	.00855	$\frac{1.25}{c}$	0.48
.95	.0515	.115	.025	.0103	.0147	10.3	0.05
.96	.051	.160	.03	.0145	.0155	14.5	0.82
.95	.0528	.208	.0363	.0197	.0165	19.7	0.92
.90	0522	.353	.05	.032	.018	32.0	0.98
	.0522	. 570	• •0511	.0345	.0165	34.5	0.91
.96	0511	0.05	pH 11.		0005		
.96	.0531	.005	.01	.0004	.0096	0.4	0.51
.96	.0513	.039	.02	.00225	.0165	2.25	0./0
.96	.0528	.083	.025	.0075	.0185	7.5	1.10
.95	.051	.100	.0297	.009	.0207	9.0	1.11
.96	0532	.203	.04	.0185	.0215	18.5	1.18
.95	.0514	.290	.05	.0265	.0235	26.5	1.30
	1.0213			.032	•018	36.2	1.26

TABLE XIX

Modified B.E.T. Plot

C mg./l.	C _o -C mg./l.	X mg./gm.	1 <u>c</u> x (c ₀ -c)	с c		
он 6.9 на	-100 +150 mesh					
0.95 2.8 6.0 16.0 16.5 29.0 39.9 pH 10.3	268.25 266.4 263.2 253.2 252.7 240.2 229.3	0.33 0.39 0.49 0.605 0.575 0.605 0.625	.0106 .034 .046 .104 .113 .190 .280	.0035 .01 .022 .059 .061 .108 .148		
1.1 1.25 6.8 10.3 14.5 19.7 32.0 34.5 pH 11.0	268.1 267.95 262.4 258.9 254.7 249.5 237.2 234.7	0.42 0.48 0.65 0.8 0.82 0.92 0.98 0.91	.0098 .0097 .0399 .0497 .069 .086 .138 .162	.004 .0046 .025 .0382 .0539 .731 .119 .128		
2.25 3.6 7.5 9.0 18.5 26.5 36.2 pH 6.9	266.95 265.6 261.7 260.2 250.7 242.7 233.0 -200	0.70 0.87 1.10 1.11 1.18 1.3 1.26 +325	.012 .0156 .026 .031 .063 .084 .122	.0084 .0134 .0279 .0334 .0687 .0984 .134		
3.4 4.5 5.2 7.5 11.3 15.5 16.1 20.5 27.4 33.2 40.0	265.8 264.7 264.0 261.7 257.9 253.7 253.1 248.7 241.8 233.0 229.2	0.93 1.1 1.1 1.08 1.07 1.09 1.09 1.09 1.16 1.1 1.2 1.22	.0137 .0155 .0179 .027 .041 .056 .0585 .071 .103 .118 .143	.0126 .0167 .0193 .0279 .042 .0575 .0598 .0761 .102 .123 .149		

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TABLE XX

Talc Data

1)	The experiment	al talc was di	vided into	ll aliquots		
	and samples we	re drawn from	each aliquo	t. The specific		
	gravity of the	samples was d	etermined b	y means of the		
	Bethlehem Tensiometer apparatus in toluene solutions.					
	The values are	listed below.				
	Talc Aliquot		Specific			
	Wt. Gm.	-	Gravity	-		
	44.8		2.789			
	46.8		2.726			
	48.2		2.797			
	50.5		2.810			
	49.5		2.790			
	49.5		2.740			
	49.8		2.802			
	51.4		2.778			
	33.4		2.191			
	Average specif	ic gravity of	experimenta	al talc is 2.781.		
2)	Mixed mesh tal	c was boiled i	in concentra	ated HCl and HNO ₃		
	acids.					
	Init. Sample	Final Sample	Soluble	<pre>% Soluble</pre>		
	Wt. Gm.	Wt. Gm.	Wt. Gm.	Impurity		
	1.002	0.976	0.026	2.6		
	1.004	0.974	0.03	3.0		
	Average per cent soluble impurity is 2.8 $\frac{+}{-}$ 0.2%.					

TABLE XX (cont'd)

3)	One gram mixed mesh samples of talc were dried at 200°F					
	and ignited in porcelin crucibles at 910°C.					
	Init. Talc Wt. Gm.	Sample Wt. After Ignition	% Loss			
			Contraction of the second s			
	1.010 1.021	0.961 0.971	4.83 4.99			
	0.998	0.949	4.90			
	Average per cent ign	nition loss is 4.91	⁺ 0.08%, roughly			
	0.11% greater than t	the expected value	of 4.8%.			
4)	Experimental talc we	eight after 6 - 10	minutes of dry			
	grind in Abbé ball mill.					
	Talc Mesh	Talc Wt.				
	Size	Gm.				
	-65 +100	134 5				
	-100 +150	112.9				
	-150 + 200	94.0				
	-200 +325	66.8 				
	Total	talc wt. 408.2				

BIBLIOGRAPHY

- l. Gaudin, A.M., Flotation, 2nd ed. McGraw-Hill (N.Y.)
 (1957).
- Sutherland, K. and Wark, I., "Principles of Flotation" AIMM, Melbourne (1955).
- 3. Fuerstensteau, F. and Aplan, D., "Froth Flotation", Chap. 7, AIMMPE, N.Y., (1962).
- 4. Azaroff, L.V., "Introduction to Solids" McGraw-Hill N.Y. (1960).
- 5. Pyror, E.J., "Mineral Processing", p. 779, Elsevier Publishing Co., N.Y. (1965).
- 6. Eithel, W., "Silicate Science", Acad. Press, N.Y. (1966).
- 7. Booth, R. and Freyberger, W. Chap. 10 in reference 3.
- Gaudin, A.M., Miaw, H.L., and Spedden, H.R., Proc.
 Second Intl. Congress of Surface Activity, Vol. III
 Butterworth's Lond. 1957 p. 202.
- 9. Pauling, L., Proc. Natl. Acad. Sci. <u>16</u>, 123, (1930).
- 10. Gruner, J.N., Ceramic Abstr. <u>14</u> [2], 50, (1935).
- 11. Hendricks, S.B., Ceram. Abstr. 18 [10], 278, (1939).
- 12. Brown, G., Amer. Mineral, <u>51</u>, 259, (1966).
- 13. Raynor, J. and Brown, G., Nature 212, 1352, (1966).
- 14. Ross, M. and Ashton, W., American Mineralogist <u>53</u>, 751, (1968).
- 15. Pask, J. and Warner, M., J. Am. Ceram. Soc. <u>37</u> [3], 118, (1954).

- 16. Stemple, I. and Brindley, G., Amer. Ceram. Soc. <u>43</u>, 34, (1960).
- 17. Private Communication from G. Brindley, June 1971.
- 18. Private Communication, N.A. Wooster, June 1971.
- 19. See ref. 4 p. 137.
- 20. Dana, E., "Textbook of Mineralogy", p. 677-8, 4th ed. John Wiley and Sons, (1966).
- 21. Dupré, A., "Theorie Mechanique de la Chaleur", Paris, 1869, p. 368.
- 22. Adam, N.K., Nature 180, 809, (1957).
- 23. Gould, R., (editor), Contact Angle, Wettability, and Adhesion., Am. Chem. Soc. (1964) Chap. 1, 2, 3.
- 24. Adamson, A., "Physical Chemistry of Surfaces", 2nd ed. Interscience Publishers (1967).
- 25. Bartell, F. and Zuidema, H., J. Am. Chem. Soc. <u>58</u>, 1449, (1936).
- 26. Fawkes, F. and Harkins, W., J. Am. Chem. Soc. <u>62</u>, 3377, (1940).
- 27. Strel'tsyn, G.S., Obogasheh Rud. 13[2], 27, (1968).
- 28. Kruyt, H.R., "Colloid Science", Vol. I, Elsevier Publ. Co., Amsterdam, (1952).
- 29. Gouy, G., Ann. Phys. 7[9], 129, (1917).
- 30. Chapman, D., Phil. Mag. 25[6], 475, (1913).
- 31. Debye, P. and Huxkel, E., Phys. 2. <u>25</u> <u>93</u>, (1924).

- 32. Stern, O.Z., Elektrochem. 30, 508, (1924).
- 33. Delahay, P., "Double Layer and Electrode Kinetics, Interscience, N.Y., (1965).
- 34. Lyklema, J. and Overbeek, J., J. Colloid Sci. <u>16</u>, 595, (1961).
- 35. Brien, F. and Kar, G., Trend Eng. Univ. Wash. <u>20</u>
 [1], 8, (1968).
- 36. Lafaye, J. and Jacauelin, G., Peintures, Pigments, Vernis, <u>45</u>, 313, (1969).
- 37. Parks, J.A. and deBruyn, P.L., J. Phy. Chem. <u>66</u>, 967, (1962).
- 38. Parks, J.A., Chem. Rev. 65, 177, (1965).
- 39. Van Olphen, H., "An Introduction to Clay Colloid Chemistry" Intern. Publ., N.Y. (1963).
- 40. Berube, Y.G., Onoda, G.Y., and de Bruyn, P.L., Surface Sci., 8, 448, (1967).
- 41. Smith, G. and Salman, T., Can. Metalurgical Quarterly, <u>2</u>, 405, (1963).
- 42. Yoon, R.N., Masters Thesis, (1971) McGill Univ.
- 43. Parks, G.A., "Advances in Chemistry Series", <u>67</u>, 121, (1967).
- 44. Razouk, R. and Mikhail, R., J. Phys. Chem., <u>62</u>, 920, (1958).
- 45. Bolt, G. Trans. Intern. Congr. Soil. Sci. (7th), Madison, Wisc., 2, 321, (1961).

- .

- 46. Fripiat, J., Leonard, A. UyHerhoeven, J.B., J. Phys. Chem. 69, 3274, (1965).
- 47. Grim, R. "Clay Mineralogy", Chap. 7, McGraw-Hill, N.Y., (1953).
- 48. See reference 39. p. 244-45.
- 49. Iswaki, I., Cooke, S., Choi, H., AIME Trans. <u>220</u>, 394. (1961).
- 50. Robinson, N., Pask, J., and Fuerstenau, D., J. Amer. Ceram. Soc., <u>47</u>, 516, (1964).
- 51. Martinez, E. and Zucker, G., J. Phys. Chem. <u>64</u>, 924, (1961).
- 52. Pauling, L., "Nature of Chemical Bond", p. 558, Cornell Univ., Ithica, (1960).
- 53. Hair, M., "Infrared Spectroscopy in Surface Chemistry", Marcel Pecker Inc., Chap. 1,2,4,5. (1967).
- 54. Young, D. and Crowell, A., "Physical Adsorption of Gases", Butterworth, London, (1962).
- 55. Langmuir , J. Am. Chem. Soc. 40, 1361, (1918).
- 56. Bruneauer, S., Emmett, Teller, J. Am. Chem. Soc. 60, 309, (1938).
- 57. Fu and Bartell, J. Phys. and Colloid Chem. 52, 374, (1948).
- 58. Hansen and Bartell, J. Phys. and Colloid Chem., <u>53</u>, 769, (1949).
- 59. Bartell, J. Phys. Chem. 56, 665, (1952).
- 60. Freundlich, "Colloid and Capilary Chemistry, "Methuan and Co. (1926).

—).

- 61. Brunauer, S., "The Adsorption of Gases and Vapours" Vol. I, Princeton Univ. Press, (1945).
- 62. Giles, C., MacEwan, T., Nakhura, S., and Smith, D., J. Chem. Soc. 3973, (1966).
- 63. Bethlehem Balance Index of Specific Gravities, Bethlehem Instr. Co., P.A.
- 64. "Dictionary of Organic Compounds", Vol. 4. p. 2715, Eyre and Spottiswoode Publ. Ltd. (1965).
- 65. Bishop, W., Lorand, E., Reese, J., U.S. Patent 2, 467,369 (1945).
- 66. Weast, R. (editor), "Handbook of Chemistry and Physics", 50th ed. Chemical Rubber Co. (1970-71).
- 67. Private Communication Hercules Canada Limited (1971).
- Gordy, W., Smith, W., and Trombanito, R., "Microwave Spectroscopy", Wiley and Sons, N.Y. (1953).
- 69. Mizushima, S. and Shimanouchi, T., Ann. Rev. Phys. Chem. 7, 445, (1956).
- 70. Hughes, E., ibid 6, 261, (1955).
- 71. Leftin, H.P. and Hobson, M.C., Advan. Catalysis, <u>14</u>, 115, (1963).
- 72. Hunt, J., Nisherd, M., and Bunhum, L., Anal. Chem. 22, 1478, (1950).
- 73. Farmer, V.C., Min. Mag. 31, 829, (1958).
- 74. Launer, P., Amer. Min. 37, 764, (1952).
- 75. Mathieu, J.P., "Spectres de Vibration et Symetrie des Molecules et des Cristau", Paris, Herman and Co. (1945).

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).

- 76. Beutelspacher, H., 6th Internat. Cong. of Soil Sci. Reports, Vol. B (Commission 1 and 2) p. 329.
- 77. Nauman, A.W., Safford, G.J. and Mumpton, F., 14th Nat. Conf. on Clay and Clay Minerals p. 367-82.
- 78. Vedder, W. Amer. Min. <u>49</u>, 738-68. (1964).
- 79. Hexter, R.M. and Dows, D.A., J. Chem. Phys. <u>25</u>, 564, (1956).
- 80. Pouchert, C. "Aldrich Library of Infrared Spectra"p. 510C, Aldrich Chem. Co. (1970).
- 81. Dyer, J., "Application of Absorption Spectroscopy of Organic Compounds", Prentice Hall, N.J. (1965).
- 82. Williams, D., and Fleming, I., "Spectroscopic Methods in Organic Chemistry", McGraw-Hill, London, (1966).
- 83. Silverstein, R. and Bussler, G., "Spectroscopic Identification of Organic Compounds", Wiley and Sons. (1967).
- 84. Roberts, J. and Cassiero, M., "Modern Organic Chemistry",W.A. Benjamin, N.Y. (1967).
- 85. Liberles, A., "Introduction to Theoretical Organic Chemistry", MacMillan, N.Y. (1968).
- 86. Giles, C., MacEwan, T., Nakhura, S.and Smith, D., J. Chem. Soc. 3973, (1960).
- 87. Haisman, PhD Thesis, London, (1959).
- 88. Cummings, Garven, Rahman, Snedden and Stewart, J.
 535, 1958.

132

- 89. Galbraith, Giles, Halliday, Hassan, McAllister, Macauly, MacMillan, J. Appl. Chem. 8, 416, (1958).
- 90. Hansen and Craig, J. Phys. Chem. 58, 211, (1954).
- 91. Adam , Proc. Ray. Soc. A 103, 676, (1923).
- 92. Greenberg, S., J. Phys. Chem. <u>60</u>, 325, (1956).
- 93. Cotton, F., "Advanced Inorganic Chemistry", 2nd ed., Interscience Publ. Co. (1966).
- 94. Volkova, Z., Serb-Serbina, N., and Saporoshez, A., Kolloid Z., <u>71</u>, 230, (1935).
- 95. Clemmer, J. and Cooke, S., U.S. Bur. Mines Dept. Investigation 3314, (1936).
- 96. Norman, J., O'Meara, R., and Baumert, F., Bull. Am. Ceramic Soc. <u>18</u>, 292, (1939).
- 97. Berkelhamer, L., Bull. Am. Ceramic Soc. 22, 227, (1943).
- 98. Buckenham, M., Rogers, J., White, C., New Zealand J. Sci. Techn. 37B, 437, (1956).
- 99. Baranovskii, N., Izv. Vysshikh, Uchelon. Zavedenii Gorn. Zh. <u>8(5)</u>, 168, (1965).
- 100. Manser, R.M., "Flotation Areas of Some Silicate Minerals" to be published.
- 101. Bain, J., Briggs, D., May, F., Inst. Mining and Metallurgy, May, 1971, p. 77-84.
- 102. Mercade, V., U.S. 3, 459, 299, 4 pp. (1967).
- 103. Klassen, V., and Mokrousov, V., "An Introduction to the Theory of Flotation", Butterworth. (1963).

- 104. Sutherland, K.C., J. Phys. Colloid Chem. <u>52</u>, 394, (1948).
- 105. Taggart, A.F., "Handbood of Ore Dressing", Wiley and Sons, N.Y. (1945).
- 106. Meloy, T.P., Chap. 9. See ref. 3.
- 107. Charles, G., and Mason, S., J. Colloid Sci., <u>15</u>, 236, (1960).
- 108. Evans, L., Ind. Eng. Chem. 46, 2420, (1954).
- 109. Allen, R., Charles, G., and Mason, S., J. Colloid Sci. <u>16</u>, 150, (1961).
- 110. Ohtsuki, M., Japan Analyst (Bunseki Kagaku), <u>19</u> (9), 1191, (1970).
- 111. Bervenmark, H., Pharm. Sueciica, 5, 579, (1968).
- 112. Parks and Debruyn, J. Phys. Chem. 66, 967, (1962).
- 113. Modi, H., and Fuerstenau, D., J. Phys. Chem., <u>61</u>, 640, (1957).
- 114. Gaudin, A., and Sun, S., AIME Tech. Pub. 2005, May 1946.
- 115. Gaudin, A., and Bloecher, F., AIME Trans. <u>187</u>, 499, (1950).
- 116. Leja, J., and Shulman, J. i) AIME Trans 199, 221, (1954).
 ii) Mining Eng. Feb. (1954).
- 117. Leja, J., Bull. Inst. of Mining and Metallurgy <u>607</u>, 425, (1957).
- 118. Osipow, L., "Surface Chemistry", Reinhold Publ. Co. N.Y. (1964).
- 119. Salman, T., PhD Thesis, McGill Univ. 1956.
- 120. Kini, K., Manser, R., Joy, A., J. Phys. Chem. <u>72</u>, 2127, (1968).

134

- 121. Van der Hall, H., and Lyklema, J., Vol II. p. 140, London and Breuch Source (1967).
- 122. Smith, H. and Hurley, R., J. Phys. Colloid Chem. <u>53</u>, 1409, (1949).
- 123. Giles, G., and Nakhura, S., J. Appl. Chem. <u>12</u>, 266, (1962).
- 124. Greenland, and Quirk, Proceedings of the 9th Nat. Conf. of Clay and Clay Minerals, Vol. 9. p. 484, (1960).
- 125. Patterson, PhD Thesis, McGill. 1965.
- 126. Hendricks, D., Masters Thesis. McGill Univ. 1971.
- 127. Bartell, F., and Donahue, D., J. Phys. Chem., <u>56</u>, 665, (1952).
- 128. Czerniawski, Roczniki Chem. 39,(9), 1275, (1965).
- 129. Greenland, O., and Quirk, J., J. Phys. Chem., <u>67</u>, 2886, (1963).
- 130. Verwey, E., and Overbeek, J., "Theory of the Stability of Lyophobic Colloids", Elsevier, N.Y., 1948.

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