

FLOTATION WITH INSOLUBLE REAGENTS

Thesis submitted for the Degree of Doctor of
Philosophy of the University of London

by

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1959

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A C K N O W L E D G M E N T S

This work was carried out in the Mining Department, Imperial College of Science and Technology in the University of London.

I should like to express my sincere thanks to Dr. A.R. Burkin for his continued advice and encouragement.

I should also like to thank the Department of Scientific and Industrial Research for their financial assistance.

A B S T R A C T

In the introduction a short outline is given of the use of insoluble oils in flotation. The object of this work is explained and the reasons for the choice of the dodecylamine quartz system are examined. A short survey of the literature on the subject follows.

In the next section the methods of manufacture of emulsion and measurement of their physical properties are described, together with a description of bubble pick-up and beaker cell methods for examining the flotation characteristics of the system. Descriptions of the streaming current and electrophoresis methods for measuring the zeta potentials of quartz particles and oil droplets follow together with a radioactive tracer technique for measuring the partition of dodecylamine between oil and water under various conditions.

The flotation of quartz is shown to be possible at greatly reduced amine concentrations if an emulsified oil is added. This result is not repeated in the beaker cell tests. The potentials of the oil and quartz surfaces are shown to be dependent upon pH, and to be varied, but not changed in sign, by non surface active salts. Amine changed the sign of both. The results of the radioactive tracer measurements are described.

Methods for interpretation of zeta potential results are discussed. Derjaguin's theory of the hetero-coagulation

of dissimilar particles is examined and curves are drawn from his formulae for the calculation of energy barriers between approaching particles.

The flotation results are discussed and the energy barriers between oil and quartz are calculated. They show that flotation occurs under theoretically impossible conditions. This anomaly is examined. The adsorption data of other workers are then applied to the system

I N T R O D U C T I O N

The use of insoluble reagents preceded that of soluble polar reagents as collectors in froth flotation. In these early methods the oil was present in concentrations of up to 200 pounds per ton of ore. The oil was presented to the ore either as an emulsion or in bulk. It was so mixed with the ore, either in the grinding circuit or in a separate conditioning stage, that it was smeared onto the surface of the sulphide minerals. The oxide minerals were not coated by oil so a separation resulted. The reason suggested by Truscott⁽¹⁾ for the selectivity of oil collectors was the low interfacial tension between oils and sulphide minerals.

With the discovery by Keller⁽²⁾ that soluble alkali xanthates could be used for flotation of sulphide minerals the use of oils was discontinued in most fields of flotation. Since then the bulk of flotation research has been directed to studying the interaction of soluble collector and mineral surface. With some minerals the use of oils has continued. The most important of these fields are those of the flotation of non-polar minerals such as sulphur or graphite, the flotation of phosphates, coal flotation and manganese flotation.

In the flotation of the non-polar minerals such as sulphur or graphite the oil is presented as an emulsion to mineral surfaces which have a strong natural tendency to float.

Indeed these minerals have been floated with only a frother see Gaudin⁽³⁾ and Taggart⁽⁴⁾. Phosphate flotation is more complex in that the oil is added to a system which already contains a fatty acid collector. The oil is used in cases where the mineral is spongy and the use of sufficient collector to give good flotation would result in a bad froth. The addition of mineral oil allows the use of less collector. No adequate explanation of the role of oil in this system has been given.

The greatest use of oils in flotation has been in the coal industry. A survey of the literature relevant to the interaction of oil and coal has been made by Bramley⁽⁵⁾. The principal reagents used in British coal flotation are creosote and cresylic acid, although the addition of fuel oil is beneficial. Various modifiers can be added. The main effect of these modifiers is upon the magnitude and sign of the zeta potentials at the surfaces of the particles of coal and gangue, possibly of the droplets of collector, and when air is admitted, of the bubbles. The changes in zeta potential influence the magnitude of the energy barrier opposing the true contact of these elements. Other effects are the improvement of froth formation and, possibly, the assistance of the spreading of the oil on the coal once it has been brought into contact.

Bramley's work showed that under relatively quiescent fluid conditions and using a 'pre-made' emulsion, although

there might be encounters between oil droplets and coal particles, there were no true collisions except when a detergent, Lissapol NDB, was present. The measurement under various conditions of the zeta potentials of the oil and coal showed that there was an energy barrier, preventing approach of the oil and coal particles, which was significantly lowered in the presence of Lissapol NDB. It was concluded that the presence of Lissapol rendered violent agitation unnecessary.

Fahrenwald records that in manganese flotation at Manganese Inc. Nevada, the principal reagents employed are 1) a primary activating agent and 2) an emulsion consisting of a neutral oil, soap and a wetting agent. He suggests that the role of the primary activating agent is to prepare the surface for adsorption of the soap. The soap is not itself the collecting agent but has a twofold action. 1) It behaves as an emulsifying agent for the oil. 2) It provides a water repellent, oil soluble, surface layer on the mineral which enables the covering of the surface by the oil. He also suggests that this method can only be employed with non-crystalline minerals.

To determine whether the effects of Lissapol in coal flotation, and the mixture of oil and fatty acid in phosphate and manganese flotation, was of general application in mineral flotation, and to study the forces involved in such a system

it was necessary to examine a mineral-collector system which had been extensively studied in the absence of an insoluble oil. The flotation of quartz by dodecylamine salts satisfied this requirement and had the added advantage that both mineral and collector are stable in water. This system could then be studied to determine whether the addition of smaller quantities of amine than those used in froth flotation would allow flotation in the presence of an emulsified oil, and to determine the forces of interaction of the oil and the mineral under various conditions.

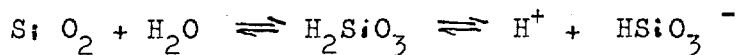
Section I Part 1

Quartz Flotation With Amines With Particular Reference
to Dodecylamine

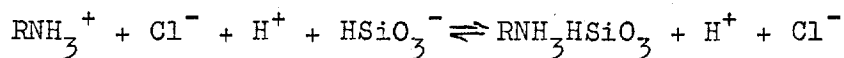
Quartz has probably been more studied, with regard to flotation, than all other silicate minerals put together. It is known that clean quartz has no native flotability⁽⁷⁾ and it was shown by early studies that it is not floated by fatty acids or soaps⁽⁸⁾⁽⁹⁾. No positive evidence has yet been produced to show that it can be floated by any other anionic collectors although it has been shown⁽¹⁰⁾ that many metallic ions activate quartz for soap collection.

As early as 1936 Wark⁽¹¹⁾ discovered that Hexadecyltrimethyl ammonium bromide is a collector for quartz, and in 1939, stimulated by their large scale commercial production and relatively low cost O'Meara, Norman and Hammond⁽¹²⁾ studied quartz flotation with various long chain primary amines. They found that it could be floated in acid solution from a pulp containing quartz and feldspar, using fluoride as a depressant for the latter. In 1943 Taggart, Kellogg and Arbiter⁽¹³⁾ studied amine flotation with various metals and minerals and reached the conclusion that in solution the amine ion is dissociated, being partially present as the aminium ion RNH_3^+ . It was suggested by the same authors that the action of sodium silicate as an activator for quartz was due to its ability to depress what they thought to be the collector coating compound $(\text{RNH}_3)(\text{HSiO}_3)$. Taggart

advanced the hypothesis that collection took place as a result of hydration and dissociation of the silica surface according to the equation



Kellogg and Vasquez Rosas⁽¹⁴⁾ calculated the various forms in which dodecylamine is present in test liquors. Their calculations were based on a careful determination of the ionisation constant of dodecylamine⁽¹⁵⁾. However their curves have been modified by Gaudin⁽¹⁶⁾ who bases his calculations on a later value for the solubility of dodecylamine in water; that of Brown⁽¹⁷⁾. The curves show that the reagent distributes itself into three forms. 1) Ionically dissolved as RNH_3^+ . 2) Molecularly dissolved as RNH_2 and 3) Precipitated. The ionically dissolved form can only exist below a certain pH. Above pH 12 less than 10^{-6} moles/litre is present in this form the rest being present in the molecular and precipitated forms. On the basis of this curve Kellogg and Vasquez-Rosas suggest that the collecting equation in a dodecylamine chloride solution is as follows



The authors also give figures for the amount of silica present in solution at various pH values. They interpret these figures as indicating that at high pH values the above reaction is aided by the presence of large quantities of

$(\text{HSiO}_3)^-$ ion in solution.

The contact angle of the system was shown to increase with increasing collector concentration at a pH of 5.8. This was attributed to the large quantities of RNH_3^+ in solution. In 1946 Taggart and Arbiter⁽¹⁸⁾ showed that the contact angle increases to a maximum and then decreases as the collector concentration continues to increase.

Contact Angle Tests

The contact angles of air bubbles in dodecylamine quartz systems have been studied by a number of workers including the two mentioned above. The critical pH curves obtained by the various workers differ to some extent. Plante⁽¹⁹⁾, using 25 mg/l of dodecylamine acetate, obtained contact between pH 4 and 14. No other worker obtained contact above pH 12. It is possible that the reason for this discrepancy lay in the impurity of Plante's collector. Maximum contact has been found at pH 9.5, the angle remaining constant until pH 10.5 and then falling off rapidly to zero at pH 12 (20). At pH 5.8 ± 0.3 Buckenham and Rogers⁽²⁰⁾ using 25 mg/l of dodecylamine hydrochloride report an angle of 15° . Kellogg and Vasquez-Rosas⁽¹⁴⁾ report an angle of 63° at the same pH and collector concentration. Philippoff, Cooke and Caldwell⁽²¹⁾ mention that at this pH considerable time was required to reach equilibrium and they record an angle of 32° . It is obvious that the differences quoted above are considerable. They might be caused by differing lengths

of induction time or alternatively by different purity of collectors. In this connection Sutherland⁽²²⁾ determined the contact angles of two samples of purified dodecylamine on sphalerite. The specially prepared amine of the higher purity showed the lower contact angle. Using 4×10^{-5} moles/litre of dodecylamine acetate Gaudin and Marrow⁽²³⁾ recorded contact at a pH of less than 2, which is in disagreement with all other workers, although Buckenham and Rogers report that cylinder tests showed some degree of flotation at 2.2.

Buckenham and Rodgers give critical pH and concentration curves for dodecylamine chloride and quartz, determined by the bubble pick-up method of Cooke⁽²⁴⁾. These showed that 'pick-up' could be obtained between pH 4 and 12 at about 20 mg/l and between 6 and 12 at 2.5 mg/l. No pick-up could be obtained above 2000 mg/l or below 0.5 mg/l. The limits of 'cling' (slight tendency to flotation) were pH 2, and 2×10^{-2} mg/l at pH 8. These results are confirmed by Robinson⁽²⁵⁾ using Armac 12D. The critical pH curve of De Bruyn⁽²⁶⁾ using dodecylamine acetate, differs greatly from that of Buckenham and Rodgers, and of Robinson. While the latter found that the minimum collector concentration could be used at pH 7 De Bruyn found this minimum at pH 12. De Bruyn's curve, however, was obtained with the captive bubble technique while the other workers used the bubble pick-up method. Buckenham and

Rodgers as a result of tests using both methods, conclude that the bubble pick-up technique is the more sensitive, so we may consider their results more trustworthy than those of De Bruyn.

Hallimond Tube and Fagergren bell Tests

Buckenham and Rodgers, using 25 mg/l of dodecylamine hydrochloride and floating for one minute in the Hallimond tube, found that recovery was very low at pH 2, rising to some 5% at pH 6 and then rising very rapidly to about 90% at pH 8. It then remained steady until pH 12 and dropped off sharply to zero at pH 12.2. The same authors performed a number of tests in the Fagergren cell, under the same conditions, but using a flotation time of 3 minutes. The results showed minimum recovery at pH 2 rising to about 85% at pH 5 then more gradually to 95% at pH 9.5 when it fell off sharply to zero at pH 12.

Adsorption Studies

Both Gaudin and Bloecher⁽²⁷⁾ and De Bruyn⁽²⁶⁾ have studied quantitatively the adsorption of dodecylamine acetate onto quartz from solutions of various concentrations using radio active tracers. Gaudin and Bloecher used an adsorption column technique while De Bruyn also used an agitation technique. Their results showed that at low collector concentrations that is from 10^{-7} to 2×10^{-4} moles/sq.cm. adsorbed, the amount adsorbed varies directly with the square root of the reagent concentration i.e.:

$$T = K \sqrt{C}$$

where T is the adsorption/cm² of quartz surface.

K is a constant and C is the solution concentration. At higher reagent concentrations the adsorption was dependent on a higher value of C than $\sqrt{C}$. Gaudin and Bloecher showed that the reagent concentration necessary to form a complete monolayer on the quartz surface is similar to that at which micelles form in solution, however before a monolayer is complete polymolecular adsorption begins.

By replacing adsorbed unmarked amine with radioactive amine and vice versa the reversibility of the dodecylamine adsorption was demonstrated. This was also indicated by showing that the equilibrium conditions of adsorption could be approached from above as well as below, although the equilibrium state is not exactly repeated. Gaudin and Bloecher also suggest that marked amine coatings can be removed from quartz by washing in water or with a weaker amine solution. They did not however consider the exchangeability sufficient to satisfy a kinetic view in which adsorption - desorption is regarded as akin to evaporation and condensation.

Data taken from Gaudin and Bloecher's experiments show that in the range of practical flotation concentrations the adsorbed coating is very incomplete. It is only 7% complete at 10 mg/l, which gives more than 95% flotation. A 4% complete coating gives 90% recovery and a change of coating density from 1 to 1.5% produces a 15% change in recovery,

hinting at lateral mobility of the collector coating.

Streaming Potential Studies

Gaudin and Fuerstenau⁽²⁸⁾ showed that quartz is negatively charged in water the potential determining ions being hydrogen and hydroxyl ions. The isoelectric point was found at pH 3.7. It was also demonstrated that increasing collector concentration decreased the zeta potential to zero at 3×10^{-3} mol/l; it being positive at higher collector concentrations. The action of salts which were not surface active was to depress the zeta potential without changing its sign. They showed⁽²⁹⁾ that the adsorption was cationic and therefore involves the aminium ion and not the undissociated amine molecule. Gaudin and Fuerstenau advanced the hypothesis that at high collector concentrations the adsorption is hemi-micellar i.e. a multi-ionic layer similar to micelles in the bulk solution. At very high concentration a second, reversed layer is adsorbed above the first layer.

Theories of Collection

Gaudin and Fuerstenau's studies show that the collecting mechanism is that of cationic adsorption. At high pH values, although the quantity of aminium ion in solution is rapidly reduced with increase of pH, the recovery in the Hallimond tube remains constant. Sutherland and Wark⁽³⁰⁾ interpret this as showing that collection is in part by the free amine molecule which is at constant concentration throughout this range. Robinson⁽³¹⁾ suggests that the precipitation of free

amine on the mineral surface causes high contact angles and high recoveries, whereas in the Fagergren cell violent stirring prevents such precipitation and the recovery decreases above pH9.5. This observation is supported by bubble pick-up results which show that in solutions of low concentration pick-up is possible at pH 9 while it is not possible at pH 10 and above.

Taggart and Arbiter suggest that the collecting mechanism is that of chemical adsorption, a chemical compound being formed between the dodecylammonium ion and silicic acid in the quartz surface. However Gaudin and Bloecher's tests on the reversibility of the dodecylamine adsorption suggest that adsorption is physical. A chemically adsorbed coating of dodecylammonium ion would not be so easily reversible as the adsorption tests showed the collector coating in this system to be. It may therefore be concluded that collection is by a physically adsorbed hydrophobic layer of dodecylammonium ion on the quartz surface.

Section I Part 2

The surface Structure of Quartz

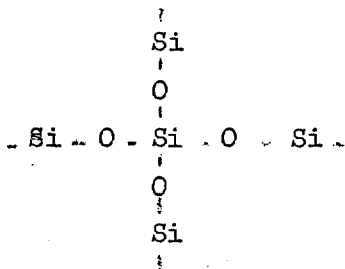
Silica occurs in four major forms at normal temperatures. These are; the amorphous form (as in glasses) quartz and two high temperature forms, tridymite and cristobalite, which are metastable below 870°C.

The temperature variation of silica is described by Sidgwick⁽³²⁾.

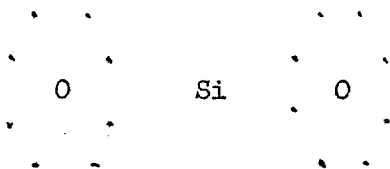
Quartz 870°C Tridymite 1470°C Crystobalite 1770°C liquid.

Each of these crystal types occurs in both a low temperature and a high temperature form; the α and β forms. In quartz the transition temperature occurs at 575° .

α quartz, the form with which this research was concerned, belongs to the hexagonal crystal system. It is formed from singly linked giant molecules of silicon and oxygen with the groupings



It is common in diagrams to show the chemical bonding between the oxygen and the silicon atoms with the electrons all attached to the oxygen atoms.



Hückel⁽³³⁾, however, points out that there is a considerable electron density between the atoms and that the structure may by no means be considered ionic.

The basic crystal structure is that of an SiO_4 tetrahedron each oxygen atom being common to two such tetrahedra. Frederickson⁽³⁴⁾ took electron microscope photographs of quartz etched with water vapour at temperatures up to 360° and pressures up to 300 atm. He concluded that quartz has a mosaic structure and consists of sheets that are aggregates of rods approximately 9×10^{-4} mm in diameter and 0.009 to 0.05 mm long.

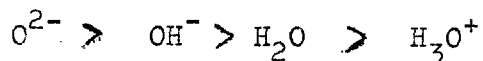
In this research we are primarily concerned with the surface structure of quartz. This has been studied by a large number of workers principally in connection with silicosis studies. Measurements of the solubility and solubility rate of powdered quartz in water showed that an initial period of rapid dissolution occurs, after which the quartz dissolves more slowly. cf Briscoe et al⁽³⁵⁾ and Holt and King⁽³⁶⁾. This initial period of rapid dissolution was also shown by Benton and Elton⁽³⁷⁾ who noted a rapid increase in the conductivity of water upon the addition of silica. Kitto and Patterson⁽³⁸⁾ and later Clelland and Ritchie⁽³⁹⁾ attributed the initial rapid dissolution of quartz to the presence of a disturbed surface layer which may be likened to a Beilby layer. Recently Neglichmidt, Gordon and Griffin⁽⁴⁰⁾ determined the quartz content of different sands as a function of particle size by X-ray diffraction.

The finest fractions had only 68% of the volume as the undistorted quartz structure. By carefully etching the powder the quartz content could be raised. They estimated that each grain was coated by a distorted layer 0.3μ thick. Dempster and Ritchie⁽⁴¹⁾ showed that the highly reactive surface layer was not found only in quartz but also in crushed silica. They suggested that this indicated that the increased reactivity of the quartz surface was not necessarily due to an amorphous surface zone. Indeed Holt and King⁽³⁶⁾ report that Heavens⁽⁴²⁾ obtained sharp Kikuchi patterns in electron diffraction photographs of the surface of a freshly fractured and an acid washed quartz crystal, proving the absence of any thick layer of non-crystalline material.

Holt and King⁽³⁶⁾ studied the solubility of crushed silica surfaces by a radiotracer technique. They showed that silica surfaces will adsorb silicic acid and that the adsorbed layer is identical with the high solubility layer mentioned by other workers. This layer is removed by alkali and reformed from silicic acid solutions even if the concentrations are well below that of a saturated solution. They divide published solubility data into two parts. The first, the 'high solubility layer' may be attributed to the dissolution of the adsorbed silicic acid layer; the second portion represents the attack of water on the true silica lattice. They point out that the rate of dissolution of quartz will depend on the particle size and since the equilibration of

quartz with water has never been accomplished at normal temperatures and at neutrality all published data must be considered with respect to the quartz particle employed.

Weyl⁽⁴³⁾ discusses the surface of quartz in relation to the size, charge and polarization properties of the ions. He points out that surface phenomena are governed by the polarization and deformation of ions, because they involve the asymmetrical groups cation-anion-space or anion-cation-space. From studies of those phenomena where mutual deformation of ions plays a decisive role he concluded that the screening of cations is a basic principle governing surface phenomena, and that the degree of screening of a cation depends on the number size and polarizabilities of the surrounding anions as well as the cation-anion distance. He also points out that in the reactions of solids with water, the polarizability and therefore the ability to screen a surface ion, decreases in the order



Weyl lists four structural changes by which a homogeneous solid can lower its surface energy. These are:

- 1) Polarization of the surface ions.
- 2) Increasing the number of the most polarizable and decreasing the number of the least polarizable ions in the surface.
- 3) Advancing the most polarizable ions into the extreme outer layer and retracting the least polarizable ones. (This produces an electrical double layer and must have a depth action).

4) Chemisorbtion of molecules or ions. If quartz is ground dry only the third method is available, which may give rise to the amorphous layer reported by other workers (see above). In the case of wet grinding, however, the fourth method can also be employed and the quartz surface would attract OH^- ions when they were available.

Weyl reports that Ruff and Hirsch⁽⁴⁴⁾ found that fine quartz powder can produce a pH of 4.85 in water. He concludes that the system quartz-water can lower its free energy by a process in which H_2O dissociates and the OH^- ions are made available for the screening of Si^{4+} ions in the quartz surface. The OH^- ions impart a negative charge to the quartz, and the corresponding number of protons may be responsible for the acidity of the supernatant liquid if ions like Na^+ are available for the double layer.

It may be concluded that although it has not been proved that an amorphous Beilby type layer does exist on quartz, there is considerable evidence that it does in the case of dry ground quartz. If wet ground quartz shows such a layer it would be to a smaller extent. The anomalous solubility phenomena can be best explained by Holt and King's observations which suggest a surface monolayer of silicic acid which can be removed in water and replaced in silicic acid solutions. The electrokinetic phenomena studied in this research may be attributed to the cation screening action of the hydroxyl ions in water leading to a negatively charged surface.

Section 2A

Experimental Methods

2.A.1 - Preparation of Emulsions

Choice of Method of Manufacture of Emulsions

In this research it was intended that the collector should be presented to the mineral as a solution in an emulsified oil. The most suitable type of oil for the purpose was a short chain aliphatic hydrocarbon one. That used was Shell Printing Ink Oil No.11. Emulsions of such oils are in frequent use in commercial practice, but in most cases an emulsifying agent is used in their manufacture. It is believed that the effect of this agent is to lower the interfacial tension at the oil-water interface, or to raise the zeta-potential of the oil drops. In many cases the agent collects to such an extent at the interface that it forms a viscous layer which prevents coagulation of the droplets. The properties of the emulsion depend to a large extent on the emulsifying agent. Because it was necessary to examine the properties of the oil-amine system in the absence of other surface active materials it was impossible to use such an agent so a mechanical method was necessary.

Mechanical methods of making emulsions are of two principal types:- a) stirring and b) homogenization. In the absence of an emulsifying agent the former method is not satisfactory with mineral oils unless very violent. It was

necessary therefore to use the latter method, which consists essentially of forcing the phase to be dispersed through an orifice into the continuous phase. The instrument chosen for this was a paint spray gun.

Method of Making Emulsions

Emulsions were prepared with a De Vilbis Aerograph type MPS spray gun fitted with a No 2 nozzle. De-ionised water (and in later experiments double-distilled water), was supplied under pressure from a 20 litre reagent storage bottle. The water was fed into the inlet to the gun normally used for air. The oil was poured into the paint reservoir. Pressures could be varied from 0 to 22 p.s.i. by a reduction valve fitted to the laboratory air line. Maximum pressure was used in all test work.

2.A.2. Analysis of Emulsions

a) Size Frequency Distribution

For the calculation of the forces involved in particle interactions it was necessary to know the sizes of the oil droplets in the emulsions. A number of possible methods were considered: the principal among these are

- a) Photomicrographic analysis
- b) Sedimentation analysis
- c) Direct microscopic count
- d) Light scattering techniques

The scope of the research did not extend to an intensive examination of the emulsions so the qualities looked for in

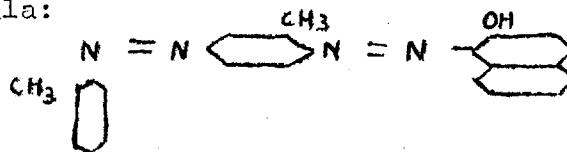
the chosen method were those of simplicity and speed. This latter was a very important limitation because the low specific gravity of the oil caused rapid creaming and hence rapid changes in particle size distribution. This rendered the direct microscopic count unusable. Sedimentation analysis was dismissed as being unpracticable because of the dilution of the emulsions used, and the time involved in the measurement. The light scattering technique was not investigated.

The principal problems of photomicrographic analysis arose from the transparency of the oil. A preliminary microscopic examination indicated that the oil droplets were completely indistinguishable from the surrounding water. To obtain contrast between the oil and the water it was therefore necessary to add a dye to the oil. It was essential that this dye should have a very low surface activity so that its presence would not alter the properties of the oil-water interface. A sample of Waxoline OS was obtained from I.C.I. Ltd. This dye is described in the Colour Index⁽⁴⁵⁾ and has the following properties:

Composition: O-toluene-azo-O-toluene-azo- β naphthol

Molecular formula : $C_{12} H_{20} N_4 O$

Structural formula:



Appearance: A dark reddish brown powder

Solubility: Insoluble in water but soluble in oils.

Although possessing one hydroxyl group in the molecule the surface activity of the dye is very low, so the requirements may be considered to have been met. The dye was present in the oil in all tests and any slight effects it might have had on the properties would have been equally in evidence in all results.

When saturated with the dye the oil had a cherry red colour but contrast was still poor. A further difficulty was presented by the rapid movement of the droplets in the emulsion. It was therefore necessary to satisfy conflicting requirements. A sufficiently fast exposure was needed to stop movement and yet the poor contrast of the subject necessitated a long exposure time. The technique which best satisfied these requirements was the following: emulsion samples were placed in a petri dish on the stage of a Beck microscope fitted with a 16mm projection objective. The image was cast onto the ground glass screen of an MPP 'Micro-Press' camera at double extension. The source of illumination was a mercury vapour lamp. Copper sulphate in an optical cell acted as a heat absorbing filter and rendered the light source monochromatic. For purposes of droplet size measurement the magnification was first determined by photographing a calibrated graticule placed on the stage. Seven exposures, the remainder of one roll of film were then made of the emulsion. Enlarged prints were made from the film and the final magnification was approximately $\times 180$. The apparatus is shown

in diagrammatic form in Fig 1.

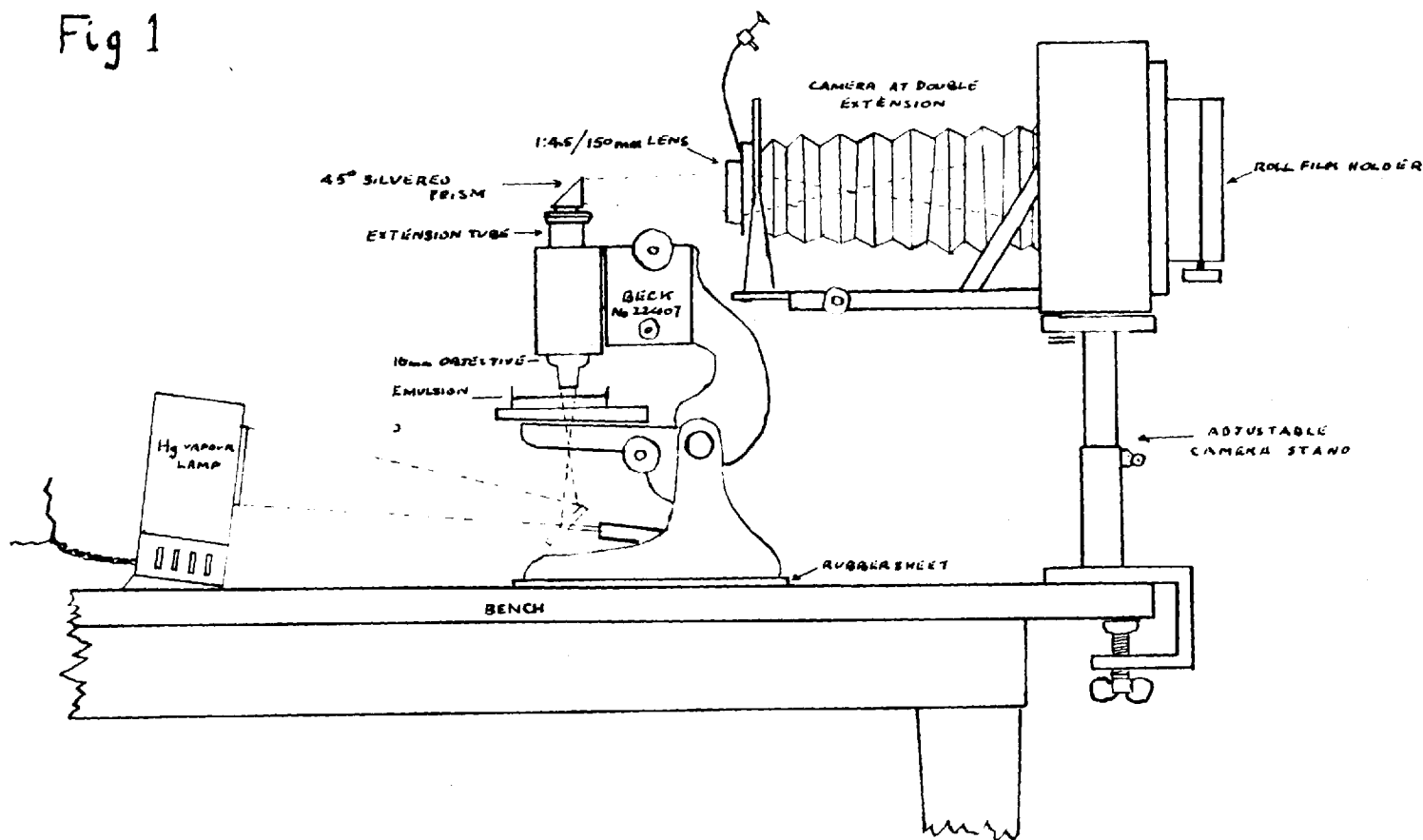
b) Proportion of Oil to Water by Weight.

For determining amine concentrations and distributions it was essential that an accurate method should be used for determining oil concentrations in emulsions. The following method was employed.

Approximately 100 ml of emulsion was placed in a 250 ml separating funnel of known weight. This sample was always taken by the same means as that used in the flotation test concerned. The funnel and contents were weighed. The oil was then completely extracted from the emulsion in the usual manner, with four successive portions of chloroform of about 20 ml each. The oil-in-chloroform solution thus obtained was then made up to 100 ml with chloroform. This solution was left standing overnight over calcium chloride to remove water which might precipitate and alter the optical density. The concentration of oil in chloroform was then determined using a Unicam spectrophotometer.

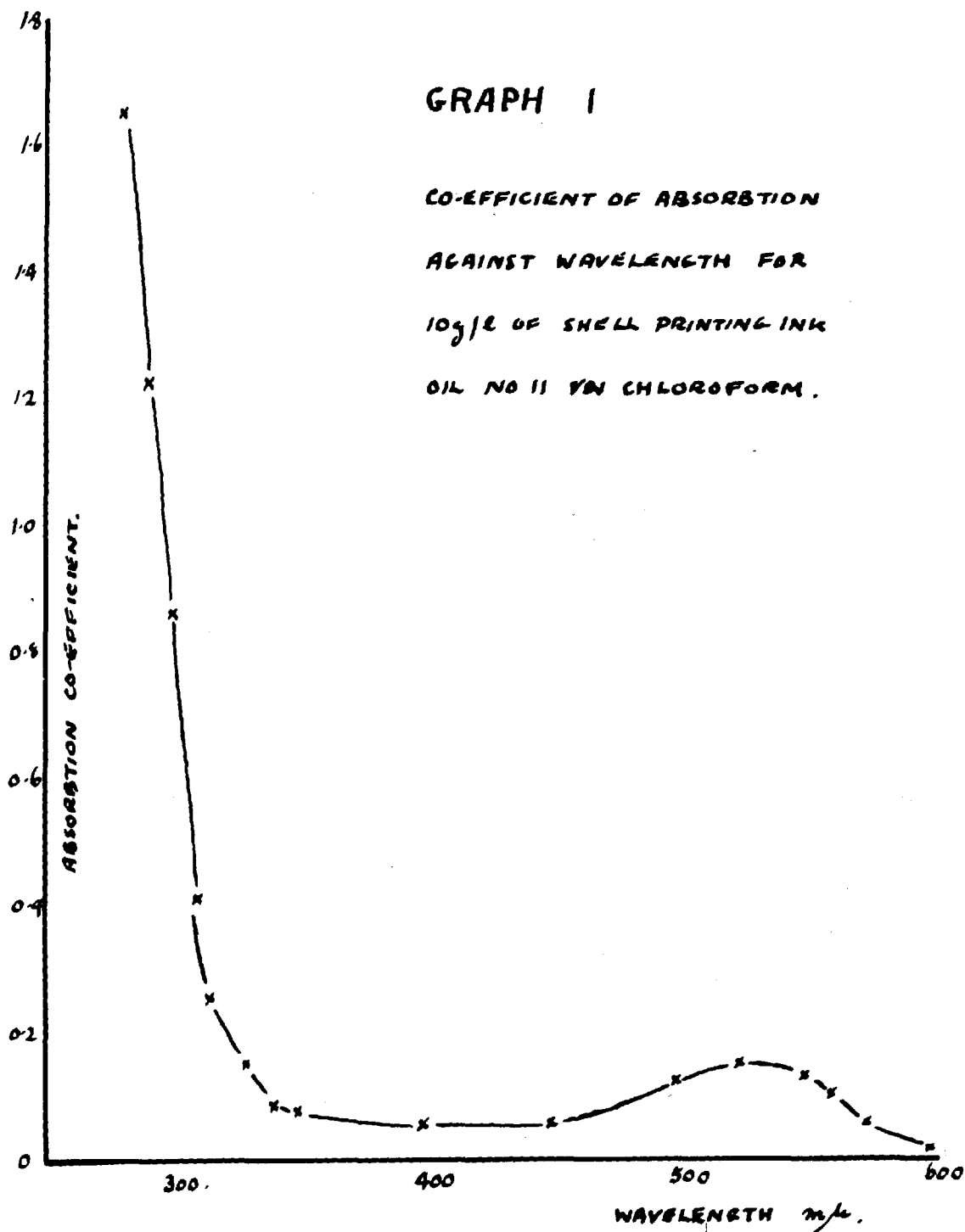
The spectrophotometer was calibrated by plotting a curve of adsorbtion co-efficient against wavelength using 10g/l of dyed oil in chloroform. The curve (graph 1) indicated that wavelengths below $280 \text{ m}\mu$ would be suitable at a lower concentration than 10g/l. Measurement of absorbtion co-efficients made at various wavelength between 245 and $280 \text{ m}\mu$ showed that a wavelength of $260 \text{ m}\mu$ at a slit width of 0.49 was most satisfactory. A curve (graph 2) was plotted of

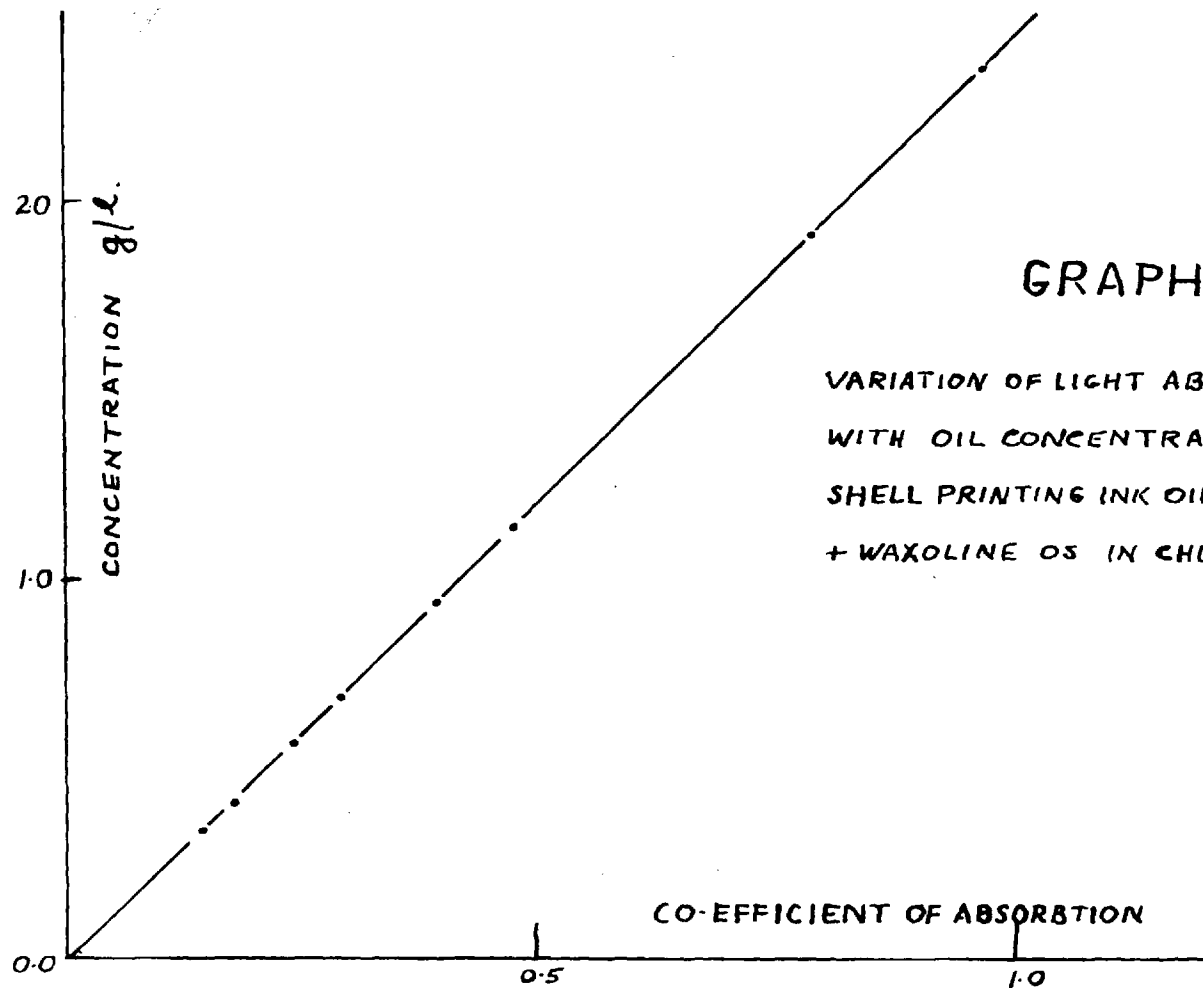
Fig 1



EMULSION PHOTOGRAPHY

ALSO USED FOR ELECTROPHORESIS (FOR MODIFICATIONS SEE TEXT)





GRAPH 2

VARIATION OF LIGHT ABSORPTION
WITH OIL CONCENTRATION
SHELL PRINTING INK OIL NO 11
+ WAXOLINE OS IN CHLOROFORM.

absorbtion co-efficient Vs concentration at this wavelength, which gave a straight line thus showing that the system obeys Beer's law at absorbtion co-efficients of below 1.0. All future oil concentrations were read from this curve. In later tests a second sample of dyed oil was used and the spectrophotometer was recalibrated.

Section 2.A.3. Bubble Pick-up Methods

a) The Method

This description of the bubble pick-up test method is largely taken from Robinson⁽⁴⁶⁾. It is based on that described by Cooke and Digre⁽²⁴⁾. It was designed to explore pure mineral response to collectors and modifiers. It was claimed by Cooke and Digre that the method is more sensitive than captive bubble tests. This claim is supported by Robinson and by Buckenham and Rogers⁽²⁰⁾. The method is quick and simple and has been shown to be both reliable and reproducible. If the basic method is not greatly altered the personal error can be reduced to a very low degree. Thus one worker can repeat the work of another and very little difference is found between the results obtained.

Essentially the method consists of bringing a captive air bubble into contact with a bed of conditioned mineral particles and observing the mineral behaviour when the bubble is withdrawn. The mineral behaves in one of three ways: when 'pick-up' occurs the mineral particles adhere to the bubble and are not dislodged when the bubble holder is tapped. When 'cling' occurs one or several mineral particles adhere to the bubble ~~holder~~. When 'no pick-up' occurs, no particles stick to the bubble when it is withdrawn from the mineral bed. In practice there is no difficulty in distinguishing between pick-up and cling except at high collector concentrations when

precipitated collector may render the solution cloudy.

In each test about 0.1 g of -72 ~~#~~ + 100 ~~#~~ mineral was taken. This was conditioned in the actual test cell. Tests were designed to show the variation of flotation characteristics with changes of pH and collector concentration. It is not possible to obtain the same boundary line between pick-up, cling and no pick-up when the boundaries are approached from pick-up as when they are approached from no pick-up. This difficulty is caused by the difference between the advancing and receding contact angles between the air bubbles and the conditioned mineral surfaces. In flotation practice the conditioning is concerned with the advancing contact angles, it was therefore considered more correct to approach the boundaries from no pick-up. For this purpose all tests were performed by adding the mineral to a solution whose pH was outside the cling region. Thus at each collector concentration tested the pick-up curve was approached from the acid and alkaline sides in different tests.

The test procedure was as follows; 100 ml of the test solution was made up in a standard flask at the desired collector concentration and transferred to the petri dish. The pH was then adjusted to the desired value with hydrochloric acid or sodium hydroxide solution. A few drops of the ground mineral were introduced and the solution stirred. With practice the mineral could be made to settle in the centre of the dish when stirring ceased. After conditioning for five

minutes a bubble about 1/4 inches in diameter was pressed onto the heap of mineral. When ten seconds had elapsed, (in some tests a time of 30 seconds was used), the bubble was raised and the holder tapped with the forefinger. The pH was measured again after examining for pick up. After modification of the pH the procedure was repeated.

The tests were all performed at room temperature i.e. 18°C to 21°C. pH modifications were done with normal, N/10 and N/100 solutions of acid and alkali and with care serious alterations in the collector concentration could be avoided. pH values were measured with a Pye pH meter.

The results obtained were plotted in a graph in the manner illustrated in graph 5. Although the tests are dynamic the curves do not give a measure of the collector concentrations which would be required in practice to float the mineral in a flotation cell, when the limits of flotation would be found to lie well within the range indicated in the bubble pick-up tests.

b) Pick-up Tests in the Presence of Emulsions

The bubble pick-up test method used in these cases was essentially the same as that used for the tests where the collector was presented as a solution of a soluble salt. One or two alterations were however introduced. The method employed is outlined below.

The method of preparation and storage of mineral was unaltered and is described in Section 2.A.5. The

dodecylamine was dissolved in the oil before making the emulsions. In each case a known weight of amine was added to a small known volume of oil and the mixture was warmed to above 30°C to ensure dis-solution of the amine in the oil. The emulsions were prepared in the usual manner in a beaker which had been filled to just under the brim with water of about pH 9. This alkaline pH was chosen because at this point most of the amine was thought to be in the oil. The emulsion was sufficiently stable that two or three series of points could be taken from one emulsion source. After being made the emulsion was allowed to stand for some time while the larger drops creamed to the surface. Meanwhile the quartz was tested for cleanliness in a petri dish in pure water both before and after the addition of modifiers. If cling was obtained the mineral was considered to be dirty and was discarded. If not the pH was then taken outside the expected cling range.

A sample of emulsion was next transferred from the beaker in sufficient quantity to give the required concentration of amine. It was not possible to estimate to within 50% of the strength used until after analysis of the emulsion sample which was siphoned into a weighed separating funnel immediately after the addition of the test sample to the petri dish.

In the third series of bubble pick-up tests the dod-

ecylamine was added as the hydrochloride salt and the emulsion was added separately. In these cases a blank test was performed in the emulsion before addition of the amine and if the mineral proved to be clean the amine was then added and the tests performed in the usual manner.

Determination of Amine Concentrations in Bubble Pick-up Tests

The amine concentrations in bubble pick-up tests performed in the presence of emulsions were calculated from the oil concentrations of the test solutions and from the partition co-efficient of the amine between the oil and the water. Thus if the emulsion were made at pH 9.3 the ratio of the concentration of amine in oil to that in water would be 290:1 (see Section 2.B.7.). When the emulsion sample was taken for bubble pick-up testing some of the oil had creamed and the total amine in the sample was:

$$\frac{V_1}{V_2} \times C_1 + \frac{V_3}{V_4} \times C_2$$

where V_1 = Volume of emulsion sample
 V_2 = Total water used in make up of emulsion
 V_3 = Volume of oil in emulsion sample
 V_4 = Total oil used in make up of emulsion
 C_1 = Concentration of amine in water
 C_2 = Concentration of amine in oil

Section 2.A.4. Beaker Cell Tests

To determine whether bubble pick-up results were valid under conditions of violent agitation a series of tests was performed in a laboratory cell. The cell which recommended itself, by reason of its ease of handling, the small size of the sample which could be used, and its cleanliness was the beaker cell. This cell was designed and made in the Mineral Dressing Department of the Royal School of Mines. It is formed from an electrically driven laboratory stirrer, which is modified by replacing the stirrer with an impeller inside an impeller shaft fitted with baffles. The baffles are of a size which will fit into a 400 ml beaker. The beakers used with these cells must be carefully chosen because too great a variation in the clearance between the baffles and the beaker walls might lead to variable results. The cell is fitted with a variable speed drive so a lower degree of agitation can be used for conditioning than is used for flotation. The cell can be operated at velocities varying between 0 and 2000 rpm.

Material

Preliminary tests were performed with deslimed - 72 mesh silver sand but this proved difficult to float, probably owing to the inert condition of its surface. Pure crystal quartz provided by Hilger and Watts was used in its place. This was reduced to -1 inch by hand crushing then handpicked

to remove impure crystals, and reduced to $-\frac{1}{16}$ inch in a bench jaw crusher. It was finally stage ground to -72 mesh + 150 mesh in a porcelain pebble mill. It was stored under deionised water containing hydrochloric acid to remove any iron impurities remaining after the crushing.

Method

For each test about 45g. of quartz were transferred in a glass spoon to a 400 ml beaker. These samples were leached in 2N HCl to remove any remaining impurities. The acid was removed by stirring and decantation with deionised water. The pH was then adjusted to the required value. The beakers used in the tests were graduated so that the volume of liquid in the beaker could be adjusted without drying the quartz. The emulsions, whether or not they contained amine, were made up at the same pH as the test solutions. Samples of emulsion were then added to the beakers and a five minute conditioning period was given to each. One drop of pine oil was then added and a further one minute conditioning period given. The air was then introduced and froth drawn off for two minutes, or until barren. Emulsion analysis was done by the usual method.

Section 2.A.5. The Measurement of Zeta-Potential

A. The Streaming Current Method

The method chosen for measurement of the zeta potential of quartz was the streaming current method.

A large number of methods has been used for the measurement of streaming potential and current. The technique upon which the method used in this work was based is that of Buchanan and Heymann⁽⁴⁸⁾ who describe streaming potential and streaming current methods for the measurement of the zeta potential of barium sulphate crystals. Work has also been published by Gaudin and Fuerstenau^(28,29) by Li⁽⁴⁹⁾, and by Bull and Gortner⁽⁵⁰⁾ on quartz. By Rabinov and Heymann⁽⁵¹⁾ and by Stanley⁽⁵²⁾ who measured streaming potentials on plugs of textile fibres, by O'Connor and Buchanan⁽⁵³⁾ of cassiterite; and by Edelberg and Hazel⁽⁵⁴⁾ of phosphor^uys.

The development of the technique employed in this work was largely carried out by Bramley⁽⁵⁾. It was originally intended to measure zeta potentials by the streaming potential technique and for this purpose an apparatus was designed which was based on that described by Lauffer and Gortner⁽⁵⁵⁾. This design is shown in most textbooks of surface chemistry. The electrodes were made of 52 BS mesh platinum gauze discs 1 cm in diameter and attached to bare platinum leads sealed into the walls of the vessel. The E.M.F. across the electrodes was to be measured by a Marconi pH meter and the plug resistances

by using a d.c. voltage source and a sensitive Tinsley galvanometer in series with the plug.

Preliminary tests showed that the electrodes were subject to a large degree of polarization. Plating them with a silver/silver chloride surface after the method of Jones and Hartman⁽⁵⁶⁾ only partially prevented this. For the same reason the Marconi meter was replaced by a Crompton potentiometer of the type used for thermocouple measurement.

Further work indicated the necessity for screening all leads and earthing the screening and glassware. Polarization was reduced by having a 1 megohm resistance in series with the Tinsley galvanometer when finding the null point with the potentiometer. This resistance was gradually reduced to zero as the null point was approached. Further attempts were made to render the electrodes non-polarizable and finally a method taken from Janz and Taniguchi⁽⁵⁷⁾ enabled production of a pair of electrodes differing in potential by not more than 0.01 mV. It was found however that these electrodes were poisoned by coal so the method was abandoned in favour of streaming current methods. This latter method was developed for coal and gave satisfactory results, it was therefore decided to use it for quartz also.

The streaming Current Method

In this method a relatively low resistance Tinsley galvanometer is connected across the electrodes. When liquid is streamed through the plug the current flowing

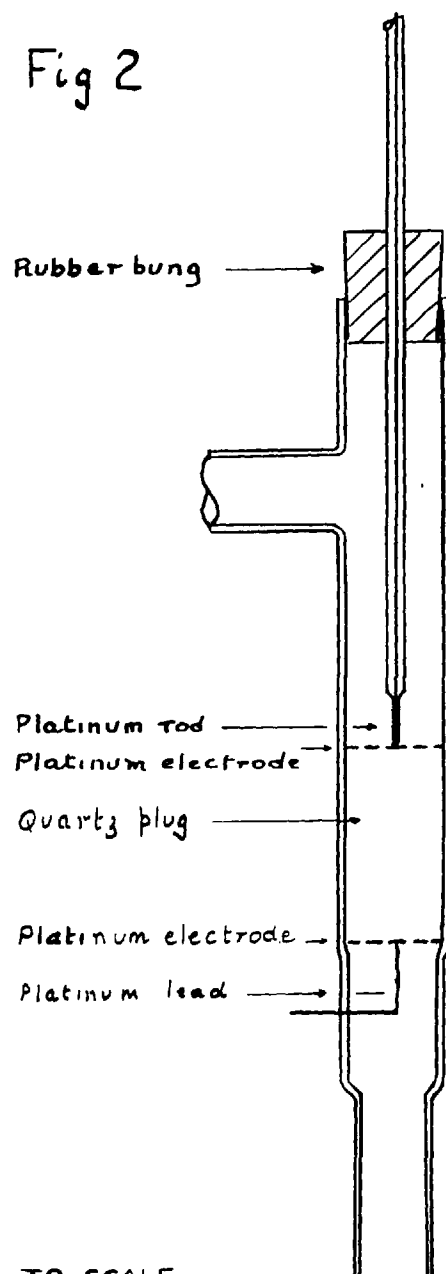
can be measured directly. The effective streaming potential can then be calculated, the resistances of the galvanometer and the plug being known.

Because the electrodes are shorted through the galvanometer no polarization potential can build up, and all such effects are minimized. Buchanan and Heymann⁽⁴⁸⁾ and O'Connor⁽⁵⁸⁾ found that bright platinum electrodes could be used. These are not normally polarized in solutions of normality below $\frac{1}{100}$. If any polarization does occur its effect can be eliminated by taking the streaming current as the difference in deflection between the rest position when streaming and the rest position after streaming stops. With no flow a potential difference existed between the electrodes due to their irreversibility.

The Streaming Current Apparatus

The streaming current apparatus^{is} based on that of Buchanan and Heymann. It is shown in diagrammatic form in figure 2. It is essentially a length of precision bore glass tubing of 1.2 cm diameter and two platinum electrodes. The glass tubing is slightly constricted at the lower end to provide a rigid support on which the lower electrode rests. The electrodes consist of two bright platinum discs of slightly less than 1.2 cm diameter. Each electrode is drilled with a large number of concentrically placed holes of 0.25 mm diameter. A length of 1.5 mm diameter platinum rod is attached to the centre of each disc. The rod on the lower electrode is connected to a length of fine gauge platinum

Fig 2



THE STREAMING CURRENT APPARATUS

wire which is sealed through the glass and provides a lead to the galvanometer. The platinum rod attached to the upper electrode is sealed into a narrow bore glass tube, with a watertight seal. It is connected through this to the galvanometer. This electrode is not fixed to the cell and is sufficiently robust to withstand the pressure to which it is subjected when compressing the plug. The rubber bung which seals the upper electrode into place does not come into contact with the electrolyte during test work.

The current was measured with a Tinsley galvanometer of resistance 136ohms and sensitivity 184 mm/ μ A.

The resistance of the plug was measured with a wide range 'Cintel' a/c bridge. The alternating current used was of approximately 1600 cycles per second, and 16 volts are applied across the resistance to be measured.

The streaming cell was connected by polyvinylchloride tubing to a manometer and head tank. The water was driven through the cell by hydrostatic pressure only.

Experimental Details

Cleaning. All glassware was cleaned with a mixture of concentrated nitric and sulphuric acids. If the apparatus had been in contact with organic reagents the acid was applied hot. The acid was removed by copious washing with tap water, followed by distilled water and followed finally by conductivity water. The polyvinyl chloride tubing was initially cleaned with

the acid cleaning mixture. This however proved to be difficult to remove by washing so in later tests the tubing was cleaned by repeated rinsing in distilled and conductivity water.

Preparation of Solutions

All solutions were prepared with conductivity water and Analar grade reagents in stoppered one litre flasks. The pH was set, in most cases, about 24 hours before use. It was adjusted with hydrochloric acid or sodium hydroxide solution. It proved very difficult to set pH's in the range 7 to 9. This was probably due to absorption of carbon dioxide gas. These solutions were therefore given a final pH adjustment on the morning of use.

Preparation of Mineral

The quartz used in these tests was prepared by the method used in bubble pick-up tests. That is, by crushing and hand picking followed by wet stage grinding in a porcelain pestle and mortar. Two fractions were taken, one was accurately sized to $-72\# + 100\# \text{ BSS}$. The other was about $+36\# - 10\#$. Bull and Gortner⁽⁵⁰⁾ studied the variation of zeta potential with mineral size. Their curves show that little variation occurs above 160μ i.e. about 100 mesh. Many other workers (e.g. Gaudin and Fuerstenau⁽²⁸⁾) have used material of $-36 \text{ mesh} + 65 \text{ mesh Tyler}$; however the sensitivity of the galvanometer used in this work did not allow for the high

currents which would have been obtained with such coarse material.

Cleaning of Mineral

The mineral was cleaned by allowing it to stand overnight or for two or three days in cold concentrated hydrochloric acid. It was then washed with copious quantities of conductivity water and allowed to stand under conductivity water until it was required for use. This method of cleaning is not so extreme as that used by others working with quartz. Thus Gaudin and Fuerstenau boiled their samples in concentrated hydrochloric acid followed by copious washing, while Bull and Gortner digested their material for 6 hours in aqua regia followed by 40 decantations with distilled water and 10 with conductivity water. They then dried it on a Buchner funnel and heated it in a muffle furnace at 800°C for 8 hours. It was thought that the effect of such cleansing methods on the surface of the quartz was too uncertain to allow for their use. The effect of heating in a muffle has already been shown in bubble pick-up work to give a surface differing greatly in behaviour from that obtained by digesting in strong acid solutions. It was found in this work that the method of preparation of the mineral had an important effect on the value obtained for the zeta potential.

Water

All water used in these tests was of conductivity of about

1.3×10^{-6} mho/cm. It was produced by double distillation, the second distillation being done in the presence of acidified potassium permanganate. In earlier tests some treble distilled water of about 1×10^{-6} mho/cm was used but since the results obtained with the double distilled water were identical this was no longer used. It was not found necessary to exclude carbon dioxide gas from the water.

Experimental Procedure

The apparatus was set up and the cell and all the tubing filled with conductivity water. A layer of coarse quartz was then washed into the cell onto the lower electrode, followed by the main bulk of the material, which was - 72 mesh + 100 mesh. A layer of coarse material was then added above this and the plug was compacted as tightly as possible by tapping the walls of the cell and by pressure from the top electrode. Care was taken to prevent air from becoming entrained in the plug or under the electrodes. The cell was then connected to the conductivity bridge and conductivity water streamed through until the resistance of the plug was steady and in excess of 5 megohms. The water in the head tank was then replaced by the first test solution which was run through until the resistance was constant. The Cintel bridge was then disconnected and the cell leads shorted to remove any residual E.M.F. The cell was then connected to the galvanometer and a reading taken after streaming for

one minute. A further reading was then taken after five minutes of alternate streaming and standing. If this was the same as the first reading the plug was assumed to have reached equilibrium. The resistance was again tested and the solution in the head tank was replaced by a second solution and the process repeated. Measurements were in almost all cases completed in under one half hour so that the conditions were similar to those obtaining in conditioning for flotation. A new plug was used for each series of tests, that is for each curve.

The greatest possible care was taken in all tests to ensure that no grease came into contact with any part of the apparatus. No taps were greased and the head tank was kept covered while experiments were in progress. It was not possible to keep the temperature constant during the tests; it was therefore taken at each reading of the current and the formula altered to compensate for temperature variations.

When a complete series of solutions had been tested the cell constant of the plug was determined. A $\frac{1}{10}$ normal solution of KCl was passed through and the resistance and temperature recorded when a steady resistance was attained.

Section 2 A. 5.

B. The Electrophoresis Method.

The method chosen for measuring the zeta potentials of the oil droplets was electrophoresis.

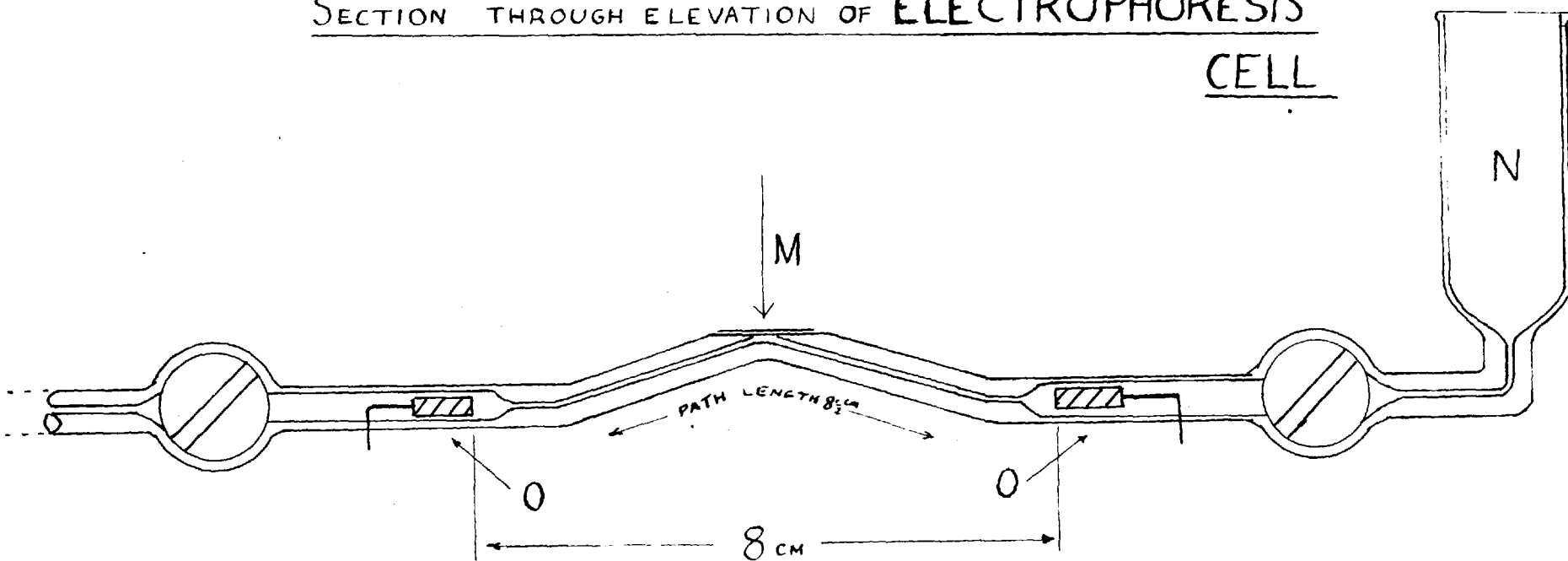
The Apparatus.

The principal details of the design of the electrophoresis cell are the same as that employed by Schenkel (59). It is shown in fig. 3. The cell is formed from a standard bore 1 mm capillary tube of $8\frac{1}{2}$ cm in length. At each end the tube is increased in area to house the electrodes O O. The tube itself is curved vertically and at the apex of the curve the glass wall has been ground down so as to just expose the capillary. A flat cover slide M is fitted over the exposed capillary with araldite; an adhesive insoluble in all the liquids used in the tests. The tube is fitted with glass side arms to give it strength and a base for support on the microscope stage. The electrodes of sheet platinum are wound into the form of two cylinders, the axes of which lie on the axis of the capillary tube. The leads from the electrodes are taken out through the walls of the glass tube. Liquid is fed into the tube from a reservoir N and both entry and exit are provided with stopcocks.

The cell is mounted horizontally on the stage of a Beck microscope. The light source is a mercury vapour lamp. Copper sulphate solution in an optical cell renders

FIGURE 3

SECTION THROUGH ELEVATION OF ELECTROPHORESIS
CELL



the light source monochromatic and acts as a heat absorbing filter. The image from the microscope is projected onto the ground glass screen of an MPP camera at double extension. The microscope eyepiece is fitted with a graticule divided into 100 divisions. This was calibrated using a stage micrometer.

The potential gradient applied to the cell is supplied by a Victor dry cell giving voltages of between 12 and 120 volts.

Experimental Details:

The emulsions tested were made in a one litre beaker in the usual manner. The water used was double distilled water of conductivity 2.5×10^{-6} mho/cm. The pH of the liquid was set roughly before making the emulsion. During the making of the emulsion sufficient carbon dioxide gas was introduced from the air to reduce the pH value. It was, therefore, necessary to set its pH accurately about 15 minutes after preparation. It was difficult to obtain an exact measure of pH because the presence of oil in the liquid to some extent upset the behaviour of the pH meter. If, however, this was frequently calibrated with buffer solutions it was possible to measure pH's to within 0.15 units. After the emulsion had been given about half an hour to become stabilized a portion of the liquid was poured off into a 100 ml. measuring cylinder from which it was added to the reservoir in the electrophoresis tube

as required. Any required modifiers were added in the measuring cylinder.

The vertical travel of the microscope was operated by a control knob fitted with a micrometer gauge. If this was set at zero when the microscope was focussed on the underside of the coverglass, readings could be taken at regular intervals in the vertical plane of the tube. Before taking any readings of the mobilities of the oil droplets in the emulsion it was necessary to locate the centre of the capillary as accurately as possible. This was done by focussing the microscope on the bottom of the capillary and moving the stage in a horizontal direction until that point was found at which the focus was furthest from the zero level of the micrometer. Because the tube was curved in a vertical direction it was also necessary to find the apex of the bend. At any other level the travel of the microscope would not be perpendicular to the axis of the tube. A stopwatch, reading to 0.1 sec. was used to obtain the mean rate of passage of a number of the droplets moving in focus along the superimposed graduated scale of the eyepiece graticule.

Readings were taken at 13 horizontal levels in the capillary tube and curves were plotted in each test of velocity of droplet movement against level. At each level the reading plotted was the average of a number of droplets in focus at that level. It was found that when

the potential gradient across the tube was zero there was a drift of particles towards the effluent end of the tube, although the stopcock at the feed end was in the closed position. This drift was in the same direction throughout the tube and was not altered if the potential was applied for some time and then removed. The speed of drift was usually slower at the edges of the tube than in the centre. When measurements were made at any given applied voltage and were then repeated with the voltage applied in the reverse direction it was found that the difference between the readings obtained was accounted for by the drift at zero potential. It was evident that the drift did not affect the magnitude of the droplet mobility and was not an electrical effect. It was probably a thermal or specific gravity effect.

In preliminary tests readings were taken in the same direction as the drift, then readings of the drift were taken, followed by readings with a reversed potential field. It was found, however, that movement in the opposite direction to that of the drift required some time to settle down to an equilibrium velocity. Since the oil had a low specific gravity creaming took place and frequent changes of emulsion were necessary. Changing of the emulsion was not desirable, particularly in the presence of amine, so to reduce the time taken to measure a complete series of mobilities, readings were taken in only one direction and

were corrected for the value of the drift.

Tests in the Presence of Amine.

In these tests the amine was dissolved in the oil before emulsification. This was necessary to avoid the use of a soluble amine salt, which would have produced a variable not present in previous tests.

The presence of dodecylamine introduced difficulties absent in other electrophoresis tests. Its low specific gravity caused the oil to cream at an appreciable rate, even after a long stabilization period. This meant that although the ratio of amine dissolved in oil to amine dissolved in water remained constant throughout the whole volume, the creaming produced local variations in this ratio. It was, therefore, necessary to transfer the emulsion samples from the beaker to the electrophoresis tube as rapidly as possible. A sample was taken for analysis of emulsion strength as soon as possible after the placing of a sample for electrophoresis in a measuring cylinder. The sample taken for analysis could only be accepted as an approximate measure of the sample eventually studied in the electrophoresis tube.

A second source of difficulty occurred in the mobility measurements. It proved impossible to obtain reproducible results because consecutive samples of emulsion from the reservoir had different mobilities. A possible reason for this phenomenon was the creaming of the emulsion both

in the reservoir and in the tube. The former leads to varying amine strength throughout the reservoir and consequently in successive samples. The latter gives rise to a layer of creamed oil on the upper surface of the tube. This alters the oil to water ratio of all subsequent samples and because it gives rise to differing charges on the glass, causes local variations in the electro osmotic movement of the water. These difficulties could be avoided by taking measurements only from the first sample run into the electrophoresis tube.

Section 2 A. 6

Radiotracer Measurements.

A. Measuring Apparatus.

Measurements of amine concentrations were carried out in an EKCO Scintillation counter type N612 using an EKCO automatic sealer type N530E.

The counter is a special purpose scintillation counter for assaying low energy beta particles with high efficiency and convenience of operation. In their technical instruction bulletin (60,61) EKCO describe the machine as follows:

"The counter comprises a specially chosen fourteen stage photo-multiplier tube which, together with a novel source coupling unit, is contained in a lead shield fitted with a spring counter-balanced lid.

"The shielded counter assembly is mounted in a steel case which also contains a five valve wide band linear amplifier.

"The source coupling unit is an aluminium alloy casting fitted with a Pyrex glass window in its lower face. Immediately above the window is a light proof shutter and above this a tray to hold the special Pyrex glass sample holder.

"A light proof lid covers the sample holder and interlocks with the shutter to prevent extraneous light from reaching the photo multiplier tube. To improve the

light collecting efficiency, a liquid coupling medium is used between the sample holder and the window.

The principle of operation is as follows: The energy of the beta particles emitted by the test sample is converted to light energy by liquid phosphor. The resulting light photons impinge upon the cathode of the photo multiplier tube and release photo-electrons which are then accelerated towards the first dynode. Each dynode emits some three or four secondary electrons for each primary electron reaching it. This results in an overall gain of about one hundred million between the photo-cathode and the collector. The signal at the collector is then amplified still further, by the built in linear amplifier, to a level sufficient to operate any conventional scaler or rate meter requiring a positive going input signal of five volts minimum.

The scaler is an EKCO automatic scaler type N530E. It is a combined six decade scaler and Timer. It may be used to time a pre-determined count, to count a pre-determined time, or as a manually operated scaler. The instrument may be set to a wide variety of counting and timing ranges, varying from 100 to 1,000,000 counts and from 100 to 100,000 seconds. It can be worked with either a 110 to 120 volts or 200 to 250 volt A.C. supply at 50 or 60 c/s. The mains consumption is 130 watts. The scaling and timing circuits are stable to mains voltage

fluctuations of up to - 10%, however the timing circuit is directly dependent on the mains frequency and needs to be checked frequently.

Counting Statistics.

In scintillation counting devices the counting of the sample must be done in the presence of a background count the size of which is characteristic of the counter and its environment. The background count is caused by a variety of sources including cosmic rays, radioactive decay in the phosphorous dye, radioactive impurities in the lead shield and other sources of stray radiation. The radioactive disintegration of the sample itself is a random process, and even in the measurement of a sample of constant activity the number of disintegrations observed in successive short periods of fixed duration will not remain constant. therefore the counting tests must be so designed that the statistical fluctuations of both sample and background are made negligible in comparison with other experimental errors.

The statistics of radioactive counting has been discussed by G.B. Cook and J.F. Duncan (62) and by R. Loevinger and Mones Berman (63).

In any radioactive sample the number of atoms which disintegrate is very small compared with the total number of atoms. Therefore in the statistical sense radioactive disintegrations are rare events and their frequency may be described by a Poisson distribution. In these studies it

must be assumed that the true physical disintegration rates are constant while counts are being taken and that the overall efficiencies of the counter and its auxiliary/re-apparatus remain constant. It will also be assumed that all counts number at least 10. In this case the Poisson distributions are approximately normal and the theory of the propagation of errors for normal populations may be assumed.

In the study of the normal distribution the true average value of the counting rate may be taken as that obtained by counting for an infinite time. The standard deviation σ is an estimate of the chance of any one observation of the counting rate being within a given error from the mean value. The standard deviation is defined as the square root of the arithmetic mean of all the deviations from the average value. Thus if Δ_i is the difference between the average count, $\bar{x}$, and one particular count, x_i , of n determinations of the sample then:

$$\sigma^2 = \frac{1}{n} \sum \Delta_i^2 = \frac{1}{n} \sum (\bar{x} - x_i)^2$$

By statistical theory there is a 2.15 to 1 chance that the result will differ from the true value by less than the standard error, and a one in twenty chance that the deviation will be greater than twice the standard error.

In the case of the normal distribution the standard deviation is the square root of the total number of counts i.e. $\sigma = \sqrt{N_i}$ where N_i is the total number of counts.

In the determination of the strength of solutions

containing a radioactive salt the important factor, for measurement, is the counting rate R_i , where $R_i = N_i/T_i$ if T_i is the time taken to record N_i counts. There is associated with the counting rate a standard deviation defined by the following equation

$$\sigma_i = \sqrt{\frac{N_i}{T_i}} = \sqrt{\frac{R_i}{t_i}}$$

An estimate of the per cent. standard deviation or the per cent. error may be obtained from the co-efficient of variation V_i where V_i is defined as $100\sigma_i/R_i$.

Much of the enquiry into counting statistics has been concerned with samples of low activity see Loevinger (63) and Haigh (64). In these cases the radioactive disintegration of the sample occurs at a rate equal to or a little above the background counting rate. In such circumstances it is important that the background count should be as low as possible and should remain constant from day to day. Hence, in these cases, study has been directed towards finding the minimum time for a sample count which will eliminate all statistical sample and background fluctuations. In this research the radioactive isotope Cl^{14} was used and the disintegration rate of the sample was sufficiently high for the fluctuations of the background, during sample counting, to be ignored. Loevinger states that "The counting of samples for which r i.e. (sample rate/background rate) > 10 can be considered "high level" in the sense that the background is so small that it does

not contribute appreciably to the uncertainty in the estimate of the sample strength, provided that the background count meets the condition of "equation 27."

$$N_b \geq N_t / (0.23 r^2 - 2.46 r + 1.23)$$

where N_t is the value of sample count and N_b is the value of the background count.

It was found that the background count varied to a large degree from day to day and it was necessary to determine the value daily. Therefore it was only necessary to evaluate the minimum counting time necessary to give both background and sample counting rates to a given degree of accuracy. This can be done by using the formula for V_i , where R_i can be obtained approximately while counting is being performed. From the formula σ can be determined and hence N_i and T_i .

$$V_i = \frac{100 \sigma_i}{R_i}$$

$$\text{and } R_i = T_i \cdot \sigma_i^2$$

Optimum Operating Conditions.

The method of finding the optimum operating conditions of the counter is described by Loevinger (63), Haigh (64) and the relevant EKCO publication (60).

The sensitivity of a scintillation counter may be defined as $R_s/s = e$ where R_s is the counting rate due to the sample s . R_b may be taken to represent the background count.

Loevinger gives a formula for the minimum time T_{min} needed to determine R_s to a r.s.m. error of $V_s\%$.

$$T_{min} = \frac{(100)^2}{(V_s)^2} R_b (\sqrt{r}-1)^2$$

where $r = R_t/R_b$ is a measure of the signal to noise ratio of the counter and $R_t = R_s + R_b$.

The merit of a counter is determined by the following factors.

- 1) The sensitivity e and
- 2) The quantity e^2/R_b .

The counter having the largest e and e^2/R_b is always superior.

For strong samples with $R_s^2 \gg R_b$ the performance is characterised almost entirely by e . For weak samples with R_s and R_b of the same order e^2/R_b is the dominant factor and signal/noise ratio decides the least measurable sample activity. Thus for a particular counter the best operating conditions at all sample strengths are those giving a maximum value of e^2/R_b . In practice one can use R_s^2/R_b where R_s is the counting rate due to a standard sample of any convenient strength.

The optimum conditions for counting are those where the combination of amplifier gain, pulse discriminating voltage E_d and dynode chain potential E_m give a maximum value of R_s^2/R_b . This point is found by using a standard preparation of the isotope concerned, in this case C_{14} , yielding a rapid counting rate. Values are measured of

$R_t f(Ed)$ and $R_b f(Ed)$ at various values of E_m and at various values of the amplifier gain. Hence it is possible to obtain curves of $R_s f(Ed)$ and hence R_s^2/R_b .

In many cases the maxima of the R_s^2/R_b curves are not sharply defined and there are a number of conditions providing a value of R_s^2/R_b near the greatest value obtainable.

It is necessary to inspect the characteristics of the counter at the points of maximum R_s^2/R_b to ascertain that they are suitably stable with regard to the applied voltages.

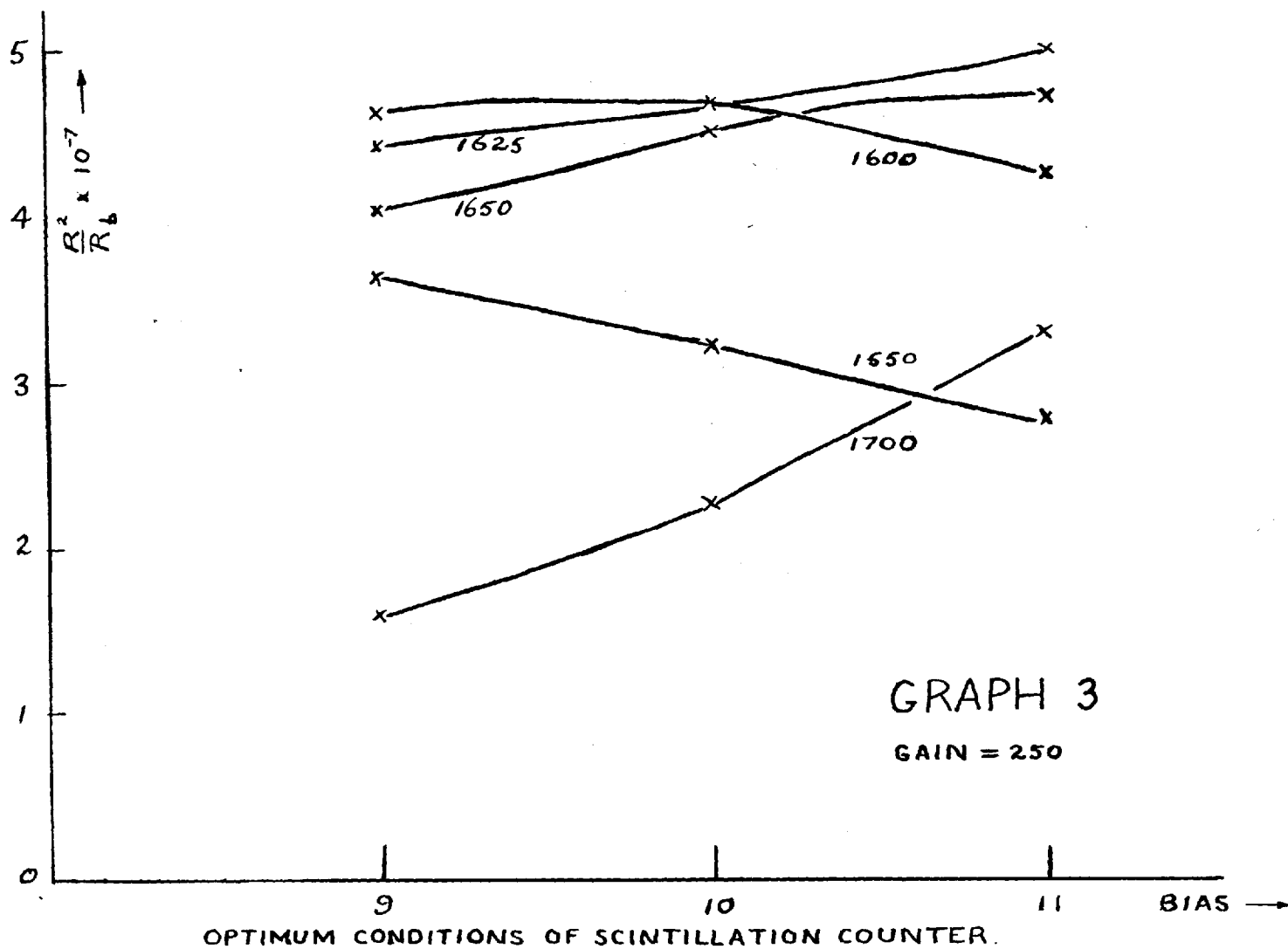
The sensitivity of the instrument tends to change more rapidly with dynode voltage than with amplifier gain or pulse discrimination level, it is advisable therefore to choose that point which yields the most stable R_s^2/R_b maximum. In cases where the sample is considerably stronger than the background it is advisable to take the most stable maximum rather than the highest one.

The counter was tested as described above with radioactive stearic acid solutions. Curves were drawn up which indicated that suitable maxima appeared at:

- i) Gain 1000. Bias 5V. High voltage. 1350v.
- ii) Gain 500. Bias 5V. High voltage. 1400v.
- iii) Gain 250 Bias 10V. High voltage. 1625v.

The three values were tested at a lower stearic acid concentration and the most stable was found to be (iii).

A curve is drawn in graph 3. showing the character-



istics of the counter in the region of the chosen conditions. The curves drawn up for the counter behaviour over the whole range of testing have not been given since it was found that the background variations from day to day led to large fluctuations in the value of R_s^2/R_b .

B. The Analysis of Radioactive Amine Solutions.

The amine was present in these tests in two forms. These were a) dissolved in oil and b) dissolved in water. The solutions in oil were measured directly after addition of the fluorescent dye. A sample of about 0.5 ml of the radioactive oil was run into a Pyrex sample holder. To this was added 5 ml of sulphur free toluene and 25 ml of the dye

The amine was extracted from aqueous solution by the following procedure: The solution was made strongly alkaline with a few millilitres of 5Normal sodium hydroxide. It was then extracted by shaking in a separating funnel with 4 successive lots of about 5 ml each of chloroform. The chloroform was run directly into a pyrex sample holder and was carefully evaporated to dryness. 5 ml of sulphur free toluene were then added, followed by 25 cc of the phosphor dye.

The solution of the phosphor dye was made by dissolving in one litre of sulphur free toluene a mixture of 4g. of the dye DPO and 0.18g. of the dye POPOP.

These solutions could be counted directly.

The radioactive amine was synthesised by Dr. A.R. Burkin of the Royal School of Mines.

C. The Partition Co-efficient of Dodecylamine Between Oil and Water.

A portion of about 0.002g of radioactive dodecylamine hydrochloride was accurately weighed into a suitable container. A known volume of pure water, about 25 ml, was then added and the container was warmed to above 30°C to ensure complete dissolution of the dodecylamine hydrochloride. A portion of about 5 ml was then accurately pipetted into a 100 ml separating funnel containing 50 ml of double distilled water at the required pH. The water was made 10^{-4} normal with respect to sodium perchlorate. A weighed amount of oil, about 0.5g, was then added and the mixture shaken. The separating funnel was then allowed to stand overnight to come to equilibrium. The following morning the water was carefully run out of the funnel into a clean beaker and a 25 ml portion was pipetted into a separating funnel for the extraction of the amine. A small portion of oil was pipetted into a sample holder as is described above

Section 2 B 1.

1. Creaming Rate of Emulsions.

a) In absence of Amine

A test was performed to determine the rate at which an average emulsion creamed. An emulsion was prepared in a two gallon bucket and samples were taken from it at various time intervals. All samples were taken from the same level in the bucket. Analysis of the samples yielded the following results:-

TABLE 1.

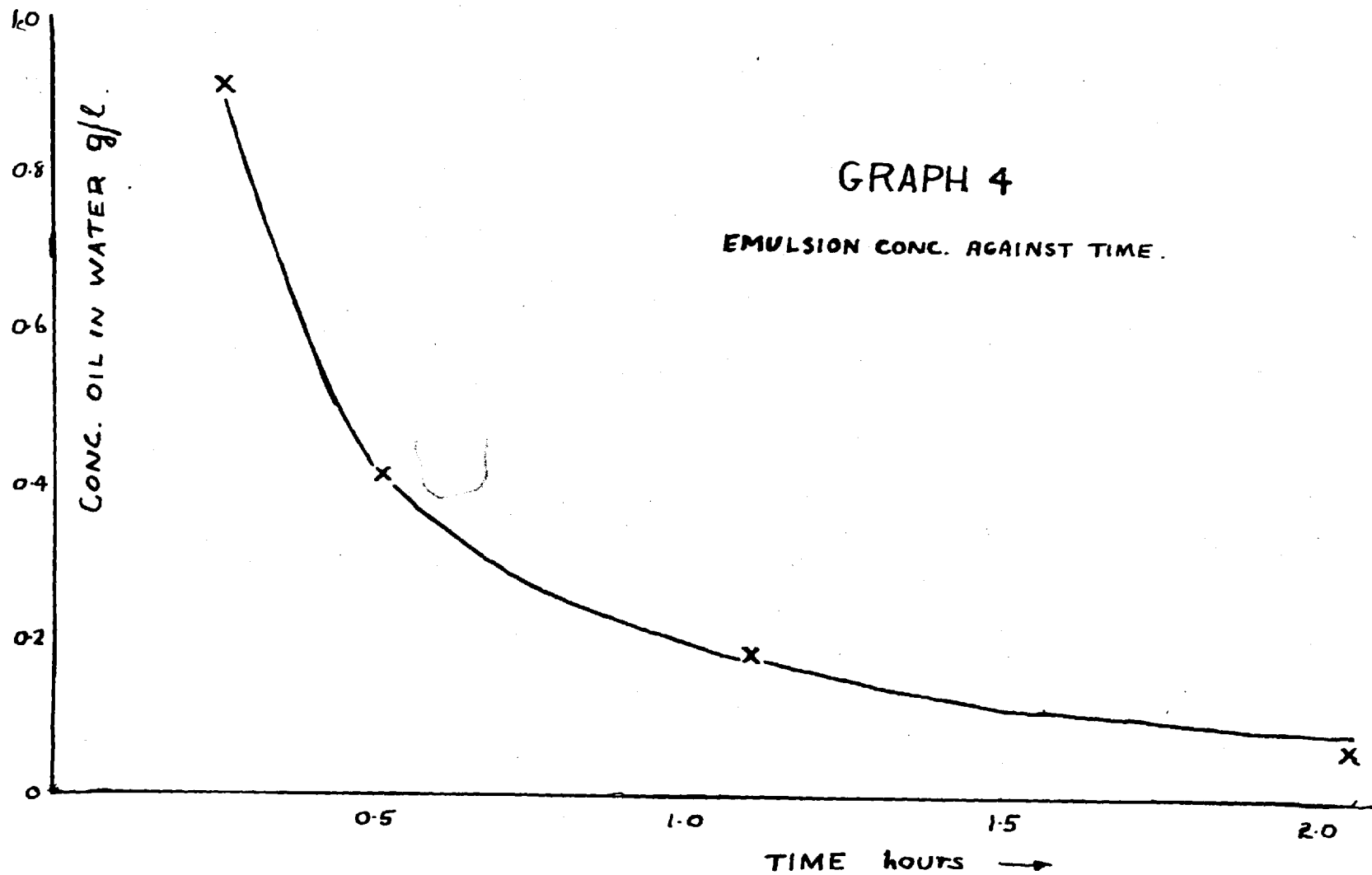
<u>Time after making Emulsion.</u>	<u>Concentration of Emulsion.</u>
16 mins.	0.916 g/l
31 mins.	0.41 g/l
67 mins.	0.18 g/l
125 mins.	0.045 g/l

These results have been plotted on a curve in Graph 4.

The high creaming rate of the emulsion coupled with the low specific gravity of the oil suggested that the oil creamed by sedimentation.

b) Creaming Rate of Emulsion in Presence of Amine.

A test was performed to determine what, if any, was the effect of dissolved amine on the creaming rate of the emulsion. Four samples of emulsion were prepared, each containing the same proportion of dedecylamine to oil. One emulsion was made at each of the following pH values: pH2, pH5, pH7 and pH9. By visual examination it was found that

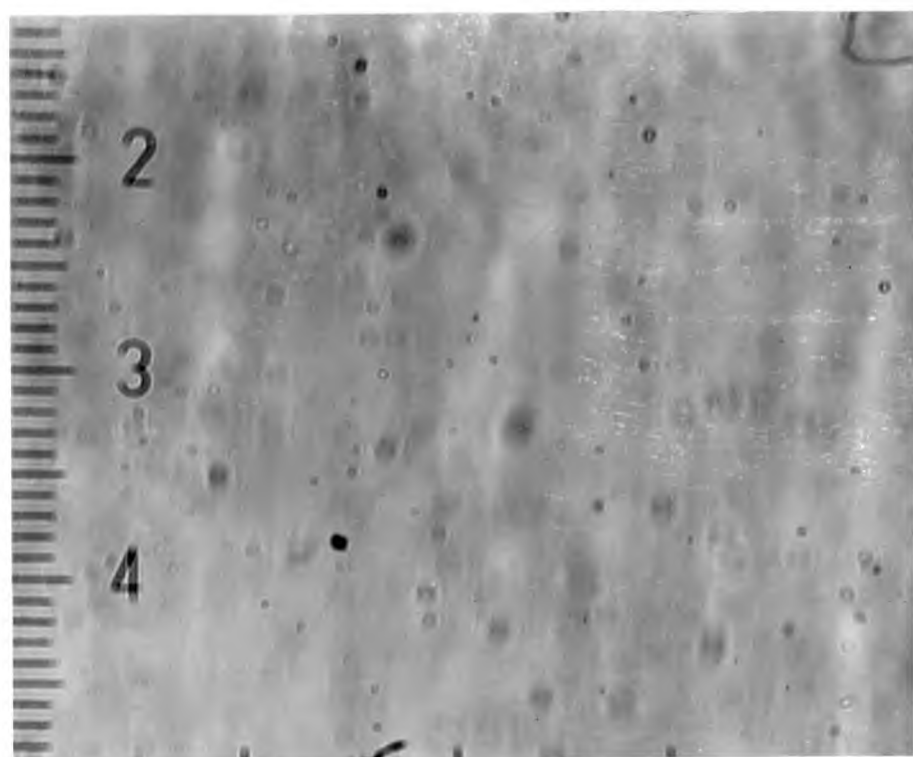


the amine had a stabilizing effect on the emulsions at all values of pH, the effect being small in acid solution and large in alkaline solution. In all cases a definite gradation of strength from top to bottom of the emulsion could be seen. This confirmed that creaming was controlled by sedimentation.

Section 2B 2.

Photo micrographic Measurements of Emulsions.

It was found that due to the creaming of the oil the size distribution of the droplets varied considerably during any test. No photograph could therefore be representative of the test during which it was taken. The photograph given with this section gives some idea of the distribution of the droplets, after about 10 minutes creaming. The scale is about X180.



Section 2 B. 3.

Bubble Pick-up Tests.

a) Cleaning Methods for Bubble Pick-up Tests.

Before proceeding with the main test works an examination was made of the principal methods employed in cleaning minerals for bubble pick-up tests. Batches of mineral, prepared by each of various methods were tested at 10mg/l concentrations of dodecylamine in the presence of sodium perchlorate in sufficient quantity to give a total ionic strength of $1/12.5$ Normal at neutral pH. The five principle methods examined were as follows:-

- a) Igniting in muffle furnace for $\frac{1}{2}$ hr. at 800°C .
- b) Standing overnight in 2N HCl.
- c) Igniting in muffle furnace at 800°C followed by an acid wash.
- d) Standing overnight in N/10 NaOH.
- e) Igniting in furnace at 800°C followed by alkali wash.

All samples had been previously ground and sized in deionised water.

The results were as follows:-

Methods d) and e) proved unusable, it being impossible in either case to obtain a blank in double distilled water. It also proved difficult to obtain a perfect blank with material which had been ignited, particularly when this had been followed by an acid wash. The most satisfactory method proved to be b). Upon comparing the results shown

by the tests, material prepared by method b) was found to behave similarly to material prepared by method c) although it was more difficult to obtain a blank in the latter case. An allowance was made in the test performed on material prepared by method c) for the one or two particles which adhered weakly to the bubble in the blank test.

The material cleaned by method a) gave the following results. Those obtained by the acid cleaned material are given for comparison.

TABLE 2.

<u>Cleaning Method.</u>	<u>Lower Critical pH.</u>	<u>Boundary between Pick-up and Cling.</u>
a) after 2 hours	below 1.3	1.3
a) after 24 hours	1.8	2.1
b) and c)	3.8	4.8

At high pH values no significant differences were observed between the various methods.

b) Bubble Pick-up Tests.

1. System Quartz-dodecylamine Hydrochloride.

Although flotability curves have been obtained by other workers investigating the quartz-dodecylamine system it was considered necessary for two reasons to repeat the work to a high degree of accuracy. These are:- (1) To find whether the test method employed would give trustworthy results i.e. whether any personal errors were being introduced. (2) Because an accurate curve for the

system was essential for comparison with curves which were obtained in other tests when the amine was present in an emulsion.

The quartz used in the test had been cleaned by standing overnight in 2N HCl solution. Tests were only performed on material which had given a perfect blank in the absence of collector.

In order to examine a theory advanced by Robinson suggesting that anomalous results might be obtained at neutral pH if the total ionic content of the solution was too low sodium perchlorate was added in each test in sufficient quantity to make the total ionic content 1/12.5 Normal. A certain amount of difficulty was experienced in measuring pH values at about pH 11, but this was overcome by buffering the pH meter at 11.4 with a mixture of solutions of sodium hydroxide and sodium hydrogen phosphate. For details of these solutions see Britton (65).

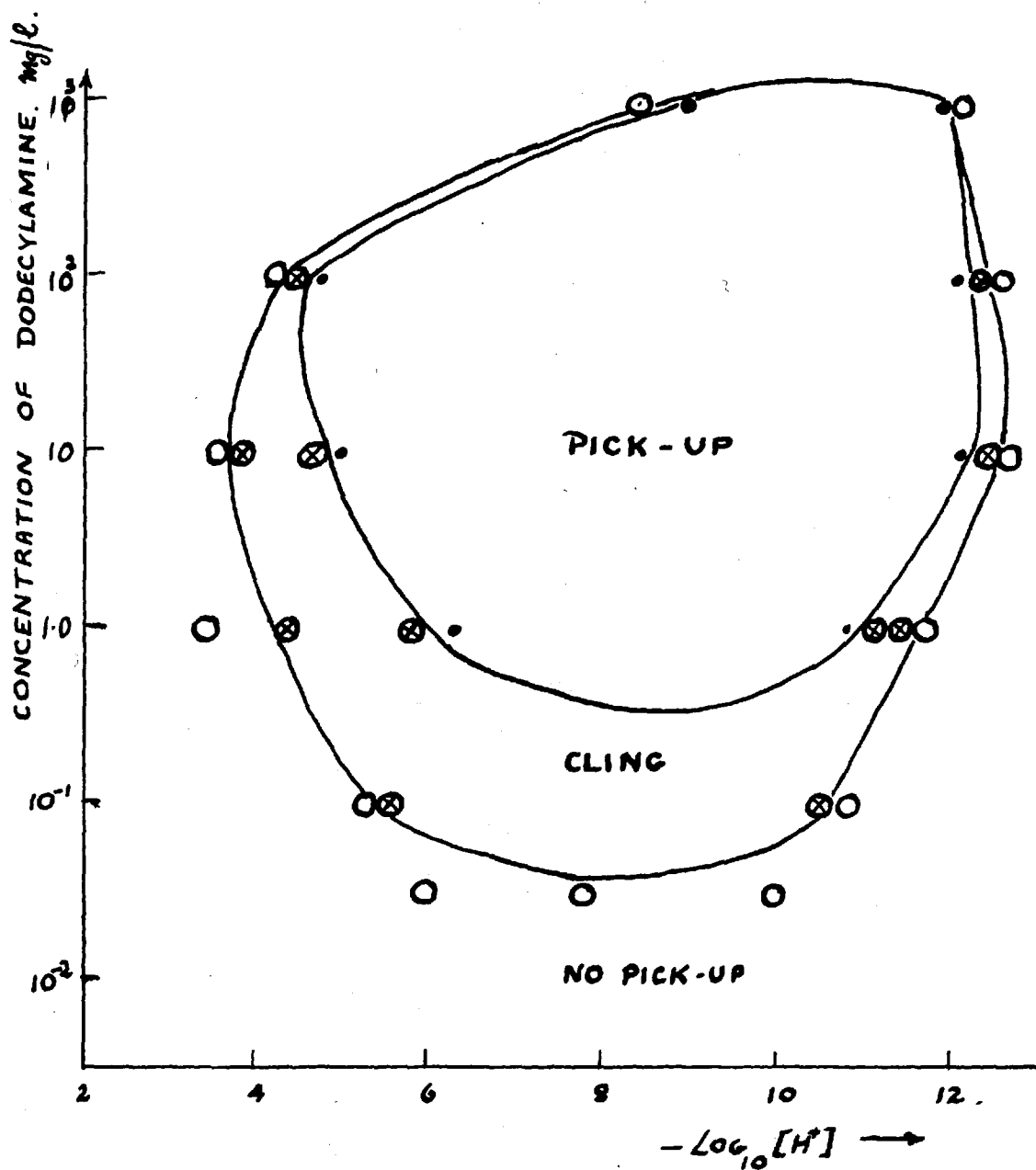
The flotability curve, which was determined to an accuracy of about 0.2 of a pH unit is given in graph 5.

2. Bubble Pick-up Tests in an Emulsion.

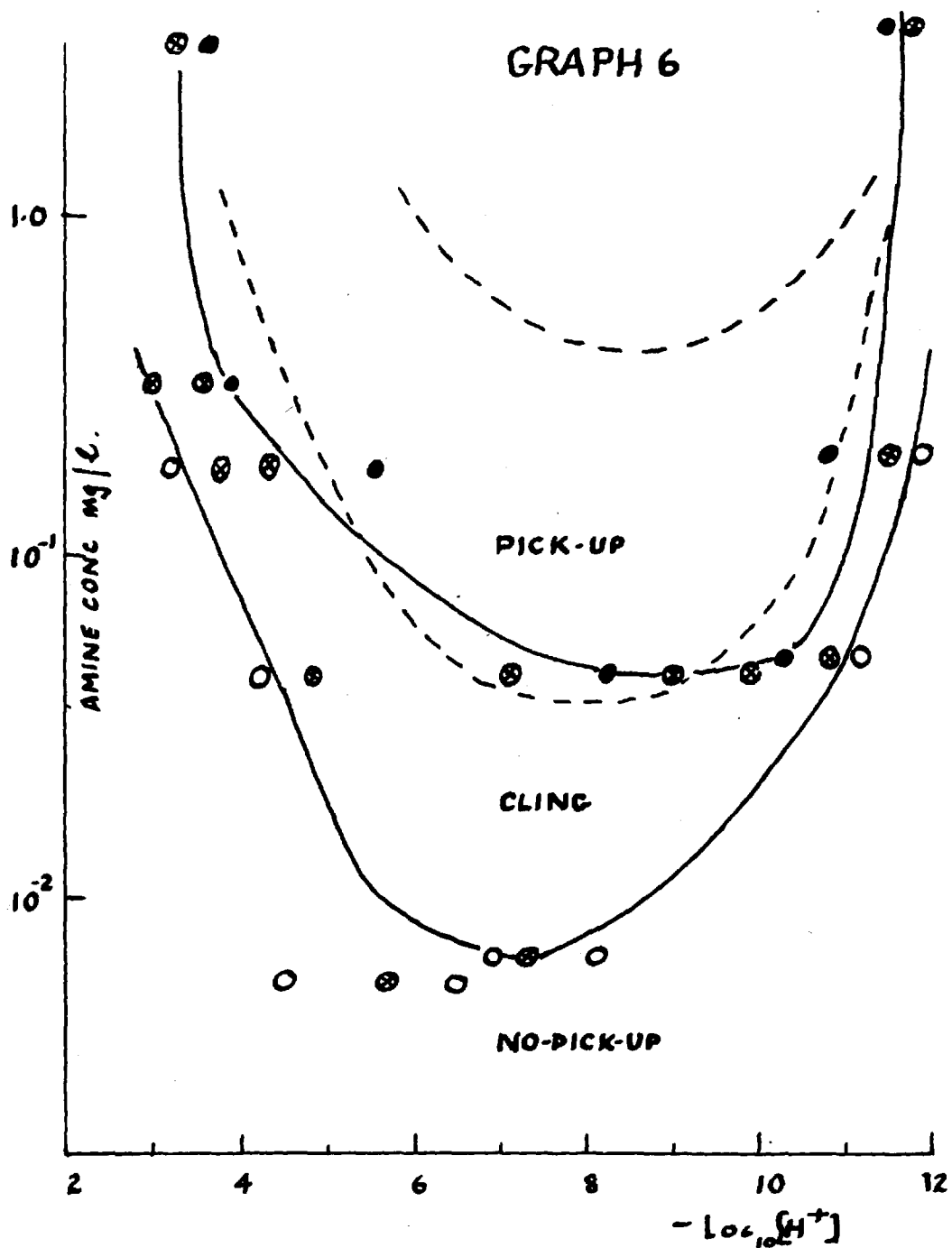
System - quartz-dodecylamine in oil.

To compare the flotation characteristics of the quartz-dodecylamine system, when the amine is present as a dissolved salt, with the same system when the amine is

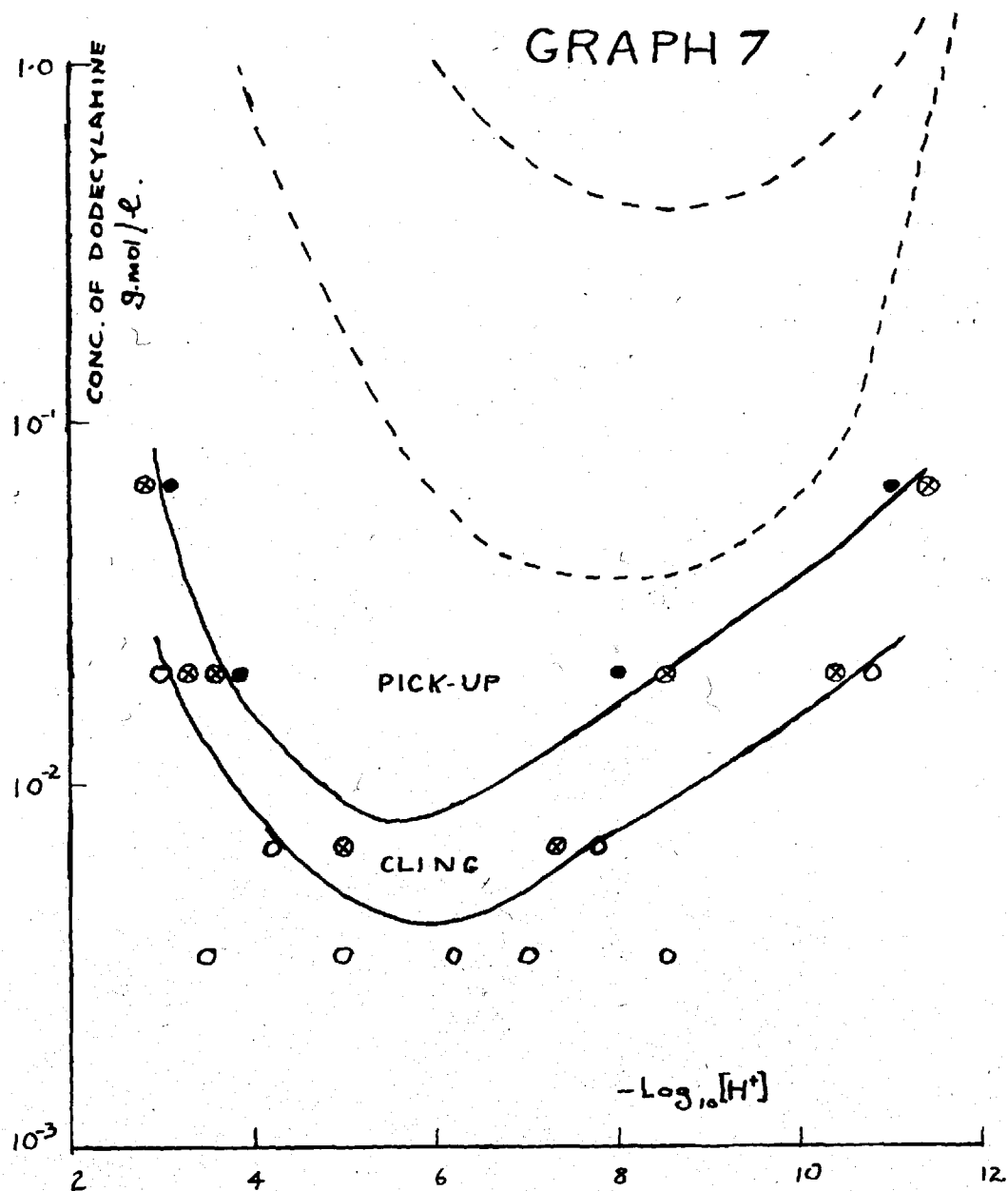
GRAPH 5



FLOTABILITY CURVE FOR QUARTZ IN
DODECYLAMINE HYDROCHLORIDE SOLUTION.



FLOTABILITY CURVE FOR QUARTZ IN DODECYLAMINE.
 DODECYLAMINE DISSOLVED IN EMULSIFIED OIL
 BROKEN LINE GIVES CURVE FOR DODECYLAMINE HCl .
 WITHOUT OIL



FLOTABILITY CURVE FOR QUARTZ IN 10. DODECYLAMINE
HYDROCHLORIDE.

FULL LINE ... IN PRESENCE OF EMULSION.

DOTTED LINE...IN ABSENCE OF EMULSION.

present in an emulsified oil, pick-up tests were performed on both systems.

Before proceeding with the test series an initial test was performed with an emulsion formed from an oil which contained no added dodecylamine. This was done to determine whether or not a blank could be obtained with quartz in the presence of oil. The test was performed with different samples of quartz at various pH values, using oil to which in some cases dye had been added, in others not. Emulsion concentrations varying between one and one hundred per cent. were tested. In all cases except that of extremely strong emulsions a perfect blank could be obtained. In these latter slight cling was observed.

The bubble pick-up curve obtained with the amine added as a solution in an emulsified oil is given in graph 6.

System quartz-dodecylamine hydrochloride - oil.

A further test was performed, in the presence of an emulsion, with the amine added as a hydrochloride solution. This test was performed because certain workers had noticed that amine is sometimes lost from solution during test work particularly when the solution comes into contact with metal. This might occur in the spray gun. This test was therefore designed as a check on the previous series performed with the amine dissolved in the oil. The results are given in graph 7. The curve for dodecylamine

hydrochloride in the absence of emulsion is given for comparison.

3. Equilibrium Tests.

A test was performed to determine the time required for the bubble pick-up test system to reach equilibrium after a pH change had been made. The solution was set at a pH outside the cling region and in the alkaline range, the pH was then gradually reduced until cling was obtained. After each reagent addition the bubble was pressed onto the quartz at half-minute intervals for a further nine minutes. After cling had been obtained the pH was again adjusted to bring it outside the cling region. In each case equilibrium was obtained in less than one half minute.

4. Contamination Test.

To determine the length of time during which a mineral sample would remain uncontaminated the following test was performed. A solution, the emulsion addition which had been insufficient to cause cling, was left standing overnight with no cover. A perfect blank could still be obtained the following morning.

Section 2B. 4.

The Beaker Cell Tests.

A preliminary test was performed at pH 9. 50 ml. of concentrated emulsion were added to 250 ml. of water containing quartz. No dodecylamine was present. The test showed that 2.3% of the mineral could float without any amine.

A. Variation of Flotability with concentration of Collector

Two series of tests were performed, one at pH 9 and the other at pH 7 to show the relationship between flotability and amine concentration. The test at pH 9 was divided into two parts, the proportion of amine to oil differing in each case. It was intended to show whether or not this proportion was an important factor in the flotation method.

The results of these tests are given below. It should be noted that the amine concentrations are not exact and are liable to an error of up to 10%. This is because not all the oil was used in making the emulsions. A certain volume remained in the gun. This volume was not measured but has been estimated and allowed for in the calculation of the amine concentrations. These concentrations were calculated using the figure for the partition co-efficient of amine between oil and water given in Section 2B 7.

TABLE 3.

TEST 1. A. Concentration of Amine in oil. Before emulsification 1.4 g/l. Emulsion made up at about pH 9.3 Floats performed at pH 9.

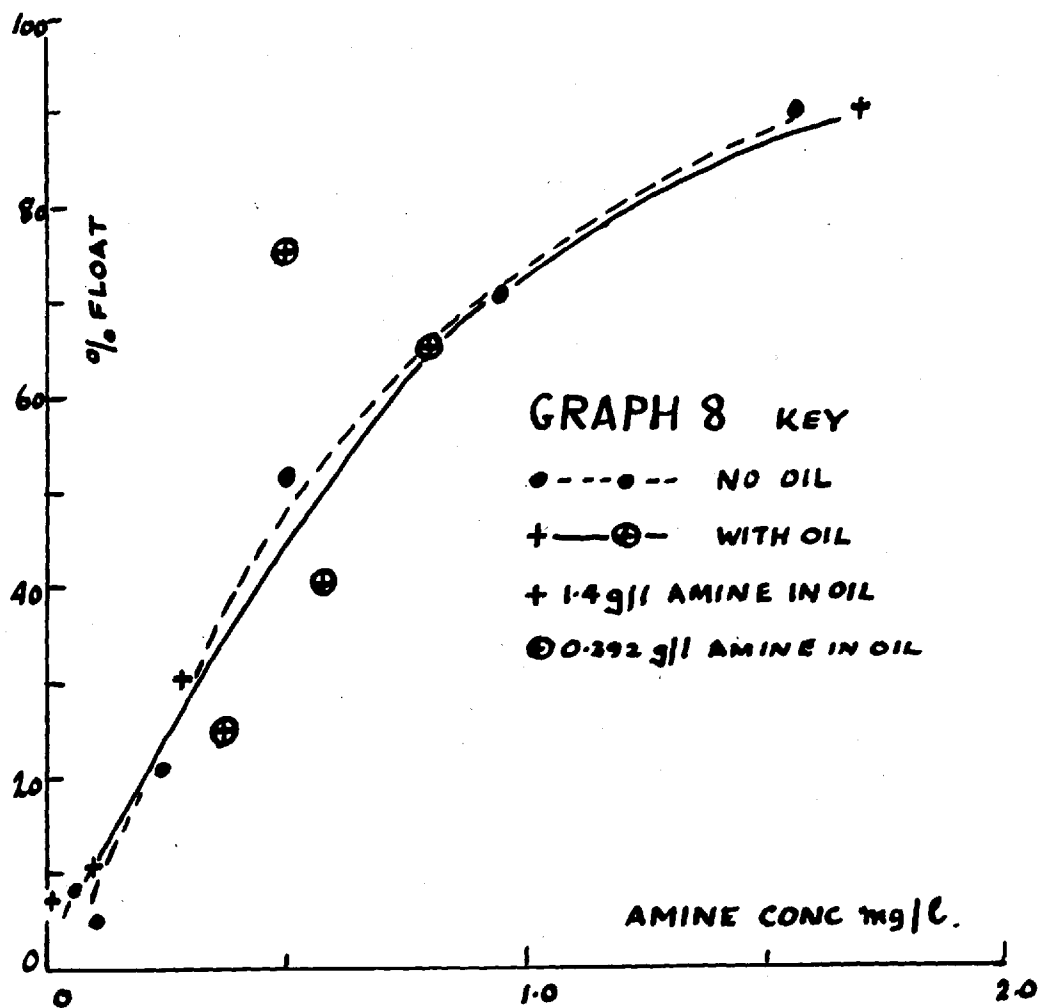
<u>Float No.</u>	<u>Vol. of emulsion added.</u>	<u>Conc. of emulsion added.</u>	<u>Total Vol. of Liquid.</u>	<u>Amine Conc.</u>	<u>% Float</u>
1	100 ml	2.11 g/l	290 ml	1.7mg/l	89.6
2	20 ml	0.84 g/l	261 ml	0.28mg/l	30.2
3	8 ml	0.47 g/l	298 ml	0.10mg/l	10.8
4	1.2 ml	0.47 g/l	290 ml	0.016mg/l	7.8

TABLE 4.

TEST 1. B. Concentration of amine in oil before emulsification. 0.392 g/l. Emulsion made up at about pH 9.3. Floats performed at pH 9.

<u>Float No.</u>	<u>Vol. of Emulsion added.</u>	<u>Conc. of Emulsion added.</u>	<u>Total Vol.</u>	<u>Amine Conc.</u>	<u>% Float</u>
5	100 ml	1.03 g/l	282 ml	0.43 mg/l	76.6
6	20 ml	0.8 g/l	281 ml	0.081 mg/l	65.7
7	8 ml	0.34 g/l	281 ml	0.038 mg/l	23.4
8	1.2 ml	0.35 g/l	283 ml	0.0058 mg/l	38.9

Tests 1 to 8 are summarised in graph 8. Together with tests 54 to 63.



VARIATION OF PERCENT FLOAT WITH AMINE CONC

TABLE 5.

TEST 2. Concentration of amine in oil before emulsification.

0.69/g/l. Emulsion made up at pH 7. Floats performed at pH 7.

<u>Float No.</u>	<u>Vol. of emulsion</u>	<u>Conc. of emulsion</u>	<u>Total Vol.</u>	<u>Amine Conc.</u>	<u>% Float</u>
9	150 ml	3.55 g/l	283 ml	2.7 mg/l	88.4
10	100 ml	1.60 g/l	282 ml	1.7 mg/l	57.7
11	50 ml	1.12 g/l	282 ml	0.95mg/l	39.0
12	25 ml	0.68 g/l	256 ml	0.51mg/l	15.4
13	10 ml	0.59 g/l	292 ml	0.18mg/l	15.2
14	200 ml	0.53 g/l	283 ml	3.70mg/l	79.4
15	100 ml	3.48 g/l	284 ml	1.85mg/l	76.0
16	100 ml	1.83 g/l	283 ml	1.80mg/l	86.0
17	70 ml	1.17 g/l	303 ml	1.10mg/l	64.8
18	40 ml	1.02 g/l	273 ml	0.70mg/l	54.2
19	20 ml	0.84 g/l	243 ml	0.39mg/l	33.2
20	3 ml	0.48 g/l	250 ml	0.06mg/l	6.92

B. Conditioning Tests.

It was originally thought that the beaker cell tests would give full information concerning the "cling" region of the bubble pick-up curve with the amine present in an emulsion. For this purpose curves similar to those drawn at pH 7 and pH 9 were to have been done at other pH values. However, since the above curves showed that very little flotation could be expected within this cling region it was decided to abandon this method and plot one curve of flotability against pH at a given amine concentration. However, to obtain the same concentration of amine in a number of beakers it would be necessary to add the emulsion samples to all the beakers at the same time. Before proceeding with the test series it was necessary to

determine whether or not the different conditioning times resulting from the simultaneous addition of emulsion to a number of beakers would affect the results. To test this the same quantity of emulsion was added to a number of beakers of flotation feed at the same pH. The flotability of each was then tested after varying lengths of time, under identical conditions. Three series of curves were plotted, the results being as given in graph 9. These show that no regular variation in flotability was produced with an increase of conditioning time. The region between 30% and 60% is probably the most difficult for obtaining reproducible results in flotation tests, so the variations in the curve can be considered to be within the limits of the experimental error of the method.

The condition of the tests and the results were as follows:-

Concentration of amine in oil = 0.69 g/l.

Emulsion made up at about pH 9.3

Samples tested at pH 9.

TABLE 6a.

a) Vol. of emulsion added 50 ml. Total Vol. of liquid 287ml
Amine conc. of solutions 0.353 mg/l.

<u>Float No.</u>	<u>Time before float</u>	<u>% float</u>
21	12 min.	14.8
22	23 min.	11.1
23	51 min.	12.8

CONDITIONING TESTS.

GRAPH 9

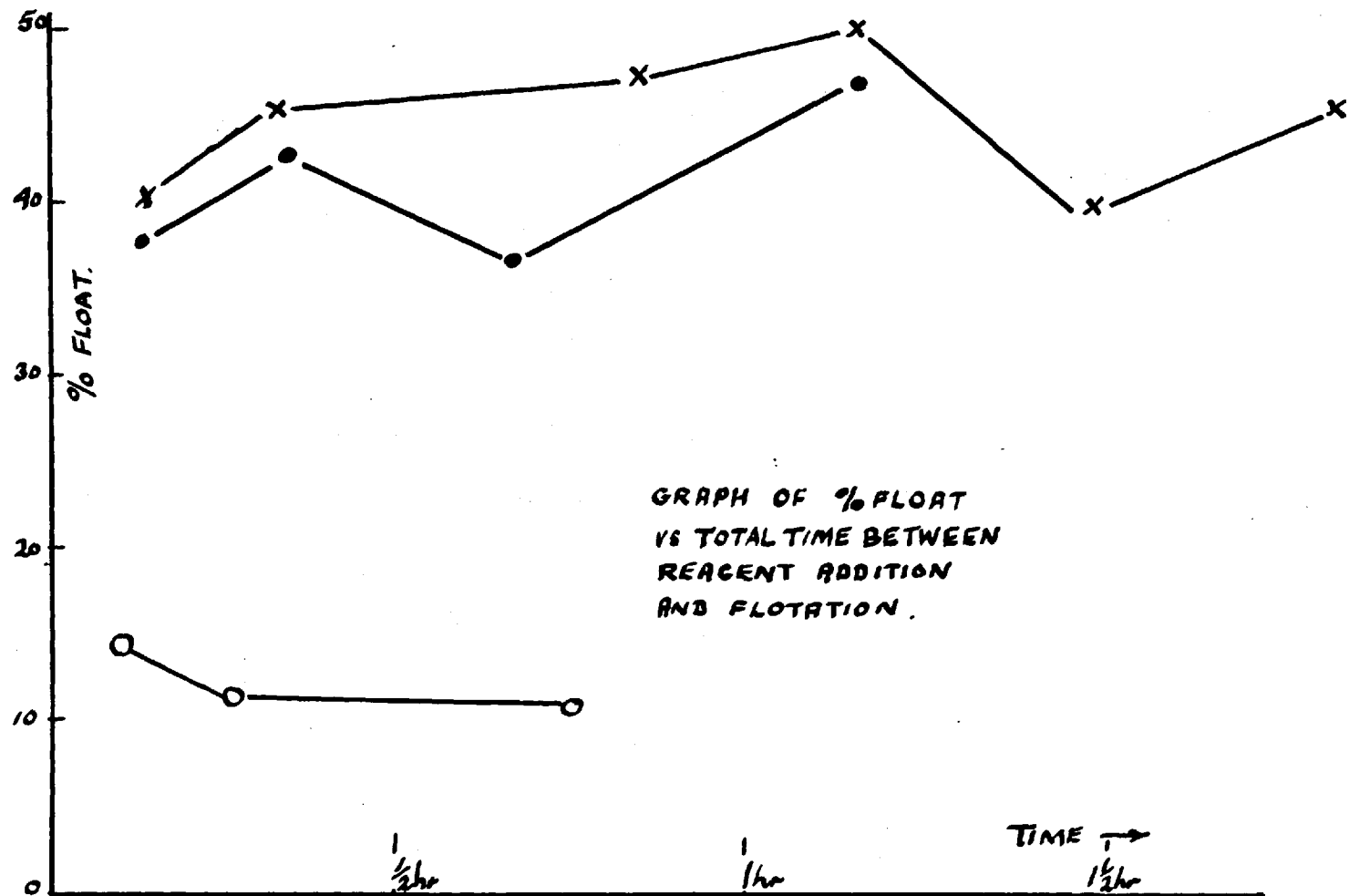


TABLE 6b.

b) Vol. of emulsion added 60 ml. Total Vol. of liquid 294ml

Amine concentration of solutions 0.441 mg/l.

<u>Float No.</u>	<u>Time before float</u>	<u>% float</u>
24	14 min.	40.3
25	26 min.	45.1
26	55 min.	47.2
27	75 min.	50.5
28	96 min.	39.1
29	116 min.	46.2

TABLE 6c.

c) Vol. of emulsion added 50 ml. Total Vol. of liquid 286 ml

Amine concentration 0.388 mg/l.

<u>Float No.</u>	<u>Time before float</u>	<u>% float</u>
30	14 min.	37.2
31	26 min.	43.1
32	35 min.	36.7
33	74 min.	47.6

C. Variation of Flotability with pH.

A number of tests were performed to indicate the effect of variations of pH on the flotability of quartz at various collector concentrations both in the presence and absence of oil.

TABLE 7a.

a) Volume of emulsion added, 100 ml. Conc. of emulsion

0.64 g/l. Conc. of amine 1.3 mg/l. Total Vol. 285 ml

<u>Float No.</u>	<u>pH</u>	<u>% float</u>
34	2.0	3.8
35	2.9	4.7
36	3.9	10.0
37	4.9	13.2
38	6.1	23.5
39	7.1	34.0

Contd.

TABLE 7a. contd.

<u>Float No.</u>	<u>pH.</u>	<u>% float</u>
40	8.5	37.9
41	9.6	91.5
42	10.7	84.6
43	12.3	4.93

TABLE 7b.

b) Vol. of emulsion added 100 ml. Total volume 285 ml.
Amine concentration 1.5 mg/l.

<u>Float No.</u>	<u>pH</u>	<u>% float</u>
44	3.15	6.45
45	6.2	36.6
46	7.35	59.3
47	8.35	82.0
48	9.2	69.4
49	10.0	92.2
50	10.6	94.3
51	11.4	59.2
52	11.85	11.25
53	12.1	2.8

Tests 34 to 53 are summarised in graph 10.

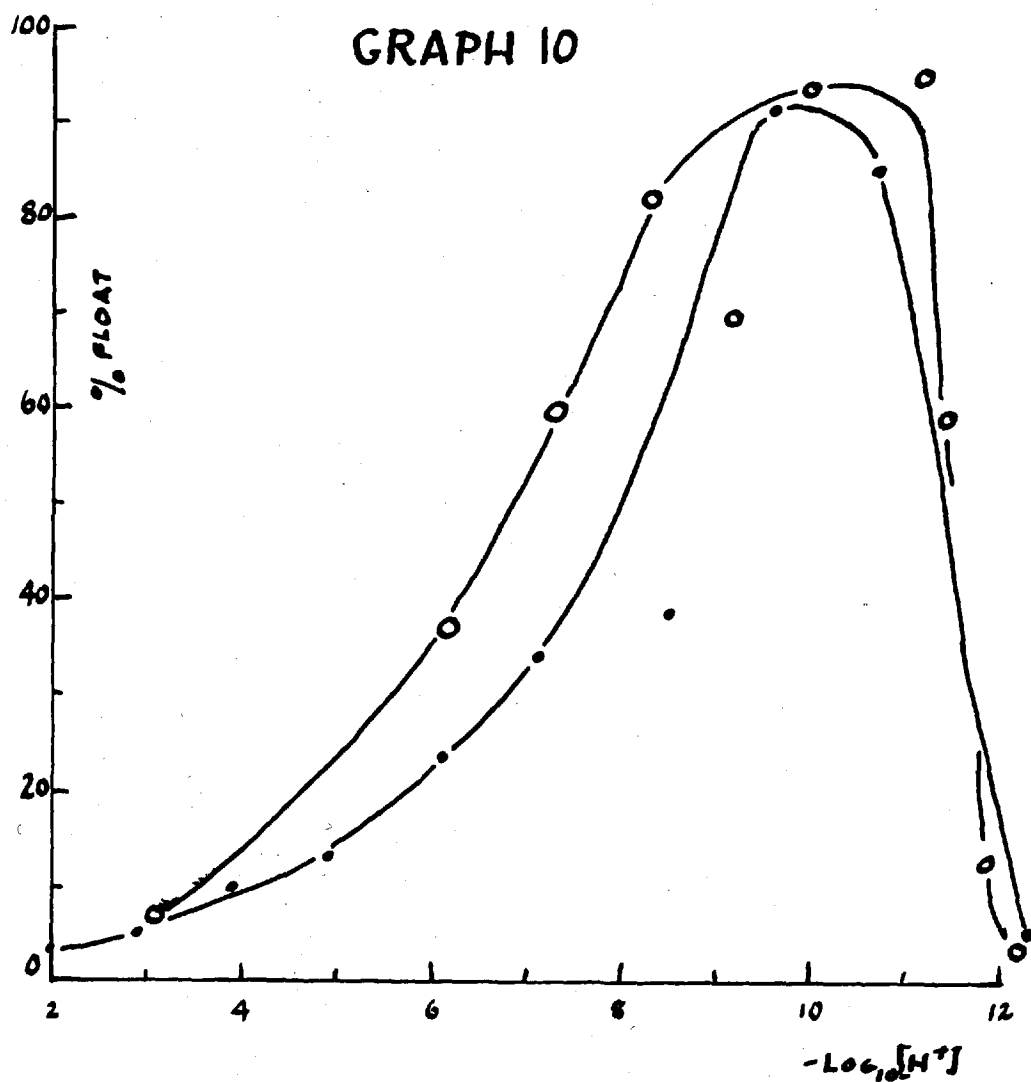
TABLE 7c.

c) Variation of Flotability with collector concentration
in absence of oil.

<u>Float No.</u>	<u>Amine Conc.</u>	<u>% float</u>
54	29.8 mg/l	99.8
55	11.2 mg/l	97.8
56	5.47mg/l	91.6
57	2.94mg/l	89.6
58	1.56mg/l	89.4
59	0.92mg/l	71.6
60	0.51mg/l	53.2
61	0.24mg/l	20.8
62	0.12mg/l	5.07
63	0.06mg/l	8.35

D. Variation of Flotability with Amine Concentration.

To check the tests in which the amine was presented



VARIATION OF % FLOAT WITH pH
QUARTZ AND DODECYLAMINE IN OIL

—○— 1.5 mg/l
—●— 1.3 mg/l .

to the quartz as a solution in an emulsified oil two tests were performed in which the amine was presented as the solution of the hydrochloride salt. 50 ml. samples of amine free emulsion were added in each case. The results were:-

TABLE 8

<u>Float No.</u>	<u>Amine Conc.</u>	<u>% float</u>
64	0.20 mg/l	9.1
65	0.43 mg/l	31.0

Section 2B. 5.

Streaming current.

a) Preliminary Tests.

Test i. Variation of current with head.

The equation for the calculation of zeta potential requires that E should be directly proportioned to P i.e. that the current flowing should be directly proportional to the head.

To test the apparatus a series of measurements of current were taken over a wide range of head values.

The conditions of the test were:-

Mineral Quartz - 72 + 100 mesh

Solution 5×10^{-6} normal aqueous sodium perchlorate.

pH 9.0

Temperature 26°C .

Specific Conductivity of Plug:-

Cell constant 12.85

The data obtained are given in Table 9 and graph 11.

Test ii Measurements in Sodium Chloride Solutions.

To compare results with those of other workers measurements were taken of the streaming current in solutions of sodium chloride at pH values of 6.7 and 10.3. A preliminary measurement was made in water to which no modifiers of any kind had been added.

The conditions of the test were:-

Mineral: Quartz - 72 + 100 mesh.

Solution: Various concentrations of aqueous sodium chloride.

pH. a) 6.7

b) 10.3

Temperature 26°C.

Specific conducting of plug: varied.

Cell constant: a) 13.12

b) 11.91

The data obtained are given in Table 10 and graph 12.

b) Measurements in Sodium Perchlorate Solutions.

Test iii Variation of potential with concentration of sodium perchlorate

Sodium perchlorate having been used as the non-surface active salt in flotation tests it was necessary to measure the properties of quartz in solutions of this salt. Sodium perchlorate solutions of various strengths were tested at pH 9.

The conditions of the test were:

Mineral. Quartz -72 + 100 mesh.

Solution. Sodium perchlorate solutions of various strengths.

pH.. 9

Temperature: Varied 24 to 25°C.

Specific conductivity of plug. Varied.

Cell constant: 12.85

The data obtained are given in Table 11 and graph 13.

Test IV. Variation of zeta-potential with pH at constant concentration of sodium perchlorate.

To determine the effect on the zeta-potential of variations in the H^+ ion concentration at constant electrolyte concentration, a series of 10^{-4} normal sodium perchlorate solutions were tested at pH's varying between 2.75 and 10.65.

The conditions of the test were:

Mineral: Quartz -72 + 100 mesh.

Solution $10^{-4}N$ sodium perchlorate.

pH Varied.

Temperature. 23.4 to 25.5°C.

Specific conductivity of plug: Varied.

Cell constant: 13.4

The data obtained are given in table 12 and graph 14.

c) Measurements in dodecylamine hydrochloride Solutions.

Test V. Variation of zeta-potential with pH at constant concentration of dodecylamine hydrochloride.

To determine the effect of varying pH on the zeta-potential of quartz in dodecylamine hydrochloride solutions a series of tests was performed in solutions of constant concentration of sodium perchlorate.

The conditions were:

Mineral. -72 + 100 mesh Quartz.

Solutions: 10^{-4} Normal aqueous sodium perchlorate.

a) 1.0 mg/litre dodecylamine hydrochloride

b) 9.6 mg/litre dodecylamine hydrochloride.

pH. Varied.

Specific conductivity: varied.

Cell constant: a) 13.3

b) 13.3

The data are given in table 13 and graph 15.

Test VI. Variation of zeta-potential with varying pH and concentration of dodecylamine hydrochloride.

It was apparent from graph 15 that an amine addition of 9.6 mg/l did not lower the zeta potential as much as one of 1.0 mg/l below pH 9. This result was considered unlikely and was possibly caused by a difference in the condition of the plugs used for the tests. To obtain further information on this point a test was done on the same plug with three strengths of dodecylamine hydrochloride. The solutions containing no amine were examined first, followed by those containing 0.96 mg/l, those containing 9.6 mg/l being used last.

The conditions of the test were:

Mineral: -72 100 quartz.

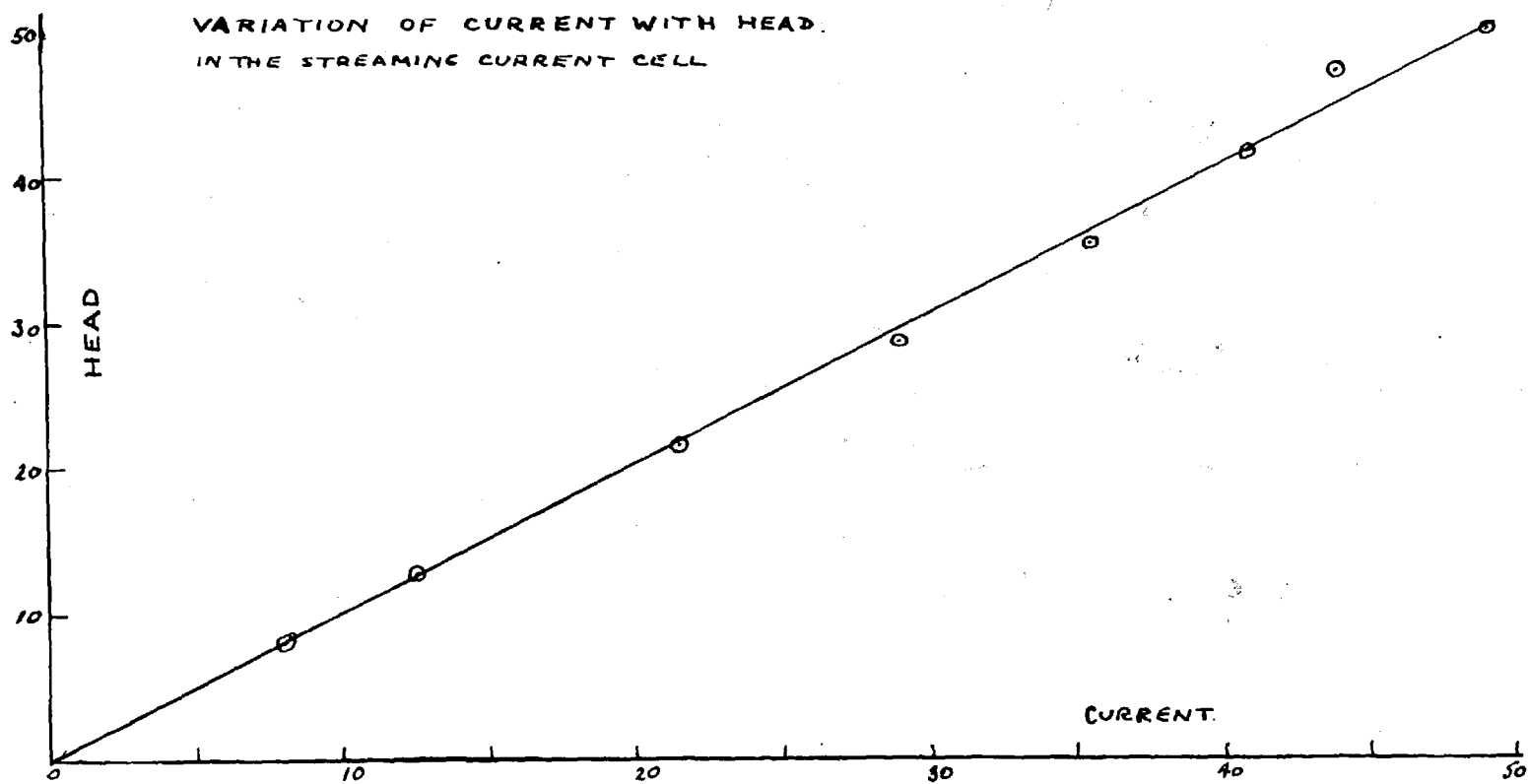
Solutions. a) 10^{-4} Normal sodium perchlorate.

b) 10^{-4} Normal sodium perchlorate
0.96 mg/l dodecylamine amine hydrochloride.

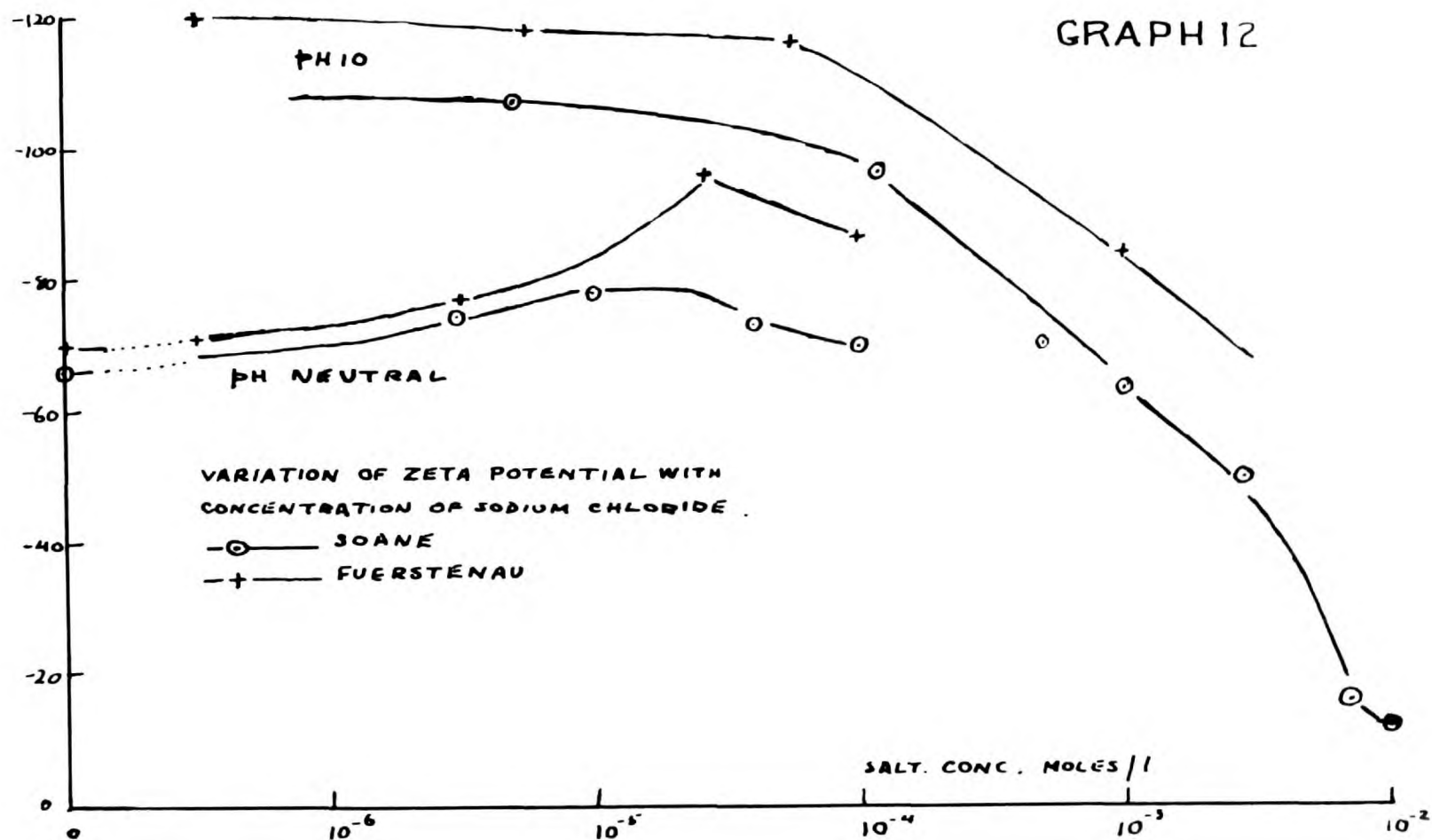
c) 10^{-4} Normal sodium perchlorate 9.6mg/
litre dodecylamine hydrochloride.

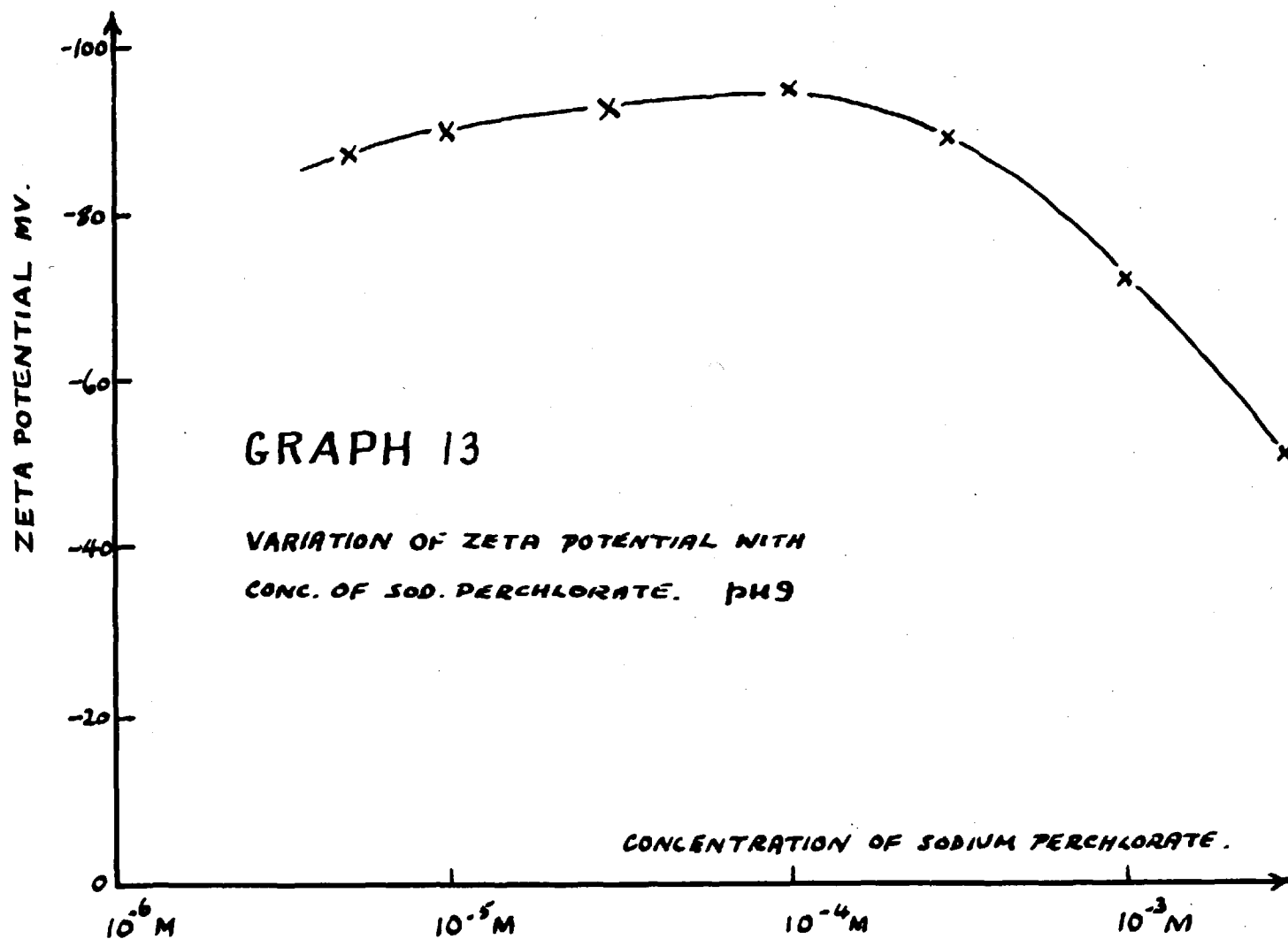
GRAPH II

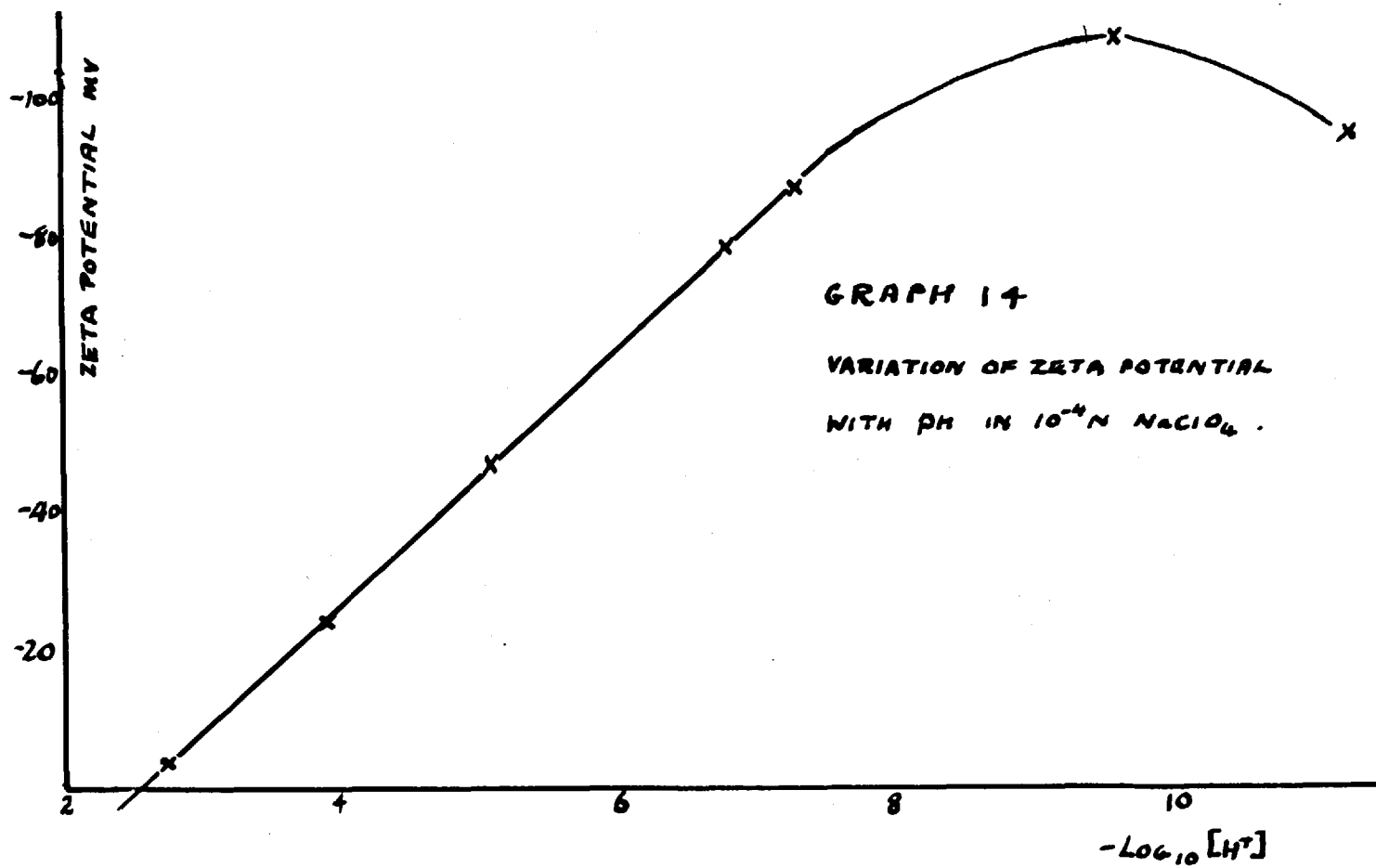
VARIATION OF CURRENT WITH HEAD.
IN THE STREAMING CURRENT CELL



GRAPH 12

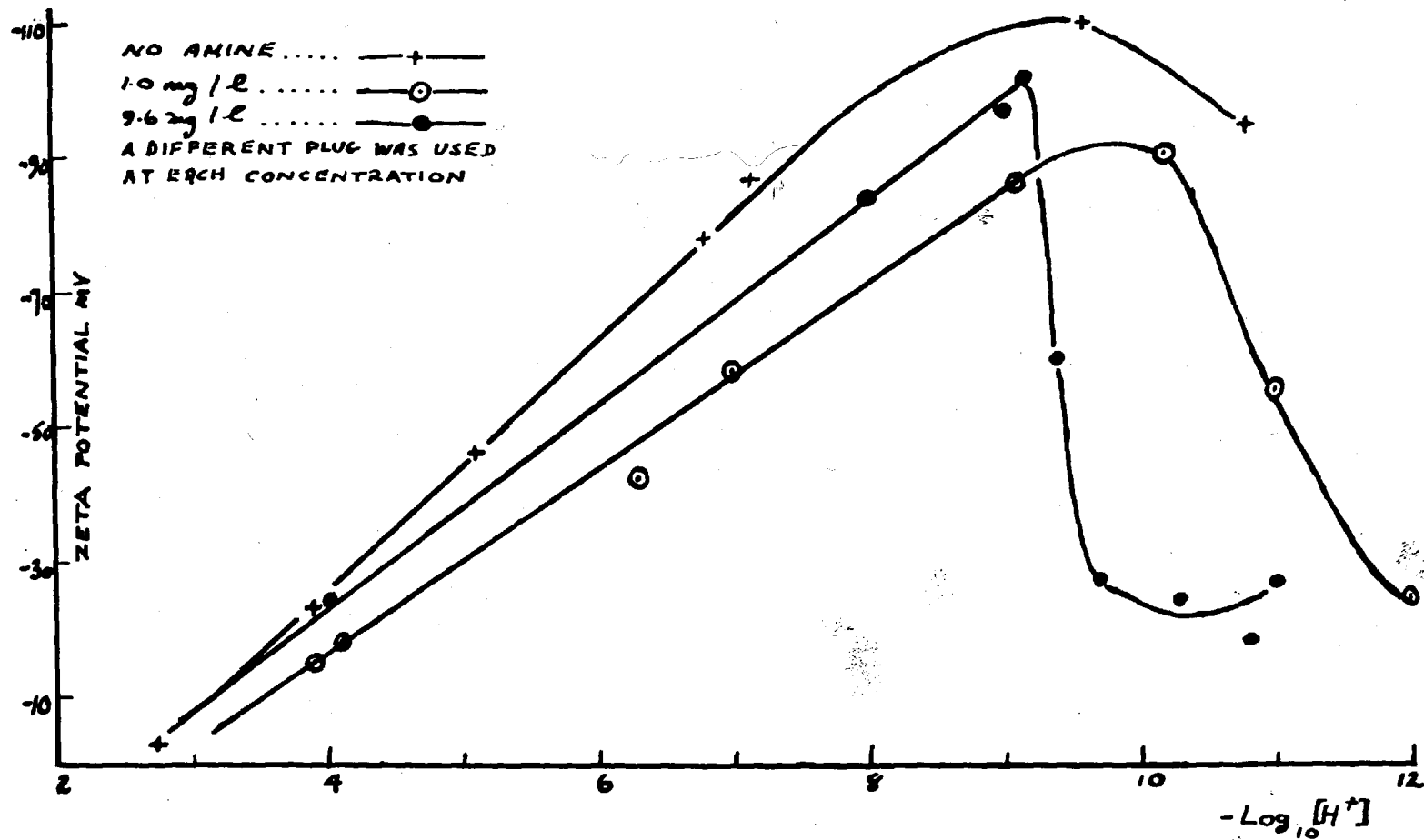




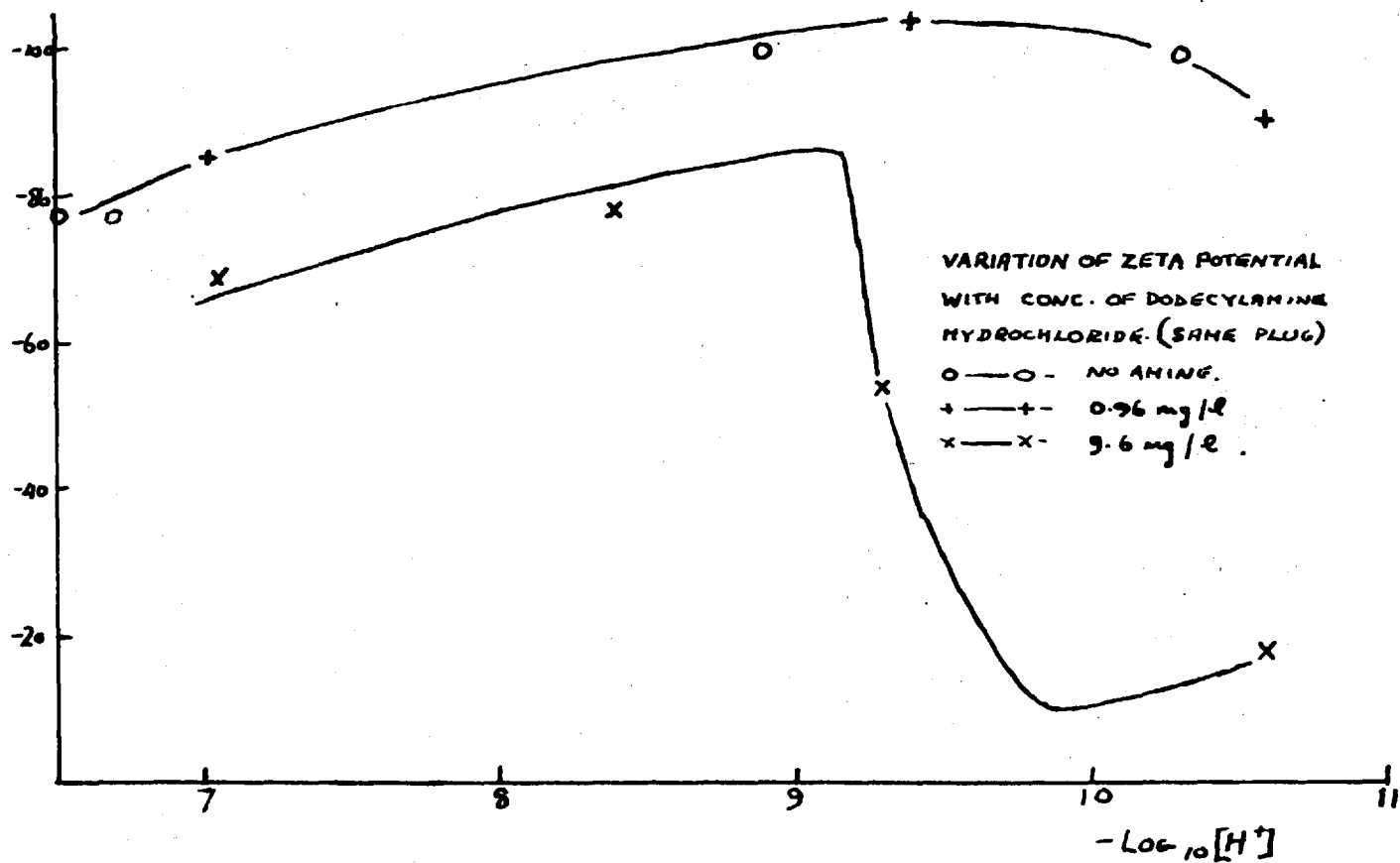


GRAPH 15

VARIATION OF ZETA-POTENTIAL WITH pH
IN DODECYLAMINE HYDROCHLORIDE SOLN.



GRAPH 16



pH. Various.

Specific conductivity of plug: Various.

Cell constant: 10.4

The plug had been standing in conductivity water for 4 days before use.

The data obtained are given in Table 14 and graph 16.

TABLE 9.

VARIATION OF STREAMING CURRENT WITH HEAD.	
Net Galvanometer Deflection mm.	Head cm Water
49.2	50.3
48.9	50.2
44.0	47.4
44.0	47.2
41.0	42.0
35.5	35.6
29.0	29.1
21.5	21.9
12.5	13.2
8.0	8.5

TABLE 10.

VARIATION OF ZETA POTENTIAL WITH SALT CONCENTRATION

pH.	Molarity of Solution	Temp. °C.	Head cm Water	Net Galv- onometer Deflection mm.	Zeta Potent- ial, mV.
6.7	0	26.0	52.2	38.8	-69
6.7	5x10 ⁻⁶	26.1	50.4	47.4	-74.2
6.7	10 ⁻⁵	-	52.3	49.7	-78
6.7	4x10 ⁻⁵	-	50.1	47.5	-73.1
6.7	10 ⁻⁴	-	50.5	44.4	-70
10.3	5x10 ⁻⁶	21.0	50.5	59.0	-107
10.3	10 ⁻⁴	21.7	49.6	51.9	-95.7
10.3	5x10 ⁻⁴	21.9	50.95	38.5	-69.7
10.3	10 ⁻³	22.0	53.2	35.7	-63.6
10.3	3x10 ⁻³	22.5	50.4	27.5	-50
10.3	7x10 ⁻³	22.8	51.0	8.2	-15.3
10.3	10 ⁻²	22.8	51.0	6.9	-12.2

Resistance in N/10 KCl. pH 6.7 series 1050 ~ pH 10.3 ~ 1000 ~

TABLE 11.
PH. 9.0. VARIATION OF ZETA POTENTIAL WITH SOD. PERCHLORATE CONCENTRATION.

<u>Molarity of Solution.</u>	<u>Temp. °C.</u>	<u>Head cm Water.</u>	<u>Mean Galv. Deflection mm.</u>	<u>Zeta Potential.</u>
5x10 ⁻⁶	25.0	42.9	41	-87.5
10 ⁻⁵	24.1	50.5	49.8	-90
3x10 ⁻⁵	24.5	50.9	50	-92.6
10 ⁻⁴	24.7	50.3	52	-95
3x10 ⁻⁴	24.2	49.9	47.5	-88.6
10 ⁻³	24.3	50.2	38.5	-72
3x10 ⁻³	24.3	49.5	27	-50.7

Resistance in N/10 KCl Solution 1000 ~ at 27°C.

TABLE 12.
VARIATION OF ZETA POTENTIAL WITH pH.

<u>pH.</u>	<u>Temp. °C.</u>	<u>Head cm Water.</u>	<u>Mean Galvanometer Deflection mm.</u>	<u>Zeta Potential mv.</u>
2.75	23.0	47.9	1.5	-3
3.9	25.8	48	12	-23.5
5.05	25.5	47.8	24	-46.7
6.8	25.2	48.4	40	-78.4
7.3	24.2	47.6	43	-87.6
9.6	23.3	48.6	54	-110
10.65	23.	48.3	46	-94.5

Resistance in N/10 KCl 25.8°C. 1020 ohms.

TABLE 13a.
VARIATION OF ZETA POTENTIAL WITH pH IN 1.0 mg/l DODECYLAMINE SOLUTION.

<u>pH.</u>	<u>Temp. °C.</u>	<u>Head cm Water</u>	<u>Mean Galvanometer Deflection mm.</u>	<u>Zeta Potential mV.</u>
3.9	22.7	49.5	8.15	-16.3
4.1	22.3	49.	9.2	-18.8
6.3	21.9	48.9	21.0	-43.1
7.0	21.7	48.5	28.5	-59.4
9.1	21.3	48.5	41.5	-87.
10.2	25.4	48.4	43.	-90.6
11.0	23.6	48.5	28.	-56.
11.9	23.4	48.	12.	-24.6

Resistance in N/10 KCl at 25°C. 1040 ohms.

TABLE 13b.
VARIATION OF ZETA POTENTIAL WITH pH in 9.6 mg/l
DODECYLAMINE SOLUTION.

pH.	Temp.	Head cm-Water	Mean Galvonometer Deflection mm.	Zeta Potent- ial-mV.
4.5	23.2	49.	12	-24.5
8.	-	48.8	41.	-84.1
9.	-	48.9	47.5	-97.3
9.15	-	50.	52.	-102.
9.4	-	49.	30.	-60.
9.7	-	49.	13.5	-27.
10.3	-	49.	13.	-24.2
10.8	-	48.9	10.5	-19.5
11.	-	48.7	14.5	-107.
11.3	-	48.5	7.	-5.

Resistance in N/10 KCl at 25.3°C. 1025 Ω

TABLE 14.
VARIATION OF ZETA POTENTIAL WITH pH at VARIOUS CONCENTRA-
TIONS OF DODECYLAMINE.

a) No Dodecylamine Hydrochloride.				
pH.	Temp. °C.	Head cm Water.	Mean Galvonometer Deflection mm.	Zeta Potent- ial-mV.
6.7	24.8	46.8	47.5	-75.5
8.9	24.8	46.7	63.	-100.
10.3	24.8	46.5	62.	-99.5
b) 0.96 mg/l Dodecylamine.				
7.05	24.3	45.9	52.	-85.4
9.4	24.2	46.7	63.5	-102.8
10.6	24.0	46.7	55.5	-90.
c) 9.6 mg/l Dodecylamine.				
7.1	23.7	48.4	44.	-69.3
8.4	24.2	48.	50.	-74.
9.3	25.0	47.2	30.	-47.
10.6	25.6	48.6	10.	-15.

Resistance in N/10 KCl 790 Ω 26.7°C.

Section 2B. 6.

ELECTROPHORESIS.

a) Preliminary Tests.

To study the effect of dodecylamine on the electrical properties of the oil/water interface it was necessary to perform a preliminary series of experiments to determine the properties of this interface in the absence of surface active modifiers. Two series of tests were performed. The first indicated the effect of a change of pH on the charges at the droplet surfaces. The second indicated the effect of varying concentrations of a neutral electrolyte. Sodium perchlorate was used in concentrations varying from zero to $1/10$ Normal at a pH of 9.2. Tests were performed at room temperature i.e. $20^{\circ} - 22^{\circ}\text{C}$.

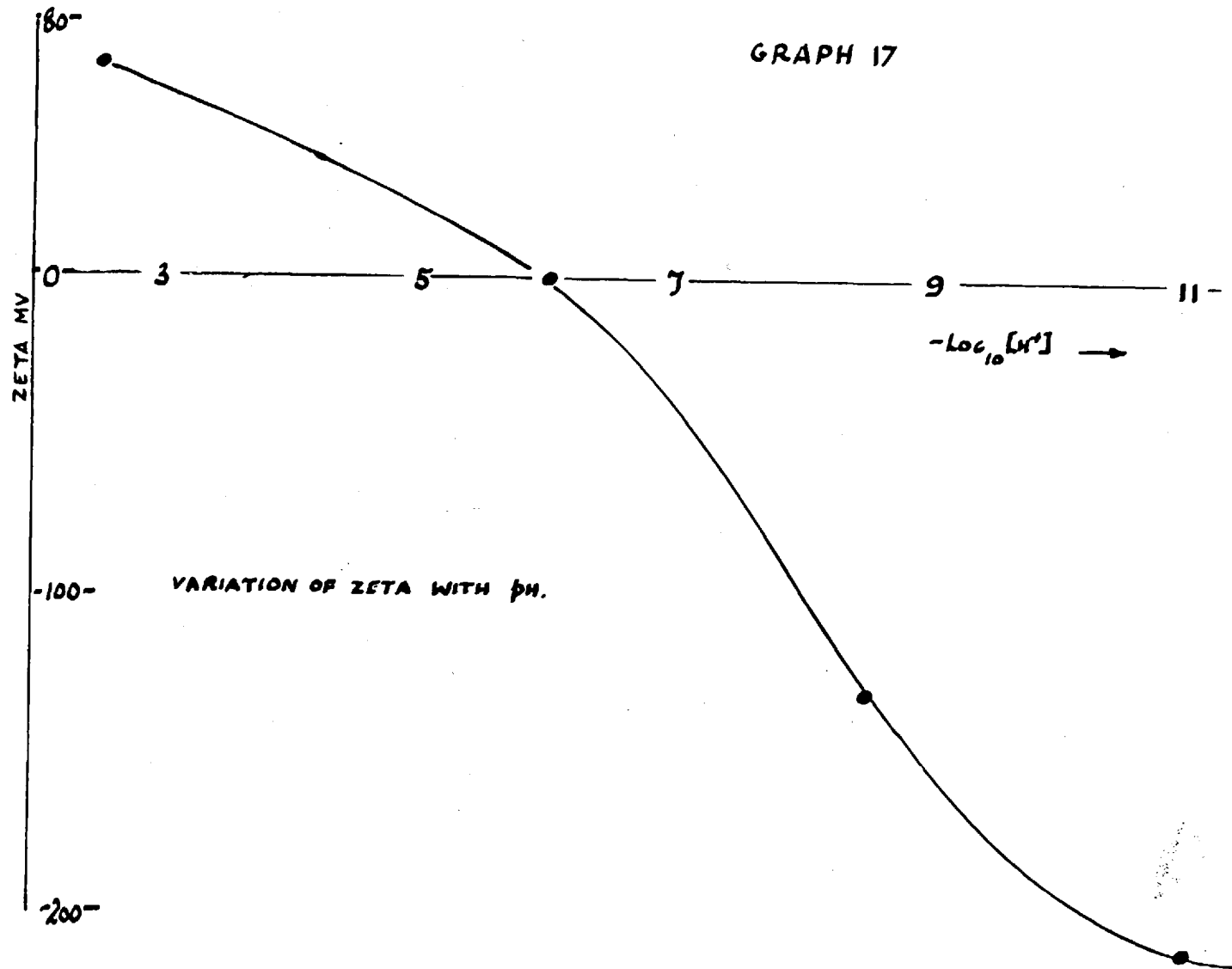
The results of the tests are given in tables 15 and 16 and graphs 17 and 18. A typical parabola, which shows that the electrophoresis equations were applicable to the system, is shown in graph 20.

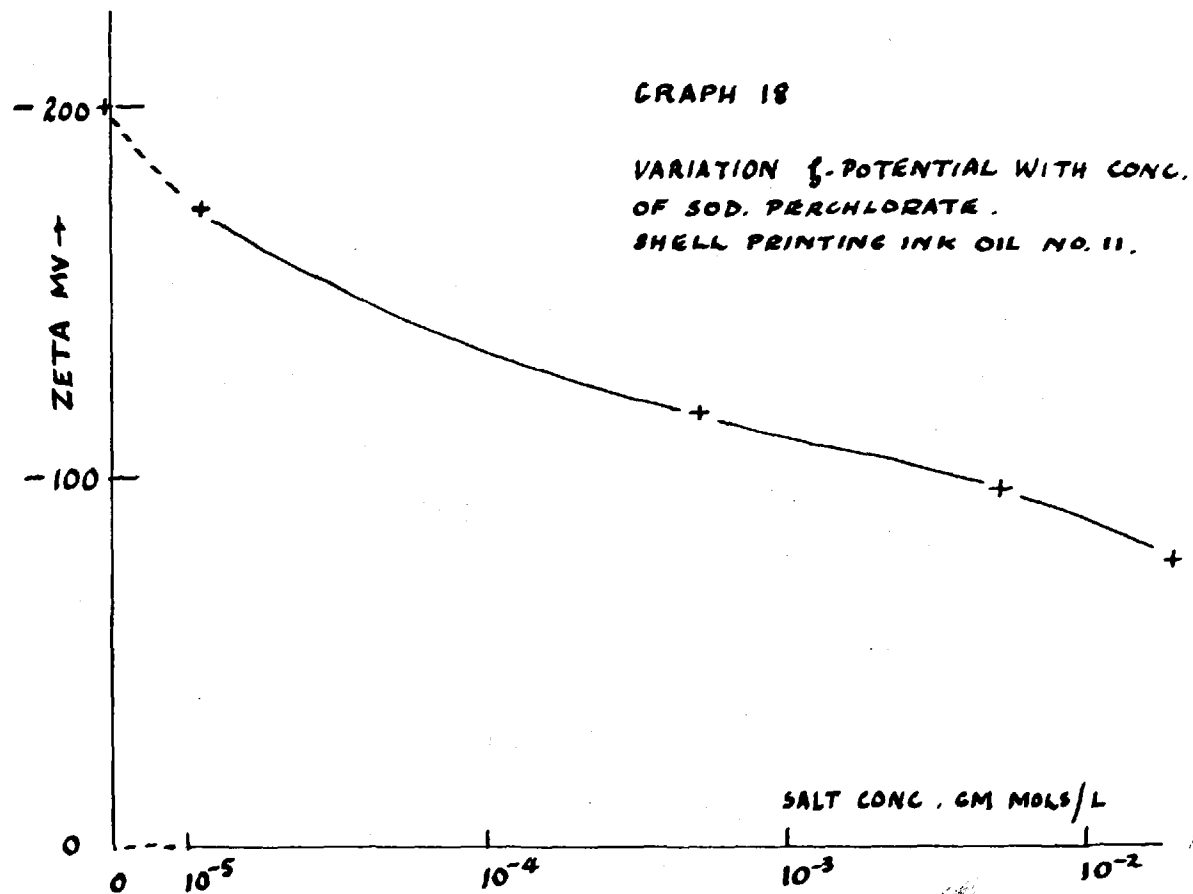
The results have been corrected, in the tables, for both relaxation and variations of potential with salt concentration. These corrections are explained in Section 3B.

b) Tests in dodecylamine solutions.

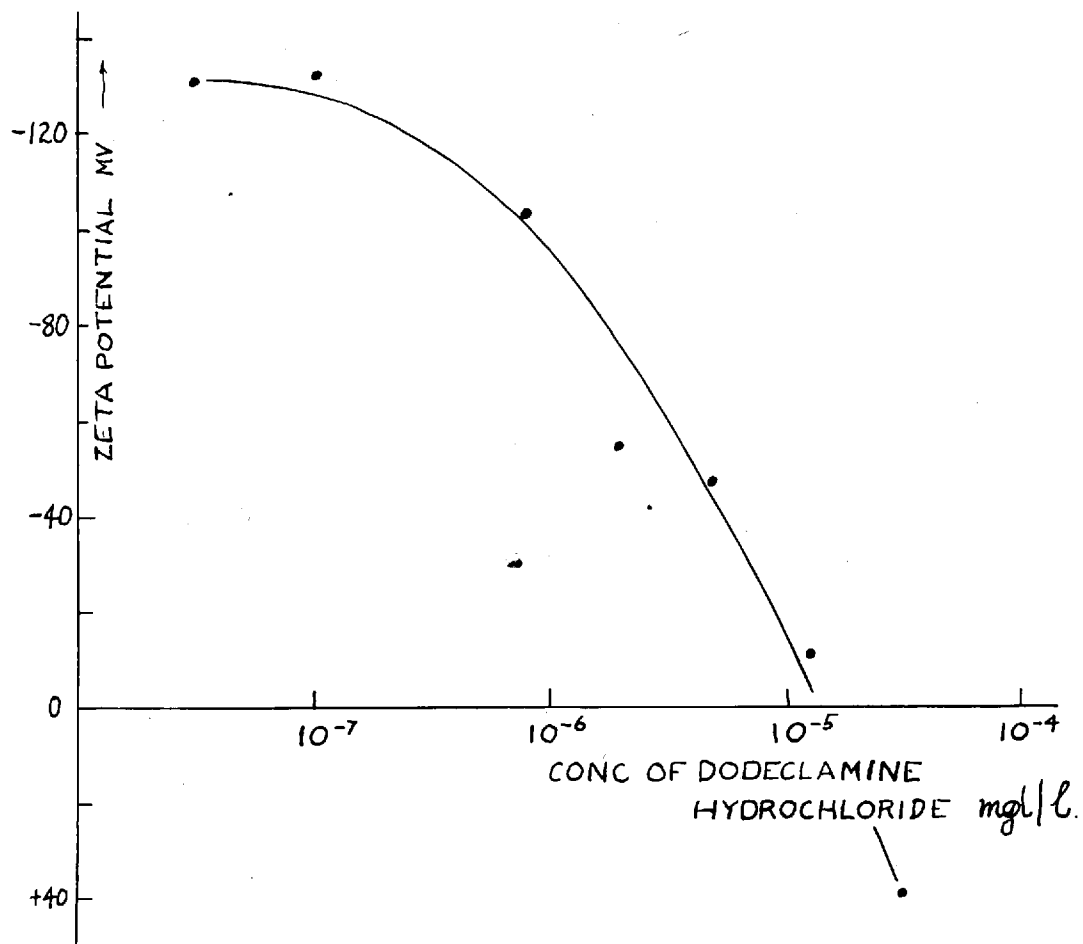
These tests were divided into two parts. In the first the dodecylamine was dissolved in the oil before emulsification. For reasons which will be described

GRAPH 17





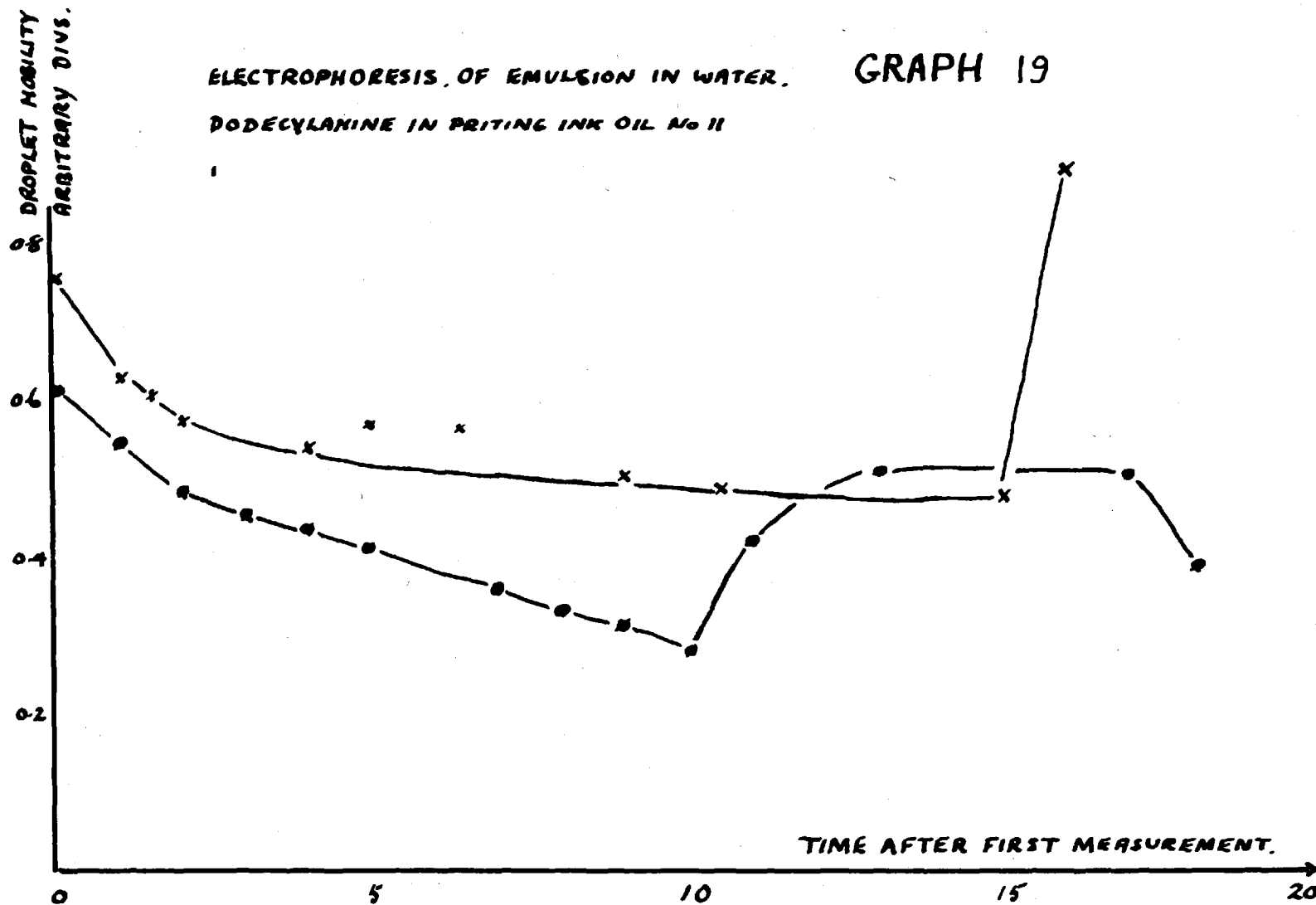
GRAPH 18b.



VARIATION OF ZETA POTENTIAL WITH AMINE CONCENTRATION
SHELL PRINTING INK OIL NO. 11

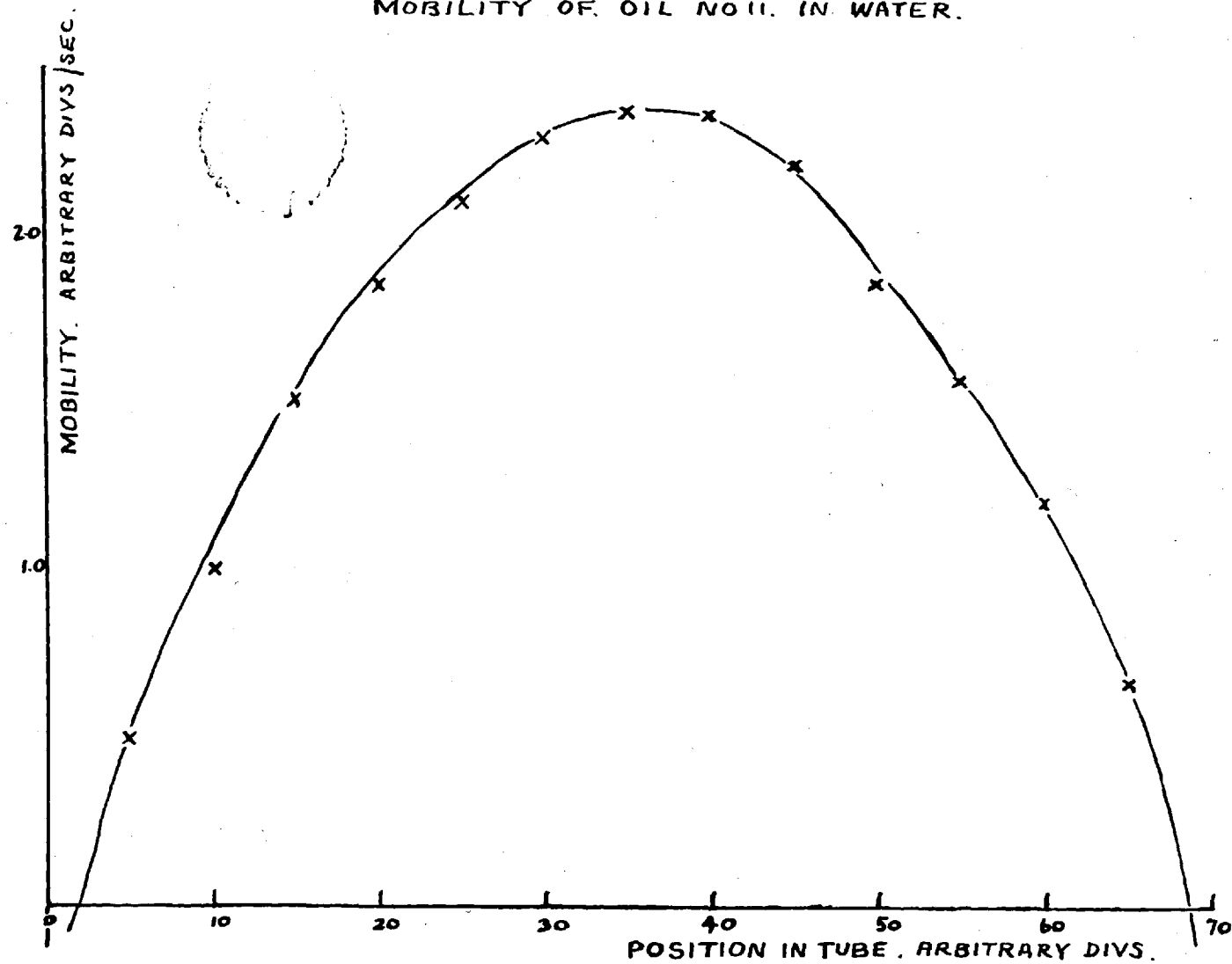
ELECTROPHORESIS OF EMULSION IN WATER.
DODECYLAMINE IN PRITING INK OIL No 11

GRAPH 19



GRAPH 20

MOBILITY OF OIL NO 11. IN WATER.



below this yielded few useful results. In the second series of tests the dodecylamine was added to the system in aqueous solution as the hydrochloride salt.

An account of some of the difficulties encountered in the tests where the amine was dissolved in the oil before emulsification, has been given in section 2A5. Measurements with the revised technique showed that the mobilities of droplets at one level in the capillary, and from the same sample, varied with time. When the voltage was applied the mobility slowly decreased until it reached a minimum value, when it suddenly increased to a value about the same as the initial one. A curve illustrating this is shown in graph 19. If further samples were run in from the reservoir their behaviour was similar to the first but did not yield the same initial and final values of mobility. In some of the weaker amine solutions a complete reversal of charge occurred. This behaviour was repeated after the apparatus had been cleaned with more than ordinary care, and after the water used for making up the emulsion had been boiled free from carbon dioxide gas.

To explain the phenomenon noted above it is necessary to explain the cause of the two phases. 1) The gradual reduction of mobility with time. 2) The sudden change after a period of time.

The gradual reduction of mobility was probably caused by adsorption of amine by the glass walls of the apparatus,

with subsequent reduction of amine concentration in the oil. This would occur slowly until a form of equilibrium was reached. To prevent the changes of mobility caused by this process it would be necessary to prepare the walls beforehand by passing through a solution of amine in water of the strength to be used in the test. This could not be done in this series because the strength of the emulsion was never known until after it had been analysed. A second series of tests is described below, in which the precaution was taken. The system was rendered more complex by oil which creamed onto the upper surface of the tube making amine concentrations in this region very complicated.

The sudden change in velocity after a period of time may have been caused by internal circulations of the oil droplets, which can occur in emulsions. It is probable that such circulation would slowly build up until it finally set the droplet circulating in the liquid. This would cause sudden alteration in all droplet mobilities.

It was not possible to draw accurate quantitative conclusions from the first series of tests in the presence of amine. However, it was shown that its addition to the oil, before emulsification, caused a reversal of the sign of the zeta-potential. Zeta potentials of the order of -35 mV were obtained with about 10 mg/l of amine in the emulsion. The lowest concentrations tested were of the order of 0.8mg/l. These also greatly reduced or changed

the sign of the zeta potential giving an unstable emulsion with a zeta potential of about zero.

In the second part of the electrophoresis tests in dodecylamine solutions the amine was added to the emulsion as a solution of the hydrochloride salt. Before passing the emulsion into the tube an amine solution of the same strength was run through for 10 or 15 minutes. All tests were performed at pH 9.3 to 9.4 and room temperature with a P.D. of 60 volts. All solutions contained 0.1 gm. mols. of sodium perchlorate per litre. The results are given in Table 17 and graph 18b.

TABLE 15a.

VARIATION OF MOBILITY WITH pH.

pH 2.6

<u>Level in Tube</u> <u>Arbitrary Divisions.</u>	<u>Mobility</u> <u>Divisions/Sec.</u>	<u>μ/sec/V/cm.</u>
5	0.43	1.81
10	0.72	3.15
15	0.98	4.12
20	1.20	5.06
25	1.22	5.16
30	1.27	5.35
35	1.45	6.1
40	1.50	6.32
45	1.55	6.53
50	1.54	6.48
55	1.23	5.18
60	1.18	4.97
65	0.97	4.09
70	0.58	2.45
72.5	0.357	1.51

Movement to cathode. Dielectric constant 82.7
 0.146 distance gives 37.5 μ /sec/V/cm = +54.3 mV.

TABLE 15b.

VARIATION OF MOBILITY WITH pH.

<u>pH 8.5</u>		
<u>Level in Tube</u>	<u>Mobility</u>	<u>Mobility</u>
<u>Arbitrary Divisions</u>	<u>Divisions/sec.</u>	<u>μ/sec/V/cm.</u>
10	1.15	4.84
15	1.4	5.9
20	1.9	8.0
25	2.17	9.13
30	2.47	10.4
35	2.72	11.4
40	2.48	10.4
45	2.43	10.2
50	2.25	9.5
55	1.69	7.13
60	1.36	5.72
65	0.8	3.37

Movement to anode. Dielectric constant 86.4
 0.146 distance gives $4.65 \mu/\text{sec/V/cm} = -67.2 \text{ mV.}$

TABLE 15c.

VARIATION OF MOBILITY WITH pH.

<u>pH 11.</u>		
<u>Level in Tube</u>	<u>Mobility</u>	
<u>Arbitrary Divisions.</u>	<u>Divisions/sec.</u>	<u>μ/sec/V/cm.</u>
5	1.34	5.65
10	2.74	11.5
15	3.34	14.1
20	4.09	17.2
25	4.18	17.6
30	3.92	16.5
35	3.95	16.6
40	3.58	15.0
45	2.75	11.5
50	2.45	10.3

Movement to anode. Dielectric constant 80.8
 0.146 distance gives $10.7 \mu/\text{sec/V/cm} = -153 \text{ mV.}$

pH of distilled water i.e. 5.8 gave zero potential.

TABLE 16a.

VARIATION OF MOBILITY WITH SALT CONCENTRATION AT pH 9.3

No sodium perchlorate.		
Level in Tube.	Mobility	Mobility
Arbitrary Divisions.	Divs./Sec.	$\mu/\text{sec/V/cm.}$
5	0.5	2.1
10	1.0	4.2
15	1.51	6.35
20	1.85	7.8
25	2.08	8.75
30	2.28	9.6
35	2.32	9.8
45	2.22	9.3
50	1.85	7.75
55	1.56	6.55
60	1.19	5.0
65	0.66	2.8

Dielectric constant 80.4. Movement to anode.
 0.146 point 5.07 $\mu/\text{sec/V/cm.}$ = -72.3 mV.

TABLE 16b.

VARIATION OF MOBILITY WITH SALT CONCENTRATION AT pH 9.3

No sodium perchlorate.		
Level in Tube.	Mobility	Mobility
Arbitrary Divisions.	Divs./Sec.	$\mu/\text{sec/V/cm.}$
5	1.10	4.65
10	1.84	7.75
15	2.45	10.3
20	2.59	10.9
25	3.07	12.9
30	3.24	13.6
35	2.79	11.75
40	2.82	11.9
45	2.36	9.95
50	1.75	7.35
55	1.23	5.2
60	0.84	3.55

Dielectric constant 80.4. Movement to anode.
 Ar. from curve 5.7 $\mu/\text{sec/V/cm.}$ = $\int$ -80.3 mV.

TABLE 16c.

VARIATION OF MOBILITY WITH SALT CONCENTRATION AT pH 9.3

1.16×10^{-5} Molar Sodium Perchlorate.

<u>Level in Tube.</u> <u>Arbitrary Divisions</u>	<u>Mobility</u> <u>Divs/Sec</u>	<u>Mobility</u> <u>μ/sec/V/cm.</u>
5	0.64	2.7
10	1.17	4.9
15	1.67	7.05
20	2.07	8.7
25	2.25	9.5
30	2.56	10.8
35	2.08	8.8
40	2.37	10.0
45	2.25	9.5
50	1.99	8.4
55	1.63	6.85
60	1.19	5.0
65	0.67	2.82

Dielectric Constant 80.4 Movement to anode.
0.146 distance gives $5.25 \mu/s/V/cm.$ = 75 mV.

TABLE 16d.

VARIATION OF MOBILITY WITH SALT CONCENTRATION AT pH 9.3

5.25×10^{-4} Molar Sodium Perchlorate.

<u>Level in Tube.</u> <u>Arbitrary Divisions.</u>	<u>Mobility</u> <u>Divs/sec.</u>	<u>Mobility</u> <u>μ/sec/V/cm.</u>
5	0.9	3.8
10	1.48	6.25
15	2.00	8.45
20	2.23	9.4
25	2.48	10.4
30	2.72	11.5
35	2.62	11.0
40	2.48	10.4
45	2.19	9.25
50	1.96	8.25
55	1.55	6.63
60	1.15	4.85
65	0.45	1.9

Dielectric constant 80.8 Movement to anode.
0.146 distance gives $6.1 \mu/sec/V/cm$ = -84.5 mV.

TABLE 16c.

VARIATION OF MOBILITY WITH SALT CONCENTRATION AT pH 9.3

5.25×10^{-3} Molar Sodium Perchlorate.

<u>Level in Tube.</u> <u>Arbitrary Divisions.</u>	<u>Mobility</u> <u>Divs/Sec.</u>	<u>Mobility</u> <u>μ/sec/V/cm.</u>
5	0.9	3.79
10	1.53	6.45
15	2.01	8.5
20	2.31	9.75
25	2.65	11.2
30	2.65	11.2
35	2.74	11.6
40	2.61	11.0
45	2.47	10.4
50	2.04	8.6
55	1.68	7.07
60	1.40	5.9
Dielectric constant 83.6 Motion towards anode.		
0.146 distance from curve. 6.35μ /sec/V/cm. = -84. Mv.		

TABLE 16f.

VARIATION OF MOBILITY WITH SALT CONCENTRATION AT pH 9.3

2×10^{-2} Molar Sodium Perchlorate.

<u>Level in Tube.</u> <u>Arbitrary Divisions.</u>	<u>Mobility</u> <u>Divs/sec.</u>	<u>Mobility</u> <u>μ/sec/V/cm.</u>
5	0.59	2.49
10	1.10	4.63
15	1.86	7.83
20	2.0	8.42
25	2.19	9.22
30	2.25	9.5
35	2.4	10.2
Dielectric constant 93.5 Movement to anode.		
0.146 distance = 6.33μ /sec/V/cm = -77.0 mV.		

TABLE 17a.

VARIATION OF MOBILITY WITH AMINE CONCENTRATION AT pH 9.4

5×10^{-8} Molar dodecylamine hydrochloride.

<u>Level in Tube.</u> <u>Arbitrary Divisions.</u>	<u>Mobility</u> <u>Divs/sec.</u>	<u>Mobility</u> <u>μ/sec/V/cm.</u>
5	0.98	4.22
10	1.31	5.63
15	1.72	7.42
20	2.00	8.60
25	2.18	9.35
30	2.22	9.58
35	2.22	9.58
40	2.10	9.02

Dielectric constant 80.6 Movement to anode.
0.146 distance gives 5.83μ /sec/V/cm.

TABLE 17b.

VARIATION OF MOBILITY WITH AMINE CONCENTRATION AT pH 9.4

1.1×10^{-7} Molar dodecylamine hydrochloride.

<u>Level in Tube.</u> <u>Arbitrary Divisions.</u>	<u>Mobility</u> <u>Divs/sec.</u>	<u>Mobility</u> <u>μ/sec/V/cm.</u>
5	0.77	3.32
10	1.33	5.72
15	1.92	8.07
20	2.38	10.25
25	2.57	11.1
30	2.64	11.4
35	2.64	11.4
40	2.57	11.1

Dielectric constant 80.6 Movement to anode.
0.146 distance gives 5.92μ /sec/V/cm.

TABLE 17c.

VARIATION OF MOBILITY WITH AMINE CONCENTRATION AT pH 9.4

8×10^{-7} Molar dodecylamine hydrochloride.

<u>Level in Tube.</u> <u>Arbitrary Divisions.</u>	<u>Mobility</u> <u>Divs/sec.</u>	<u>Mobility</u> <u>μsec/V/cm.</u>
5	0.42	1.79
10	1.00	4.30
15	1.56	6.70
20	2.00	8.60
25	2.17	9.20
30	2.23	9.60
35	2.27	9.80
40	2.08	8.93

Dielectric constant 80.6 Movement to anode.
0.146 distance gives 4.51 μ /sec/V/cm.

TABLE 17d.

VARIATION OF MOBILITY WITH AMINE CONCENTRATION AT pH 9.4

2×10^{-6} Molar dodecylamine hydrochloride.

<u>Level in Tube.</u> <u>Arbitrary Divisions.</u>	<u>Mobility</u> <u>Divs/Sec.</u>	<u>Mobility</u> <u>μ/sec/V/cm.</u>
5	- 0.2	- 0.86
10	0.55	2.37
15	1.10	4.72
20	1.38	5.92
25	1.66	7.13
30	1.78	7.63
35	1.78	7.63

Dielectric Constant 80.6 = Movement to anode.
0.146 distance gives 2.58 μ /sec/V/cm.

TABLE 17e.

VARIATION OF MOBILITY WITH AMINE CONCENTRATION AT pH 9.4

5×10^{-6} Molar dodecylamine hydrochloride.

<u>Level in Tube.</u> <u>Arbitrary Divisions.</u>	<u>Mobility</u> <u>Divs/sec.</u>	<u>Mobility</u> <u>μ/sec/V/cm.</u>
5	0	0
10	0.39	1.66
15	0.63	2.69
20	0.72	3.08
25	0.83	3.56
30	1.0	4.30
35	1.0	4.30

Dielectric Constant 80.6 Movement to anode.
0.146 distance gives 2.06μ /sec/V/cm.

TABLE 17f.

VARIATION OF MOBILITY WITH AMINE CONCENTRATION AT pH 9.4

1.3×10^{-5} Molar dodecylamine hydrochloride.

<u>Level in Tube.</u> <u>Arbitrary Divisions.</u>	<u>Mobility</u> <u>Divs/sec.</u>	<u>Mobility</u> <u>μ/sec/V/cm.</u>
5	-0.14	-0.60
10	0.13	0.54

Dielectric constant = 80.6 Movement to anode.
0.146 distance gives 0.56μ /sec/V/cm.

TABLE 17g.

VARIATION OF MOBILITY WITH AMINE CONCENTRATION AT pH 9.4

3×10^{-5} molar dodecylamine hydrochloride.

<u>Level in Tube.</u> <u>Arbitrary Division.</u>	<u>Mobility</u> <u>Divs/sec.</u>	<u>Mobility</u> <u>μ/sec/V/cm.</u>
5	-0.29	-1.19
10	-0.42	-1.79

Dielectric constant 80.6 Movement to anode.
0.146 distance = -1.94μ /sec/V/cm.

N.B. In Tables 17f and 17g creaming was too rapid to allow more readings than those shown.

SUMMARY OF ELECTROPHORESIS RESULTS.

TABLE 15.

VARIATION OF MOBILITY WITH pH.

<u>pH.</u>	<u>Mobility</u> <u>μ/sec/V/cm.</u>	<u>Zeta Potential</u> <u>mV.</u>	<u>Zeta Corrected</u> <u>for Potential</u> <u>variations.</u>
2.6	3.75	54.3	66.7 mV.
6.0	0	0	0
8.5	-4.65	-67.2	-130
11.0	-10.7	-153	-204

TABLE 16.

VARIATION OF MOBILITY WITH SALT CONCENTRATION AT pH 9.3

<u>Molarity</u> <u>g. mol./l.</u>	<u>Mobility</u> <u>μ/sec/V/cm.</u>	<u>Zeta Potential</u> <u>Mv.</u>	<u>Corrected</u> <u>for relax-</u> <u>ation.</u>	<u>Corrected</u> <u>for potent-</u> <u>ial variat-</u> <u>ions.</u>
0	-5.40	-76.3	-83	About -200
1.16x10 ⁻⁵	-5.25	-75.0	-82	-172
5.25x10 ⁻⁴	-6.10	-84.5	-84.5	-117
5.25x10 ⁻³	-6.25	-84.0	-84.0	-96.3
2x10 ⁻²	-6.33	-77	-77.0	-77.0

TABLE 17

VARIATION OF MOBILITY WITH DODECYLAMINE HYDROCHLORIDE
CONCENTRATION AT pH 9.4

<u>Molarity</u> <u>g. mol./l.</u>	<u>Mobility</u> <u>μ/sec/V/cm.</u>	<u>Zeta Potential</u> <u>Measured</u> <u>mV.</u>	<u>Corr. for</u> <u>relaxation</u>	<u>Corr. for</u> <u>Potent-</u> <u>ial varia-</u> <u>tions.</u>
5x10 ⁻⁸	-5.83	-74.7	-80.9	-131
1.1x10 ⁻⁷	-5.92	-75.8	-81.9	-132
8x10 ⁻⁷	-4.51	-57.5	-62.1	-104
2x10 ⁻⁶	-2.58	-32.9	-32.1	-54
5x10 ⁻⁶	-2.06	-25.9	-25.9	-47.5
1.3x10 ⁻⁵	-0.56	-6.9	-6.9	-11.4
3.0x10 ⁻⁵	-0.94	24.7	24.7	40.5

Section 2B. 7.

The Partition Co-efficient of Dodecylamine Hydrochloride Between Oil and Water.

A preliminary test was performed to indicate the effect of the red dye waxoline OS, on the counting rate. It was found that the colour of the solution reduced the counting rate of the sample. The reduction in counting rate increased with increasing density of colour.

To determine the extent to which the dye reduced the count a sample made from undyed oil was counted. The counting procedure was repeated with increasing quantities of dyed oil present in the liquid.

The following results were obtained:

The undyed oil proved to have no appreciable effect on the counting rate.

The dyed oil gave the following results.

TABLE 18

<u>Counting rate</u>	<u>Weight of oil added</u>
1155 counts/sec.	None
733.4 "	0.4752g.
556.0 "	0.8395g.
466.1 "	1.0310g.
282.5 "	1.5479g.
208.7 "	2.1010g.

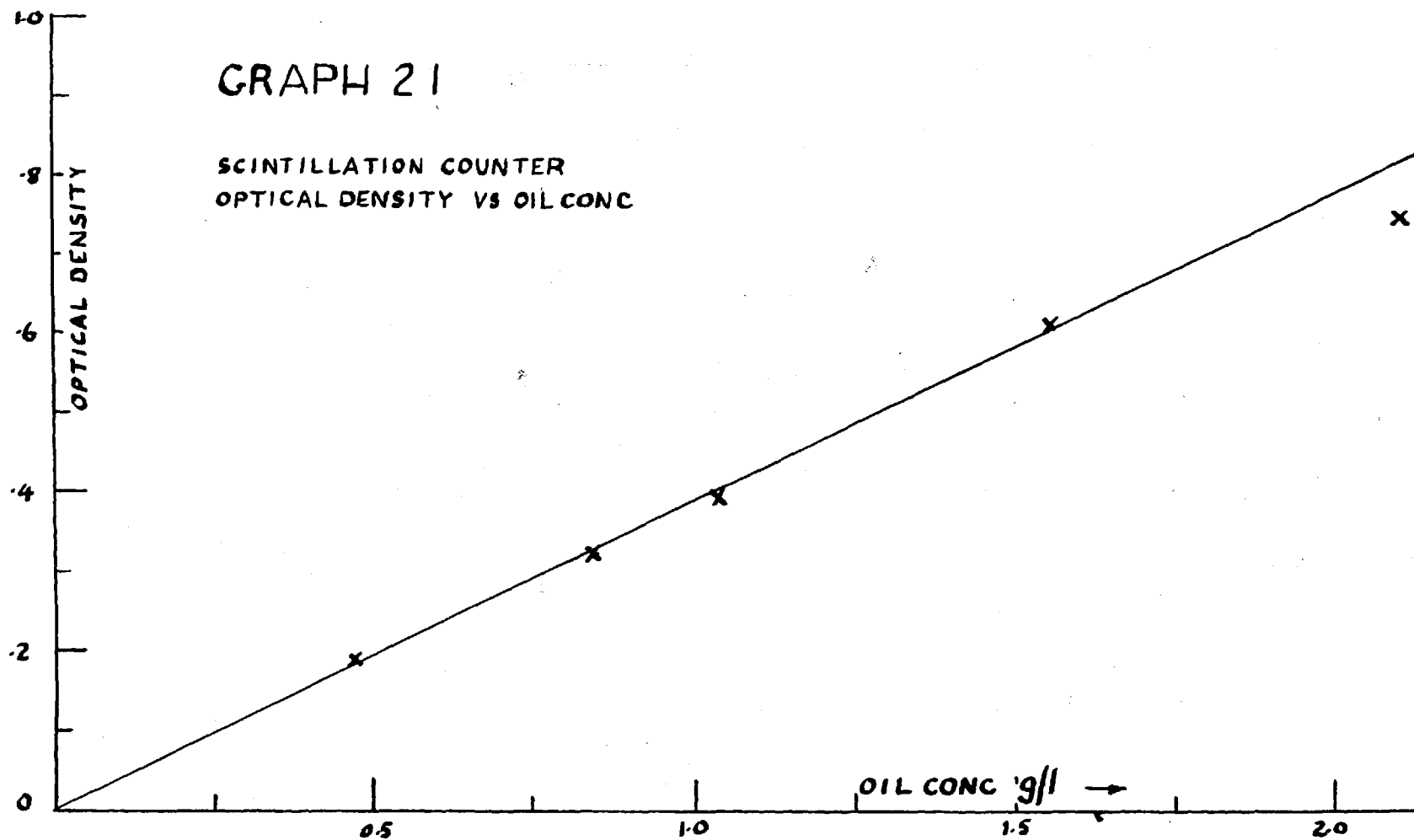
These results were interpreted by calculating the optical densities of the solutions.

The optical density is defined as the logarithm of the ratio of incident light to transmitted light.

$$\text{i.e. O.D.} = \log_{10} \frac{I_i}{I_t}$$

GRAPH 21

SCINTILLATION COUNTER
OPTICAL DENSITY VS OIL CONC



If for I_1 is substituted the count with no dye present and for I_2 is substituted the count with dyed oil present then a graph of O.D against oil concentration gives a straight line. See graph 21.

All counts from solutions containing dyed oil were corrected from the data in graph 21.

Result of Partition Co-efficient Measurements.

The partition co-efficient of dodecylamine hydrochloride between Shell Printing Ink oil No. 11 and Water is:

<u>pH</u>	<u>Conc.in oil/</u> <u>conc.in water.</u>
9.3	290 to 1
7.0	36 to 1
4.6	1.42 to 1

S E C T I O N 3.

METHODS USED IN INTERPRETATION OF RESULTS.

Section 3A.

Calculations of ξ potential.

All calculations of the ξ -potential were done with the well known streaming potential formula.

$$\xi = \frac{4\pi \eta K_c E}{D P}$$

where:

ξ	=	potential of mineral in millivolts.
η	=	Viscosity of solution in poise.
K_c	=	Conductivity of liquid in plug.- mho/cm.
E	=	Streaming potential in mV.
D	=	Dielectric constant.
P	=	Head of liquid to plug. Cm of mer- cury.

may be calculated from the expression

$$K_c = C/R$$

where:

C	=	Cell constant.
R	=	Plug resistance in solution.

C is calculated from the plug resistance in $N/10$ KCl and the specific conductivity of $N/10$ KCl solutions. A table giving the variation of the specific conductivity of $N/10$ KCl with temperature is given in appendix.

In streaming current measurements E may be replaced by $I R$ where I is the streaming current in mA and R the circuit resistance in ohms.

The value of R includes the resistance of the galvanometer and of the plug. However in this work the galvanometer resistance was 136 ohms and the lowest plug

resistance 9000 ohms so the galvanometer resistance was ignored and the final equation became:

$$\xi = \frac{4\pi n}{D} \cdot \frac{I.C.}{P} \quad \text{mV.}$$

Criticisms of the Streaming Potential Formula.

The formula for the calculation of zeta-potential from streaming current and streaming potential data is open to some criticism. The veracity of the formula is based on the assumption that the dielectric constant ~~is~~ and the viscosity of the solution in the diffuse parts of the double layer are equal to the values of these quantities in the bulk of the solution. It has not as yet been shown that this is, in fact, true. It must, therefore, not be assumed that the formulae yield essentially accurate information concerning the charges and potentials at inter-phases.

The second major ground for criticism arises from the fact that the formula assumes that the specific conductivity of the solution in the plug is the same as the specific conductivity in bulk. Many workers e.g. Smoluchowski (71) Briggs (72) Bull and Gortner (73) and Bikerman (74) have pointed out that in capillaries, and particularly in very dilute solutions the surface conductance will enter the formula. Rutgers (75) performed a series of experiments with glass capillaries. He found that in dilute solutions, up to

about 10 moles per litre, the zeta potential varied greatly with the capillary diameter. His results with KCl give a graph of the form shown in fig. 4, where ζ is the theoretical potential, and ζ^1 , ζ^2 and ζ^3 are the potentials with various capillary diameters.

The smallest capillary used by Rutgers had a diameter of about 100μ . It gave values of the zeta-potential differing from the theoretical value by about 40 mV at 4×10^{-5} mol/litre of KCl, and 160mV in 10^{-6} mol/litre KCl. To correct these errors he modified the Helmholtz-Smoluchowski streaming potential formula to include an expression for the capillary diameter. Then, by using two or more capillaries of different diameters, under similar conditions, the true zeta-potential could be calculated. Although this correction might perhaps, with certain modifications, be applied to plugs of minerals it was not found necessary to do so in this work since most of the important tests were performed at values of the pH and concentration where the correction would not be large.

The Electrical Double Layer.

The formula for zeta potential is based on the theory of the electrical double layer advanced by Stern. A very brief outline of electrical layer theory is given below.

(76)
The summary of the theory, given by Rideal is very useful.

It is accepted by most workers that the charge at the interphase between a solid and a surrounding liquid

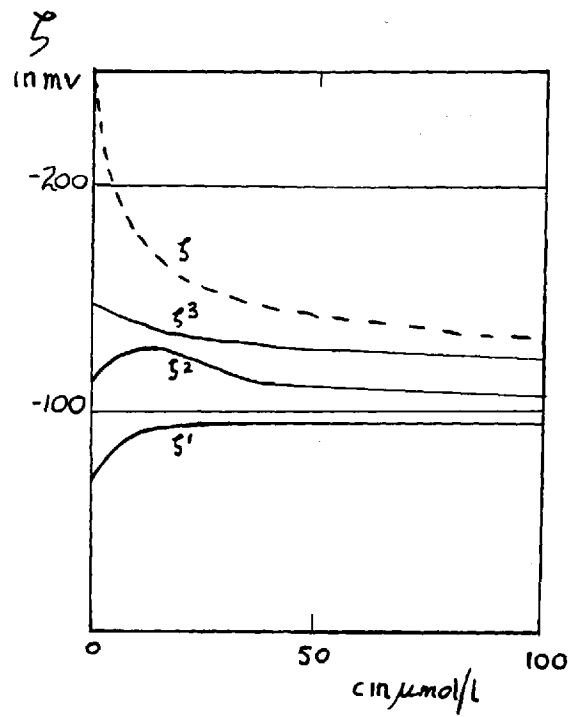


fig 4

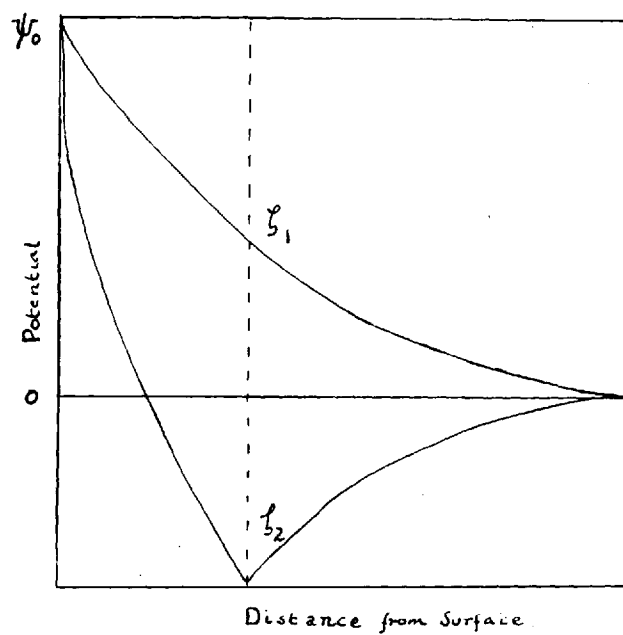


Fig 5

arises from adsorption. At the interphase there is an electrolyte held as ion pairs and one kind of ion is held more firmly than the other. The ion pair thus creates a dipole orientated with respect to the interface. Of the adsorbed ion pairs some will be dissociated, the more loosely held ion tending to drift away into solution. This surface dissociation is caused by thermal agitation and causes a charge to be imparted to the surface. The diffuse part of the ion pairs is that which gives rise to the electrokinetic phenomena.

There are three means by which the ion pairs may arise. If one phase is impermeable to ions the layer is formed by adsorption. This is known as Gouy or specific adsorption. If one of the phases is a conductor the ion pair system may be caused by the passage of electrons across the interphase. A third process of creating ion pairs is noted in those cases where one of the homogenous phases is ionogenic to form ions soluble in the other phase i.e. the boundary is selectively permeable to an ion.

Helmholtz regarded the double layer as being similar to a flat parallel plate condenser, the charge on the surface being balanced by a layer of charges of opposite sign at a certain distance from the surface. This conception of the double layer was modified by Gouy and Chapman who utilized the idea of a diffuse double layer. The solution side of the double layer was considered as being

not merely one molecule thick but extending for some distance into the solution. The potential falls exponentially with distance from the surface, the total ionic charges being equal in the bulk of the solution where the potential is zero. This conception of the double layer leads to an expression for the zeta potential which is the same as that proposed by Helmholtz.

$$\zeta = \frac{4\pi\sigma d}{D}$$

where σ is the charge on the surface and d is identifiable with $\frac{1}{K}$ the Debye-Hückel expression for the distance of the centre of moment of the ion atmosphere round a single ion in solution. This is defined by Glasstone⁽⁸⁷⁾

$$\text{as } \frac{1}{K} = \left(\frac{D T 1000 k}{\sum C_i Z_i^2 4\pi e^2 N} \right)^{\frac{1}{2}}$$

where k is 1.38×10^{-16} E is 4.802×10^{-2} , N is Avogadro's number 6.025×10^{23} . D is the dielectric constant, T the absolute temperature, C_i is the concentration of ions of the i the kind expressed in gm ions per litre and Z_i is the valency of these ions.

The Gouy-Chapman model did not take into account the size of the adsorbed ions in the double layer, so it was modified by Stern who proposed a model which combines the essential characteristics of the Helmholtz and Gouy-Chapman theories. According to Stern the distribution of counter ions in solution may be divided into two parts one of which is approximately one molecule thick and

remains fixed to the solid surface, the other being a diffuse layer which extends for some distance into the solution. The variation of potential with distance would then be as shown in fig. 5. In fig. 5 ψ_0 is the Nernst or surface potential created by the original adsorption. ψ_d is the potential at the layer dividing the mobile part of the double layer from the fixed part i.e. the potential at the Stern layer. The size of the Stern layer is greatly exaggerated in the diagram. The Stern potential is believed to be the zeta-potential which is measured in electrokinetic experiments. This potential can be altered by an alteration of the ionic concentrations of the solutions. If a neutral salt, i.e. one in which neither ion is specifically adsorbed at the interface is added to the solution the double layer is compressed and the potential at the Stern layer is reduced. No change occurs in the Nernst potential. This latter potential can be altered by a variation in the concentrations of the potential determining ions in the solution, or by the adsorption of long chain surface active organic electrolytes which have a high specific adsorption potential.

Section 3B.

THE ELECTROPHORESIS FORMULAE.

The electrophoresis measurements were plotted in the form of a graph of droplet velocity vs. vertical distance from the top of the tube. In accordance with the theory of electrophoresis measurement see (79) these curves were parabolic. This parabola is caused by the electrokinetic motion of the liquid carrying the droplets in relation to the charge on the walls of the capillary tube. The liquid motion is zero at two levels in the tube, given by Laurence S. Moyer (78) as being 0.146 of the tube width from either end of the curve. The values at these points were found from the curves obtained by measurement, and were used for the calculation of zeta potential. The formula used in the calculations was the Smoluchowski formula:

$$\zeta = \frac{4 \pi \eta \mu}{D} \times 9 \times 10^4$$

where zeta is the zeta potential in volts, η is the viscosity of the liquid and was obtained from tables given in the Chemical Engineers Handbook (79), μ is the electrical mobility of the droplets, expressed in cm/sec/volt/cm. D is the dielectric constant of the liquid. The values of D used in these experiments were obtained from curves drawn by Lotzky and Davis (80) for uni-univalent electrolytes. The salt used for varying the solution concentrations in these tests was sodium perchlorate. Although

Lattcy and Davis did not measure these values for sodium perchlorate they state that the values are the same for all uni-univalent electrolytes.

Corrections to the Electrophoresis Formula.

The assumptions in the Smoluchowski formula are stated by Henry to be as follows:

1. That the usual hydrodynamic equations for the motion of a viscous fluid may be assumed to hold both in the bulk of the liquid and within the double layer.

2. That the motion is stream-line motion and slow enough for inertia terms in the hydrodynamic equation to be neglected.

3. That the applied field may be taken as simply superimposed on the field due to the electrical double-layer.

4. That the thickness of the double-layer (ie the distance normal to the interface over which the potential differs appreciably from the bulk of the liquid) is small compared with the radius of the particle.

Henry stated that the first two assumptions are probably valid. The third can be taken as a good approximation in the absence of any better formula and that the fourth is valid if the particles are neither too small nor too irregular in shape. In cases where the double-layer is very large it is necessary to apply a correction factor. This can be taken from fig. 6 which

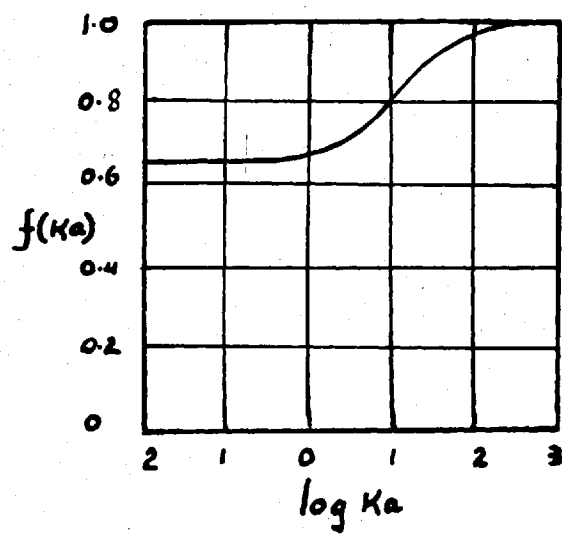


Fig 6

is taken from his paper. It is applied to the Smoluchowski formula in the following manner:

$$f = \frac{4\pi\eta\mu}{D} \times \frac{1}{f(\kappa\alpha)}$$

where κ is the inverse of the Debye-Huckel function $1/\kappa$ which gives a measure of the thickness of the double layer see section 31. α is the particle radius. $f(\kappa\alpha)$ varies between 0.66 and 1.

Table 19, from Henry, gives values of κ and $1/\kappa$ for various concentrations of electrolyte. The final column in the table gives a measure of the minimum size in microns for which the Smoluchowski equation can be used and the minimum size for which the Debye-Huckel equation can be used. Between these limits the correction factor must be taken from the graph.

TABLE 19.

Electrolyte	Concentration	κ 20° cm-1	$1/\kappa$	Diameters	
	$\times N$			(s)	(H)
Pure Water	-	1.0×10^4	1.0	600	1.0
Uni-univalent	10^{-5}	1.0×10^5	0.1	60	0.1
	10^{-3}	1.0×10^6	0.01	6.0	0.01
	10^{-1}	1.0×10^7	0.001	0.6	0.001
	10^{-5}	1.8×10^5	0.056	34	0.056
Uni-Bivalent	10^{-1}	1.8×10^7	0.00056	0.34	0.00056
	10^{-5}	2.1×10^5	0.048	29	0.048
Bi-Bivalent	10^{-1}	2.1×10^7	0.00048	0.29	0.00048

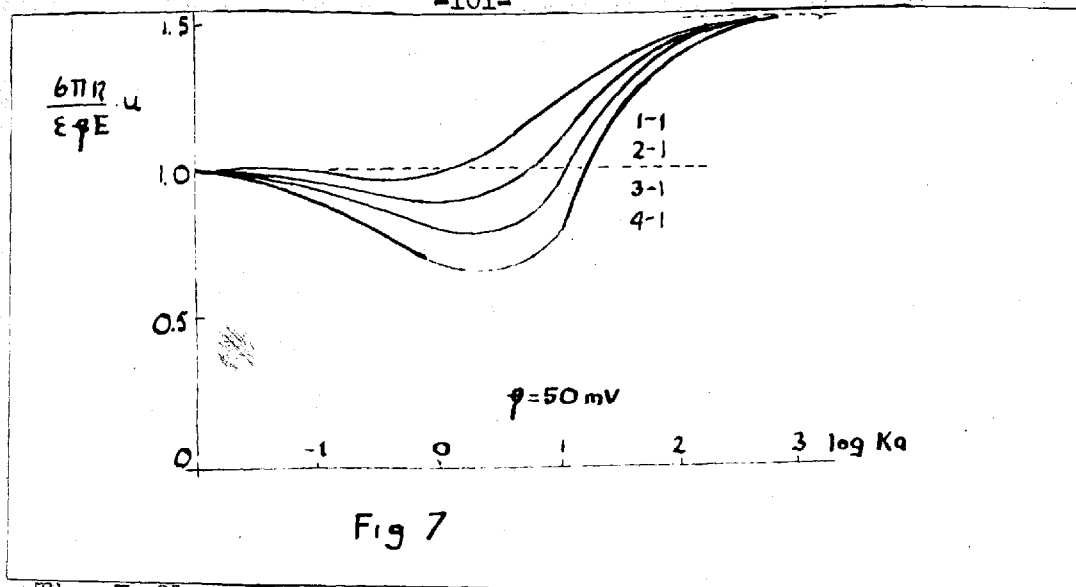


Fig 7

The Influence of Relaxation.

Overbeek has modified Henry's electrophoresis equation to allow for the relaxation effect. This effect is well described by Schenkcl.⁽⁵⁹⁾ It is caused by deformation of the double layer during movement under the influence of an external electric field. If the particle is negatively charged it will move towards the anode. The double layer, which consists mainly of positive ions, will move towards the cathode. It is thus deformed. On one side the particle seems to move out of the double layer, but since this can not happen it is constantly being built up. This building up takes a certain amount of time known as the relaxation time. The relaxation time gives rise to a force which tends to slow down the particles. Overbeek applied the treatments of Debye, Hückell, and Onsager for the relaxation effects and made certain equations available both for symmetrical and non-symmetrical electrolytes. The equations were calculated for

values of β of the order of 25 mV. However they have been shown to be valid at higher potentials.

The conclusions drawn for the applicability of Overbeck's equations are as follows:

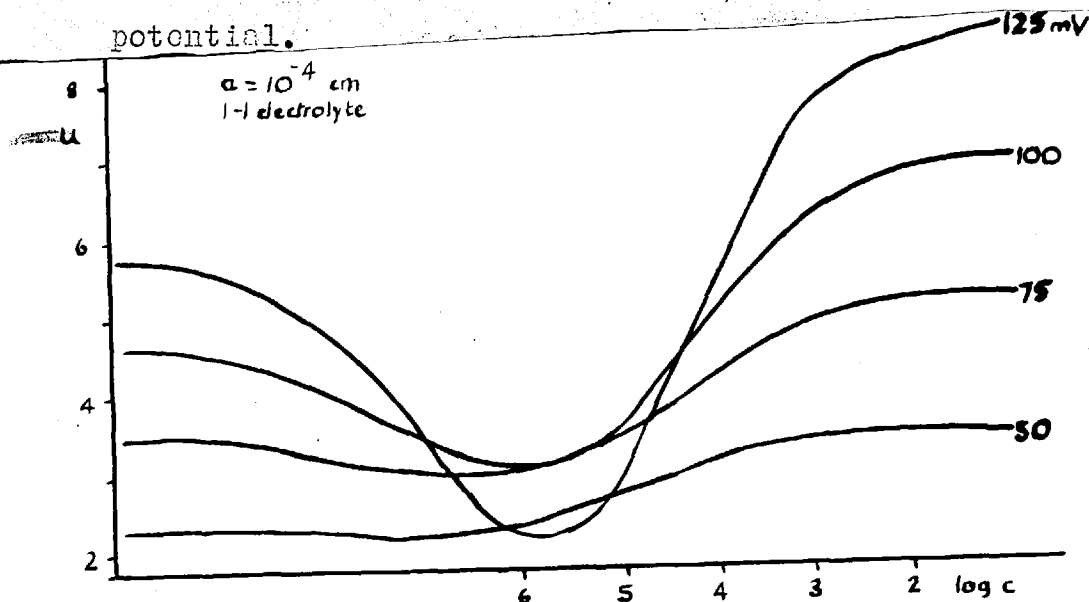
1. The relaxation correction is small for values of β less than 25 mV.

2. The relaxation correction is important for K_{∞} 's of the order of approximately 0.1 to 10.

3. For symmetrical electrolytes the valency of the counter-ion solely appears in the equation.

4. For non-symmetrical electrolytes the difference of the valency of the two ions of an electrolyte can make either a positive or negative contribution depending on the ion with the highest valency.

Fig. 7, taken from Schenkel, shows the influence of the relaxation effect as well as the importance of the ions in the bulk solution on the mobility for a constant potential.



In fig. 8, the variation of mobility with increasing potential is demonstrated.

Figs. 7 and 8 are drawn according to Overbeck's equation.

At about 50 mV. with uni-univalent electrolytes the curve for variation of mobility with particle size follows Henry's curve for the variation of mobility with $\log.Ka$. At higher values of potential the curves differ to some extent. Thus at 75 mV. the mobility in dilute solutions is even lower than Henry's curve would suggest. Particle size is not very important at lower potentials but at higher potentials it tends to push the conditions for the same mobilities to lower electrolyte concentrations.

The greatest deviations from Henry's curve in a uni-univalent electrolyte for 1μ particles occur between

10^{-6} and 10^{-4} moles/litre being greatest at about 10^{-5} . The droplets studied in the electrophoresis were about 3μ diameter. The effect of this difference in size would be to change the region of maximum effect to 10^{-7} and 10^{-6} g.mols/litre with some effect at 10^{-5} .

All tests in sodium perchlorate solutions gave potentials in the region of 80 mV. It may be estimated from the relaxation data that a factor of about 10% should be added to the values measured in the region of 10^{-5} g.moles/l. No correction will be required above 10^{-4} g.moles/l. These corrections should be added to the values found after Henry's correction has been applied. The droplets studied in the dodecylamine hydrochloride tests were about 6μ and the solutions 10^{-4} normal. The relaxation effect therefore reduced all values above about 50mV. by around 7 to 10%.

Variations of Applied Potential with Salt Concentration.

Lewis (82) has found that in the electrophoresis tube used in this work the potential applied to the cell is dependent on salt concentration. By taking measurements of applied potential, current, and resistance, he found that the system did not obey Ohm's law. The variation of potential with salt concentration was found to be as given in Table 20. The first column gives values of the salt concentration and the second column gives the potential at those values as a percentage of the true

applied potential, which was 54 volts.

TABLE 20.

<u>Salt Concentration x N.</u>	<u>% of Applied Potential</u>
1.0 x 10 ⁻⁵	47.4
2 x 10 ⁻⁵	50.7
6.67 x 10 ⁻⁵	58.7
2 x 10 ⁻⁴	65.3
1 x 10 ⁻³	78.2
3.33 x 10 ⁻³	83.8
1 x 10 ⁻²	93.1

A curve was drawn of salt concentration vs. potential and all electrophoresis results were corrected in accordance with the curve.

Section 3C.

INTERACTION OF CHARGED PARTICLES IN SOLUTION:

The forces of interaction between charged particles in solution have been studied by B.V. Derjaguin⁽⁸³⁾ in Russia and by Verwey and Overbeek⁽⁸⁴⁾ in Holland. A useful summary of the theory of interaction of similar charged particles has been given by Schenkel⁽⁵⁹⁾. Derjaguin extended the theory to cover the case of particles with dissimilar charges. The theoretical basis for Derjaguin's final deductions is given in a series of papers published between 1937 and 1941. Criteria were established, in these papers, for the adhesion of particles and the coagulation of hydrophobic sols and suspensions both weakly and strongly charged.

The following description is taken from "Hetero coagulation of dissimilar particles".

"Let us first consider a plane-parallel layer of thickness h formed by a solution of binary electrolyte between the surfaces of plates 1 and 2 charged to potentials ψ_1 , and $\psi_2 > \psi_1$, respectively. We shall assume that the potential in the electrolyte solutions obeys the equation:

$$\frac{d^2\psi}{dz^2} = \frac{a}{2} \exp(z, b\psi) - \exp(-z, b\psi) \quad (1)$$

where $b = e/kT = F/RT$, e is the electron charge, F is the Faraday, K is the Boltzmann constant, T is the

absolute temperature, z_1 and z_2 are the valencies of the cation and anion respectively:

$$a = (8\pi l/D) eNC = (8\pi l/D) e z_1 n_1 N y = (8\pi l/D) e z_2 n_2 N y$$

D is the dielectric constant, N is the Avogadro number, C is the concentration in gm. equiv/cm³, y is the concentration in moles cm⁻³, n_1 and n_2 are the number of anions and that of cations, respectively in a molecule of the electrolyte.

On introducing the parameter $\beta = z_2/z_1$ and the dimensionless variables,

$$\phi = z_1 b \psi \quad X = x/d \quad = kx.$$

$$\text{where } k = 1/d = \sqrt{a b z_1}$$

equation (1) reduces to:

$$d^2\phi/dX^2 = \frac{1}{2} (\exp(\phi) - \exp(-\beta\phi)) \quad (2)$$

On integrating eqn (2) we obtain:

$$(d\phi/dX)^2 = \exp \phi - (1/\beta) \exp(-\beta\phi) - C \quad (3)$$

where the value of C must be so chosen as to make the difference $X_1 - X_2$ for which $\phi = -\phi_1 = z_1 b \psi_1$ and $\phi = z_1 b \psi_2$ respectively, be equal to $H = h/d$.

The repulsion between the plates has earlier been shown to be equal to:

$$P = \frac{kTNC}{z_1} \quad (4)$$

$$\text{where } W = C - 1 - (1/\beta) \quad (5)$$

To build up a complete picture of the variation of repulsive force with distance between particles it is

necessary to obtain in graphical form W vs. H i.e. repulsion vs. distance. It is very difficult to do this directly so Derjaguin suggested the adoption of the reverse process viz. determining H as a function of W for various values of ϕ_1 and ϕ_2 and the parameter β .

For this purpose a series of integral curves $\phi = \phi(X, C)$ were plotted according to equation (3) for various values of C , and hence of W , and passing through the point $X = 0, \phi = \infty$ i.e. having the ϕ axis as an asymptote.

There are three major types of isodynamic curves, as these curves are called:

1) Where $W < 0$ $d\phi/dX$ differs from zero for any values of ϕ and the integral of equation (3) may be expressed in the form:

$$X = \int_{\phi}^{\infty} \frac{d\phi}{\sqrt{\exp \phi + \frac{1}{\beta} \exp(-\beta \phi) - 1 - \frac{1}{\beta} - W}} \quad (6)$$

2) When $W = 0$ the integral curve has the axis of abscissae as an asymptote.

3) When $W > 0$ each curve has a minimum with an ordinate of $\phi = \phi_0$ defined by the equation.

$$\exp \phi_0 + \left(\frac{1}{\beta}\right) \exp(-\beta \phi_0) = C = 1 + \left(\frac{1}{\beta}\right) + W \quad (7)$$

which has one positive root.

The abscissa for the minimum is given by

$$X_m = \int_{\phi_0}^{\infty} \frac{d\phi}{\sqrt{\exp(\phi) + \frac{1}{\beta} \exp(-\beta \phi) - \exp(\phi_0) - \frac{1}{\beta} \exp(-\beta \phi_0)}} \quad (8)$$

For $X \leq X_m$ the integral of equation (3) is also expressed by equation (6).

$$\text{For } X > X_m$$

$$X' = 2X_m - \int_{\phi}^{\infty} \frac{d\phi}{\sqrt{\exp(\phi) - (1/\beta)\exp(-\beta\phi) - 1 - (1/\beta) - W}}$$

The intersections of one of the isodynamic curves which corresponds to a definite value of $W = \text{const.}$ with two straight lines parallel to the axis of abscissae drawn at the heights $\phi = \phi_1$ and $\phi = \phi_2$ gives the possible abscissae of the respective surfaces X_1 and X_2 whose difference equals H .

For $W < 0$ each straight line crosses the isodynamic curves in one place. This corresponds to attraction at all values of H . At $W = 0$ there is absence of interaction. For $W > 0$ repulsion occurs instead of attraction. In this case each straight line $\phi = \text{const.} > \phi_0$ crosses the isodynamic curve twice. Thus there is more than one possible distance of separation of the particles which will give a certain repulsion.

A maximum repulsion for a given value of ϕ , occurs when the straight line $\phi = \phi_1$ is a tangent to the isodynamic curve W_m and hence when:

$$W = W_m = \exp(\phi_1) + (1/\beta)\exp(-\beta\phi_1) - 1 - 1/\beta$$

When $W > W_m$ the straight line $\phi = \phi_1$ will fail to intersect the isodynamic curve so that such values of W cannot occur.

The isodynamic curves have been drawn and are given in graph 22.

The Isodynamic Curves:

The equation for the isodynamic curves:

$$X = \int_0^{\infty} \frac{d\phi}{\sqrt{\exp \phi - 1/\beta \exp(-\beta \phi) - C}}$$

was integrated numerically by Simpson's rule.

Simpson's Rule states that the area $y = f(x)$ between two ordinates y_1 and y_3 , at a distance of $2h$ apart is nearly $\frac{1}{3} (y_1 + 4y_2 + y_3)$ where y_2 is the mid-ordinate.

The rule may be extended to a large odd number of ordinates and can then be stated:

$$\int_a^b f(x) dx \approx \frac{1}{3} h [y_1 + y_{2n+1} + 4(y_2 + y_4 + \dots + y_{2n}) + 2(y_3 + y_5 + \dots + y_{2n-1})]$$

where y_1 and y_{2n+1} are the end ordinates at a and b respectively,

$$\text{and } h = \frac{b - a}{2n}$$

The proportional error in the integral is of the order of h^4 and thus decreases very rapidly with h . The accuracy of the integral therefore increases very much with an increase in n . To estimate the accuracy of the integration at any interval difference tables can be drawn up. If the third differences are more or less constant then the curve approximates to a parabola and Simpson's Rule may be applied.

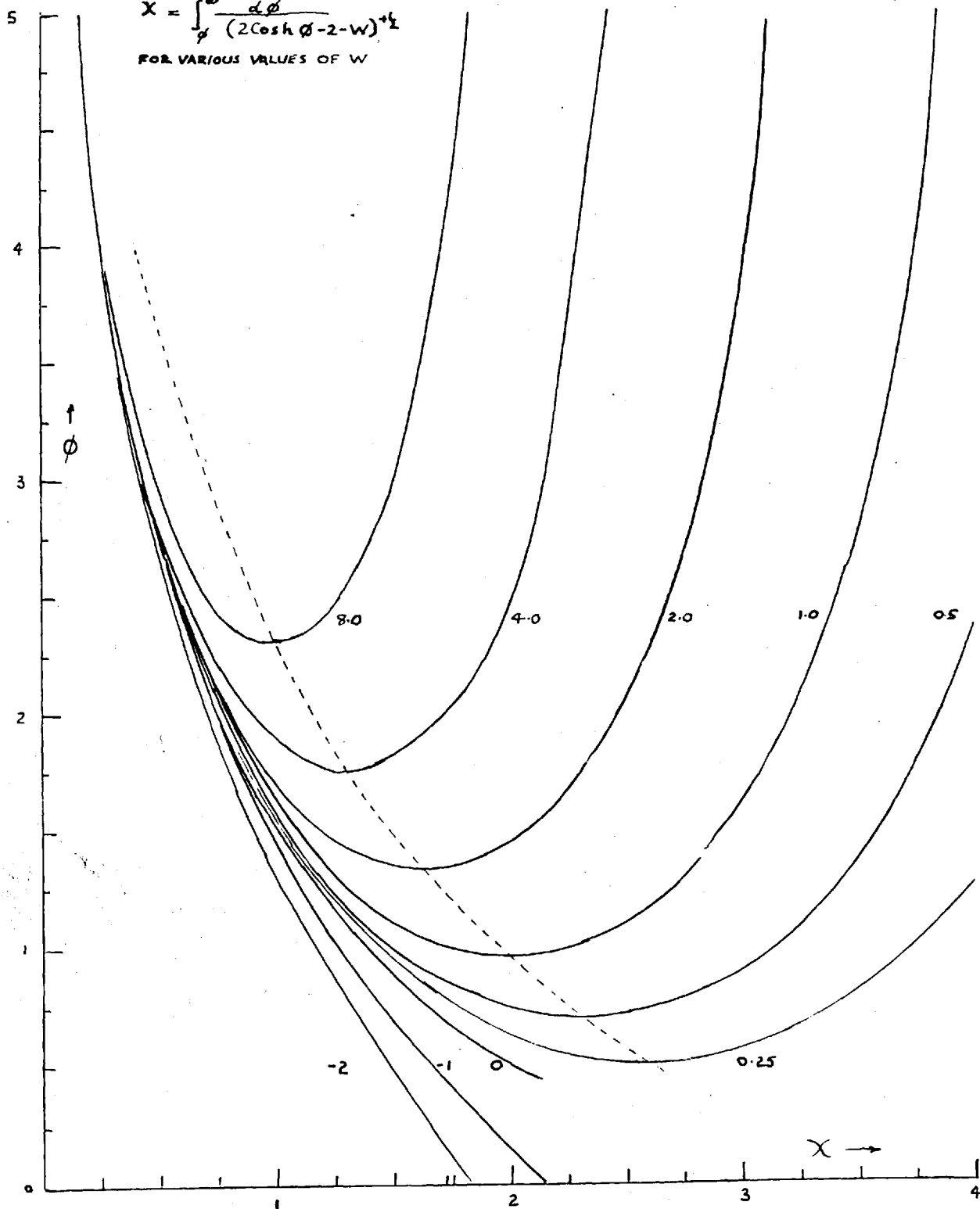
Curves were plotted of X vs. ϕ for 9 values of W .

GRAPH 22

ISO DYNAMIC CURVES

$$X = \int_{\phi}^{\infty} \frac{d\phi}{(2\cosh\phi - 2 - W)^{1/2}}$$

FOR VARIOUS VALUES OF W



It was impossible to integrate numerically to ∞ . At $\phi = 10$ the value of the integral becomes very small. This was therefore taken as the upper limit.

For each value of W a table was drawn up giving values of ϕ , $\cosh \phi$ and $1/\sqrt{(2 \cosh \phi - C)}$. The figures in the last column were then plotted against ϕ . It was found that in the case of $W \geq 0$ the curves did not cross the axis of abscissae and hence could not be integrated to the minimum value of ϕ . To find the integral at this point equation (8) was used. This can be expressed as

$$W_m = \int_{\phi_0}^{\infty} \frac{d\phi}{\sqrt{2 \cosh \phi - 2 \cosh \phi_0}}$$

This equation has been integrated by Verwey and Overbeek and gives an elliptical function which may be solved from tables. The appropriate table is given in Table IX "Theory of the Stability of Lyophobic Colloids" (84). In this table z may be taken as 10, U as ϕ_0 and y as ϕ . Then X is the same as $-X_d$. A curve was drawn from table IX and the minimum readings taken by interpolation. This curve is also plotted in graph 22.

The figures employed in drawing the curves are given after this section to save other workers the large amount of time necessary for their calculation. The isodynamic curves are shown in graph 22.

In all calculations the values of H and X are based

on Derjaguin's definition of H , i.e. half the distance between the plates, hence for calculation of the energy barrier the values of H in graph 22 must be doubled.

The values of ϕ , $\cosh \phi$ and $\frac{1}{\sqrt{2 \cosh \phi - 2 - W}}$ used for the calculation of the isodynamic curves are given below.

TABLE 21a

$W = -2$

ϕ	$\cosh \phi$	$\frac{1}{\sqrt{2 \cosh \phi - 2 - W}}$	ϕ	$\cosh \phi$	$\frac{1}{\sqrt{2 \cosh \phi - 2 - W}}$
0.0	1.00100	0.70711	3.6	18.31278	0.16524
0.1	1.00500	0.70534	3.8	22.36178	0.14953
0.2	1.02007	0.70012	4.0	27.30823	0.13531
0.4	1.08107	0.68008	4.2	33.3507	0.12244
0.6	1.18547	0.64944	4.4	40.7316	0.11079
0.8	1.33744	0.61143	4.6	49.7472	0.10025
1.0	1.54308	0.56923	4.8	60.7593	0.09068
1.2	1.81066	0.52549	5.0	74.2099	0.08208
1.4	2.15090	0.48214	5.5	122.3480	0.06393
1.6	2.57746	0.44044	6.0	201.7156	0.04979
1.8	3.10747	0.40113	6.5	332.571	0.03877
2.0	3.76220	0.36456	7.0	548.317	0.03020
2.2	4.56791	0.33085	7.5	904.021	0.02352
2.4	5.55695	0.29996	8.0	1490.479	0.01832
2.6	6.76901	0.27178	8.5	2457.385	0.01426
2.8	8.25273	0.24614	9.0	4051.54	0.01111
3.0	10.06766	0.22285	9.5	6679.87	0.00865
3.2	12.28665	0.20173	10.0	11013.24	0.00674
3.4	14.99874	0.18258			

All values of $\cosh \phi$ taken from: Comrie ⁽⁸⁵⁾

All values of square roots from: P. Barlow ⁽⁸⁶⁾

W = -1

TABLE 21b

ϕ	Cosh ϕ	$(2\text{Cosh}\phi - C)^{-1/2}$	ϕ	Cosh ϕ	$(2\text{Cosh}\phi - C)^{-1/2}$
0.0	1.00000	1.00000	3.2	12.28665	0.20596
0.1	1.00500	0.99503	3.4	14.99874	0.18570
0.2	1.02007	0.98052	3.6	18.31278	0.16754
0.3	1.04534	0.95752	3.8	22.36178	0.15123
0.4	1.08107	0.92764	4.0	27.30823	0.13657
0.5	1.12763	0.89255	4.2	33.3507	0.12337
0.6	1.18547	0.85407	4.4	40.7316	0.11148
0.7	1.25517	0.81370	4.6	49.7472	0.10076
0.8	1.33744	0.77269	4.8	60.7593	0.09109
0.9	1.43309	0.73202	5.0	74.2099	0.08236
1.0	1.54308	0.69274	5.5	122.3480	0.06406
1.2	1.81066	0.61765	6.0	201.7156	0.04985
1.4	2.15090	0.55033	6.5	332.571	0.03880
1.6	2.57746	0.49059	7.0	548.317	0.03021
1.8	3.10747	0.43790	7.5	904.021	0.02352
2.0	3.76220	0.39150	8.0	1490.479	0.01832
2.2	4.56791	0.35059	8.5	2457.385	0.01427
2.4	5.55695	0.31444	9.0	4051.54	0.01111
2.6	6.76901	0.28241	9.5	6679.87	0.00865
2.8	8.25273	0.25396	10.0	11013.24	0.00674
3.0	10.06766	0.22860			

W = 0

TABLE 21c

ϕ	Cosh ϕ	$(2\text{Cosh}\phi - C)^{-1/2}$	ϕ	Cosh ϕ	$(2\text{Cosh}\phi - C)^{-1/2}$
0.55	1.15510	1.7960	2.7	7.47347	0.27792
0.60	1.18546	1.6420	2.8	8.25273	0.26256
0.65	1.21879	1.5117	2.9	9.11458	0.24823
0.70	1.25516	1.3998	3.0	10.06766	0.23479
0.75	1.29468	1.3026	3.1	11.12150	0.22225
0.80	1.33743	1.2173	3.3	13.57476	0.19941
0.85	1.38353	1.1418	3.5	16.57282	0.17918
0.90	1.43308	1.0745	3.7	20.23601	0.16123
0.95	1.48633	1.0141	3.9	24.71135	0.14521
1.0	1.54308	0.95950	4.1	30.1784	0.13090
1.05	1.60379	0.91000	4.3	36.8567	0.11809
1.1	1.66851	0.86484	4.5	45.0141	0.10658
1.2	1.81066	0.78536	4.7	54.9781	0.09625
1.3	1.97091	0.71762	4.9	67.1486	0.08694
1.4	2.15090	0.65913	5.1	82.0140	0.07856
1.5	2.35241	0.60804	5.3	100.1709	0.07101
1.6	2.57746	0.56300	5.5	122.348	0.06419
1.7	2.82832	0.52295	6.0	201.7156	0.04991
1.8	3.10743	0.48709	6.5	332.571	0.03883
1.9	3.41773	0.45476	7.0	548.317	0.03022
2.0	3.76220	0.42547	7.5	904.021	0.02353
2.1	4.14431	0.39877	8.0	1490.48	0.01832
2.2	4.56790	0.37435	8.5	2457.385	0.01427
2.3	5.03722	0.35192	9.0	4051.54	0.01111
2.4	5.55695	0.33125	9.5	6679.87	0.00865
2.5	6.13229	0.31213	10.0	11013.14	0.00674
2.6	6.76901	0.29440			

W = +0.25

TABLE 21d

ϕ	Cosh ϕ	$(2\text{Cosh}\phi - C)^{-1/2}$	ϕ	Cosh ϕ	$(2\text{Cosh}\phi - C)^{-1/2}$
0.53	1.14377	5.16129	1.8	3.10747	0.50220
0.535	1.14656	4.81579	1.9	3.41773	0.46699
0.54	1.14938	4.52857	2.0	3.76220	0.43542
0.545	1.15223	4.28504	2.2	4.56791	0.38109
0.55	1.15510	4.07564	2.4	5.55695	0.33588
0.555	1.15801	3.89196	2.6	6.76901	0.29764
0.56	1.16094	3.72995	2.8	8.25273	0.26485
0.57	1.16690	3.45447	3.0	10.06766	0.23646
0.58	1.17297	3.22851	3.2	12.28665	0.21165
0.59	1.17916	3.03841	3.4	14.99874	0.18984
0.60	1.18547	2.87563	3.6	18.31278	0.17056
0.65	1.21879	2.30888	3.8	22.36178	0.15344
0.70	1.25517	1.95990	4.0	27.30823	0.13819
0.75	1.29468	1.71659	4.5	45.0141	0.10674
0.80	1.33744	1.53417	5.0	74.2099	0.08271
0.85	1.38353	1.39068	5.5	122.3480	0.06422
0.90	1.43309	1.27393	6.0	201.7156	0.04993
0.95	1.48623	1.17651	6.5	332.571	0.03884
1.0	1.54308	1.09359	7.0	548.317	0.03023
1.1	1.66852	0.95913	7.5	904.021	0.02354
1.2	1.81066	0.85395	8.0	1490.479	0.01832
1.3	1.97091	0.76882	8.5	2457.385	0.01427
1.4	2.15090	0.69812	9.0	4051.51	0.01111
1.5	2.35241	0.63825	9.5	6679.87	0.00865
1.6	2.57746	0.58672	10.0	11013.24	0.00673
1.7	2.82832	0.54180			

W = 0.5

TABLE 21e

ϕ	Cosh ϕ	$\frac{1}{2\text{Cosh}\phi-2.5}$	ϕ	Cosh ϕ	$(2\text{Cosh}\phi-2.5)^{-1/2}$
0.78	1.31994	2.74718	1.350	2.0583	0.78647
0.79	1.32862	2.52188	1.357	2.1040	0.76517
0.80	1.33744	2.39137	1.400	2.1509	0.74499
0.81	1.34638	2.27759	1.425	2.1992	0.72579
0.82	1.35547	2.17737	1.450	2.2488	0.70741
0.83	1.36468	2.08799	1.5	2.3524	0.67345
0.84	1.37404	2.00771	1.55	2.4619	0.64230
0.85	1.38353	1.93506	1.6	2.5775	0.61372
0.86	1.39316	1.86884	1.65	2.6995	0.58734
0.87	1.40293	1.80815	1.7	2.8283	0.56281
0.88	1.41284	1.75230	1.75	2.9642	0.53999
0.89	1.42289	1.70065	1.8	3.1075	0.51883
0.90	1.43309	1.65256	1.85	3.2586	0.49893
0.91	1.4434	1.60852	1.9	3.4177	0.48026
0.92	1.4539	1.56595	1.95	3.5855	0.46271
0.93	1.4645	1.52677	2.0	3.7622	0.44613
0.94	1.4753	1.48971	2.1	4.1443	0.43365
0.95	1.4862	1.45495	2.2	4.5679	0.38971
0.96	1.4973	1.42191	2.3	5.0372	0.36468
0.97	1.5085	1.39076	2.4	5.5569	0.34072
0.98	1.5199	1.36092	2.5	6.1323	0.32001
0.99	1.5314	1.35099	2.6	6.7690	0.30191
1.00	1.5431	1.30616	2.7	7.4735	0.28345
1.025	1.5729	1.24508	2.8	8.2527	0.26722
1.05	1.6038	1.20309	2.9	9.1146	0.25214
1.075	1.6356	1.13872	3.0	10.0677	0.23813
1.100	1.6685	1.09304	3.1	11.1215	0.22506
1.125	1.7024	1.06246	3.2	12.2866	0.21285
1.150	1.7374	1.01284	3.3	13.5748	0.20142
1.175	1.7735	0.92828	3.4	14.9987	0.19441
1.200	1.8107	0.94429	3.5	16.5728	0.18064
1.225	1.8490	0.91366	3.6	18.3228	0.17118
1.25	1.8884	0.88496	3.7	20.2360	0.16228
1.275	1.9291	0.85807	3.8	22.3618	0.15389
1.300	1.9709	0.83285	3.9	24.7113	0.14599
1.325	2.0140	0.80900	4.0	27.3082	0.13852

W = +1

TABLE 21f

ϕ	Cosh ϕ	$(2\text{Cosh } \phi - C)^{-1/2}$	ϕ	Cosh ϕ	$(2\text{Cosh } \phi - C)^{-1/2}$
1.0	1.54308	3.40681	1.95	3.58548	0.48965
1.01	1.55491	3.01759	2.0	3.76220	0.47013
1.02	1.56689	2.73403	2.1	4.14431	0.43484
1.03	1.57904	2.51515	2.2	4.56791	0.40370
1.04	1.59134	2.33967	2.3	5.03722	0.37598
1.05	1.60379	2.19486	2.4	5.55695	0.35106
1.06	1.61641	2.07250	2.5	6.13229	0.32854
1.07	1.62919	1.96730	2.6	6.76901	0.30805
1.08	1.64214	1.87554	2.7	7.47347	0.28932
1.09	1.65525	1.79459	2.8	8.25273	0.27211
1.10	1.66852	1.72250	2.9	9.11458	0.25625
1.125	1.70244	1.57159	3.0	10.06766	0.24158
1.150	1.4511	1.45118	3.2	12.28665	0.21530
1.175	1.77348	1.35214	3.4	14.99874	0.19246
1.200	1.81066	1.26860	3.6	18.31278	0.17245
1.225	1.84896	1.19700	3.8	22.36178	0.15482
1.250	1.88842	1.13457	4.0	27.30823	0.13919
1.275	1.92907	1.07949	4.2	33.3507	0.12529
1.300	1.97091	1.03042	4.4	40.7316	0.11289
1.325	2.01399	0.98629	4.6	49.7472	0.10180
1.350	2.05833	0.94632	4.8	60.7593	0.09186
1.375	2.10396	0.90988	5.0	74.2099	0.08293
1.400	2.15090	0.87645	5.5	122.3480	0.06432
1.45	2.24884	0.81713	6.0	201.7156	0.04997
1.500	2.35241	0.76588	6.5	332.571	0.03886
1.55	2.46186	0.72099	7.0	548.317	0.03024
1.60	2.57746	0.68122	7.5	904.021	0.02354
1.65	2.69952	0.64563	8.0	1490.479	0.01832
1.70	2.82832	0.61353	8.5	2457.385	0.01427
1.75	2.96419	0.58437	9.0	4051.51	0.01111
1.80	3.10747	0.55772	9.5	6679.87	0.00865
1.85	3.25853	0.53323	10.0	11013.24	0.00673
1.90	3.41773	0.51061			

W = +2

TABLE 21g

ϕ	Cosh ϕ	$(2\text{Cosh}\phi - C)^{-1/2}$	ϕ	Cosh ϕ	$(2\text{Cosh}\phi - C)^{-1/2}$
1.335	2.03158	3.97900	1.8	3.10747	0.67192
1.3375	2.03600	3.72675	1.85	3.25853	0.63031
1.3400	2.04045	3.51605	1.9	3.41775	0.59386
1.3425	2.04490	3.33700	1.95	3.58548	0.56157
1.3450	2.04936	3.18268	2.0	3.76220	0.53267
1.3475	2.05384	3.04739	2.1	4.14431	0.48288
1.3500	2.05833	2.92774	2.2	4.56791	0.44126
1.3525	2.06284	2.82079	2.3	5.03722	0.40574
1.3550	2.06735	2.72472	2.4	5.55695	0.37493
1.3575	2.07188	2.63741	2.5	6.13229	0.34783
1.3600	2.07643	2.55774	2.6	6.76901	0.33548
1.365	2.08555	2.41756	2.7	7.47347	0.30225
1.37	2.09473	2.29742	2.8	8.25273	0.28278
1.375	2.10396	2.19308	2.9	9.11458	0.26510
1.38	2.11324	2.10128	3.0	10.06766	0.24895
1.385	2.12258	2.01963	3.2	12.28670	0.22047
1.390	2.13196	1.94655	3.4	14.99870	0.19613
1.395	2.14140	1.88040	3.6	18.31280	0.17507
1.40	2.15090	1.82030	3.8	22.36180	0.15670
1.41	2.17005	1.71473	4.0	27.30820	0.14056
1.42	2.18941	1.62474	4.2	33.3507	0.12629
1.43	2.20900	1.54672	4.4	40.7316	0.11362
1.44	2.22881	1.47824	4.6	49.7472	0.10233
1.45	2.24884	1.41751	4.8	60.7593	0.09225
1.46	2.26910	1.36310	5.0	74.2099	0.08321
1.47	2.28958	1.31401	5.5	122.3480	0.06446
1.48	2.31029	1.26942	6.0	201.7156	0.05004
1.49	2.33123	1.22862	6.5	332.571	0.03889
1.50	2.35241	1.19113	7.0	548.317	0.03025
1.525	2.40638	1.10923	7.5	904.021	0.02354
1.55	2.46186	1.04047	8.0	1490.479	0.01833
1.575	2.51888	0.98164	8.5	2459.885	0.01426
1.6	2.57746	0.93052	9.0	4051.54	0.01111
1.65	2.69952	0.84544	9.5	6679.87	0.00865
1.7	2.82832	0.77693	10.0	11013.24	0.00674
1.75	2.96419	0.72012			

W = +4

TABLE 21h

ϕ	Cosh ϕ	$(2\text{Cosh}\phi - 2 - W)^{-1/2} \phi$	ϕ	Cosh ϕ	$(2\text{Cosh}\phi - 2 - W)^{-1/2}$
1.9	3.41773	1.09404	3.6	18.3128	0.18070
1.925	3.50051	0.99950	3.8	22.3619	0.16070
1.95	3.58548	0.92412	4.0	27.3082	0.14342
1.975	3.67269	0.86214	4.2	33.3507	0.12835
2.00	3.76220	0.80993	4.4	40.7316	0.11512
2.05	3.94832	0.72612	4.6	49.7472	0.10342
2.1	4.14431	0.66102	4.8	60.7593	0.09304
2.15	4.35067	0.60843	5.0	74.2099	0.08379
2.2	4.56791	0.56471	5.5	122.3480	0.06445
2.3	5.03722	0.49541	6.0	201.7156	0.05016
2.4	5.55695	0.44221	6.5	332.571	0.03895
2.5	6.13229	0.39953	7.0	548.317	0.03028
2.6	6.76901	0.36423	7.5	904.021	0.02356
2.7	7.47347	0.33432	8.0	1490.479	0.01833
2.8	8.25273	0.30853	8.5	2457.385	0.01427
2.9	9.11458	0.28596	9.0	4051.54	0.01111
3.0	10.06766	0.26598	9.5	6679.87	0.00865
3.2	12.28665	0.23204	10.0	11013.24	0.00674
3.4	14.9987	0.20414			

W = +8

TABLE 21j

ϕ	Cosh ϕ	$(2\text{Cosh}\phi - C)^{-1/2} \phi$	ϕ	Cosh ϕ	$(2\text{Cosh}\phi - C)^{-1/2}$
2.4	5.55695	0.94750	4.4	40.7316	0.11829
2.45	5.83732	0.77275	4.6	49.7472	0.10571
2.5	6.13229	0.66452	4.8	60.7593	0.09469
2.55	6.44259	0.58873	5.0	74.2099	0.08500
2.6	6.76901	0.53164	5.5	122.3480	0.06527
2.70	7.47347	0.44961	6.0	201.7156	0.05042
2.8	8.25273	0.39207	6.5	332.571	0.03907
2.9	9.11458	0.34860	7.0	548.317	0.03034
3.0	10.06766	0.31411	7.5	904.021	0.02358
3.2	12.28665	0.26195	8.0	1490.479	0.01835
3.4	14.99874	0.22362	8.5	2457.385	0.01428
*3.8	22.36178	0.16970	9.0	4051.54	0.01112
4.0	27.30823	0.14971	9.5	6679.87	0.00865
4.2	33.3507	0.13280	10.0	11013.24	0.00674
*3.6	31.1278	0.19380			

A typical difference table is given below:-

TABLE 22

$$W = +2 \quad f(\phi) = (2 \cosh \phi - C)^{-1/2}$$

ϕ	$f(\phi)$	Δ^I	Δ^{II}	Δ^{III}
1.5	1.19113	0.15166		
1.55	1.04047	0.10995	0.04271	0.01784
1.60	0.93052	0.08508	0.02487	0.00830
1.65	0.84544	0.06851	0.01657	0.00487
1.70	0.77693	0.05681	0.01170	0.00309
1.75	0.72012	0.04820	0.00861	0.00212
1.80	0.67192	0.04161	0.00659	0.00143
1.85	0.63031	0.03645	0.00516	0.00100
1.90	0.59386	0.03229	0.00416	0.00077
1.95	0.56157	0.02890	0.00339	
2.0	0.53267			

A smaller interval is necessary below $\phi = 1.6$

The Intervals used in The Integration by Simpson's Rule were as follows:-

TABLE 23

Value of W	ϕ_2 to ϕ_1	Interval	Value of W	ϕ_2 to ϕ_1	Interval
- 2	10 to 5	0.5	+ 1	10 to 5	0.5
	5 to 0.2	0.2		5 to 3.0	0.2
	0.2 to 0.0	0.1		3.0 to 2.0	0.1
				2.0 to 1.4	0.05
- 1	10 to 5	0.5		1.4 to 1.1	0.025
	5 to 1.0	0.2			
	1.0 to 0.0	0.1	+ 2	10 to 5.0	0.5
0	9.5 to 5.5	0.5		5.0 to 3.0	0.2
	5.5 to 4.7	0.2		3.0 to 2.0	0.1
	4.7 to 3.1	0.2		2.0 to 1.6	0.05
	3.1 to 1.1	0.1		1.6 to 1.5	0.025
	1.1 to 0.5	0.05		1.5 to 1.4	0.01
				1.4 to 1.35	0.005
				1.35 to 1.335	0.0025
+ 0.25	10 to 4	0.5			
	5 to 2	0.2	+ 4.0	10 to 5.0	0.5
	2 to 1	0.1		5 to 3.0	0.2
	1 to 0.6	0.05		3 to 2.2	0.1
	0.6 to 0.56	0.01		2.2 to 0.05	0.05
	0.56 to 0.53	0.005		2.0 to 1.9	0.025
+ 0.5	10 to 4	-	+ 8.0	10 to 5.0	0.5
	4 to 2	0.1		5 to 3.0	0.2
	2 to 1.5	0.05		3 to 2.6	0.1
	1.5 to 1.00	0.025		2.6 to 2.4	0.05
	1.0 to 0.78	0.01			

The Results of the Numerical Integration are:-

TABLE 24

W	ϕ_1	X
- 2	9	0.00874
	7	0.04692
	5	0.15070
	4.2	0.23143
	3.0	0.43270
	2.2	0.65145
	1.8	0.79750
	1.4	0.97380
	1.0	1.18402
	0.6	1.42831
	0.2	1.69964
	0.0	1.84239
- 1	9.0	0.00874
	7.0	0.04693
	5.0	0.15088
	4.2	0.23204
	3.0	0.43579
	2.2	0.66363
	1.8	0.82060
	1.4	1.01730
	1.0	1.26485
	0.8	1.41129
	0.4	1.75240
	0.0	2.14237
0.0	8.5	0.01543
	7.5	0.03374
	6.5	0.06448
	5.5	0.11492
	4.7	0.17822
	3.9	0.27343
	3.1	0.41794
	2.1	0.71764
	1.7	0.90035
	1.3	1.14519
	1.1	1.30265
	0.8	1.60951
	0.5	2.07157

(Continued next page)

TABLE 24 Continued

W	ϕ_1	X	X'
+ 0.25	6.0	0.08621	5.0936
	4.0	0.25911	4.9207
	2.8	0.49154	4.6883
	2.0	0.75732	4.4235
	1.4	1.08730	4.0925
	1.0	1.43435	3.7454
	0.8	1.69175	3.4880
	0.7	1.86442	3.3154
	0.6	2.09884	3.0810
	0.56	2.22895	2.9508
	0.53	2.35907	2.8207
	0.4949	2.5899	2.5899
+ 0.5	4.0	0.25915	4.3808
	3.0	0.43926	4.2007
	2.0	0.77921	3.8608
	1.5	1.04247	3.5975
	1.3	1.19201	3.4480
	1.0	1.50201	3.7380
	0.9	1.64856	2.9914
	0.78	1.89563	2.7444
	0.69315	2.3200	2.3200
+ 1.0	8.0	0.02316	3.9874
	7.0	0.04695	3.5406
	6.0	0.08622	3.9244
	5.0	0.15125	3.8593
	3.8	0.28910	3.7215
	3.0	0.44458	3.5660
	2.0	0.78196	3.2286
	1.7	0.94278	3.0678
	1.4	1.16383	2.8468
	1.25	1.31272	2.6979
	1.1	1.51922	2.4914
	1.02	1.67895	2.3316
	0.9624	2.0053	2.0053
+ 2.0	9.0	0.00874	3.2693
	7.0	0.04694	3.2521
	5.0	0.15143	3.1266
	4.2	0.23394	3.0441
	3.0	0.44896	2.8290
	2.0	0.81037	2.4676
	1.6	0.08666	2.1913
	1.5	1.19738	2.0806
	1.4	1.34195	1.9360
	1.35	1.45444	1.8236
	1.335	1.50506	1.7729
	1.3169	1.6390	1.6390

(Continued next page)

TABLE 24 Continued

W	ϕ_1	χ	χ'
+ 4.0	5.0	0.15180	2.4316
	3.8	0.31755	2.2659
	3.0	0.45848	2.1249
	2.2	0.76253	1.8209
	2.0	0.89309	1.6903
	1.9	0.98644	1.5960
	1.763	1.2917	1.2917
+ 8.0	5.0	0.15260	1.8274
	4.2	0.23801	1.7420
	3.0	0.48170	1.4983
	2.6	0.64246	1.3385
	2.4	0.78169	1.1983
	2.2922	0.990	0.990

The abscissal of the minima are as follows:

$$\text{from } \chi_m = \int_{\phi_0}^{\infty} \frac{d\phi}{\sqrt{2 \cosh \phi - 2 \cosh \phi_0}}$$

The results were obtained by interpolation in Table 9, Venvey and Overbeck, "Theory of the Stability of hyophobic Colloids".

For values of W exceeding W = 0 i.e where $\chi = \chi' > \chi_m$.

$$\chi' = 2\chi_m - \chi$$

TABLE 25

W	ϕ_0	χ_m
+ 0.25	0.4949	2.5899
+ 0.5	0.69315	2.320
+ 1.0	0.96242	2.0053
+ 2.0	1.31696	1.6390
+ 4.0	1.7626	1.2917
+ 8.0	2.29224	1.990

Section 4 Conclusions and Discussion of Results

The purpose of this research was the study of insoluble collectors. To this end the system quartz-dodecylamine was chosen because of the stability of both the mineral and the collector and the extensive study to which the system has been subjected. The dodecylamine was to be presented to the quartz as a solution in an emulsified oil. The flotation characteristics of the system, together with those factors which influenced the interaction of mineral and oil particles were studied, with particular attention being paid to the highly alkaline solutions where much of the amine was dissolved in the oil.

It was desired to form the emulsion without using the great degree of agitation employed in practice. An emulsifying agent could not be used because of its very nature it would be surface active and would interfere with the reactions of the dodecylamine at the oil/water interface. The method chosen for reasons which are outlined in section 2.A.1., employed a paint-spray gun. This was found to give satisfactory results and produced emulsions in which the droplet size ranged down to 1 or 2 microns. This method had been previously employed in the Royal School of Mines but various modifications were made which are described in the text.

For a detailed knowledge of the flotation system a method of measuring the oil content and droplet size distribution of

the emulsions was required. The analytical methods which were chosen were photomicrography for the droplet size distribution and spectrophotometric measurement of the chloroform extract for the ratio of oil to water by weight. For both these methods it was necessary to introduce a red dye to the system. This is described in section 2.A.2. It was concluded from tests performed both in the presence and absence of this dye, on various aspects of the system, that the dye was not sufficiently surface active to affect the results in any way. The concentration of dye was never above a few mg.per litre of oil, which is very much lower than the equivalent amine concentrations.

The test described in Section 2.B.1. showed that the oil creamed by sedimentation. If graph 4 is plotted on a logarithmic scale a straight line is obtained which is in accordance with this observation. The sedimentation was caused by the low specific gravity of the oil, 0.825 and ensured that a defined emulsion could never be presented to the quartz. The droplet size distribution could not be predicted, and varied considerably even during one test. It was thought, therefore, that an investigation of this factor during each test could yield no accurate results so no such information was sought in later test work. The photograph given in Section 2.B.2 shows an emulsion which has been creaming for only about 15 minutes. The droplet size

variation in older emulsions would be considerably less.

The bubble pick-up test method was chosen as being most suitable for establishing the flotation characteristics of the system. The first system studied was that of quartz with aqueous dodecylamine hydrochloride as a collector. A neutral electrolyte was added to define the total ionic concentration and to study Robinson's theory that results in the presence of such an electrolyte should differ, at neutral pH, from those in its absence. It was hoped that the curve obtained would agree well with that of other workers. This was in fact so and the agreement between graph 5 and the curve published by Buckenham and Rogers⁽²⁰⁾ is very good. The agreement with Robinson is not quite so good, but his collector was a commercial one with some degree of impurity. The agreement indicates that the writer introduced no personal errors into his bubble pick-up test method and also that Robinson's theory was wrong. This is more fully discussed later in this section.

Before the system was studied in the presence of an emulsified oil a discussion of the results of the cleaning tests in section 2.B.3a is appropriate. No standard technique is employed in the literature for cleaning minerals for fundamental flotation tests. It was found in both the bubble pick-up tests and the streaming current tests that the method of cleaning the mineral had a significant effect

on the results obtained in the experimental work. The latter case will be considered more fully in the discussion of the streaming current results. In the bubble pick-up tests it was found that quartz could be floated at a pH of 1.3 if it had been first ignited in a furnace at 800°C. Acid treatment and other cleaning methods did not allow flotation below a pH of 3.8. If, after ignition, the quartz stood in water its reactivity at low pH's slowly approached that of the unignited quartz. Acid treatment after ignition brought the quartz rapidly to the condition of the unignited mineral. These observations may be examined in the light of tests performed by various other workers, and described in Chemical Abstracts. Zhdanov⁽⁸⁸⁾ found that the adsorption characteristics of quartz ground in vacuo differed from those of quartz which was calcined at 600° in vacuo. The adsorption and desorption isotherms for vacuum ground quartz indicated complex physical and chemical reactions with water and the irreversible character of the hydration. Grinding in vacuo was a fracturing of the crystal faces and edges. The broken Si - O bonds brought about electrostatic free charges $\text{>Si}^+ \text{O}^-$ which caused reaction with water molecules and H^+ and OH^- ions producing the surface presented in bubble pick-up tests. Washing with dilute or even concentrated acids would not

permanently alter this surface to any large degree. In the dehydration process by calcining in vacuo the hydroxide laden quartz brings about only a reaction between neighbouring OH^- groups, the removal of H_2O and a compensation of valencies to form groups like $\text{>Si} = \text{O}$ or $\text{>Si} \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{Si} <$ without electrostatic charges remaining. De Boer and Vleeskens⁽⁸⁹⁾ concluded that reaction could occur between the OH^- groups on adjacent Si atoms or on one Si atom with two such groups, giving both rehydratable and non-rehydratable Si - O - Si groups. The surface shows a reduction in the number of OH^- groups. Il' in, Kiselev and Krail'Nekov⁽⁹⁰⁾ examined the influence of the nature of the surface of silica on its adsorption properties. They studied gels but the results can probably be extended to quartz. The temperature of ignition had an important effect on the hydration and dehydration properties and even after 5 days the properties of surfaces produced at different temperatures were not identical. The adsorption of methane was dependent on the hydration of the surface and it is probable that this would apply also to amines. These observations help to explain the different results shown in Table 2. The ignited quartz surface would be only partially rehydrated and would adsorb strongly at low pH values. With time it would approach the condition of hydration of an unignited surface. The washing of an ignited surface with acid has not been studied in the literature

but it would probably greatly increase the hydration rate and decrease the strength of adsorption at low pH.

From the bubble pick-up tests in the presence of an emulsion, both with the amine added as a salt and as a solution in the emulsified oil, it may be concluded that the presence of a non-polar oil is, in itself, incapable of causing flotation, but in the presence of a surface active collecting agent flotation does occur. The concentration of amine needed to bring about flotation is much lower than that in the absence of oil. To understand the forces which produce this result an understanding of the interaction of dodecylamine and quartz in aqueous solution is necessary. This has been briefly discussed in Section 1. Graphs 5 to 7 can be interpreted by the method used by Robinson⁽³¹⁾. If Philipoff's equation for the relation between surface coverage and contact angle was accepted as being correct then the pick-up curve indicated conditions of similar surface coverage by the active species of the collector. Along that line the minimum contact angle had been developed which balanced the disrupting force of gravity. Thus in the system examined it should be possible to obtain evidence of the effects of hydrogen ion, sodium ion, and free amine concentrations on the adsorption of the dodecylammonium ion, which is thought to be the active species of the collector.

For the three pick-up curves the ratio of dodecylammonium

ion to hydrogen ion has been calculated on the acid side of neutral and the dodecylammonium ion and free amine concentrations on the alkaline side. The ratio of dodecylammonium ion to amine molecule was calculated from the expression:

$$K_b = \frac{[\text{RNH}_3^+][\text{OH}^-]}{[\text{RNH}_2]}$$

where K_b is given by Ralston⁽⁹¹⁾ as 4.3×10^{-4} . The solubility of dodecylamine, 2.0 ± 0.2 mg/l, was taken from Brown⁽¹⁷⁾.

The calculations yielded the information given in tables 25 to 27. From Table 25 it may be concluded that in the absence of oil, the competition between hydrogen ion and dodecylammonium ion determine the flotation characteristics below a pH of 5 or 6. When the hydrogen ion concentration is sufficiently low, i.e. between 5 and 7, the dodecylammonium ion concentration becomes the dominant factor. Robinson thought that the ratio of dodecylammonium ion to hydrogen ion should be decisive at neutral pH. His figures showed that it was not so at pH7 and he concluded that the anomaly was caused by the low total ionic concentration of the solution. That this is not so is shown by these results. There is in fact no anomaly. Above pH7 the dodecylammonium ion alone is dominant. However the necessary concentration

of this species does increase between 9 and 12. Robinson suggested that this apparent increase may be caused by the adsorption of free amine molecules at the air interface. These molecules would be more strongly adsorbed than the amine ion and would produce a considerable reduction in the free surface energy of the interface. As a result the contact angle necessary to lift the particle would have to be somewhat larger than in the absence of amine molecules. The apparent decrease noted by Robinson between 10 and 12 appears to be due to a wrong value for the solubility of amine i.e. 8.5×10^{-7} mol/l as opposed to the value of 1.07×10^{-5} mol/l given by Brown. The sodium ion appears to have little effect if any. It increases some 10,000 times between 7 and 11 but produces no great change in the dodecylammonium ion concentration required for flotation. Buckenham and Rogers⁽²⁰⁾ performed a test in which quartz, conditioned in 25 mg/l amine solution, was placed in a molar sodium chloride solution. The contact angle was reduced from about 60° to 35° . They concluded that sodium chloride had a significant effect on the system. However if so large a salt concentration causes only this change it may be concluded that the smaller concentrations used in bubble pick-up tests would have no effect. The free amine concentration increases by 10^5 between 8 and 12. But apparently has little, if any effect on the flotation.

The figures from the tests in emulsions are given in Tables 26 and 27. A represents the case where amine was presented as a hydrochloride salt and B where it was dissolved in the oil. It may be seen that in alkaline solutions the two methods yield very similar results. The dominant factor in this region appears to be the concentration of dodecylammonium ion, as it is in the absence of oil. However the necessary dodecylammonium ion concentration is about $\frac{1}{10}$ of that in the case discussed above. This indicates that it is not only the amine which enables the quartz to cling to the air bubble, but that the oil must have become spread over the quartz surface in such a way that it is the dominant factor in the interaction of quartz and air. The surface free energy between oil and quartz is probably higher than that between quartz and water. Therefore in the absence of amine the oil will not adhere to the quartz. Since no chemical bond can be found^{med} there is no attraction between the two substances. When a small quantity of amine is adsorbed on to the quartz its surface free energy with the water rises at the points where amine is adsorbed. To lower this energy mineral oil, which collides with the surface, becomes spread over the amine covered portions as a thin film. Flotation then becomes possible. It is, however, evident from the figures that the factor of major importance in the spreading of the oil on the quartz is still the dodecylammonium ion concentration. The same gradual rise in the

TABLE 25

pH	Collector Conc. mg/l	RNH_3^+ gm ion/l	RNH_2 gm/mol/l	$\frac{\text{RNH}_3^+}{\text{H}^+}$
3				
4	1.6	8.7×10^{-6}	-	8.7×10^{-2}
5	0.16	8.7×10^{-7}	-	8.7×10^{-2}
6	6.3×10^{-2}	3.4×10^{-7}	-	3.4×10^{-1}
7	4.5×10^{-2}	2.4×10^{-7}	-	2.4
8	4×10^{-2}	2.2×10^{-7}	5.1×10^{-10}	-
9	4×10^{-2}	2.2×10^{-7}	5.1×10^{-9}	-
10	6.3×10^{-2}	2.8×10^{-7}	6.4×10^{-8}	-
11	2.2×10^{-1}	3.6×10^{-7}	8.5×10^{-7}	-
12	2.0	4.5×10^{-7}	1.04×10^{-5}	-

TABLE 26

pH	Collector Conc mg/l		$\text{RNH}_3^+/\text{H}^+$	
	A	B	A	B
3	2.2×10^{-2}	3.2×10^{-1}	1.2×10^{-4}	1.7×10^{-3}
4	8.5×10^{-3}	7.5×10^{-2}	4.6×10^{-4}	4.1×10^{-3}
5	5×10^{-3}	1.9×10^{-2}	2.7×10^{-3}	9.8×10^{-3}
6	4×10^{-3}	7.5×10^{-3}	2.2×10^{-2}	4.1×10^{-2}
7	5×10^{-3}	6.7×10^{-3}	2.7×10^{-1}	3.6×10^{-1}

TABLE 27

pH	Collect. Conc. mg/l		RNH_3^+ gm ion/l		RNH_2 gm ion/l	
	A	B	A	B	A	B
7	5×10^{-3}	6.7×10^{-3}	2.7×10^{-8}	3.6×10^{-8}	6.2×10^{-12}	8.3×10^{-12}
8	7.1×10^{-3}	8×10^{-3}	3.9×10^{-8}	4.4×10^{-8}	9.0×10^{-11}	1.0×10^{-10}
9	1×10^{-2}	1×10^{-2}	5.3×10^{-8}	5.3×10^{-8}	1.2×10^{-9}	1.2×10^{-9}
10	1.6×10^{-2}	1.8×10^{-2}	7.2×10^{-8}	8.1×10^{-8}	1.6×10^{-8}	1.8×10^{-8}
11	2.2×10^{-2}	5×10^{-2}	3.6×10^{-8}	8.2×10^{-8}	8.4×10^{-6}	1.9×10^{-7}

necessary concentration as was found in Table 25 is present in this case but to a greater degree. It might be partially ascribed to the same cause. However in the presence of emulsions another factor has entered the system. The amine is partitioned between the oil and the water, as is shown in Section 2.B.7. It may be concluded from these tests that not only the molecularly dissolved form is partitioned but also the ionically dissolved, for if this were not so no amine would be dissolved in the oil at low concentrations. The partition co-efficient is strongly dependent on pH so between pH7 and 11 the concentration of amine in oil is rising by a factor of about 20. This does not affect the concentration in water until between 10 and 11 because the proportion of oil to water was very low in the bubble pick-up tests. The increasing concentration of amine in oil would probably cause a decrease in the surface-free energy at the oil-water interface. In this case more amine might be necessary on the quartz surface to assist the spreading of the oil once contact between oil and quartz is made, thus causing a gradual rise in the dodecylammonium ion concentration.

An anomalous situation is seen in comparing the acid sides of graphs 7 and 8. Although the system in each case requires a greatly reduced amine concentration to allow collection the disagreement between the two curves is considerable. In neither case does the collection depend entirely

on the hydrogen ion to dodecylammonium ion ratio, suggesting that the adsorption of amine on quartz is not the only factor controlling the spreading of oil on the mineral. However the discrepancy between the two curves is greater than their internal discrepancies. The only difference between the two methods rests in the oil concentrations used in the solutions of low amine concentration. In graph 6 these low concentrations were attained by dilution of an emulsion source containing a high concentration of amine. In graph 7 the low concentrations were attained by adding a quantity of dodecylamine hydrochloride solution and a standard amount of concentrated emulsion. The oil concentrations in test 7 were therefore much higher than those in test 6. It is probable therefore that for a reason which is not understood the oil concentration is important in acid solutions, while it is not important in alkaline solutions.

The streaming current measurements yielded interesting information with regard to the cleaning of minerals. It was shown that under what appeared to be the same conditions different plugs gave different values for the zeta potential. This can be seen in graph 13 where the potential in a 10^{-4} normal sodium perchlorate solution at pH9 is given as -95mV. In graph 14 under the same conditions the potential is -104mV. Similarly in graph 15 a large difference is found between the

zeta potentials of solutions of 0.96 mg/l of dodecylamine and solutions containing no surface active additives. In graph 16 it is shown that no such difference exists. This discrepancy in zeta potentials can best be explained by slight differences between the conditions of the quartz plugs used in the tests. All the quartz was cleaned in the same manner in acid and was washed in double distilled water, but the various samples were exposed to water for varying lengths of time before use. For example the material used in Test 3 had been standing in water longer than that used in Test 4. Similarly the material used in Test 5a had only been standing in water for a few hours while that used in Test 5b had been standing for several days. It is evident that although shaking with conductivity water removes most of the acid, it does not remove all immediately, but will do so with time. Bramley⁽⁵⁾ tested quartz which had been boiled in concentrated hydrochloric acid and then washed and left standing in conductivity water. He found that the conductivity of the water increased over a period of some days. This showed that the last traces of acid were only very slowly removed from the quartz surface.

If acid remains on the mineral surface the pH of the solution near the surface is low compared with that in the bulk of the solution. Since it is the OH^- ion concentration in the surface region which determines the zeta potential

insufficient removal of H^+ ions will give low zeta potentials. It may also be deduced that the stonger the acid attack on the mineral surface the more difficult it will be to remove all acid. This might explain why the writer obtained an iso-electric value for quartz at pH2.6, while Gaudin and Fuerstenau⁽²⁸⁾, who repeatedly boiled their quartz in concentrated acid, report a value of 3.75.

Although the streaming current results agree on the whole with those in the literature a number of discrepancies can be found.

The value found for the zeta potential in conductivity water was -68mV. Gaudin and Fuerstenau⁽²⁸⁾ found a value of -70mV. Overbeck and Wijga⁽⁶⁶⁾ obtained a value of -70mV for powdered glass and -140mV for a capillary of the same glass. In 2×10^{-4} normal potassium chloride solution these values were -98mV and -112mV. These differences can be explained by surface conductance effects. The surface conductance makes a greater contribution to the conductances of mineral plugs than of capillaries. It should be pointed out that it can be dangerous to compare results obtained with glass, with those obtained with quartz. The structure and composition of the former are more complex than those of the latter.

Some workers have measured the zeta potential of quartz by electrophoresis. Blake and Whitney⁽⁶⁷⁾ found a value of

-44mV, Fründlich⁽⁶⁸⁾ of -50mV, and Gaudin and Sun of -36mV. All of which are lower than the results gained with streaming current or potential. Comparison of the results of electrophoresis and streaming potential is difficult because of the difficulties inherent in the electrophoresis and the calculation of results found with it.

Benton and Elton⁽⁶⁹⁾ measured the zeta potential and surface charge on quartz by the sedimentation method. They attempted to trace a relationship between these properties and the conductivity of the solution. Conductivities between 0.2 and 1.0 gemmho were used. The writers reported that an increase in the conductivity of water, caused by dissolution of atmospheric carbon dioxide, was accompanied by an increase in the zeta potential of quartz. To explain their results, contrary to accepted belief, they suggested that the bicarbonate ion was potential determining at the quartz-solution interface. However, the equation by which they calculated surface charges contains an expression for the specific conductivity of the solution. Any errors in the derivation of the equation would lead to an apparent variation of zeta potential with conductivity. That such errors exist is very likely since many assumptions are made in the derivation of the equations. The results of Benton and Elton are not confirmed by other workers who studied the same effect with streaming potential techniques. Lachs and Biczyn⁽⁷⁰⁾

are reported to have found a decrease of zeta potential with increasing conductivity. They worked with solutions of higher conductivity. Wood^(70b) found no apparent variation of zeta potential with conductivity.

The results obtained in the tests with varying concentrations of sodium chloride and sodium perchlorate agree well with the *Stern* theory of the double layer. Neither sodium, chloride or perchlorate ions are preferentially adsorbed at the quartz-solution interface. The effect of these ions is therefore simply to compress the double layer and reduce the value of the zeta potential. They can not change its sign. In the tests at pH 7 and 9 an increase in zeta potential is found, which reaches a maximum at 10^{-4} Normal and drops with further increase in concentration. In the test at pH 10.3 no initial rise was found. The theory demands that the maximum potential should be in pure water and this should be decreased by any increase in the electrolyte concentration. In the tests at pH 7 and 9 the effect of surface conductance prevents this from being noticed. It is not until 10^{-4} Normal that the double layer is so compressed that the total ionic strength has more effect on zeta than does the surface conductance. In solutions stronger than this results obey the theory. at pH 10 the concentration of sodium hydroxide is about 10^{-4} Molar and the sodium chloride has no effect until its con-

centration is equal to this (see Graph 12)

Test IV and graph 14 confirms that the zeta potential of quartz is dependent upon the hydrogen and hydroxyl ions concentrations of the solution. Above pH 10 the potential falls because the high electrolyte concentration compresses the double layer and has a stronger effect than that of extra hydroxyl ions in raising it.

The tests with dodecylamine hydrochloride (graphs 15 and 16) show that at low amine concentrations there is no change in the zeta potential. At higher concentrations a slight fall is noticed at all pH's with a sharp drop at 9.3. Gaudin and Fuerstenau found that in 7mg/l solutions of dodecylamine hydrochloride the sign of the zeta potential was reversed at pH 9.5 but that result was not obtained in this work. This sudden drop in potential can be attributed to strong adsorption of the dodecylammonium ions. In weaker solutions although adsorption occurs, as is shown by flotation tests (see graph 8), the adsorption is not sufficient to cause any change in the surface potential. This result suggests that any connection between changes in flotation characteristics and changes in zeta potential is simply a secondary result of the adsorption which causes both phenomena. Flotation can occur with no change in zeta potential.

In section 2.B.6. the electrophoresis tests showed

that the zeta potential of hydrocarbon oil in water is dependent upon the pH (graph 17). The iso-electric point is at about pH6. In salt solutions as with quartz increasing salt concentration caused a considerable decrease in the zeta potential (graph 18). This can be explained by Stern's theory of the double layer. In amine solutions (graph 18b) the amine ion is preferentially adsorbed at the oil/water interface. In concentrations greater than 10^{-7} Molar it causes a reduction in the zeta potential which is completely reversed at 1.6×10^{-5} normal. Increasing amine concentration increases the positive zeta potential. The tests in which amine was dissolved in the oil prior to emulsification were very difficult to interpret but gave similar results in a qualitative fashion. In these tests as with the bubble pick-up and beaker cell tests where the amine was dissolved in the oil before emulsification, it was impossible to calculate amine strengths beforehand and calculations had to be delayed until the partition of amine between oil and water was known. The results were therefore slightly inaccurate. It can be recommended that in measurements involving similar systems the surface active agent should, when possible, be added as a soluble salt.

Both the streaming current and the electrophoresis results yield information concerning the interaction of quartz particles

and oil droplets in the liquid medium. To determine the factors which influence the interaction of quartz with oil it is necessary to calculate under various conditions the energy barrier which controls the distance of approach of particles of the two materials. This can be done by the method evolved by Derjaguin (see section 3.C (3)).

The energy barrier preventing the disrupting of the water layer between any two particles in a liquid is given by the integration of the force of repulsion over the distance through which it acts. Therefore the area, A, under the WH curve, obtained for any pair of charges is a measure of the energy barrier. The numerical force of repulsion is P, which is dependent upon W and upon the electrolyte concentration of the solution. The distance over which the force of repulsion acts, i.e. h the distance between the particles is the factor H (i.e. $X_2 - X_1$) in the isodynamic curves multiplied by d, the thickness of the double layer. Therefore the actual energy barrier is:

$$E \text{ in ergs/sq cm} = (d \cdot \frac{P}{W} \times A)$$

$$\text{From the equation (4) } P = \frac{kTNWV}{Z_1}$$

p is in dynes/sq cm of flat condenser plate

k is the Boltzmann constant 1.38×10^{-16} ergs/dy

T is the absolute temperature $\frac{1}{4}$ 293 at 20°C

C is the concentration of electrolyte in gm equiv cc.

Z_1 is the valency of the anion

N is Arogadro's number - 6.02×10^{23} at 20°C

$\beta = Z_2/Z_1$, where Z is the valency of the anion and Z_2 of the cation.

$$\phi_1 = \frac{Z e \psi_1}{kT} \quad \text{and} \quad = \frac{Z e \psi_2}{kT} \quad \text{where } Z = Z_1$$

e = The charge on the electron = 4.802×10^{-10}

ψ_2 is the numerically larger zeta potential

ψ_1 is the numerically smaller zeta potential

d is the thickness of the double layer = $\left(\frac{DT}{\epsilon_0 Z_1^2 4\pi C N} \right)^{1/2}$
 where D is the dielectric constant and
 T the absolute temperature.

C_i is the concentration in gm ions / litre

Various combinations of potential and concentration relevant to the system quartz/Shell Printing Ink Oil No.11 will now be considered.

Case 1 Energy of repulsion of two quartz particles at pH9 in N/10000 sodium perchlorate.

From graph 13 ψ_1 and $\psi_2 = -96\text{mV} = 32 \times 10^{-5} \text{ e.s.u.}$

$$\phi_1 = \phi_2 = \frac{Z e \psi}{kT} = \frac{1.0 \times 4.802 \times 10^{-10} \times 32 \times 10^{-5}}{1.38 \times 10^{-16} \times 293} = 3.83$$

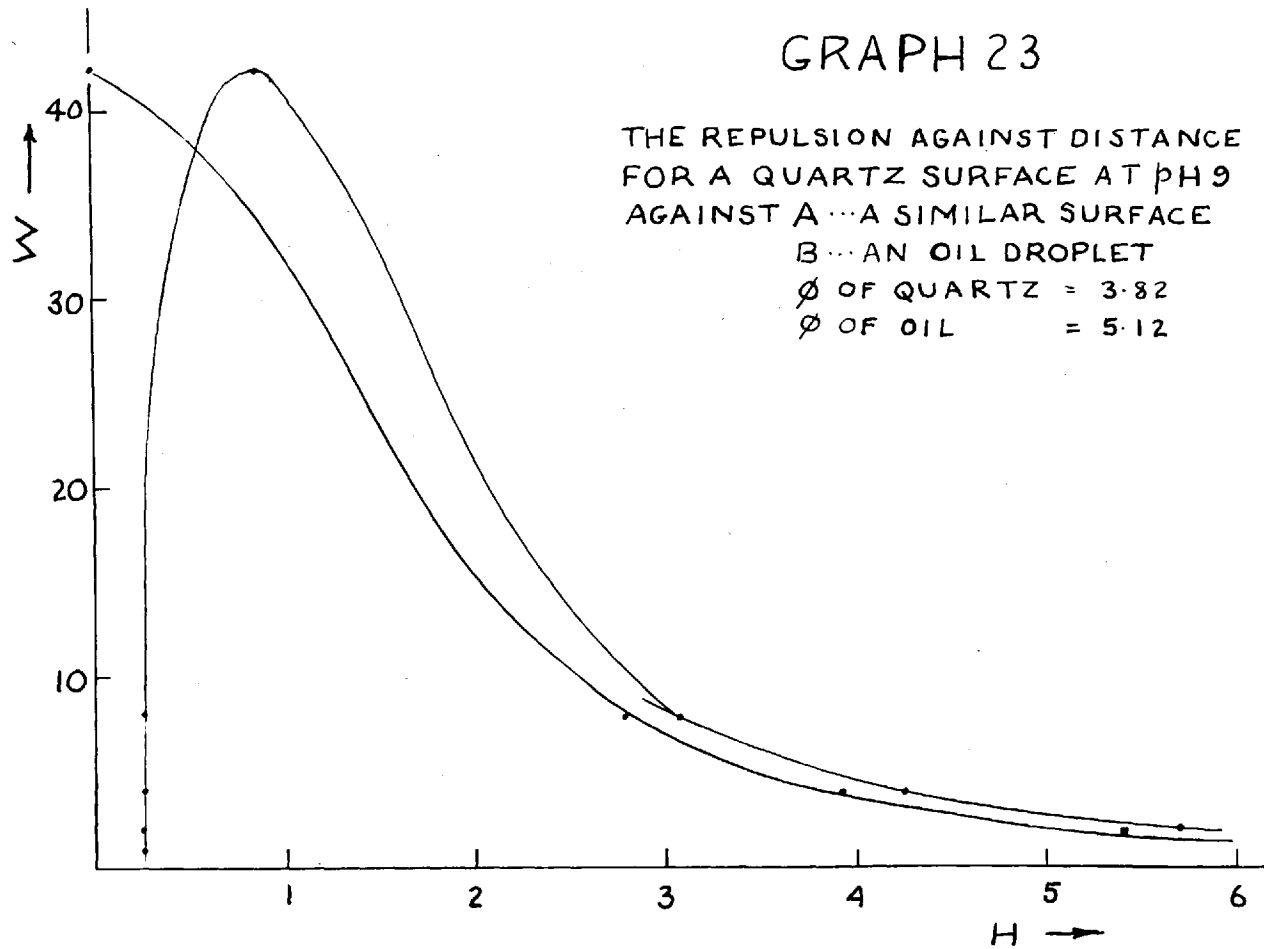
From the iso dynamic curves, graph 22, the relevant WH curve has been plotted and is shown in graph 23.

Area under curve = 86.5

(N.B. The value for X has been doubled to obtain the correct WH curve see Section 3.C.(3)

$$\frac{P}{W} = \frac{kT N c}{Z_1} = 1.38 \times 10^{-16} \times 293 \times 6.02^{23} \times 10^{-7} = 2.43 \times 10^3$$

GRAPH 23



$$d = 2.81 \times 10^{-10} \left(\frac{80.36 \times 293}{2 \times 1} \right)^{1/2} = 3.35 \times 10^{-6} \text{ cm.}$$

Therefore the energy barrier =

$$86.6 \times 2.43 \times 10^3 \times 3.05 \times 10^{-6} = 6.38 \times 10^{-1} \text{ erg/sq.cm}$$

Case 2.

The case which most concerns the present work is that of a quartz particle and an oil droplet in water.

In a 10^{-4} molar solution of sodium perchlorate at pH9:

$$\text{For oil } \psi_1 = -132 \text{ mV} = -44 \times 10^{-5} \text{ esu}$$

$$\phi_1 = 5.12$$

$$\text{For quartz } \psi_2 = -95 \text{ mV} = -32 \times 10^{-5} \text{ esu}$$

$$\phi_2 = 3.83$$

Since the lower ϕ i.e. $\phi_2 = 3.82$, is the same as it was in Case 1 the values for W are the same, at the same values, of $\chi_1' - \chi_2$, but the value of χ_1 is larger, so the curve is shifted to the right while remaining the same in area. Thus A = 86.6 and:

$$\frac{P}{W} = 2.42 \times 10^3 \quad d = 3.25 \times 10^{-6}$$

$$\text{Energy barrier} = 6.38 \times 10^{-1} \text{ ergs/sq cm.}$$

If we assume an oil droplet of diameter 6μ then the area over which the repulsion acts is that of the great circle. i.e. $2.82 \times 10^{-7} \text{ sq.cm.}$

$$\begin{aligned} \text{The energy barrier is then } & 6.38 \times 10^{-1} \times 2.82 \times 10^{-7} \\ & = 1.82 \times 10^{-7} \text{ ergs} \end{aligned}$$

We must assume that the energy necessary to break down this barrier is that of the droplet velocity = $\frac{1}{2} MV^2$.

Therefore to get collision, if we assume a 6 μ droplet moving along the central streamline the available energy is

$$\begin{aligned} E &= \frac{1}{2} MV^2 = 1.82 \times 10^{-7} \text{ ergs} \\ \frac{1}{2} \times 9.33 \times 10^{-11} \times V^2 &= 1.82 \times 10^{-7} \\ V &= 62.4 \text{ cm/sec} \end{aligned}$$

In the bubble pick-up tests the only motion was that caused by stirring of the solution to regulate the pH. It is impossible to estimate the velocity which this would impart to the droplets. It might be possible that oil droplets would get squeezed between the glass stirrer and quartz particles. In this case the available energy would not be only that of the droplet movement but would be greatly increased. It is certain that flotation did not occur in the absence of amine, therefore we may conclude that if the stirring did cause collision the oil droplet did not spread over the quartz particle. This fact is confirmed by the behaviour of the system in acid solutions. In these cases the zeta potentials of oil and quartz are dissimilar and attraction should exist. Yet no flotation occurs.

In the presence of a quantity of amine, too low by itself to cause flotation, the addition of an emulsion results in flotation. Under these conditions it is evident that the oil has been caused to spread upon the quartz surface. It is

necessary to determine whether the oil should, in fact, according to the theories of interaction, collide with the quartz under these circumstances. To calculate the minimum zeta potential which will allow collision it is necessary to assign a velocity to the oil droplets. If we say that gentle stirring imparted a motion of 10 cm/sec to the droplets then the energy available for collision is :

$$\begin{aligned}\frac{1}{2} MV^2 &= \frac{1}{2} \times 9.33 \times 10^{-11} \times 100 \text{ ergs} \\ &= 4.67 \times 10^{-9} \text{ ergs.}\end{aligned}$$

which must be equal to the energy barrier.

The bubble pick-up tests were done in solutions where the pH had been set at pH 11 or pH 3 and then modified towards the neutral point. In those tests where the amine was added as a hydrochloride salt the salt concentration was 10^{-4} molar. Hence at pH 9 the total ionic strength was 1.1×10^{-3} molar

$$\text{and } \frac{P}{W} = \frac{kTNC}{E_1} = 26,800$$

$$d = 94 \times 10^{-8}$$

$$\text{The energy barrier for a } 6\mu \text{ droplet is } \frac{4.67 \times 10^{-9}}{2.82 \times 10^{-7}} = 1.66 \times 10^{-2} \text{ ergs/sq.cm}$$

(where 2.82×10^{-7} is the droplet area)

$$\text{The area under the WH curve} = \frac{E}{(p/W)d} = 9581$$

The relevant value of zeta potential was found by trial and error to be -12 or -13mV.

In the bubble pick-up tests where the amine was added as a solution in the oil, the salt concentration was 1/25 molar.

$$\text{In this case } \frac{P}{W} = 97.3 \times 10^4$$
$$\text{and } d = 1.93 \times 10^{-7} \text{ cm.}$$

Therefore the area under the WH curve = 0.0885 and the value of zeta potential must be about - 5mV.

From graph 18b it can be seen that the concentration of dodecylamine which is required to give such low values of zeta potential is about 10^{-5} mol/l. From graph 6 and 7 it can be seen that flotation is, in fact, possible at concentrations well below this figure (N.B. 10^{-5} mol/l = 1.85 mg/l). Therefore it may be concluded that the zeta potentials of the oil and quartz surfaces were not the determining factors in emulsion flotation. Since the theories of interaction have been shown to be valid in coal flotation (see Bramley 5) it must be concluded that another factor has entered this system. A factor which has not been examined in this research is the Van der Waals attraction force. This force has been discussed by Verwey and Overbeek⁽⁸⁴⁾. It is known that it can extend as much as 1 micron into the solution. The Van der Waals forces for quartz are known to be high, but those for oil have not been measured. It has been predicted that they would be of the same sign as those of quartz. They might cause enough attraction

between the oil and the quartz to overcome the repulsive forces to which the high values of zeta potential give rise. A second factor which has not been studied is the precise nature of the potential which determines the energy barrier in the system. It was assumed for the purposes of calculation, and in the absence of any alternative theory, that this is the zeta potential. It is possible that the repulsive forces for interacting potential fields are dependent on a lower value of potential. A third possible cause of the discrepancy between observed and predicted values of zeta potential might be stirring. Bramley showed that in emulsion/coal systems where flotation did not occur under quiescent conditions, flotation did occur if the system was agitated. The degree of flotation was increased by surface active reagents.

The beaker cell tests (see graph 8) showed no apparent improvement in flotation by the addition of an emulsified oil to the system. In the beaker cell the outer edges of the impellor moved at about 400 cm/sec. Therefore the energy available for breaking down the energy barrier was that of a

6 μ . oil droplet moving at 400 cm/sec.

$$\frac{1}{2} mV^2 = \frac{1}{2} \times \frac{4}{3} \times \pi \times (3 \times 10^{-4})^3 \times (400)^2 \text{ ergs} = 9.1 \times 10^{-6}$$

This acts over an area of 2.82×10^{-7} sq.cm.

therefore the energy barrier = 32 ergs.

The tests were not done at any constant salt concentration

so the molarity of the solution must be assumed to be that of a solution at pH9 i.e. 10^{-5} gm mol/l.

$$\text{therefore } d = 9.64 \times 10^{-6} \text{ cm}$$

$$\frac{P}{W} = 244$$

$$\text{therefore area under WH curve} = 1.36 \times 10^4$$

The minimum charge which can prevent collision is therefore well above any imparted by the interaction of quartz and oil, and collision should be possible in all tests and under all conditions. However, no improvement in flotation is found in the tests. Since this cannot be due to the energy barriers between oil and quartz it must be due to either the exceedingly violent agitation or to over oiling. It is well known that oil will not float so a surface which had been over oiled would show no tendency to float. Thus the beaker cell tests simply give the flotation curves usual to amine solutions of the strengths tested.

It was shown in the discussion of the bubble pick-up curves that the determining factor in alkaline solutions is the dodecylammonium ion concentration. It would be interesting to calculate from adsorption data what surface covering these ionic concentrations give, and hence what surface covering promotes the spreading of enough oil to allow flotation. de Bruyn⁽²⁶⁾ found that the amount of amine adsorbed on quartz from dodecylamine acetate solutions is dependent on the square root of the solution concentration.

$$\text{i.e. } \Gamma = K \sqrt{C}$$

where Γ is the amount adsorbed/cm² and c is the amine concentration in moles./l.

A 10⁻⁶ molar solution gave 8.6 x 10⁻¹² moles/cm² of adsorption at neutral pH.

$$\text{therefore } K = 8.6 \times 10^{-9}$$

In Table 27 the minimum amine concentration which gave flotation in emulsions was 5 x 10⁻³ mg/l (i.e. 2.7 x 10⁻⁸ moles/l) at neutral pH.

$$\text{Therefore } \Gamma = 8.6 \times 10^{-9} \times 2.7 \times 10^{-8} = 1.4 \times 10^{-12} \text{ moles/cm}^2.$$

The reagent coverage necessary to give a monolayer is reported by Gaudin and Bloecher⁽²⁷⁾ to be 7.1 x 10⁻¹⁰ moles/cm². Therefore we may conclude that a surface coverage 2 x 10⁻¹ per cent complete allows flotation in emulsions. That allowing pick-up is somewhat higher than this and is approximately the same as that allowing cling in the absence of oil.

The figures used in the above calculations have been criticised by Edwards and Ewers who are reported by Sutherland and Wack⁽⁹⁴⁾ to have tried to repeat the results of Gaudin and Bloecher and de Bruyn. They could not do so, but obtained adsorptions of about 1/20 of those given above. They were suspicious of a fritted glass filter used by Gaudin and Bloecher and the use of the unstable acetate salt. Their work is unpublished. From the authors own experience it appeared that the time factor allowed in amine adsorption experiments

would be critical. It was found that if 2 mg/litre solutions were left standing overnight about 80% of the amine had gone from solution onto the walls of the apparatus the following morning. If, as seems possible, amine continues to precipitate without reaching a chemical equilibrium de Bruyn's and Gaudin and Bloecher's results would be open to suspicion, and the amine adsorption in the flotation tests would be lower than that calculated above.

It is evident that an understanding of the quartz - dodecylamine - mineral oil system requires further study of the Van der Waals forces in the oil, the nature of the potential giving rise to the energy barrier, and the adsorption of amine on quartz.

Summary of Conclusions

It may be concluded that the addition of a quantity of a surface active reagent, too small, in itself, to allow flotation, enables an insoluble hydrocarbon oil to spread on the surface of quartz. Flotation is then possible.

The critical factor in quartz flotation with dodecylamine, both in the presence and absence of oil, is shown to be, in alkaline solution, the dodecylammonium ion concentration. The ratio of dodecylammonium ion to hydrogen ion is critical in acid solution, but other factors also are of importance in emulsions. It may be concluded that the spreading of oil is controlled by adsorption of the dodecylammonium ion. The adsorbed layer necessary for flotation has been calculated from adsorption data to be about 0.2% of a monolayer, but more recent adsorption data suggest that the coating may be about 1/20 of this.

Cleaning methods for fundamental flotation testing and zeta potential measurements have been examined and it has been shown that the choice of method is of critical importance. It was concluded that for tests concerned with the mineral surfaces presented in flotation acid washing is the most advisable method.

The partition co-efficient of dodecylamine hydrochloride between oil and water is strongly dependent on the pH of the water. The free amine molecule is not the only species

of the salt which is partitioned. The partition coefficient rises by a factor of 200 in favour of the oil between pH 4.5 and 9.3.

The zeta potentials of both oil and quartz are dependent on pH. Salts which are not surface active compress the double layer and reduce the value of the potential. They do not change its sign. Surface conductance effects reduce the measured potential in streaming current measurements at low concentrations. Dodecylamine, which is surface active reverses the sign of the zeta potential of the oil if added in sufficient quantity. It greatly reduces the zeta potential of quartz at high pH.

The energy barriers between oil and quartz particles in water have been calculated. They appear to be too large to allow collision where flotation is known to occur. It is suggested that the Van der Waals attraction may account for this. The relationship between the zeta potential and the value ψ in the interaction calculations has been questioned.

A P P E N D I X I

Particle Impingement

Bubble pick-up tests with emulsion in the absence of surface active agents indicated that no flotation can be obtained by oil alone. This led to a study of the factors affecting impingement between a quartz particle and an oil droplet in a liquid medium. This subject has been examined by Stairmand⁽⁹²⁾. His work deals primarily with the filtration of dust from air.

Stairmand considers first the impingement of a dust particle on a cylinder or rod lying transverse to the air stream.

The possibility of the particle touching the rod is determined by the following factors

- a) The particle mass
- b) The approach velocity of the particle
- c) The position of the particle relative to the central streamline.

If particles initially at a distance $\frac{D^1}{2}$ from the central streamline just graze a rod of diameter D , then D^1 is the target diameter. The ratio D^1/D is termed the target efficiency symbol (η_r).

Stairmand states that the target efficiency is a function of the dimensionless group $\frac{Dg}{Vf}$ where D is the diameter of the obstacle, g is the gravitational constant,

V is the velocity of approach and f is the terminal velocity of the particle in the particular fluid medium.

Stairmand also considered the application of the above principle to spray tower performance. The target efficiency in the case of a dust particle and a spherical water droplet was found to be a different function of D_g/V_f where:

$$\left[\frac{D^1}{D} \text{ spheres} \right]^2 > \left(\frac{D^1}{D} \right) \text{ cylinders}$$

V is the difference in terminal velocities between the dust particle and the water droplet. The particle diameter is much smaller than that of the water droplet. In this case for impingement D_g/V_f must be less than 16.

Although the figure 16 may not apply to the present circumstances Dr. Heywood⁽⁹³⁾ states that it should not be more than 20% in error.

Case of Oil Droplet and Quartz Particle in Water

The 72 mesh quartz particle is prismoidal and its volume co-efficient (Heywood) may be taken as 0.3. From the tables and method due to Heywood the terminal velocity of such a particle is 1.16 cm/sec. This is the same as a quartz sphere of diameter 130μ .

Therefore $D = 0.013 \text{ cm}$ $V = 1.16 \text{ cm/sec.}$

The oil droplet diameter may be taken as 10 microns or 0.01 cm. The specific gravity of Shell Printing Ink Oil

No 11 is 0.825. Hence the terminal velocity of the oil droplet may be calculated from Stoke's equation:

$$f = \frac{d^2}{18} \cdot \frac{(\sigma - \rho) g}{\eta}$$

$$= \frac{(0.001)^2 (0.175) 981}{18 \times (0.01)}$$

If we assume that both quartz particle and oil droplet are moving at their terminal velocities then:

$$\frac{Dg}{Vf} = \frac{(0.013)(981)(18)(0.01)}{(1.16)(0.001)^2(0.175)(981)} = 1.15 \times 10^4$$

Therefore impingement cannot take place.

For impingement to occur the function Dg/Vf would be equal to 16. The velocity approach of the oil droplet and the quartz particle would then need to be :

$$V = \frac{Dg}{16f}$$

$$= \frac{(0.013) \times 981 \times 18 \times (0.01)}{16 \times 10^{-6} \times (0.175) \times 981} = 0.837 \times 10^3 \text{ cm/sec.}$$

In the bubble pick-up tests no speed of this order occurred. In the beaker cell the maximum speed of the impellor was about 2000 rpm. At this speed the outer edges of the blades were moving at 397 cm/sec which is below the velocity given above.

Case of Oil droplet and Air bubble

Droplet diameter, 10 microns; bubble diameter 1mm

Bubble terminal velocity (turbulent flow), 11.5cm/sec

$$\text{Hence } \frac{Dg}{Vf} = \frac{(0.1) \times (981) \times (18) \times (0.01)}{(11.5) \times (0.001)^2 \times (0.175) \times (981)} = 8.95 \times 10^3$$

Potential Flow Around Spheres

The generally accepted theory of potential flow around spheres gives the equation of a streamline as:

$$\sin^2 \theta = \frac{C r}{r^3 - a^3} \quad (\text{ref. fig })$$

where C is a constant for the streamline. Thus when C=0 and $r > a$, $\sin \theta = 0$ and $\theta = 0$. When C = 0 and $r > a$, $\sin \theta$ is indeterminate and all values of θ are possible. Thus for c = 0, the streamline, which is the central one, envelops the sphere.

At y_0 , $\sin \theta = y_0/r$ and a is negligible compared with r. Thus substitution in the basic streamline equation gives

$$y_0 = \sqrt{C}.$$

At y_1 $\theta = 90^\circ$, and $r = y_1$.

$$\text{Hence } y_1^3 - a^3 - C y_1 = 0$$

$$\text{or } y_1^3 - a^3 - y_0^2 y_1 = 0$$

Applying the above equations to the droplet/particle system necessitates the assumption that the quartz particles can be taken as spherical. Some allowance would have to be made for the droplet size, but it can be assumed (from calculations of Stairmand's function) that the droplets will not deviate from the Streamline round the leading edges of the quartz particle.

Approximately, from the foregoing theory, an oil droplet approaching a 200 micron quartz particle at a distance of 3 microns from the central streamline would pass within 300 Angstroms of the particle surface.

A P P E N D I X I I

Values of $4\pi\eta/D$ used in calculating zeta potential

When the streaming and zeta potentials are given in millivolts and when the hydrostatic head is measured in centimetres of mercury, the value of $4\pi\eta/D$ at 20°C is 1.06×10^5 . (Alexander and Johnson).

Calculating from the results that they published(48)

Buchanan and Heymann used the values:

$$1.17 \times 10^5 \text{ at } 16^\circ\text{C}$$

$$0.985 \times 10^5 \text{ at } 24^\circ\text{C}$$

For the purposes of the calculations of which the results are reported in this thesis, the three above values were plotted against temperature. Values at intermediate temperatures were then read from the graph.

A P P E N D I X I I I

A Quantitative Method of Bubble Pick-up Testing

Since bubble pick-up test methods form an important operating technique in the study of flotation reagents an attempt was made to render them to some extent quantitative. It was hoped that this would give more detailed information concerning the 'cling' region of the critical pH curve for the system under investigation.

The method examined was based on one reported by Bramley (Private communication) as being in use in flotation research at Leeds University. In this method the bubble of air is blown under an inverted cup attached vertically by a glass rod to a cantilever beam. The deflection of the beam is a measure of the weight of particles picked up. A modified form of this apparatus was made by adopting a torsion balance previously used for the measurement of surface tension. Instead of a cantilever beam, a 6" length of aluminium rod was clamped to a taut, fine gauge steel piano wire, and from the end of the aluminium rod was suspended a vertical glass rod carrying a polythene bubble-holder. The bubble-holder was raised by twisting the piano wire and the necessary deflection provided a measure of the 'pick-up' weight. Most of the glass rod as well as the bubble holder was immersed in the test solution in order to prevent the polythene from floating. This apparatus did not prove sufficiently sensitive

to record the pick-up of a small quantity of -72 mesh +100 mesh garnet particles. To improve sensitivity a much longer beam or a much thinner wire would have been necessary. However neither of these corrections could be applied to a sufficient extent to give the required sensitivity.

In place of the torsion balance an attempt was made to obtain suitable sensitivity with a quartz spring, suspended vertically, the bubble-holder being suspended from the spring. The spring was protected from draughts by a glass tube which could be moved so that the whole length of the spring was always enclosed. The bubble-holders were again made of polythene the glass rod being on this occasion very narrow. To prevent the bubble-holder from floating a length of platinum spiral was placed so that it rested on the upper surface of the polythene cup. The overall weight on the spring could then be reduced to a few milligrammes, which was well within its elastic limit. The extension of the spring upon pick-up was measured by a horizontally mounted microscope. Upon testing it was found that although the spring was sufficiently sensitive to record the weight picked up, it was not possible to obtain a constant zero point. Errors amounting to as much as the weight of 10 particles were caused by a slight displacement of the bubble holder. Since this difficulty could not be overcome without the expenditure of an unreasonable amount of time, and in consideration of the fact that

the investigation was entirely subsidiary to the main research project, it was decided that the method should be abandoned in favour of the standard test method.

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