KINETIC STUDY OF ADSORPTION OF ALKALINE

ANIONS ON TITANIUM (IV) OXIDE IN DRY CELL

BY

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DEPARTMENT OF CHEMICAL ENGINEERING

SCHOOL OF ENGINEERING AND ENGINEERING

TECHNOLOGY

FEDERAL UNIVERSITY OF TECHNOLOGY

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NOVEMBER 2004

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A RESEARCH PROJECT SUBMITTED TO THE DEPARTMENT

OF CHEMICAL ENGINEERING AND ENGINEERING
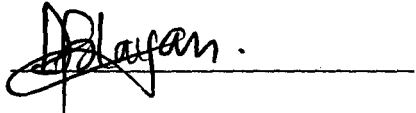
TECHNOLOGY, FEDERAL UNIVERSITY OF TECHNOLOGY

MINNA,

IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE AWARD

OF BACHELOR OF ENGINEERING IN CHEMICAL ENGINNERING.

NOVEMBER 2004

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DECLARATION

I here by declare that this project is my original work and has not been presented else where for the award of any degree or its equivalent.
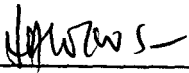
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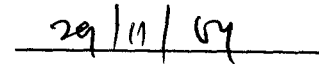
(REG. NO. 98/6933EH)

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CERTIFICATION

This is to certify that this project work titled "kinetic study of adsorption of alkaline anions on Titanium (iv) oxide in dry cell was carried out by Dadi Afolayan Julius (98/6933EH) of Department of Chemical Engineering, Federal University of Technology, Minna, under the supervision of Dr. Duncan Aloko.

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Dr. DUNCAN ALOKO   **DATE**

(*Project supervisor*)

_____   _____
Dr. F. ABERUAGBA   **DATE**

(*Head of Department*)

_____   _____
EXTERNAL EXAMINER   **DATE**

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DEDICATION

This project work is dedicated to the glory of Almighty God whose grace makes me what I

m today.

nd also to my parents MR and MRS SAMEUL DADI.

ACKNOWLEDGEMENT

ABSTRACT

"The kinetic study of adsorption of alkaline anions on Titanium (IV) Oxide in dry cell" was carried out using graphical method of analyzing the rate equation. The alkaline anions on which this research work was based are Chloride and Bromide ions, while concentration of 1M, 0.1M, 0.01M, and 0.001M of each ion are used for the potentiometric titration at temperature of $29^{o}C$ and $35^{o}C$. The rate of adsorption of Br^{-} and Cl^{-} on TiO_2 at $29^{o}C$ are derived to be $-r_{cl} = 0.00040_{cl}$ and $-r_{Br} = 0.50_{Br}$, while at $35^{o}C$, the rate of adsorption was found to be $-r_{cl} = -r_{Br} = 4.0 \times 10^{-13} mol/cm^2 min$ for both anions. The order of the adsorption rate of alkaline anions at $29^{o}C$ is first order while at $35^{o}C$ was found to be Zero order. Also, the determination of surface area of TiO_2 gave an area of $6175.34 m^2/g$.

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NOMENCLATURE

E   Surface electric charge, $\mu Cmol/cm^2$

Cs   Concentration of stock solution

F   Faraday number, 96500C

M.w   Molecular weight

n   Number of charge on ion

Nm   Number of adsorption sites

No   Avogadro's number, 6.02×1023

C   Concentration, M, g/cm^3, mol/dm^3

S   Specifc surface area, cm^2/g

S.G   Specific gravity, g/ml

θ Adsorption capacity, or coverage, $gmol/cm2$

ΔV Change in volume of titrant, ml

Br^- Bromide ion

Cl^- Chloride ion

NaBr   Sodium Bromide

NaCl   Sodium Chloride

$-r_{cl}$ Rate of adsorption of Cl^-

$-r_{Br}$ Rate of adsorption of Br^-

K   Rate constant

θ_{cl} Adsorption of Cl

θ_{Br} Adsorption of Br^-

CHAPTER ONE

1.0   INTRODUCTION

1.1 Background

This research work "Kinetic of adsorption of alkaline anions on titanium (iv) oxide used in a dry cell" is based on Leclanche dry cell, which is widely used today as battery. This project work is focused on an attempt to provide detailed analysis of the Kinetics that involve in the adsorption of alkaline anions, which have as influence on the cell life span.

Battery is a device that changes chemical energy into electrical energy. It consists of a number of connected units called cells and this converts the energy of chemical reaction into an electric current (3).

In a common usage, the term battery is also applied to a single cell, such as flash light battery. There are generally two types of batteries. Indeed, this research work is based on the primary battery and in particular the Leclanche dry cell.

The leclanche dry cell is an improved type of primary cells (voltaic pile) in the line of inventory the first primary cell was invented by Alessandro Volta. There are many variables (parameter) that affects the rate of an electrode reaction, which consequently determines the effectiveness of a battery. The variables are:

1) Electrode Variables: material surface area (A), geometry and surface condition of the electrode.

2) Mass transfer variables: mode (diffusion, convection), surface concentration and adsorption.

3) External variable: Temperature, pressure, and time.

4) Electrical variables: Potential (E), current (i) and quantity of electricity (Q)

5) Solution Variables: Bulk concentration of electro active species, concentration of another species (electrolyte, pH....), solvent (4).

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A leclanche's cell has a negative electrode of zinc, ammonium chloride electrolyte and a positive electrode of finally divided carbon and manganese (IV) oxide (MnO$_2$) packed around a carbon rod terminal.

Manganese (IV) oxide is present to act as a depolarizer by adsorbing the hydrogen gas that is formed at the positive electrode; the two electrodes are separated by moistened paper, starch gel or some other porous non- conductor.

Meanwhile, Titanium (IV) oxide (TiO$_2$) can be also be used in the leclanche cell as a depolarizer, which is the basis of this research work.

General, the non-conductor contain zinc and mercuric chlorides is used to amalgamate the zinc in order to increase the storage life. When the cell is made in cylindrical form, the zinc usually serves both as the negative electrode and as the container.

The reaction at the negative electrode is

$$Zn + 2OH^- \longrightarrow ZnO + H_2O + 2e^- \text{----------} 1.1$$

Where e denotes electron and OH denotes hydroxyl ion, both from the ionization of water

$$H_2O \longrightarrow H + OH^- \text{---------} 1.2$$
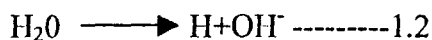
The reaction at the positive electrode depends on whether the discharge rate is slow or high. For slow discharge, when TiO$_2$ used as a depolarizer, we have

$$2 TiO_2 + NH_4^+ + 2e^- \longrightarrow Ti_2O_3.H_2O \text{------------------} 1.4$$

The ammonium ion (NH$_4^+$) comes from ionic dissociation of ammonium chloride. The overall reaction at the two electrodes is:

$$Zn + H_2O + 2TiO_2 \longrightarrow Ti_2O_3.H_2O + ZnO \text{-------------} 1.5$$

The hydrogen gas produced seriously reduces the efficiency of the dry cell due to two reasons.

1) The hydrogen layer set-up a back e.m.f in the cell in the opposition to that due to the copper and zinc.

2) The gas partially insulates the plates and hence increases the internal resistance of the cell, thus the current in the circuit is greatly reduced. This effect is called polarization of the cell, (1).

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The titanium (iv) oxide in the cell serve to minimise polarization i.e. act as a depolarizer.

The polarization reaction can be given as:

$$H_2 + 2TiO_2 \longrightarrow H_2O + Ti_2O_3 \dots\dots\dots\dots 1.6$$
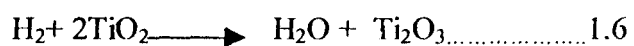
1.2 Scope of Work

In order to propose the kinetic rate relationship that exists between some selected anions and the cells (leclanche) performance, some particular alkaline anions are being employed, they are Cl^- from aqueous sodium chloride salt and Br^- bromide from aqueous sodium bromide salt.

The data obtained from the potentiometric titration of trixonitrate (V) acid, $HNO_{3(aq)}$ (titrant) against each of the anions mentioned earlier (titrands) at various concentration and temperature are being used extensively for this research work.

1.2 Aims and Objective.

The aim of this research work is to study the kinetic rate relationship that exist between some selected alkaline anions and titanium (IV) oxides, (TiO_2), after blending TiO_2 with both Cl^- and Br^- from their respective sodium salts to improve its depolarization performance and to enhance the longevity of the leclanche dry cell.

1.3 Approach

Data obtained from both adsorptions from solution and potentiometric titration experiments were used to determine the rate of adsorption.

Then, at a particular pH of solution, the plots of the logarithm of rate of adsorption against the logarithm of the adsorption are used to ascertain the order of reaction by finding the slope.

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CHAPTER TWO

2.0   LITERATURE REVIEW

2.1 Historical Development

Towards the and of the eighteenth century, Luigi Galvani, while dissecting a frog, noticed that is leg- muscle twitched when one of his assistants produced an electric spark in another part of the room. He also found that when a frog's leg muscles was hung by a copper hook from an iron stand, the muscle twitched whenever it swung so as to touch the stand.

Galvanic suggested that the electricity which caused the twitching was generated within the muscle but his fellow countryman, Alessandro Volta, believed that it arose from the contact of the two dissimilar metals. Volta turned out to be right and in 1799 he discovered how to obtain from two metals a continuous supply of electricity by placing a piece of cloth soaked in brine between copper and zinc plate and the arrangement is called a voltaic cell. The use of Volta's invention quickly led to a number of important discoveries (1).

One of special interest was introduced by William Wallastan (1816) copper plate doubled around zinc plates with a space between the plate were submerged in dilute acid when the battery is in use and with drawn when not use. This battery was a precursor of modern reserve cell. An important stage is the evolution of the battery was the invention of Daniel cell, in 1836 by English chemist John Frederic Daniel, this cell was the first to include a depolarizer.

In 1868, the French chemist George Leclanche invented a forerunner of today's zinc- carbon dry cell. The leclanche cell used a liquid solution of ammonium chloride as an electrolyte. The first true dry cell, using a paste electrolyte containing ammonium chloride was developed by carl grasner in 1886 (5).

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2.2 Types of Electric Cell

Cells may be divided into two kinds; primary cells secondary cells. In a primary cells the chemical reaction used up the available electrode material. This causes the electrode to deteriorate when they wear out.

The secondary cells however, are constructed so that the electrode does not deteriorate. Upon discharge, the cell can be recharged by an electrical generator. The generator is connected to the cell so that the flow of current through it is a direction opposite to the flow during discharge. In effect, the chemical reaction in the cell is run backwardly restoring its ability to produce current.

2.2.1 Primary Cells.

Primary cells are those in which current is produced as a result of an irreversible chemical change (6).

Initially, they are assembled with drawn as electrical energy at some latter times. The electrolyte and electrodes have to be replaced when they wear out they can be divided into four types: dry cell, wet cells, resever cells and fuel cells.

Dry cells: Dry primary cells are non-spill able and non-refillable. It is called a dry cell because the electrolyte is a moist paste, rather than a liquid.

This makes the cell less likely to leak or spill. The electrolyte usually is immobile (contained in adsorbent material). Because of this immobility, ion migration is slower in dry cells than wet cells. Dry cells, therefore, sustain lower current that wet cells. Because dry cells are non-spill able, they can be used on a person e.g. in hearing aids. Dry cell made in appreciable quantities on the leclanche alkaline- manganese (IV) oxide and mercury cells. Silver chloride and silver oxides cell are made in lesser amounts, others in limited quantities, (3)

2.2.2 Leclanche dry cells

It uses an amalgamated zinc anode, an electrolyte of ammonium and zinc chloride dissolved in water and a manganese dioxide cathode has dominated the primary battery market since its introduction is the 1860's. In present- day dry cells, the cathode is MnO_2

with Ca 10-30 weight % acetylene black to improve the matrix conductivity. The anode is usually the zinc can or a zinc sheet. Amalgamation of zinc with mercuric chloride minimises corrosion and associated hydrogen evolution.

The electrolyte layer in the dry cell is also a separator, which prevents a short circuit of the cathode and anode (7).

The two general categories for the leclanche dry cell are the round and the flat cells whose difference is chiefly physical, not chemical the cell has open- circuit potential of 1.6V when fresh. Discharge current density, shelf life is an important factor and can be controlling at low discharge rates. Service life also is dependent on the relative lime of operation and recuperation period.

The popularity of leclanche dry cells is based in part on their relatively low cost, availability in many voltages and size, and suitable for intermittent and light- to – medium current- grain capability (8).
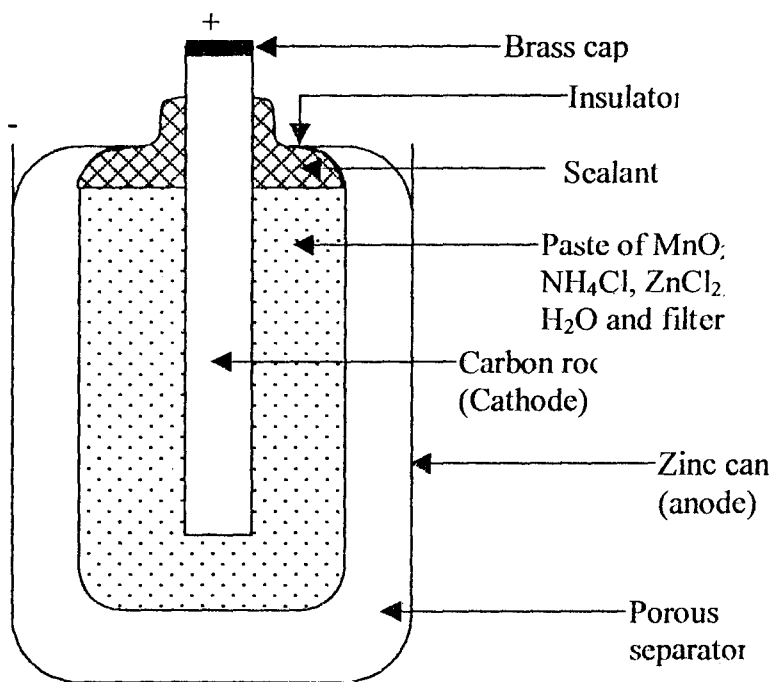
Fig. 2.1 Leclanche dry cell

2.3 Defect of a Simple Cell

There are two serious defect of a simple cell. These are known as polarization and local action, (6).

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2.2.3 Polarization

The working of a cell involves the release of hydrogen bubbles. These bubbles collect at the positive electrode and insulate it. This slows down and eventually stops the working of the cell. This defect is called polarisation. Polarization can be cut down either by occasionally brushing the plates, which is highly inconvenient, or by use of what is called a depolarizer, such as manganese dioxide, which oxides hydrogen to form water and so removes the hydrogen bubbles.

2.3.1 Local action

Impurities in the zinc can also interfere with the operation of the cell. Copper, iron or carbon in the zinc set up tiny cells within the electrode itself, wearing it away faster and producing energy that is wasted in the form of heat. Such local action can be prevented in either of two ways- the cathode can be made of very pure zinc, or a coating of mercury can be applied to the zinc surface.

2.4   Chemistry of Batteries

An electrochemical cell consists basically of two electrodes of unlike material placed in a solution. Electrodes are conductors in the form of rods or plates. The solution can conduct electricity and is called an electrolyte. The electrodes may be placed in the same or in different solution. A reaction takes place between one of the electrodes and the electrolyte, releasing electrons. This is an oxidation reaction and the electrode is called a negative electrode. The positive electrode takes on electrons in what is known as a reduction reaction. If an external wire connects the electrodes, excess electrons will flow from the negative to the positive electrode. This flow of electrons is as electrical current it can be used to power lights, motors, electronic circuit, or other useful devices.

The overall reaction taking place within a battery is known as oxidation-reduction reaction. Tais reaction is driven by the chemical differences between the electrode materials. One material tends to give up electrons, the other to give electrons. When two half- reactions are combined the resulting- reactions proceeds automatically, and current flows.

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In any electrochemical cell the electrical pressure (Voltage) depends upon the materials used to make up that cell and not upon the size of the cell or the arrangement of materials within it. All batteries having electrodes of the same materials have the same voltage. The range of voltage voltages produced by the various types of cell is not large, about 1.25 to 2 volts.

For example, the standard flash light battery produces 1.5 volts. Higher voltages are obtained by connecting cells in series. Thee two batteries usually found in a flashlight are connected in series to yield 3 volts. Current in battery are measured in amperes and capacity in ampere-hours. The ampere-hour is a measure of both how much current a battery gives and for how long [5].

2.5   Adsorption

Adsorption is the selective collection and concentration, on to solid surface of a particular types of molecules contained in a liquid or gas. Solids that are used to adsorb gases or dissolve substances are called adsorbents; they adsorbed molecules are usually referred to collectively as the adsorbate.

Adsorption refers to the taking up of molecules by the external surface or internal surface (walls of capillaries or crevices) of solid or by the surface of liquids. Absorption, with which it is often confused, refers to processes in which a substance penetrates into the actual interior of crystals, of blocks of amorphous solid, or of liquids. Sometimes the word sorption is used to indicate the process of the taking up of gas used or liquid by a solid without specifying whether the process is adsorption or absorption. Two types of adsorption may occur (7).

2.5.1 Physical adsorption.

Physical adsorption is non specific and somewhat similar to the process of condensation. The forces attracting the fluid molecules to the solid surface are relatively weak, and the heat evolved during the exothermic adsorption process is of the same order of magnitude as the heat of condensation, 0.5 to 5 Kcal/gmol. The adsorption is made

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possible by the transfer of the adsorbed molecules kinetic energy of approach into many vibrational mode of the solid.

An example of physical adsorption is the adsorption of helium on tungsten.

2.5.2 Chemisorption.

This is a process in which a strong bond is formed between adsorbent and substrate, characterized by a large heat of adsorption.

In chemisorptions, the adsorbed molecules are actually chemically bonded to one or a few surface atoms. Example of this is the dissociate adsorption of hydrogen on tungsten.

However, molecules with high kinetics energy are not likely to be adsorbed at all, but simple to rebound. One can treat such rebounding as an elastic collision which a single surface atom.

2.5.3 Adsorption isotherm.

A.   Langmuir adsorption isotherm.

Langmuir proposed simple formulations of rates of adsorption and desorption of gases (applicable also to liquid) on solid surface. It is derived on the basis of several assumptions namely:-

1) All the surface of the solid has the same activity for absorption, e.g. it is energetically uniform.

2) There is no interaction between absorbed molecules; this means that amount absorbed has no effect on the rate of adsorption per site.

3) All the adsorption occurs by the same mechanism, and each adsorbed complex has the same structure.

4) The extent of adsorption is less than one complete monomolecular layer on the surface (9).

In the system of solid surface and gas, the molecules of gas will be continually striking the surface and a fraction of those will adhere. However, because of their kinetic rotational and vibrational energy, the more energetic molecules will be continually leaving the surface. Equilibrium will be established such that the rate of which molecules

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strikes the surface, and remain for an appreciable length of time by the rate of which molecules leave the surface.

The rate of adsorption r_a will be equal to the rate of collusion r_c of molecules with the surface multiplied by a factor F representing the friction of the collecting number of molecules that adhere. At a fixed temperature the number of collusion will be proportional to the pressure P of the gas (or its concentration), and the fraction F will be constant. Hence the rate of adsorption per unit of bare surface will be r_c x F. this equal to K P, where K is constant involving the friction F and the proportional between rc and p.

Since the adsorption is limited to complete coverage by a monomolecular layer, the surface may be divided into two parts: the fraction 0 covered by the adsorbed molecules and the fraction $1 - \theta$ which is bare. Since only those molecules striking the uncovered part of the surface can be adsorbed, the rate of adsorption per unit of total surface will be proportional to $1 - \theta$, that is

$$r_a = KP(1-\theta) \text{------------------} 2.1$$

The rate of desorption will be proportional to the friction of covered surface

$$r_d = K' \theta \text{ -------------------------} 2.2$$

The amount adsorbed at the equilibrium is obtained by equating r_a and r_d and solving for 0. The result is called the langmuir isotherm, is

$$0 = \frac{kP}{k' + kP} = \frac{KP}{1 + KP} = \frac{v}{v_m} \quad \text{................................} 2.3$$

Where $K = k/k^1$ is the adsorption equilibrium constant, expressed in unit of gas adsorbed, v, since the adsorption is less than a monomolecular layer. Hence equation (3) may be regarded as a relationship between the pressure f the gas and the volume adsorbed this is indicated by writing as $\theta = V/V_m$ where is V_m the volume adsorbed when the all the active sites are covered i.e. when there is a complete monomolecular layer.

The concentration from of equation (2.3) can be obtained by introducing the concept of an adsorbed concentration C, expressed in moles per gram of solid. Following the same procedure above we have to be

$$\theta = k_cCg$$

$$\overline{1 + k_cCg} \text{ ------------------2.4}$$

Where $K_c = {}^{kc}/_{k'c}$ = equilibrium constant.

Cg = concentration of adsorption component in the gas.

B. other isotherms.

Two other well-known isotherms may be classified in terms of the ΔHa-θ dependency.

1) The temkin isotherm may be derived from the langmuir isotherm by assuming that the heat of adsorption drops linearly with increasing θ. The result is

$$\theta = K_2 + K_1 \log c \text{ ------------2.5}$$

Where K_1 and K_2 are constant at a given temperature.

i)   The freundlich isotherm can be derived by assuming a logarithmic decrease in ΔHa be with θ, that is

$$\Delta Ha = -\Delta Ho \ln \theta \text{ -----------2.6}$$

The isotherm itself has the form

$$\theta = kc^n \text{ ----------2.7}$$

Where n has a value greater than unity, owning to its flexibility, the freundlich isotherm usually fits experimental data over a reasonable range of concentration, (7).

In conclusion, note two points first the freundlich isotherm can be reduced to either the langmuir or the temkin form by proper simplification. It may be considered a general empirical form encompassing the other more specific types. Second a single isotherm to fit data over the entire range of θ.

It has been shown that a straight line drawn through a plot of log θ versus log C should give a positive intercept of K and a positive slope of n.

Also, from recent experimental work on adsorption in a journal titled "oxide and oxide film," this was shown that this relationship

$$\theta = \Delta V. C \qquad \text{holds-----------2.8}$$
$$\overline{\text{S.1000}}$$

Where θ = Adsorption gmol/cm^2, Δv = change in volume of titrant cm^3 and S =

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surface area of the adsorbent cm^2/g (10).

2.6 Practical Method of Adsorption

Generally the adsorption analysis as it relates this research work could be achieved through three broad methods of analysis namely;

1) Electro kinetic method.

2) Radio chemical method.

3) Potentiometric titration method i.e. method of interest.

2.6.1 Electric kinetic method.

The Electro kinetic phenomena are that which is associated with the movement of a continuous medium of a charged surface. The four principal Electro kinetic phenomena are electrophoresis, Electro osmosis, streaming potential and sedimentation potential or Dorn effect.

2.6.2 Radio chemical method

This method embrace the application of radioactive isotopes. In a unique application of radio chemical studies (like in adsorption) an understanding of diffusion is of considerable important because the rate at which chemical reactions species can diffuse through a medium to the point of reaction or adsorption. For example, to the point of reaction or process depends upon the rate of oxidation of copper ions to the metal surface.

2.6.3 Potentiometric titration(general principle)

The procedure involved measurement of the e.m.f between two electrodes, an indicator electrode, the potential of which is a function of the concentration of the ion to be determined, and a reference electrode of constant potential.

In potentiometric titrations, the measurements are made while the titration is in progress. The equivalence point of the reaction will be revealed by a sudden change in

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potential in the plot of e.m.f reading against the volume of the titrating solution, any method which will detect this abrupt change of potential may be used.

One electrode must maintain a constant, but not necessarily known potential while the other electrode must serve as an indicator of the changes in ion concentration and must respond rapidly. The solution must be of course be stirred during the titration.

A simple arrangement of potentiometric titration consists of a reference electrode indicator, magnetic stirrer and the solution to be titrated is contained in a beaker to be titrated is contained in the beaker. When the solution requiring the exclusion of the atmospheric carbon dioxide or air are to be titration, it is advisable to use a tall lipless beaker equipped so that nitrogen may be bubbled through the solution is determined and relatively large increment (1-5ml) of the titrant solution are added until the equivalence point is approached, the e. m. f is determined after such addition.

The approach of the e.p is indicated by a somewhat more rapid change of the e.m.f. In the vicinity of the equivalence point, equal increment-(e.g. 0.1 or 0.05ml) should be added, the equal addition in the region of the e.p are particularly important when the e.p is to be determined by an analytical method. Sufficient time of approximately two munites should allowed after each addition for the indicator electrode to reach a reasonably constant potential, before the next increment is introduced. To measure e.m.f., the electrode system must be connected to either a pH meter reading which gives directly the varing pH values as titrations proceeds, or the meter may be used in milli volts mode, so that the e.m.f. values are recorded [11].
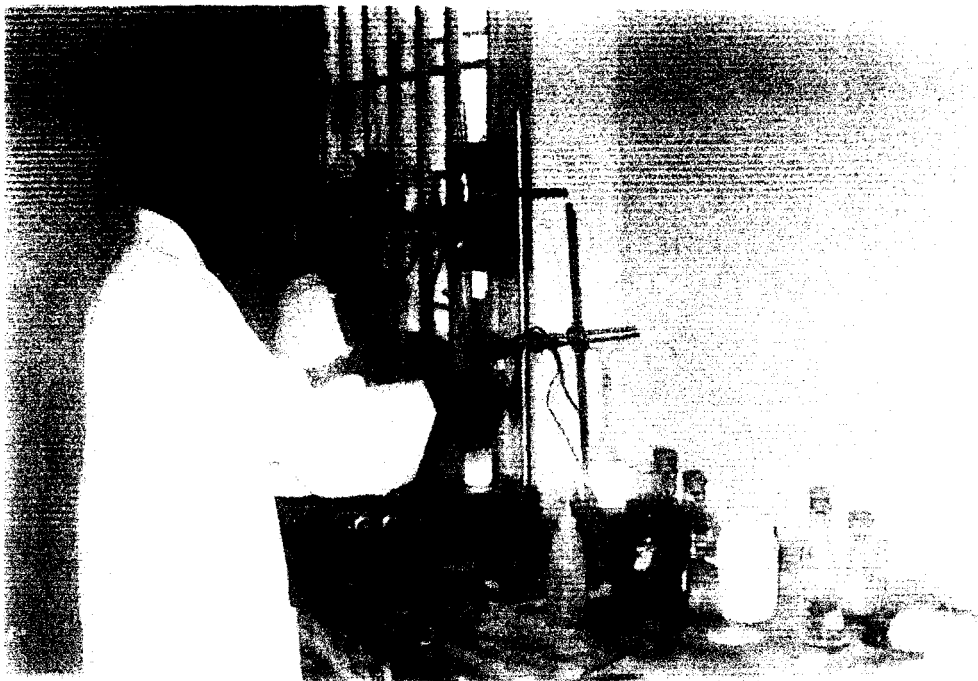
Fig. 2.2: Potentiometric Titration set- up

2.7   Titanium (IV) Oxide

Titanium (IV) oxide, TiO_2 is an oxide of titanium which exist at a room temperature in three forms:- rutile, anatase and brookite, each of which occurs naturally.

Each contain six co-ordinate titanium but rutile is the common form, both in nature and as produced commercially and the others transform onto it on heating.

2.7.1 Properties of TiO_2

1) Texture: powdery

2) Colour: white

3) Solubility: soluble in water

4) Density: $155g\ cm^{-3}$

5) Melting point temperature: it varies from 1892^0C when heated in an atmosphere of O_2 to 1943^0C when heated in air.

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6) Molecular weight: 80g.

2.8 Electric Charge

Electric charges are the quantity of electricity that flow in electric circuit or that accumulates on the surface of dissimilar non- metallic substance that are the rubbed together vigorously. Electric charges are of two generally types: positive and negative charges.

Many fundamental or subatomic particle of matter have the property of electric charge. For example, electrons have negative charges and proton have positive charges of but neutrons have zero charge. The negative charge of each election is found by experiment to thus exist in natural this equal to the charges of an electron or a proton, a fundamental physical constant, [12]

Electric charges are considered in any system, in any chemical and nuclear reaction, the net electric charge is constant.

The surface charge, $E = n F \theta$

Where E = Surface electric charge $\mu Cmol/cm^2$

N = Forestay's constant i.e. 96500 c

θ = Adsorption $[mol/cm^2]$

2.9 Chemical Kinetics

Chemical kinetic is the study of reaction rates and of the factors that influence them.

The aims of studying chemical Kinetics are.

1) To determine experimentally the rate of a reaction and its dependence on parameters such as concentration, temperature and catalysts.

2) To understand the mechanism of the reaction that is the sequence of steps by which a reaction occurs.

In the approach to chemical Kinetics, the way kinetic laws are express depends in large part on the type of reaction we are dealing with and it may be well to consider the classification of chemical reactions [13]

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2.9.1 Classification of chemical reaction.

Chemical reactions can be classified by breaking it down according to the number and types of phases involved, the big division being between the homogeneous and heterogeneous systems.

A reaction is homogeneous if it takes place in one phase alone. A reaction is heterogeneous if it requires the presence of at least two phases to proceed at the rate that it does.

2.9.2 Variables affecting the rate of reaction

In homogenous systems the temperature, pressure and composition are obvious variable. But in heterogeneous system more than one phase is involved, hence the problem becomes more complex, since material may have to move from phase to phase during reaction, hence the rate of mass transfer can become important. Also rate of heat transfer can also be a limiting factor of rate equation when dealing with an endothermic or exothermic reaction.

2.9.3 Reaction rate.

The rate of a reaction is expressed as they change in concentration of a reactant molecule with time. Consider the stoichiometrically simple reaction.

$R \rightarrow P$ 2.10
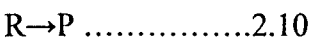
Let the concentration (in mol liter^{-1}) of R at time t, and t_2 ($t_2 > t_1$) be $(R)_1$, and $(R)_2$. the rate of the reaction over the time interval ($t_2 - t_1$) is given by

$$\frac{[R]_2 - [R]_1}{t_2 - t_1} = \frac{\Delta[R]}{\Delta t} \quad ....2.11$$

Since $[R]_2 < [R]_1$. in practice, what we are interested in, is the instantaneous rate. Using the language of calculus, as Δt becomes smaller and smaller and eventually approaches Zero, the rate of the fore-going reaction at a specific time t is given by

$$\text{Rate} = \frac{-d[R]}{dt} = \frac{d[P]}{dt} \dots\dots\dots 2.14$$

The units of reaction rate are usually MS^{-1} or $M\ min^{-1}$

In dealing with stoichiometrically more complicated reactions the rate must be expressed in an unambiguous manner.

Suppose that the reaction of interest is now

$$R \rightarrow 2P \dots\dots\dots\dots 2.15$$

The new rate equation should be written as

$$\text{Rate} = \frac{-d[R]}{dt} = \frac{1}{2}\frac{d[P]}{dt} \dots\dots\dots\dots 2.16$$

because the product P is appearing twice as fast as the reaction R is disappearing.

Therefore, the manner in which the rate of a reaction varies with reaction concentrations is called rate law.

2.9.4 Order of reaction

This is the power to which a concentration is raised in the rate equations and is a specification of the empirical dependence of the rate on concentrations. It may be zero, an integer or even a non- integer.

A)   Determination of reaction order.

Before anything can be said about the mechanism of a reaction, the first task is to determine the order of the reaction. There are a number of methods for this:

i)   Integral method.

An obvious procedure is to measure the concentration of the reactions(s) at various time intervals of a reaction and to substitute the data into the standard equations for the various form of rate order that will be derived later.

Let us examine a number of those forms:

1)   Zero order when the rate of reaction is independent of the concentration of materials or reactant concentrations. Thus

$$-r_A = \frac{-dC_A}{dt} = K \dots\dots\dots 2.17a$$

Integrating between t=0 and t=t gives

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$$\int_{C_{A0}}^{C_A} dC_A = -K\int_0^t dt \ldots\ldots\ldots\ldots 2.17b$$

$$C_{A0} - C_A = Kt \qquad \text{for} \qquad t < \frac{C_{A0}}{K} \ldots\ldots\ldots\ldots 2.18$$

As a rule, reactions are zero order only in certain concentration ranges- the higher concentrations.

2) Empirical rate equation of nth order.

When the mechanism of reactions is not known, we often attempt to fit the data with an nth –order rate equation of the form.

$$-r_A = \frac{-dC_A}{dt} = KC_A^n \ldots\ldots\ldots\ldots 2.19$$

Which on separation and integration, gives

$$\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A^n} = -K\int_0^t dt \ldots\ldots\ldots\ldots 2.20a$$

$$= C_A^{1-n} - C_{A0}^{1-1} = (n-1)Kt, n \neq 1 \ldots\ldots\ldots\ldots 2.20b$$

ii) Differential Method

The differential method of analysis deals directly with differential rate equation to be tested, evaluating all terms in the equation including the derivatives dC_A/dt and testing the goodness of fit of the equation with experiment.

The procedure is as follows:

1) Plot the C_A Vs t data and then by eye, carefully draw a smooth curve to represent the data. This curve most likely will not pass through all the experimental points.

2) Determine the slope of this curve at suitably selected concentration values- this slope $dC_A/dt = r_A$ are the rates of reaction at these composition.

3) Now search for a rate expression to represent this r_A Vs C_A data either by picking and testing a particular rate form or

Testing an nth order form, $-r_A = KC_A^n$ by taking logarithms of the equation.

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2.9.5 Elementary and non-elementary reaction.

Consider a single reaction with stiochiometric equation:

$$A + B \rightarrow R \ldots \ldots \ldots 2.21$$
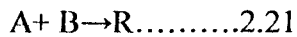
If the rate – controlling mechanism involves the collision or interaction of a single molecule of A with a single molecule of B, then the number of collisions of molecules A with B is proportional to the concentration of reactions in the mixture, hence the rate of disappearance of A is give by.

$$r_A = KC_A C_B \ldots \ldots \ldots 2.22$$

Such reaction in which the rate corresponds to a stichiometric equation are called elementary reactions. But when there is no correspondence between stoichiometry and rate than we have a non-elementary reaction.

2.9.6 Molecularity and rate constant K

The molecularity of an elementary reaction is the number of molecules involved in the reaction, and this has been found to have the value of one, two and occasionally three. Note that the molecularity refers to an elementary reaction.

Rate constant K for a given reaction does not depend on the concentrations of the reactant; it is affected only by temperature. For homogeneous chemical reaction, its dimensions for the nth –order reaction are $(time)^{-1} (concentration)^{1-n}$ which for a first-order become simply $(time)^{-1}$

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CHAPTER THREE

3.0 EXPERIMENTAL WORK

3.1 Chemical and Equipment

The chemical used for both the absorption from solution experiment to determination of specific surface area of titanium(IV) oxide and those used for the potentiometric titration are presented in Table 3.1 while Table 3.2 contains list of the equipment used.

Table 3.1 List of chemicals used

Chemical	Source	Comments
Sodium hydroxide (NaOH)	Chemproha chemical	Laboratory chemicals (Analytical)
Acetic Acid (CH_3COOH)	East Anglia chemicals	Analytical
Phenolphthalein	May and baker Ltd Dagenham England	Laboratory chemicals
Titanium (IV) oxide (TiO_2)	BDH chemical Ltd pools England	Laboratory reagent (Analytical)
Nitric acid (HNO_3)	M&B chemical company, England	Laboratory chemical.
Sodium chloride (NaCl)	M&B chemical company England	Laboratory reagent (Analytical)
Sodium bromide	M&B chemical company, England	Laboratory Chemical (Analytical)
Nitrogen gas	Supplied in cylinder	Analyticaland Industrial

Nitrogen gas was necessary used in the experiment in order to:

i)   Provide an inert environment in the titrating vessels and thus inhibit side reactions.

ii)   Drive off oxygen and carbon dioxide, which, might be present in the vessel.

Table 3.2 List of equipment used

Equipment	Source	Comment
250ml beaker	Simax Czechoslovakia	Analytical (fragile)
250ml Erlenmeyer flask with stopper	Simax Czechoslovakia	Analytical (fragile)
50ml burette	Technico England	Analytical (fragile)
100ml titration conical flasks	Schott Mianz Jena glas	Analytical (fragile)
Funnel	-	Conveying (Plastic)
Analytical balance	Ohaus U.S.A.	Analytical
25ml pipette	Techcolor west-Germnay	Analytical (Fragile)
Spatula	-	For taking sample
Wash glass	-	For taking sample
PH meter (3071)	Jenway U.K.	Analytical
Magnetic stirrer	Conning hemming	Analytical
Magnetic follower	Conning hemming	Analytical
	Techino	Analytical(fragile)
50ml burette	England	
25ml Pipette	Techcolor West Germany	Analytical(fragile)
100ml beaker	Simax Czechoslovakia	Analytical(fragile)
250ml beaker	Pyrex England	Analytical(fragile)
250ml conical flask	Pyrex England	Analytical(fragile)
250&1000ml measuring cylinders	Techino England	Analytical(fragile)

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100ml volumetric flask	Jay Tech England	Analytical
Nitrogen gas cylinder and regulator	Switzerland	Analytical and industrial
Retort stand and clamp	Technico England	Analytical

3.2 Preparation of Chemical Used

(a) Sodium chloride, NaCl

58.5g of NaCl was dissolved in some quantity of distil water and was made up to 1000cm^3 in a cleaned volumetric flask to give 1M NaCl. The molar weight of NaCl being 58.5g

After the first round of experiment with 1M NaCl, the remaining solution was diluted with appropriate volume of distil water to get a solution of 0.1M NaCl. Subsequently, 0.01M and 0.001M of the solutions were made like wise.

(b) Sodium Bromide, NaBr

102.9g NaBr was dissolved in some quantity of distil water, and was made up to 1000cm^3 in a cleaned volumetric flask to give 1M NaBr. The molar weight of NaBr being 102.9g. then, portion of 1M NaBr solution was taken and diluted with appropriate volume of distil water to get 0.1M, 0.01M and 0.001M solution of NaBr respectively.

(c) Sodium hydroxide, NaOH

4g of sodium hydroxide was dissolved in some quantity of distil water, and made up of 1000cm^3 in a cleaned volumetric flask to give 0.1M NaOH. Since the molar weight of NaOH is 40g.

d) Acetic acid and nitric acid.

Since these acids are usually stored in stock bottles, it becomes necessary to determine the concentration of the stock solution before being used.

The concentration of the stock solution was determined using the assay on the stock bottle.

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CHAPTER FOUR

4.0 RESULTS

4.1 Tables of values obtained from the experiment of determination of specific surface area of TiO_2.

Table 4.1a: Data obtained from the titration of 0.1M NaOH against various concentrations of acetic acid.

Initial conc. of Acetic acid(M)	0.15	0.12	0.09	0.06	0.03	0.015
Volume of acetic acid(ml)	25	25	25	25	25	25
Volume of 0.1MNaOH(ml)	47.05	40.92	30.52	20.25	11.35	7.64

Table 4.1b: Concentration and number of moles of acetic acid.

C1 = Initial concentration of acetic acid

Ceq = Equilibrruim concentration of acetic acid

N = Number of moles.

C1 (M)	Ceq (M)	N=Ceq(M) – C1(M)	Ceq/N
0.15	0.1882	0.0382	1.927
0.12	0.1637	0.0437	3.746
0.09	0.1221	0.0321	3.804
0.06	0.081	0.021	3.857
0.03	0.0454	0.0154	2.948
0.015	0.0306	0.0156	1.961

4.2 Tables of experimental data from potentiometric titration.

The following date were obtained from the potentyiometric (adsorption) titrationexperiment of 0.1M HNO_3 against various concentrations of both NaCl and NaBr at different temperature with and without TiO_2.

At temperature $29^{o}C$ for various concentration s of Br⁻ and Cl⁻, the following date were obtained:

Table 4.2 : Tables of data for the titration of 0.1M HNO₃ against 1M Br⁻ at 29°C.

1M Br- without TiO₂

V HNO₃(ml)	0.0	0.5	1.0	1.5	2	2.5	3	3.5	4	4.5	5
pH	4.03	2.32	2.09	1.97	1.96	1.96	1.92	1.91	1.91	1.91	1.9
V HNO₃(ml)	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10	
pH	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9	

1M Br- with TiO₂

V HNO₃(ml)	0.0	0.5	1.0	1.5	2	2.5	3	3.5	4	4.5	5
pH	6.5	5.85	5.22	4.16	3.86	3.62	3.49	3.38	3.32	3.26	3.23
V HNO₃(ml)	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10	
pH	3.18	3.16	3.12	3.10	3.08	3.07	3.06	3.06	3.06	306	

Table 4.3: Tables of data for the titration of 0.1M HNO₃ against 0.1M Br⁻ at 29°C.

0.1M Br- without TiO₂

V HNO₃(ml)	0.0	0.5	1.0	1.5	2	2.5	3	3.5	4	4.5	5
pH	6.44	4.28	4.12	4.02	3.94	3.9	3.86	3.82	3.8	3.77	3.75
V HNO₃(ml)	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10	
pH	3.72	3.7	3.67	3.66	3.64	3.62	3.6	3.59	3.54	3.52	

0.1M Br- with TiO₂

V HNO₃(ml)	0.0	0.5	1.0	1.5	2	2.5	3	3.5	4	4.5	5
pH	7.18	5.44	4.6	4.39	4.26	4.13	4.05	3.99	3.95	3.91	3.87
V HNO₃(ml)	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10	
pH	3.83	3.8	3.77	3.74	3.72	3.7	3.68	3.65	3.63	3.61	

Table 4.4: Tables of data for the titration of 0.1M HNO₃ against 0.01M Br⁻ at 29°C.

0.01M Br- without TiO₂

V HNO₃(ml)	0.0	0.5	1.0	1.5	2	2.5	3	3.5	4	4.5	5
pH	6.76	4.78	4.4	4.34	4.16	4.07	4.0	3.94	3.89	3.85	3.81
V HNO₃(ml)	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10	

| pH | 3.78 | 3.75 | 3.71 | 3.68 | 3.66 | 3.63 | 3.61 | 3.59 | 3.57 | 3.55 | |

| pH | 3.78 | 3.75 | 3.71 | 3.68 | 3.66 | 3.63 | 3.61 | 3.59 | 3.57 | 3.55 | |

0.01M Br- with TiO$_2$

V HNO$_3$(ml)	0.0	0.5	1.0	1.5	2	2.5	3	3.5	4	4.5	5
pH	6.94	5.36	4.58	4.38	4.28	4.21	4.17	4.11	4.08	4.03	4.00
V HNO$_3$(ml)	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10	
pH	3.97	3.95	3.92	3.89	3.87	3.84	3.83	3.81	3.79	3.77	

Table 4.5: Tables of data for the titration of 0.1M HNO$_3$ against 0.001M Br⁻ at 29°C.

0.001M Br- without TiO$_2$

V HNO$_3$(ml)	0.0	0.5	1.0	1.5	2	2.5	3	3.5	4	4.5	5
pH	6.92	4.57	4.33	4.21	4.13	4.17	4.1	3.97	3.93	3.89	3.87
V HNO$_3$(ml)	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10	
pH	3.83	3.81	3.79	3.76	3.74	3.72	3.7	3.68	3.66	365	

0.001M Br- with TiO$_2$

V HNO$_3$(ml)	0.0	0.5	1.0	1.5	2	2.5	3	3.5	4	4.5	5
pH	7.35	5.64	4.85	4.5	4.4	4.29	4.21	4.14	4.09	4.03	3.99
V HNO$_3$(ml)	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10	
pH	3.95	3.91	3.88	3.86	3.83	3.8	3.78	3.75	3.73	3.71	

Table 4.6: Tables of data for the titration of 0.1M HNO$_3$ against 1M Cl⁻ at 29°C.

1M Cl⁻ without TiO$_2$

V HNO$_3$(ml)	0.0	0.5	1.0	1.5	2	2.5	3	3.5	4	4.5	5
pH	7.23	4.8	4.54	4.46	4.37	431	4.26	4.21	4.17	4.14	4.1
V HNO$_3$(ml)	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10	
pH	40.7	4.04	40.1	3.99	3.96	3.94	3.93	3.91	3.89	3.88	

1M Cl⁻ with TiO$_2$

V HNO$_3$(ml)	0.0	0.5	1.0	1.5	2	2.5	3	3.5	4	4.5	5
pH	7.28	5.55	4.76	4.65	4.5	4.4	4.34	4.29	4.24	4.2	4.19
V HNO$_3$(ml)	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10	
pH	4.14	4.11	4.08	4.06	4.04	4.01	3.99	3.97	3.96	3.93	

Table 4.7: Tables of data for the titration of 0.1M HNO₃ against 0.1M Cl⁻ at 29°C.

0.1M Cl⁻ without TiO₂

V HNO$_3$(ml)	0.0	0.5	1.0	1.5	2	2.5	3	3.5	4	4.5	5
pH	6.05	4.75	4.59	4.55	4.46	4.41	4.36	4.34	4.28	4.26	4.24
V HNO$_3$(ml)	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10	
pH	4.21	4.19	4.17	4.15	4.13	4.11	4.09	4.07	4.05	4.03	

0.1M Cl⁻ with TiO₂

V HNO$_3$(ml)	0.0	0.5	1.0	1.5	2	2.5	3	3.5	4	4.5	5
pH	7.34	5.78	5.15	4.88	4.58	4.72	4.52	4.44	4.4	4.35	4.31
V HNO$_3$(ml)	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10	
pH	4.27	4.24	4.22	4.19	4.17	4.15	4.13	4.11	4.09	4.07	

Table 4.8: Tables of data for the titration of 0.1M HNO₃ against 0.01M Cl⁻ at 29°C.

0.01M Cl⁻ without TiO₂

V HNO$_3$(ml)	0.0	0.5	1.0	1.5	2	2.5	3	3.5	4	4.5	5
pH	6.71	4.83	4.65	4.44	4.36	4.32	4.29	4.26	4.23	4.2	4.18
V HNO$_3$(ml)	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10	
pH	4.15	4.12	4.1	4.08	4.06	4.04	4.02	3.98	3.95	9.93	

0.01M Cl⁻ with TiO₂

V HNO$_3$(ml)	0.0	0.5	1.0	1.5	2	2.5	3	3.5	4	4.5	5
pH	7.22	5.18	4.78	4.59	4.5	4.46	4.39	4.35	4.31	4.27	4.24
V HNO$_3$(ml)	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10	
pH	4.22	4.19	4.16	4.14	4.11	4.09	4.09	4.05	4.03	4.01	

Table 4.9: Tables of data for the titration of 0.1M HNO₃ against 0.001M Cl⁻ at 29°C.

0.001M Cl⁻ without TiO₂

V HNO$_3$(ml)	0.0	0.5	1.0	1.5	2	2.5	3	3.5	4	4.5	5
pH	6.73	4.8	4.62	4.5	4.44	4.4	4.36	4.32	4.27	4.23	4.19
V HNO$_3$(ml)	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10	
pH	4.15	4.11	4.07	4.04	4.01	3.99	3.95	3.93	3.9	3.8	

0.001M Cl⁻ with TiO₂

V HNO₃(ml)	0.0	0.5	1.0	1.5	2	2.5	3	3.5	4	4.5	5
pH	6.99	5.02	4.74	4.6	4.54	4.49	4.42	4.36	4.32	4.29	4.26
V HNO₃(ml)	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10	
pH	4.24	4.22	4.19	4.16	4.12	4.09	4.05	4.01	3.98	3.95	

At temperature 35°C for various concentrations of Br- and Cl-,,the following data were obtained:

Table 4.10: Tables of data for the titration of 0.1M HNO₃ against 1M Br⁻ at 35°C.

1M Br⁻ without TiO₂

V HNO₃(ml)	0.0	0.5	1.0	1.5	2	2.5	3	3.5	4	4.5	5
pH	5.9	2.19	1.83	1.68	1.57	1.48	1.44	1.37	1.29	1.26	1.23
V HNO₃(ml)	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10	
pH	1.2	1.14	1.12	1.11	1.09	1.05	1.04	1.02	1.01	1	

1M Br⁻ with TiO₂

V HNO₃(ml)	0.0	0.5	1.0	1.5	2	2.5	3	3.5	4	4.5	5
pH	6.55	4.01	3.21	294	2.61	2.44	2.32	2.27	2.18	2.10	2.06
V HNO₃(ml)	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10	
pH	2.02	1.98	1.95	1.93	1.87	1.84	1.82	1.8	1.78	1.77	

Table 4.11: Tables of data for the titration of 0.1M HNO₃ against 0.1M Br⁻ at 35°C.

0.1M Br⁻ without TiO₂

V HNO₃(ml)	0.0	0.5	1.0	1.5	2	2.5	3	3.5	4	4.5	5
pH	5.75	2.2	2.08	1.91	1.84	1.73	1.66	1.61	1.53	1.5	1.48
V HNO₃(ml)	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10	
pH	1.44	1.41	1.4	1.36	135	1.33	1.32	1.32	1.32	1.32	

0.1M Br⁻ with TiO$_2$

V HNO$_3$(ml)	0.0	0.5	1.0	1.5	2	2.5	3	3.5	4	4.5	5
pH	6.4	4.78	3.54	2.94	2.71	2.55	2.45	2.37	2.31	2.26	2.22
V HNO$_3$(ml)	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10	
pH	2.19	2.09	2.05	2.02	199	1.97	1.93	1.93	1.92	1.9	

Table 4.12: Tables of data for the titration of 0.1M HNO$_3$ against 0.01M Br⁻ at 35°C.

0.01M Br⁻ without TiO$_2$

V HNO$_3$(ml)	0.0	0.5	1.0	1.5	2	2.5	3	3.5	4	4.5	5
pH	5.58	2.35	2.1	1.97	1.89	1.8	1.75	1.7	1.63	1.6	1.58
V HNO$_3$(ml)	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10	
pH	1.53	1.61	1.49	1.48	1.42	1.42	1.42	1.39	1.37	1.37	

0.01M Br⁻ with TiO$_2$

V HNO$_3$(ml)	0.0	0.5	1.0	1.5	2	2.5	3	3.5	4	4.5	5
pH	6.47	4.01	3.25	2.72	2.52	2.4	2.32	2.25	2.2	2.14	2.1
V HNO$_3$(ml)	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10	
pH	2.06	2.04	2.01	1.99	1.94	1.92	1.9	1.89	1.87	1.86	

Table 4.13: Tables of data for the titration of 0.1M HNO$_3$ against 0.001M Br⁻ at 35°C.

0.001M Br⁻ without TiO$_2$

V HNO$_3$(ml)	0.0	0.5	1.0	1.5	2	2.5	3	3.5	4	4.5	5
pH	5.45	2.45	2.22	2.12	2.02	1.96	1.9	1.85	1.77	1.75	1.71
V HNO$_3$(ml)	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10	
pH	1.68	1.66	1.63	1.62	1.59	1.57	1.52	1.5	1.49	1.48	

0.001M Br⁻ with TiO$_2$

V HNO$_3$(ml)	0.0	0.5	1.0	1.5	2	2.5	3	3.5	4	4.5	5
pH	6.52	4.19	3.22	2.9	2.69	2.58	2.5	2.44	2.38	2.32	2.24
V HNO$_3$(ml)	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10	
pH	2.2	2.16	2.12	2.1	2.08	2.06	2.04	2.02	2.00	1.99	

Table 4.14: Tables of data for the titration of 0.1M HNO₃ against 1M Cl⁻ at 35°C.

1M Cl⁻ without TiO₂

V HNO₃(ml)	0.0	0.5	1.0	1.5	2	2.5	3	3.5	4	4.5	5
pH	6.62	3.02	2.77	2.73	2.66	2.59	2.48	2.44	2.4	2.37	2.3
V HNO₃(ml)	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10	
pH	2.29	2.28	2.26	2.23	2.22	2.22	2.21	2.17	2.16	2.16	

1M Cl⁻ with TiO₂

V HNO₃(ml)	0.0	0.5	1.0	1.5	2	2.5	3	3.5	4	4.5	5
pH	7.13	5.6	5	4.43	4.12	3.96	3.88	3.18	3.76	3.69	3.66
V HNO₃(ml)	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10	
pH	3.62	3.59	3.57	3.52	3.49	3.47	3.46	3.45	3.43	3.42	

Table 4.15: Tables of data for the titration of 0.1M HNO₃ against 0.1M Cl⁻ at 35°C.

0.1M Cl⁻ without TiO₂

V HNO₃(ml)	0.0	0.5	1.0	1.5	2	2.5	3	3.5	4	4.5	5
pH	6.54	3.96	3.82	3.73	3.67	3.63	3.57	3.53	3.5	3.47	3.45
V HNO₃(ml)	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10	
pH	3.43	336	3.34	3.33	3.31	3.3	3.29	3.27	3.26	3.25	

0.1M Cl⁻ with TiO₂

V HNO₃(ml)	0.0	0.5	1.0	1.5	2	2.5	3	3.5	4	4.5	5
pH	7.13	5.57	4.59	4.28	4.12	4.02	3.95	3.9	3.86	3.82	3.79
V HNO₃(ml)	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10	
pH	3.73	3.71	3.69	3.66	3.65	363	3.61	3.59	3.68	3.57	

Table 4.16: Tables of data for the titration of 0.1M HNO₃ against 0.01M Cl⁻ at 35°C.

0.01M Cl⁻ without TiO₂

V HNO₃(ml)	0.0	0.5	1.0	1.5	2	2.5	3	3.5	4	4.5	5
pH	6.3	4.06	3.9	3.78	3.73	3.68	3.6	3.56	3.53	3.5	3.48
V HNO₃(ml)	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10	
pH	3.46	3.44	3.43	3.41	3.35	3.33	3.32	3.31	3.3	3.29	

0.01M Cl⁻ with TiO₂

V HNO₃(ml)	0.0	0.5	1.0	1.5	2	2.5	3	3.5	4	4.5	5
pH	7.09	5.34	4.38	4.12	4.00	3.88	3.86	3.81	3.76	3.73	3.9
V HNO₃(ml)	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10	
pH	3.67	3.64	3.61	3.59	3.57	3.55	3.53	3.25	3.5	3.49	

Table 4.17: Tables of data for the titration of 0.1M HNO₃ against 0.001M Cl⁻ at 35°C.

0.001M Cl⁻ without TiO₂

V HNO₃(ml)	0.0	0.5	1.0	1.5	2	2.5	3	3.5	4	4.5	5
pH	6.26	4.14	3.96	3.85	3.77	3.73	3.66	3.62	3.58	3.55	3.51
V HNO₃(ml)	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10	
pH	3.48	3.45	3.42	3.38	3.36	3.34	3.32	3.3	3.28	3.27	

0.001M Cl⁻ with TiO₂

V HNO₃(ml)	0.0	0.5	1.0	1.5	2	2.5	3	3.5	4	4.5	5
pH	7.13	5.21	4.35	4.06	3.92	3.85	3.78	3.73	3.69	365	3.62
V HNO₃(ml)	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10	
pH	3.59	3.54	3.51	3.49	3.47	3.45	3.44	3.42	3.41	3.4	

4.3 Tables of data for adsorption and surface charge.

The following data shown in the table below are the extract from the plot og pH of solution against volume of titrants at various concentration and temperature(from figures 2 to 17).

See appendix C and D for the calculation of adsorption θ and surface charge E.

At temperature of 20°C, the following data were obtained.

Table 4.18: Data for 0.1M HNO₃ against 1MBr⁻ at 29°C

pH	Change in volume, ΔV (m³)	Adsorption, θ (mol/cm²)	Surface charge, E (μC)
4.5	2.82	4.566×10^{-12}	0.441
4.0	1.73	2.80×10^{-12}	0.27

Table 4.19: Data for 0.1M HNO₃ against 0.1MBr⁻ at 29°C

pH	Change in volume, ΔV (m³)	Adsorption, θ (mol/cm²)	Surface charge, E (μC)
4.5	0.88	1.425×10^{-12}	0.138
5.0	0.38	6.152×10^{-13}	0.059
5.5	0.31	5.019×10^{-13}	0.048
6.0	0.25	4.048×10^{-13}	0.039

Table 4.20: Data for 0.1M HNO₃ against 0.01MBr⁻ at 29°C

pH	Change in volume, ΔV (m³)	Adsorption, θ (mol/cm²)	Surface charge, E (µC)
4.5	0.50	8.095×10^{-13}	0.078
5.0	0.25	4.048×10^{-13}	0.039
5.5	0.19	3.076×10^{-13}	0.03
6.0	0.13	2.105×10^{-13}	0.02

Table 4.21: Data for 0.1M HNO₃ against 0.001MBr⁻ at 29°C

pH	Change in volume, ΔV (m³)	Adsorption, θ (mol/cm²)	Surface charge, E (µC)
4.5	0.9	1.425×10^{-12}	0.141
5.0	0.5	6.152×10^{-13}	0.078
5.5	0.3	5.019×10^{-13}	0.047
6.0	0.15	4.048×10^{-13}	0.023
6.5	0.1	1.619×10^{-13}	0.016

Table 4.22: Data for 0.1M HNO₃ against 1MCl⁻ at 29°C

pH	Change in volume, ΔV (m³)	Adsorption, θ (mol/cm²)	Surface charge, E (µC)
5.0	0.3	4.875×10^{-13}	0.047
5.5	0.2	3.238×10^{-13}	0.031
6.0	0.15	2.429×10^{-13}	0.023
6.5	0.1	1.619×10^{-13}	0.016

Table 4.23: Data for 0.1M HNO₃ against 0.1MCl⁻ at 29°C

pH	Change in volume, ΔV (m³)	Adsorption, θ (mol/cm²)	Surface charge, E (µC)
5.0	0.8	1.495×10^{-12}	0.125
5.5	0.4	6.476×10^{-13}	0.062
6.0	0.3	4.875×10^{-13}	0.047

Table 4.24: Data for 0.1M HNO₃ against 0.01MCl⁻ at 29°C

pH	Change in volume, ΔV (m³)	Adsorption, θ (mol/cm²)	Surface charge, E (µC)
5.0	0.25	4.048×10^{-13}	0.047
5.5	0.13	2.015×10^{-13}	0.031
6.0	0.13	2.105×10^{-13}	0.023
6.5	0.13	2.105×10^{-13}	0.016

Table 4.25: Data for 0.1M HNO_3 against 0.001MCl⁻ at 29°C

pH	Change in volume, ΔV (m³)	Adsorption, θ (mol/cm²)	Surface charge, E (μC)
5.0	0.13	2.105×10^{-13}	0.020
5.5	0.1	1.619×10^{-13}	0.016
6.0	0.06	1.02×10^{-13}	0.1
6.5	0.1	1.019×10^{-13}	0.016

Table 4.26: Data for 0.1M HNO_3 against 1MBr⁻ at 35°C

pH	Change in volume, ΔV (m³)	Adsorption, θ (mol/cm²)	Surface charge, E (μC)
3.5	0.5	8.095×10^{-13}	0.078
4	0.31	5.019×10^{-13}	0.048
4.5	0.25	4.048×10^{-13}	0.039
5	0.19	3.076×10^{-13}	0.03
5.5	0.13	2.105×10^{-13}	0.02

Table 4.26: Data for 0.1M HNO_3 against 1MBr⁻ at 35°C

pH	Change in volume, ΔV (m³)	Adsorption, θ (mol/cm²)	Surface charge, E (μC)
3.5	0.5	8.095×10^{-13}	0.078
4	0.31	5.019×10^{-13}	0.048
4.5	0.25	4.048×10^{-13}	0.039
5	0.19	3.076×10^{-13}	0.03
5.5	0.13	2.105×10^{-13}	0.02

Table 4.27: Data for 0.1M HNO_3 against 0.1MBr⁻ at 35°C

pH	Change in volume, ΔV (m³)	Adsorption, θ (mol/cm²)	Surface charge, E (μC)
3.5	0.8	1.295×10^{-12}	0.125
4	0.55	8.905×10^{-13}	0.086
4.5	0.4	6.476×10^{-13}	0.062
5	0.3	4.876×10^{-13}	0.074
5.5	0.2	3.238×10^{-13}	0.031

Table 4.28: Data for 0.1M HNO₃ against 0.01MBr⁻ at 35°C

pH	Change in volume, ΔV (m³)	Adsorption, θ (mol/cm²)	Surface charge, E (μC)
3	0.88	1.425×10^{-13}	0.138
3.5	0.8	1.295×10^{-12}	0.078
4	0.55	8.905×10^{-13}	0.048
4.5	0.4	6.476×10^{-13}	0.039
5	0.3	4.876×10^{-13}	0.039
5.5	0.2	3.238×10^{-13}	0.03

Table 4.29: Data for 0.1M HNO₃ against 0.001MBr⁻ at 35°C

pH	Change in volume, ΔV (m³)	Adsorption, θ (mol/cm²)	Surface charge, E (μC)
3	61.1	1.797×10^{-12}	0.173
3.5	0.56	9.066×10^{-12}	0.088
4	0.33	5.343×10^{-13}	0.052
4.5	0.28	6.533×10^{-13}	0.044
5	0.28	4.533×10^{-13}	0.044
5.5	0.2	3.562×10^{-13}	0.034

Table 4.30: Data for 0.1M HNO₃ against 1MCl⁻ at 35°C

pH	Change in volume, ΔV (m³)	Adsorption, θ (mol/cm²)	Surface charge, E (μC)
4.5	1.25	2.024×10^{-13}	0.195
5	0.75	1.214×10^{-13}	0.117
5.5	0.44	7.124×10^{-13}	0.069
6	0.31	5.019×10^{-13}	0.048

Table 4.31: Data for 0.1M HNO₃ against 0.1MCl⁻ at 35°C

pH	Change in volume, ΔV (m³)	Adsorption, θ (mol/cm²)	Surface charge, E (μC)
4.5	0.73	1.182×10^{-12}	0.114
5	0.5	8.095×10^{-13}	0.078
5.5	0.32	5.181×10^{-13}	0.05
6	0.27	4.371×10^{-13}	0.042
6.5	0.18	2.914×10^{-13}	0.028

Table 4.32: Data for 0.1M HNO₃ against 0.01MCl⁻ at 35°C

pH	Change in volume, ΔV (m³)	Adsorption, 0 (mol/cm²)	Surface charge, E (μC)
4.0	1.25	2.024×10^{-12}	0.195
4.5	0.5	8.095×10^{-13}	0.078
5	0.38	6.152×10^{-13}	0.059
5.5	0.25	4.048×10^{-13}	0.039
6	0.19	3.076×10^{-13}	0.03

Table 4.33: Data for 0.1M HNO₃ against 0.001MCl⁻ at 35°C

pH	Change in volume, ΔV (m³)	Adsorption, θ (mol/cm²)	Surface charge, E (μC)
4	0.19	1.619×10^{-12}	0.156
4.5	0.2	9.066×10^{-13}	0.088
5	0.31	5.019×10^{-13}	0.048
5.5	0.56	4.048×10^{-13}	0.039
6	1	3.076×10^{-13}	0.03

Table 4.34: Table of Br⁻ at pH of 6.0

Temp °C	Concentration of solution, M	Adsorption, 0 mol/cm²	Log C	Log 0
	1.0	-	0	-
29°C	0.1	4.048×10^{-13}	-1	-12.39
	0.01	2.105×10^{-13}	-2	-12.68
	0.001	2.429×10^{-13}	-3	-12.62
	1.0	-	0	-
35°C	0.1	-	-1	-
	0.01	-	-2	-
	0.001	-	-3	-

Table 4.35: Table of Cl⁻ at pH of 6.0

Temp °C	Concentration of solution, M	Adsorption, θ mol/cm²	Log C	Log θ
	1.0	2.429×10^{-13}	0	-12.62
29°C	0.1	4.857×10^{-13}	-1	-12.31
	0.01	2.105×10^{-13}	-2	-12.68
	0.001	1.02×10^{-13}	-3	-12.99
	1.0	5.019×10^{-13}	0	-12.3
35°C	0.1	4.371×10^{-13}	-1	-12.36
	0.01	3.076×10^{-13}	-2	-12.51
	0.001	3.076×10^{-13}	-3	-12.51

Table 4.36: Table of Br⁻ at pH of 5.0

Temp °C	Concentration of solution, M	Adsorption, θ mol/cm²	Log C	Log θ
	1.0	-	0	-
29°C	0.1	6.152×10^{-13}	-1	-12.21
	0.01	4.048×10^{-13}	-2	-12.39
	0.001	8.095×10^{-13}	-3	-12.09
	1.0	3.076×10^{-13}	0	-12.51
35°C	0.1	4.857×10^{-13}	-1	-12.31
	0.01	4.533×10^{-13}	-2	-12.34
	0.001	4.048×10^{-13}	-3	-12.39

Table 4.37: Table of Cl⁻ at pH of 5.0

Temp °C	Concentration of solution, M	Adsorption, θ mol/cm²	Log C	Log θ
	1.0	4.857×10^{-12}	0	-12.31
29°C	0.1	1.295×10^{-12}	-1	-11.89
	0.01	4.048×10^{-13}	-2	-12.39
	0.001	2.105×10^{-13}	-3	-12.68
	1.0	1.214×10^{-13}	0	-11.92
35°C	0.1	8.095×10^{-13}	-1	-12.09
	0.01	6.152×10^{-13}	-2	-12.21
	0.001	5.019×10^{-13}	-3	-12.30

4.38 Tables of temprature, concentration adsorption and rate of adsorption of Br⁻ at pH 5

Temp °C	Concntration of solution,M	Adsorption, θ mol/cm²	Time taken	Rate of adsorption	Log θ	Log θ /t
	1	-	-	-	-	-
29°C	0.1	6.152×10^{-13}	1.52	4.047×10^{-13}	-12.21	-12.39
	0.01	4.048×10^{-13}	1.00	4.048×10^{-13}	-12.39	-12.39
	0.001	8.095×10^{-13}	1.00	8.095×10^{-13}	-12.09	-12.09
	1	3.076×10^{-13}	0.76	4.047×10^{-13}	-12.51	-12.39
35°C	0.1	4.058×10^{-13}	1.2	4.048×10^{-13}	-12.31	-12.39
	0.01	4.048×10^{-13}	1.00	4.048×10^{-13}	-12.39	-12.39
	0.001	4.533×10^{-13}	1.12	4.047×10^{-13}	-12.34	-12.39

4.39 Tables of temprature, concentration adsorption and rate of adsorption of Cl⁻ at pH 5

Temp °C	Concntration of solution	Adsorption, θ mol/cm²	Time taken	Rate of adsorption	Log θ	Log θ /t
	1	4.857×10^{-13}	0.60	8.095×10^{-13}	-12.31	-12.09
29°C	0.1	1.295×10^{-13}	1.6	8.094×10^{-13}	-11.89	-12.09
	0.01	4.048×10^{-13}	1.00	4.048×10^{-13}	-12.39	-12.39
	0.001	2.105×10^{-13}	0.52	4.048×10^{-13}	-12.68	-12.39
	1	1.214×10^{-13}	3	4.047×10^{-13}	-11.92	-12.39
35°C	0.1	8.095×10^{-13}	1.82	4.448×10^{-13}	-12.09	-12.35
	0.01	6.152×10^{-13}	1.52	3.994×10^{-13}	-12.22	-12.40
	0.001	5.019×10^{-13}	1.24	4.048×10^{-13}	-12.30	-12.39

CHAPTER FIVE

5.0　　　　　　　　　　DISCUSSION OF RESULTS

5.1 Response of pH with Titration

During the process of titration, as the volume of the titrant added to the solution increases, the pH of the solution tends towards acidity. This is because the titrant HNO_3 is an acid.

For any given concentration of chloride and bromide ions in solution (i.e. 0.01M of Cl^- and Br^-) with and without TiO_2 it was observed that at any given equal volume of titrant added, the pH value of the solution with TiO_2 was always higher then those with out TiO_2. The reason for this is that, whenever there is TiO_2 in the solution, some of the Cl^- and Br^- ion got adsorbed unto it, resulting into lesser ion and therefore lower acidity of the solution.

While in solution with TiO_2, the whole ions are still present in solution and therefore result into higher acidity as shown in fig. 4.2-4.19. Also as the titration progresses it was noted that the rate of change of pH with respect to successive additions of the titrant decreases. This could be due tot e fact that as the adsorption of the anions progresses the number of sites available for further adsorption decreases with time. Hence the rate of change of pH values decreases until it reaches a constant amount.

5.2 Effect of pH on Surface Charge.

From the calculated values of surface charge it was observed that as the pH of the solution increases, the surface charge decreases also. This is noted for all concentration of all Cl^- and Br^- for which 0.1M HNO_3 was titrated against. This observation showed that as the pH value increases, the number of ions adsorbed also increases and therefore result into lesser charge in the solution.

5.3 Effect of Concentration on Adsorption and Surface Charge.

The adsorption and surface charge calculated for higher concentration of Cl^- and Br^- were observed to be higher than those of lower concentration. This implies that as the

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concentration of the anions decrease from 1M to 0.001M the adsorption and surface charge obtained for each concentration also follow the same trend. The reason for this is that high concentration contains more adsorbate and then more of it tends to be adsorbed as compared with low concentration solution that contains less adsorbate. But reverse was the case for Br⁻ at 35°C as shown in table 4.38.

5.4 Effect of Temperature on Surface Charge

From the calculation, it was observed that the surface charges calculated at 35°C for different concentrations of Cl⁻ and Br⁻ ions (1M, 0.1M, 0.01M and 0.001M) were little from those at 29°C . This shows that temperature was one of the factors to be considered when the number of sites available is to be determined.

From the graph plotted in fig. 4.18 to 4.21, it could be observed that all the graphs gave a positive slope and intercept as calculated in appendix E. Therefore it could be stated that the adsorption of Cl⁻ and Br⁻ follows Freundlich isotherm at all temperature and concentration investigated.

Also from fg.4.22 to 4.25, the graphs of t against log C were plotted and all of them gave positive slope K_1 and intercept and K_2 which shows that they followed Temkim isotherm for the range of temperature considered. Calculations are shown in appendix F.

5.5 Nature of the Adsorbate

From table 4.18-4.33, it was observed that Br- had greater surface charge of 0.441µC compared to that of Cl⁻ which was 0.125µC, when various concentrations of the anion were considered at 29°C. This shows that, blending the adsorbent with Br⁻ ions will enhance its adsorptive capability better than that of Cl⁻. The reverse was the case at 35oC, with Cl⁻ ion having a surface charge of 0.195µC which is greater than 0.173µC calculated for Br⁻

5.6 Kinetics of the Adsorption of Br⁻ and Cl⁻

As evident from calculations, the rate of adsorption calculated at that temperature for various concentrations of Cl⁻ and Br⁻ were a little different from those at a lower temperature.

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From table 4.38 to 4.39 it was observed that at 35°C the rate of adsorption was independent of concentration of both Br- and Cl⁻ present in solution. While at 29°C, the rate of adsorption of Cl⁻ increases, with increase in concentration from 0.001M to 1M (i.e. the calculated value of the rate of adsorption was found to be 8.095×10^{-13} mol/cm2min which is greater than 4.048×10^{-13} mol/cm^{2}min calculated for 0.001M)

The rate of adsorption of Br- also follows the same trend but it deviated at concentration of 0.001M.

CHAPTER SIX

6.0 CONCLUSION AND RECOMMENDATION

6.1 Conclusion

From the experiments carried out in this research work, the following conclusions were made:

(1.) The blending of alkaline anions like Cl^- and Br^- with TiO_2, enhances its activity as a depolarizing agent and therefore increases its life span.

(2.) That 1M of solution of bromide ion at 29^oC yielded greater surface charge. compared to other concentrations and temperature considered.

(3.) That at a higher concentration of Cl^- and Br - a higher surface charge and adsorption could be obtained

(4.) That adsorption of Cl^- and Br ions on TiO_2 follows Freundlich and Temkim isotherms at all the concentrations and temperatures investigated.

(5.) The reaction order of the adsorption of the alkaline anions assuming an elementary reaction is first order for both Cl^- and Br at 29^oC while at elevated temperature of 35^oC, it's zero order for both anions.

6.1 Recommendations

Based on the information gathered in this research work, the following recommendations were made:

(1.) Whenever a dry cell which is to use TiO2 as the depolarizer, is to be designed it should be blended with alkaline anions like Cl^- and Br - as this will improve its adsorptive capability.

(2.) That other factor that affects the rate of adsorption be investigated.

(3.) More apparatus should be provided in the chemical laboratory so that this type of research could be effectively carried out and to enhance further research in this areas or specialization –"Electrochemical Engineering".

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APPENDIX A

CALCULATIONS INVOLVED IN THE DETERMINATION OF SURFACE AREA OF TiO_2 BY ADSORPTION FROM SOLUTION

To calculate the concentration Cc of the acetic acid stock given, we make uses of the formula below

$$Cc = \frac{\% \text{ Purity x S.G x 1000}}{\text{M.M x 100}}$$

where Cc = Concentration of the stock acetic acid solution

% Purity is percentage purity of the acetic acid stock.

S.G is specific gravity of the acetic acid stock;.

M.M is molecular weight of the acetic acid stock

The assays on the stock bottle of the acetic acid are

S.G = 1.0495g/l,

 Molecular Weight = 60.05g/gmol

% Purity = 99%

$$Cc = \frac{99 \text{ x } 1.0495 \text{ x } 1000}{60.05 \text{ x } 100}$$

$$= 17.3M$$

To determine the volume of stock acid solution that must be diluted to obtain 0.15M of acid the dilution formula was applied:

Cc x Vc = Cd x Vd

Where Vc is volume of stock acid needed for dilution,

Cd is desired concentration of the needed acid solution, = 0.15M

Vd is the volume of desired solution, = 1000ml

Vc = (0.15 x 1000) / 17.3,

 = 8.67ml

Therefore, 8.67ml of the stock acid was taken and made up to 1000ml of solution to obtain 0.15M acetic acid solutions needed.

Also 80, 60, 40, 20, and 10ml of 0.15M acid solutions were made up to 100 ml with distilled water, differently, in order to get 0.12, 0.09, 0.06, 0.03, 0.015M acid solutions respectively.

(1.) To calculate the equilibrium (final) concentrations of acetic acid after adsorption from solution.

Let the final concentration of acid be C_{eq} and the volume of sodium hydroxide, V_2, be values in table 4.1A. Also, the equation of the reaction is:

$$NaOH_{(aq)} + CH_3COOH_{(aq)} \longrightarrow CH_3COONa_{(aq)} + H_2O_{(l)}$$

Let the final concentration of acetic acid C_{eq} be equal to M_1

Hence, using $M_1 \times V_1 = M_2 \times V_2$

where C_{eq} = Final concentration of Acetic acid;

V_2 = volume of NaOH

M_2 = concentration of NaOH

For 0.15 Acetic acid:

$M_1 = \dfrac{47.05 \times 0.1}{25}$ = 0.1882 moles

For 0.12 Acetic acid:

$M_1 = \dfrac{40.92 \times 0.1}{25}$ = 0.1637 moles

For 0.09 Acetic acid:

$M_1 = \dfrac{30.52 \times 0.1}{25}$ = 0.1221 moles

For 0.06 Acetic acid:

$M_1 = \dfrac{20.25 \times 0.1}{25}$ = 0.081 moles.

For 0.03 Acetic acid:

$M_1 = \dfrac{11.35 \times 0.1}{25}$ = 0.0454 moles

For 0.015 Acetic acid:

$M_1 = \dfrac{7.64 \times 0.1}{25}$ = 0.0306 moles.

All the initial concentrations of acetic acid were now acetic acid were now regarded as C_1 and all the final concentration of acetic acid (M1) as C_{eq} and tabulated as in table 4.1b of chapter four.

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(IV) Calculation of the slope of the slope from graph C_{eq}/N against C_{eq} of fig.

$$\text{Slope} = \frac{\Delta y}{\Delta x} = \frac{y_2 - y_1}{x_2 - x_1} = \frac{4.00 - 2.30}{0.13 - 0.047} = \frac{1.7}{0.083}$$

Slope = 20.482

But from the equation plotted i.e

$$\frac{C_{eq}}{N} = \frac{C_{eq}}{Nm} + \frac{1}{KNm}$$

$Nm = 1/\text{slope} = 1/20.482 = 0.0488235$

(V) Calculation of specific area, A.

Specific area of adsorptoion, $A \ (m^2/g)$ is given by

$$A = Nm \ x \ No \ x \ \sigma \ x \ 10^{-20}$$

Where Nm = Number of adsorption sites = 0.0488235

No = Avogadro's Number = $6.023 \ x \ 10^{23}$

σ = Area occupied by adsorbed molecule on the surface = 21Å

Therefore upon substitution

$A = 0.0488235 \ x \ 6.023 \ x \ 10^{23} \ x \ 21 x 10^{-20}$

$= 6175.34 m^2/g$

or $A = 61753428 cm^2/g$

APPENDIX B

CALCULATIONS INVOLVED IN THE PREPARATION OF 0.1M NITRIC ACID

(1.) To calculate the molarity, Mc of stock nitric acid given using the formula below
:

Mc = $\dfrac{\% \text{ purity x S.G x } 1000}{\text{M.M x } 100}$

Where Mc is the molarity of the stock solution.

% Purity = Percentage purity of the stock solution

M.M = Molecular weight of the stock nitric acid

The assays on the stock bottle of the nitric acid are:

S.G = 1.5g/ml

M.M = 63.01

% Purity = 95% - 98% but the average = 96.55%

Applying equation 1 above:

Mc = $\dfrac{96.5 \times 1.5 \times 1000}{63.01 \times 100}$

= 22.97M

(2.) To determine the volume of stock acid solution needed to obtain 1000ml of 0.1M
   Nitric acid.

The dilution formula is applied: Mc x Vc = Md x Md

Where Mc is the molarity of the stock =

Vc is volume of stock acid needed for the dilution

Md is the desired molarity of the needed solution = 0.1M

Volume of desired solution, =1000ml.

Vc = $\dfrac{0.1 * 1000}{22.97}$ = 4.35ml.

Therefore, 4.35ml of the stock must be made up to 1000mp with distilled water to obtain
0.1M nitric acid.

APPENDIX C

CALCULATION OF ADSORPTION

Adsorption, θ is given by $= \dfrac{\Delta V \times C}{S \times 1000}$ 1

Where θ = Adsorption ($gmol/cm^2$)

S = surface area of the adsorbate cm^2/g = $61753400 cm^2/g$

ΔV = Change in volume between when TiO_2 is used and not used

C = concentration of the titrant (M) = 0.1M HNO_3

And $E = n F \theta$

Where E = Surface electric charge in $\mu Cmol/cm^2$

       n = number of charge on the ion; 1 for Br^- and same for Cl^-

where

To calculate the adsortion at 29^oC for 1M of Cl^-, then

$\theta = \dfrac{\Delta V \times C}{S \times 1000}$

Then substituting all the values into the equation above, we have

$\theta = \dfrac{\Delta V \times 0.1}{61753400 \times 1000}$

$\theta = 1.619 \times 10^{-12} \times \Delta V$

From table 4.22, at pH 6.5, $\Delta V = 0.1 cm^3$

$\theta = 1.619 \times 10^{-12} \times 0.1$

    $= 1.619 \times 10^{-13} \, mol/cm^2$

At pH = 6

$\Delta V = 0.15$

$\theta = \dfrac{1.3 \times 0.1}{61753400 \times 1000}$ $= 2.4292 \times 10^{-13} \, mol.cm^2$

At pH = 5.5

$\Delta V = 0.20$

$\theta = 0.2 \times 0.1$ $\qquad$ $= 3.238 \times 10^{-13} \, mol.cm^2$

$\overline{61753400 \times 1000}$

$E = n F \theta$

, $\qquad = 1 \times 96548 \times 3.12 \times 10^{-12}$

$\qquad = 3.01 \times 10^{-7}$

$\qquad = 0.301 \times 10^{-6}$

$E \quad = 0.301 \, \mu Cmol/cm^2$

At pH = 5

$\Delta V = 0.30$

$\theta = \dfrac{0.3 \times 0.1}{4.1556 \times 10^7 \times 1000}$ $\qquad = 4.857 \times 10^{-13}$

Then equation 1 above was used to generate the value of θ in the remaining table by substituting the values Δv from each of tables.

APPENDIX D

CALCUALTION OF SURFACE ELECTRIC CHARGE, E

From literature, surface electric charge E is given by

$E = n F$ 1

Where E = surface electric charge in μC.

n = valency of ions (for Br and Cl ions = 1)

F = faraday constant = 96500C

θ = Adsorption in mol/cm^2

To calculate the surface charge at 29^oC for 1M of Cl^- ion using table 4.22 then at pH 6.5,

$\theta = 1.61 \times 10^{-13}$

$E = 1 \times 96500 \times 2.429 \times 10^{-13}$

$= 0.023 \ \mu C$.

At pH 5.5, $\theta = 3.238 \times 10^{-13}$

$E = 1 \times 96500 \times 3.238 \times 10^{-13}$

$= 0.031 \mu C$.

At pH 5, $\theta = 4.857 \times 10^{-13}$

$E = 1 \times 96500 \times 4.857 \times 10^{-13}$

$= 0.047 \mu C$.

Equation 1 above was then used to generate the values of E for other tables by substituting the values of θ from each table.

APPENDIX E

CALCUALTION OF CONSTANT n AND K IN ISOTHERM.

DETERMINATION FOR FREUNDLICH ISOTHERM

From fig. 4.18-4.19, which is a graph of log θ against log C at pH 5. The equation

plotted is $\log \theta = \log K + n \log C$

Where n = slope of the graph

       K = intercept on the log θ axis.

At 29°C for Br-

$n = \text{slope} = \dfrac{\Delta y}{\Delta x}$

$= \dfrac{-12.50-(-12.15)}{-2.25-(-0.75)}$

$= \dfrac{-0.35}{-1.5}$

$= 0.23$

Intercept, log K = -12

       $K = 1 \times 10^{-12}$

At 35°C for Br⁻

$n = \text{slope} = \dfrac{\Delta y}{\Delta x}$

$= \dfrac{-12.375-(-12.20)}{-2.55-(-0.75)}$

$= \dfrac{-0.175}{-1.8}$

$= 0.10$

Intercept, log K = -12.125

       $K = 7.50 \times 10^{-13}$

At 29°C for Cl⁻

$n = \text{slope} = \dfrac{\Delta y}{\Delta x}$

$= \dfrac{-12.50-(-11.55)}{-2.20-(-0.75)}$

$= \dfrac{-0.85}{-1.45}$

$= 0.59$

Intercept, $\log K = -11.40$

$$K = 3.98 \times 10^{-12}$$

At 35°C for Cl⁻

$$n = \text{slope} = \frac{\Delta y}{\Delta x}$$

$$= \frac{-12.25 - (-12.00)}{-2.20 - (-0.625)}$$

$$= \frac{-0.25}{-1.625}$$

$$n = 0.15$$

Intercept, $\log K = -11.90$

$$K = 1.26 \times 10^{-12}$$

From Fig 4.20-4.21, graph pf log 0 against log C at pH of 6.0

At 29°C for BrI⁻

$$n = \text{slope} = \frac{\Delta y}{\Delta x}$$

$$= \frac{-12.875 - (-12.25)}{-2.5 - (-0.65)}$$

$$= \frac{-0.625}{-1.85}$$

$$= 0.34$$

Intercept, $\log K = -12.025$

$$K = 9.44 \times 10^{-13}$$

At 29°C for Cl⁻

$$n = \text{slope} = \frac{\Delta y}{\Delta x}$$

$$= \frac{-12.75 - (-12.25)}{-2.10 - (-0.5)}$$

$$= \frac{-0.5}{-1.6}$$

$$= 0.31$$

Intercept, $\log K = -11.925$

$$K = 1.19 \times 10^{-12}$$

At 35°C for Cl⁻

$$n = slope = \frac{\Delta y}{\Delta x}$$

$$= \frac{-12.50 - (-12.25)}{-2.0 - (-0.25)}$$

$$= \frac{-0.25}{-1.75}$$

$$= 0.14$$

Intercept, log K = -12.20

$$K = 6.31 \times 10^{-13}$$

APPENDIX F

CALCULATION OF SLOPE K1 AND INRTERCEPT K₂ FOR TEMKIM ISOTHERM.

From Fig. 4.22-4.25, which is a graph of θ Vs log C at pH 5, the equation plotted is

$$\theta = K_2 + K_1 \log C$$

where K_1 = slope of the graph

K_2 = Intercept of the graph

At 29°C for Br⁻

$$K_1 = \frac{\Delta y}{\Delta x}$$

$$= \frac{(8.4 - 4.0) \times 10^{-13}}{0 - (-2.05)}$$

$$= \frac{4.4 \times 10^{-13}}{2.05}$$

$$K_1 = 2.15 \times 10^{-13}$$

Intercept, $K_2 = 8.4 \times 10^{-13}$

At 35°C for Br⁻

$$K_1 = \frac{\Delta y}{\Delta x}$$

$$= \frac{(5.30 - 4.0) \times 10^{-13}}{0 - (-3)}$$

$$= \frac{1.3 \times 10^{-13}}{3}$$

$$K_1 = 4.33 \times 10^{-14}$$

Intercept, $K_2 = 5.3 \times 10^{-13}$

At 29°C for Cl⁻

$$K_1 = \frac{\Delta y}{\Delta x}$$

$$= \frac{(8.10 - 4.0) \times 10^{-13}}{0 - (-2.05)}$$

$$= \frac{4.10 \times 10^{-13}}{2.05}$$

$$K_1 = 2.0 \times 10^{-13}$$

Intercept, $K_2 = 8.10 \times 10^{-13}$

At 35^oC for Cl^-

$$K_1 = \frac{\Delta y}{\Delta x}$$

$$= \frac{(10.0 - 6.0) \times 10^{-13}}{0 - (-2.125)}$$

$$= \frac{4.0 \times 10^{-13}}{2.125}$$

$$K_1 = 2.0 \times 10^{-13}$$

Intercept, $K_2 = 10.0 \times 10^{-13}$

APPENDIX G

CALCULATION OF RATE OF ADSORPTION AND ORDER OF REACTION

Rate of adsorption, = $\dfrac{\text{Adsorption (mol.cm2)}}{\text{Time taken}}$

To calculate the rate of adsorption at 29oC for various concentrations of Cl- and Br-.

At pH 5, for 0.1M Br-

Adsorption, $\theta = 6.152 \times 10^{-13}$ mol./cm^2, time taken = 1.52 min.

$r_{abs} = \dfrac{\theta}{t} = \dfrac{6.152 \times 10^{-13}}{1.52} = 4.047 \times 10^{-13}$ mol/cm^2 min

for 0. 01M Br-

$\theta = 4.048 \times 10^{-13}$ mol./cm^2, time taken = 1.00 min.

$r_{abs} = \dfrac{\theta}{t} = \dfrac{4.048 \times 10^{-13}}{1.0} = 4.048 \times 10^{-13}$ mol/cm^2 min

for 0.001M Br-

$\theta = 8.095 \times 10^{-13}$ mol./cm^2, time taken = 1.00 min.

$r_{abs} = \dfrac{\theta}{t} = \dfrac{8.095 \times 10^{-13}}{1.52} = 8.095 \times 10^{-13}$ mol/cm^{2}min

At 35°C, for 1M Br⁻

$\theta = 3.076 \times 10^{-13}$ mol./cm^2, time taken = 0.76 min.

$r_{abs} = \dfrac{\theta}{t} = \dfrac{3.076 \times 10^{-13}}{0.76} = 4.047 \times 10^{-13}$ mol/cm^{2}min

At 35°C, for 0.1M Br⁻

$\theta = 4.857 \times 10^{-13}$ mol./cm^2, time taken = 1.20 min.

$r_{abs} = \dfrac{\theta}{t} = \dfrac{4.857 \times 10^{-13}}{1.20} = 4.048 \times 10^{-13}$ mol/cm^{2}min

At 35°C, for 0.01M Br⁻

$\theta = 4.048 \times 10^{-13}$ mol./cm², time taken = 1.00 min.

$r_{abs} = \dfrac{\theta}{t} = \dfrac{4.048 \times 10^{-13}}{1.00} = 4.048 \times 10^{-13}$ mol/cm²min

At 35°C, for 0.001M Br⁻

$\theta = 4533 \times 10^{-13}$ mol./cm², time taken = 0.76 min.

$r_{abs} = \dfrac{\theta}{t} = \dfrac{3.076 \times 10^{-13}}{1.12} = 4.047 \times 10^{-13}$ mol/cm²min

Calculation for the order of reaction, n

From Fig. 4.26 – 4.27, the order of reaction at pH 5 were gotten by calculating the slopes.

At 29°C, for Br-

$n = $ slope $ = \dfrac{-11.00 - (-5.10)}{-10.9 - (-5.00)}$

$= \dfrac{5.9}{5.9}$

$n = 1$

At 35°C, for Br⁻

$n = $ slope $ = 0$

At 29°C, for Cl-

$n = \dfrac{-11.0 - (-7.0)}{10.7 - (-5.0)}$

$= \dfrac{4}{5.7}$

$n = 0.7$

At 35°C for Cl-

$n = 0.$

Fig. 4.1 Graph of Ceq /N Vs Ceq
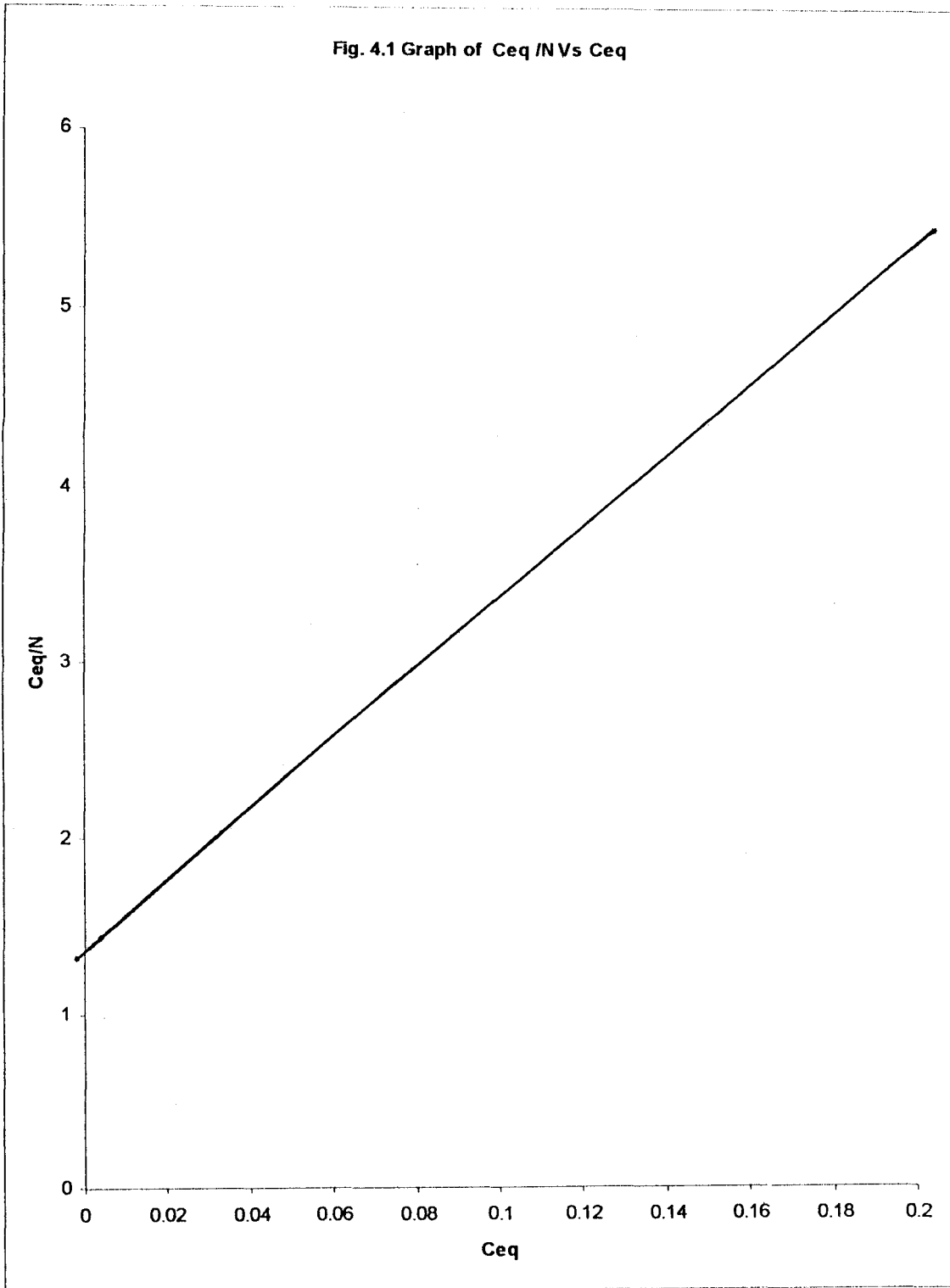
FIG. 4.2 Adsorption of 1M bromide ion at 29°C

— without TiO2
— with TiO2
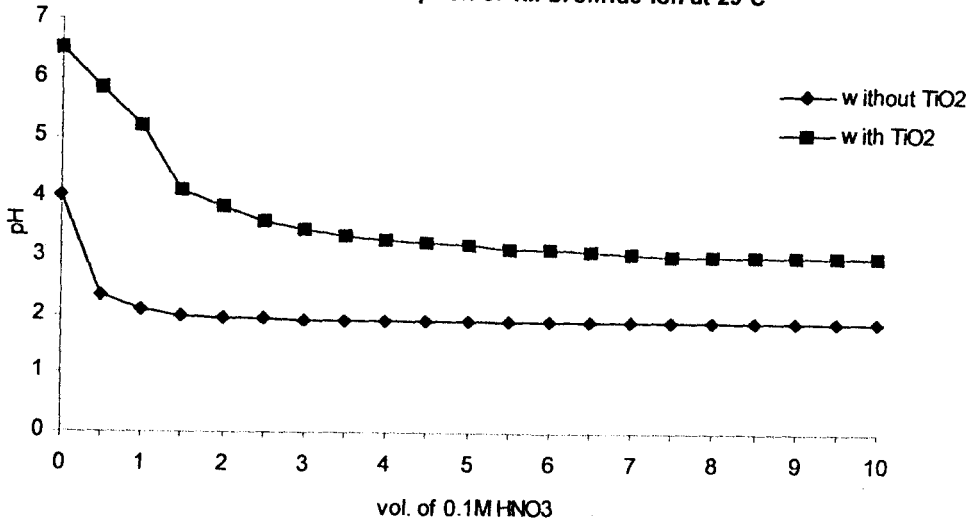
Fig. 4.3 Adsorption of 0.1M bromide ion at 29°C

— without TiO2
— with TiO2
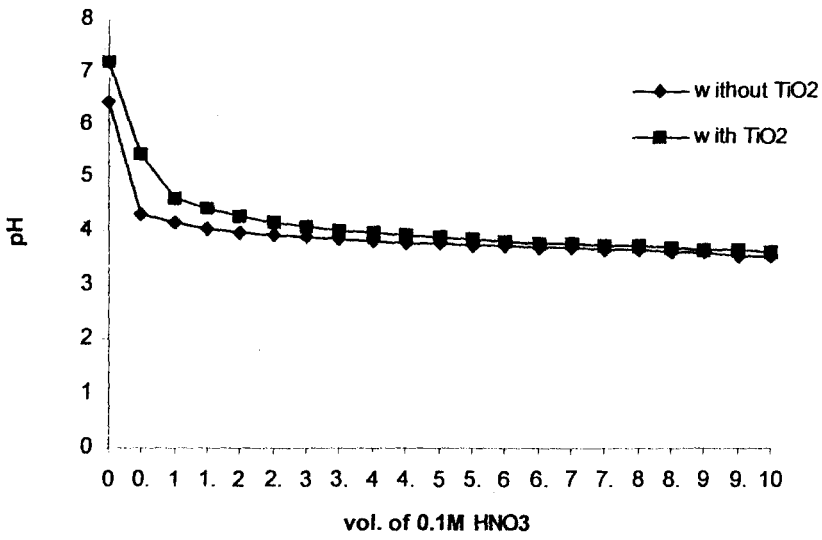
Fig. 4.4 Adsorption of 0.01M bromide ion at 29°C

— without TiO2
— with TiO2
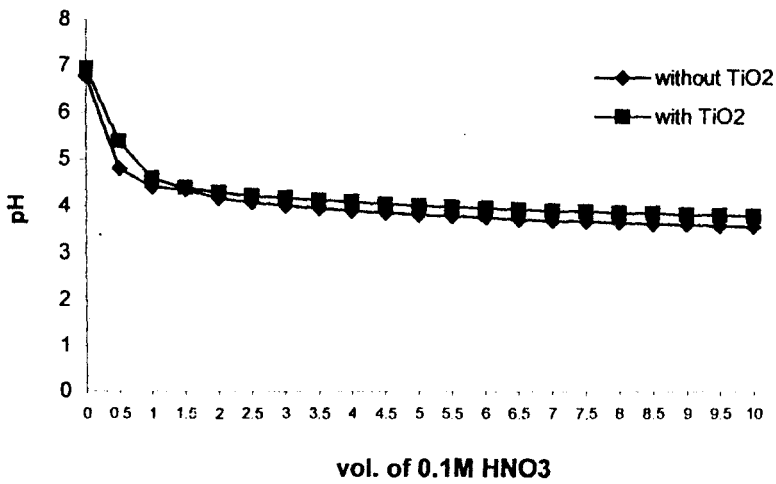
Fig. 4.5 Adsorption of 0.001M brominde ion at 29°C

Fig. 4.6 Adsorption of 1M chloride ion at 29°C


Fig. 4.7 Adsorption of 0.1M chloride ion at 29°C

Fig. 4.8 Adsorption of 0.01M chloride ion at 29°C

fig. 4.9 Adsorption of 0.001M chloride ion at 29°C
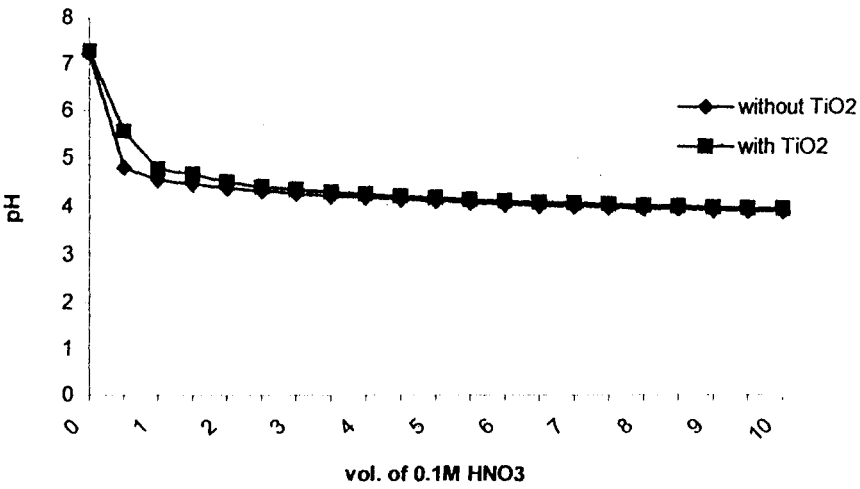
Fig. 4.10 Adsorption of 1M bromide ion at 35°C
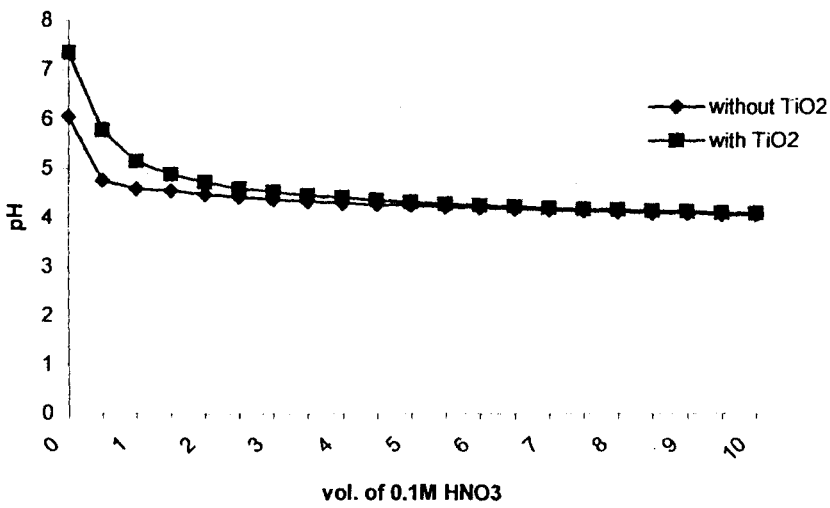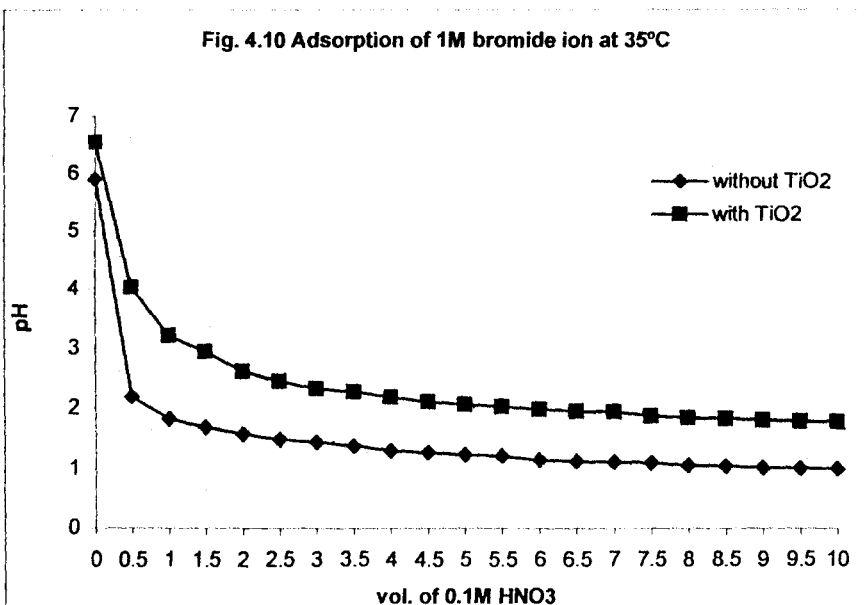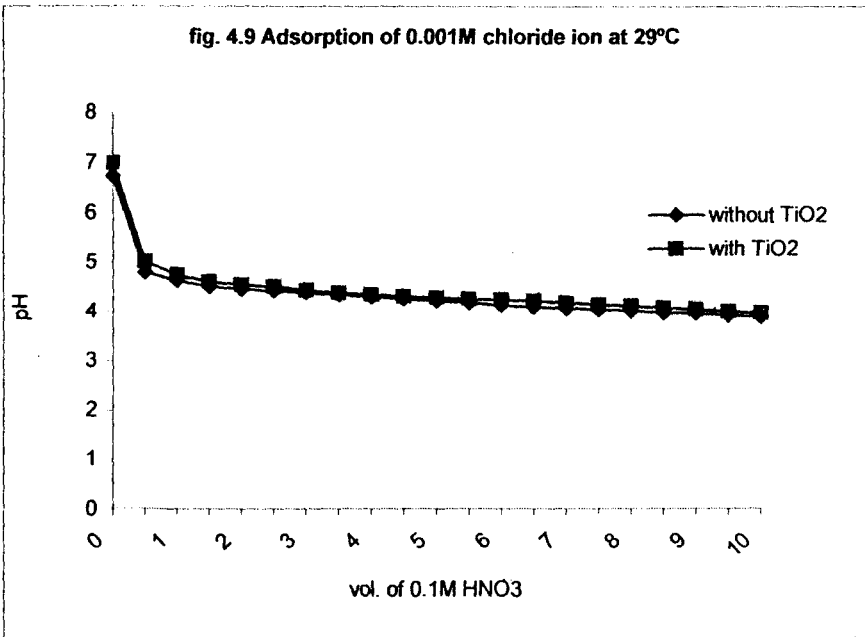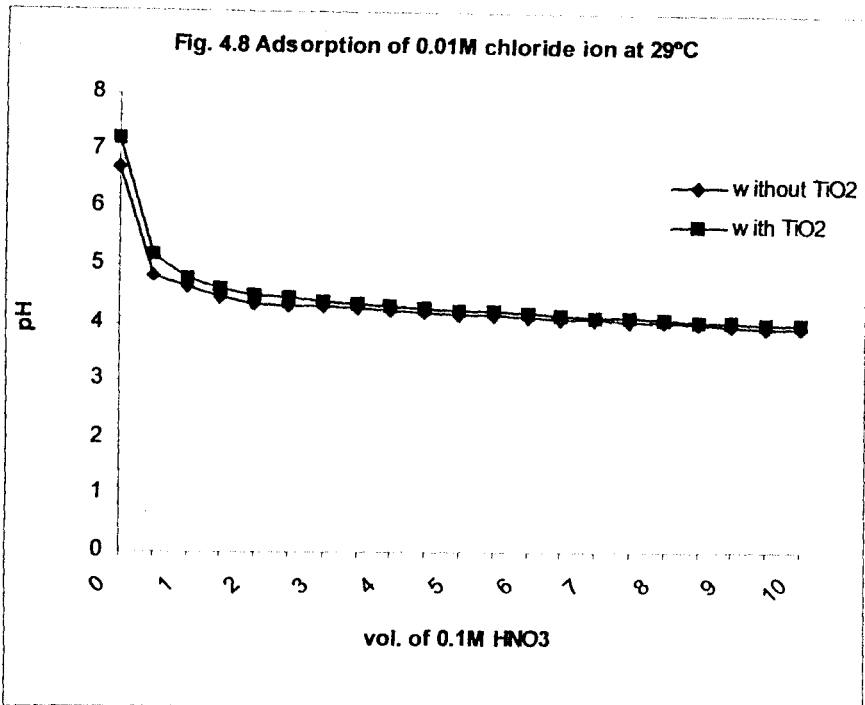
Fig. 4.14 Adsorption of 1M chloride ion at 35°C
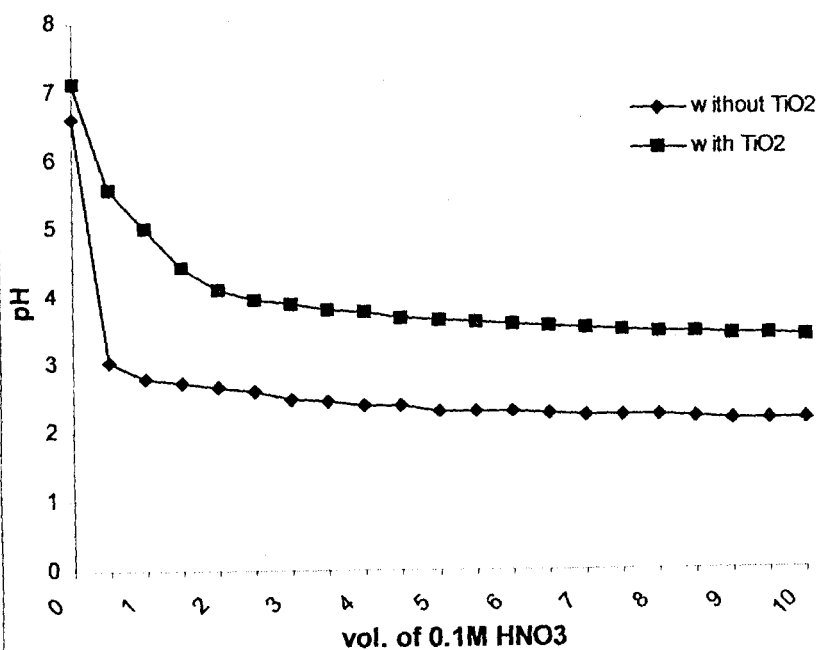
Fig. 4.15 Adsorption of 0.1M chloride ion at 35°C
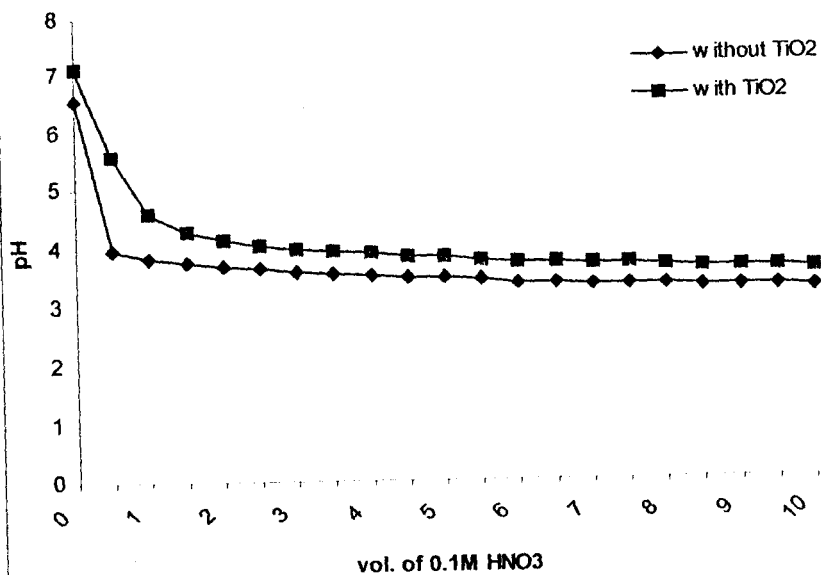
Fig. 4.16 Adsorption of 0.01M chloride ion at 35°C
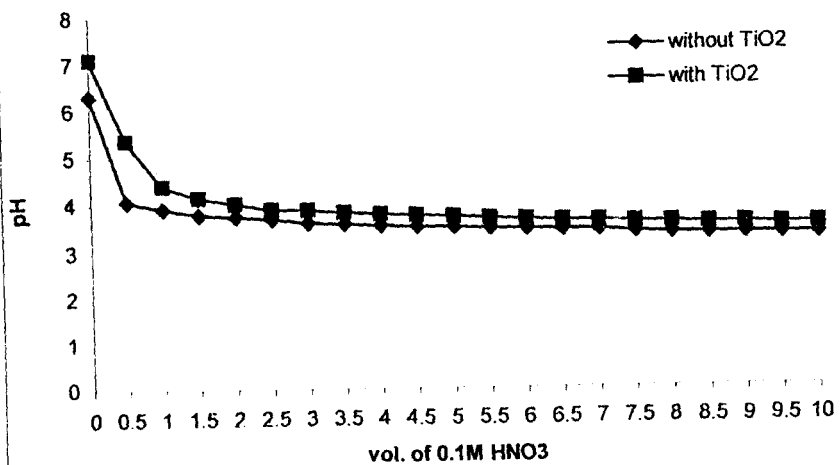
Fig. 4.11 Adsorption of 0.1M bromide ion at 35°C
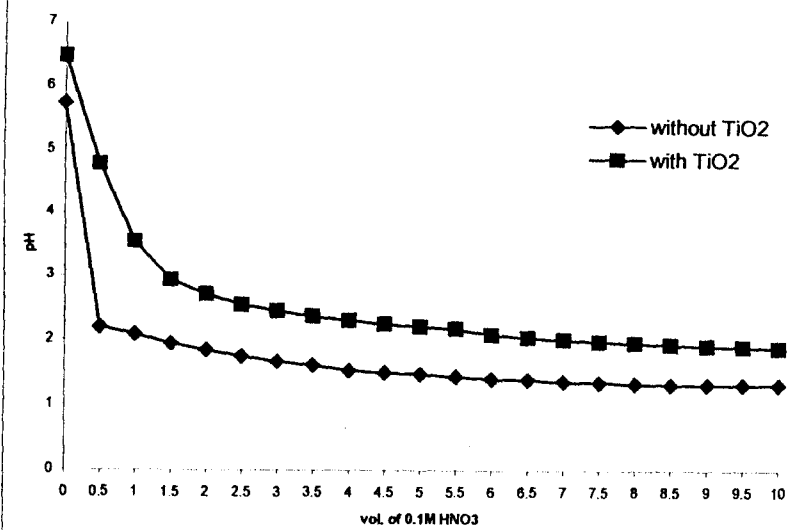
Fig. 4.12 Adsorption of .01M bromide ion at 35°C
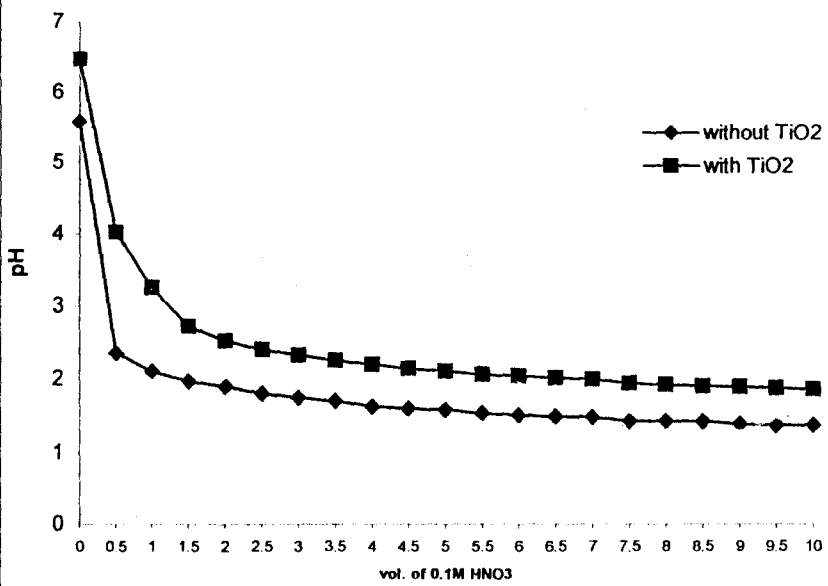
Fig. 4.13 Adsorption of 0.001M bromide ion at 35°C
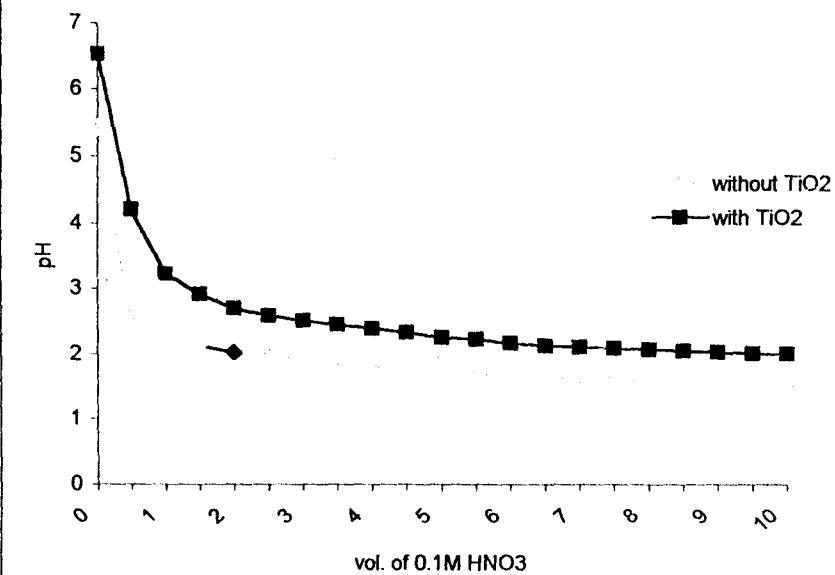
Fig. 4.18: Graph of Log θ against Log C of Br⁻ at pH 5
Scale: 4cm to rep 1unit on both axes

Log C   -3   -2   -1   -10

35°C

29°C

Log θ

-11

-12

-13
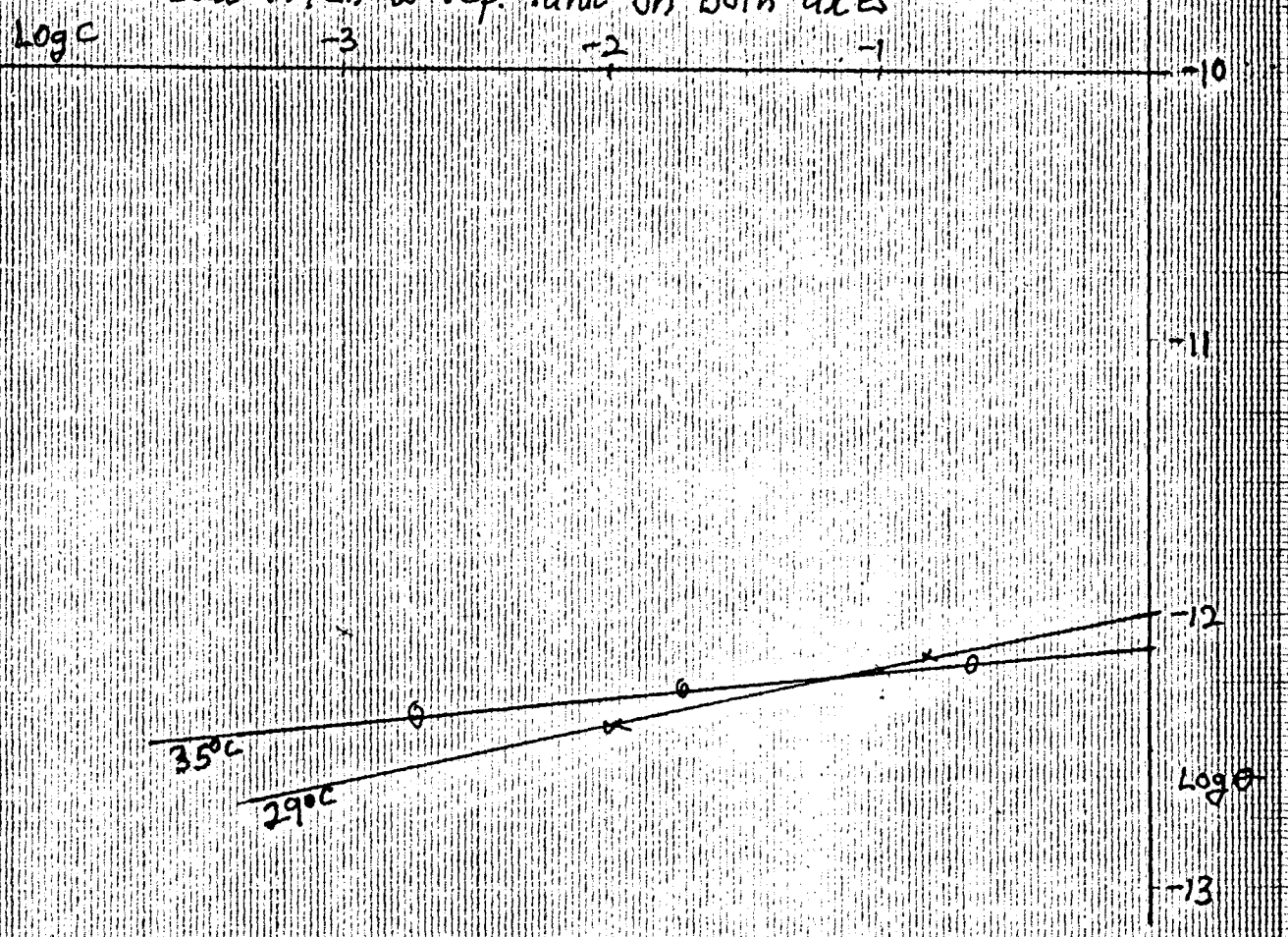
Fig. 4.19: Graph of Log θ against Log C of Cl⁻ at pH 5,
Scale:- 4cm to rep 1 unit on both axes
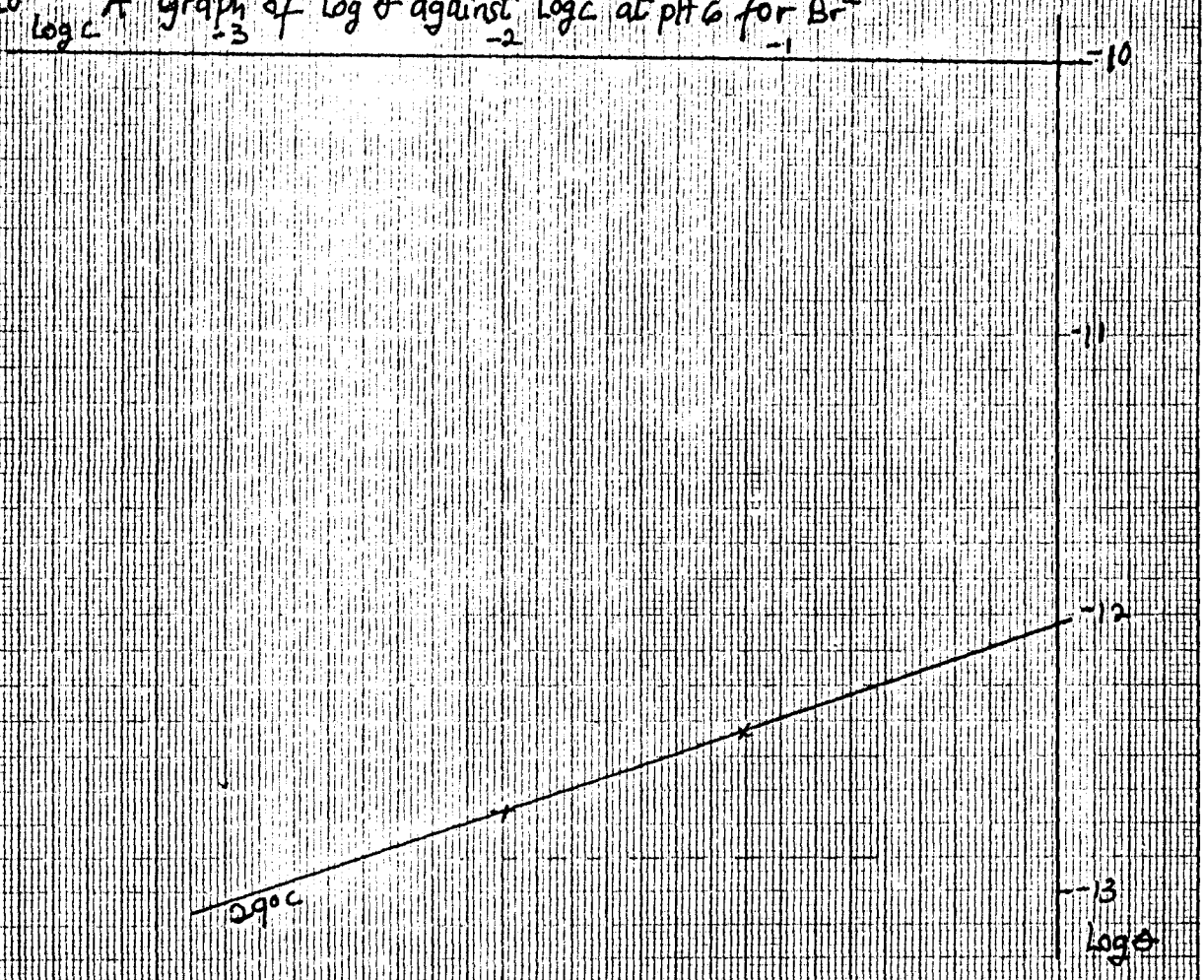
Log C   -3   -2   -1   -10

Cl⁻

-11

35°C

-12

29°C

-13

Log θ

20

Fig. 4·20 A graph of log σ against log c at pH 6 for Br⁻

Fig. 4·21 : A graph of log σ against log c at pH 6 for Cl⁻

Fig 4.22: A graph of θ against Log c of Br⁻ at PH5

Fig 4.23: A graph of θ against Log c of Cl⁻ at PH5
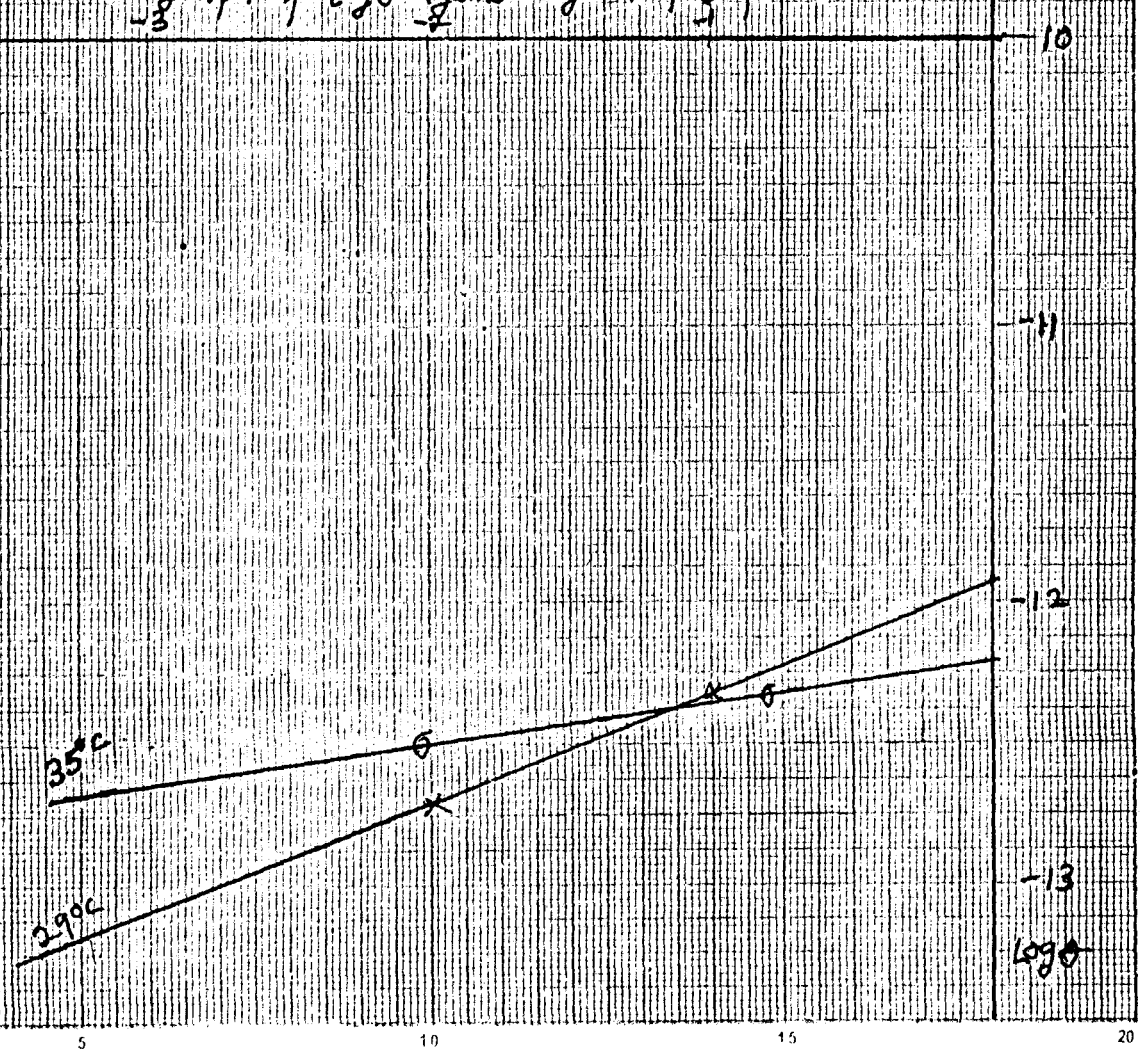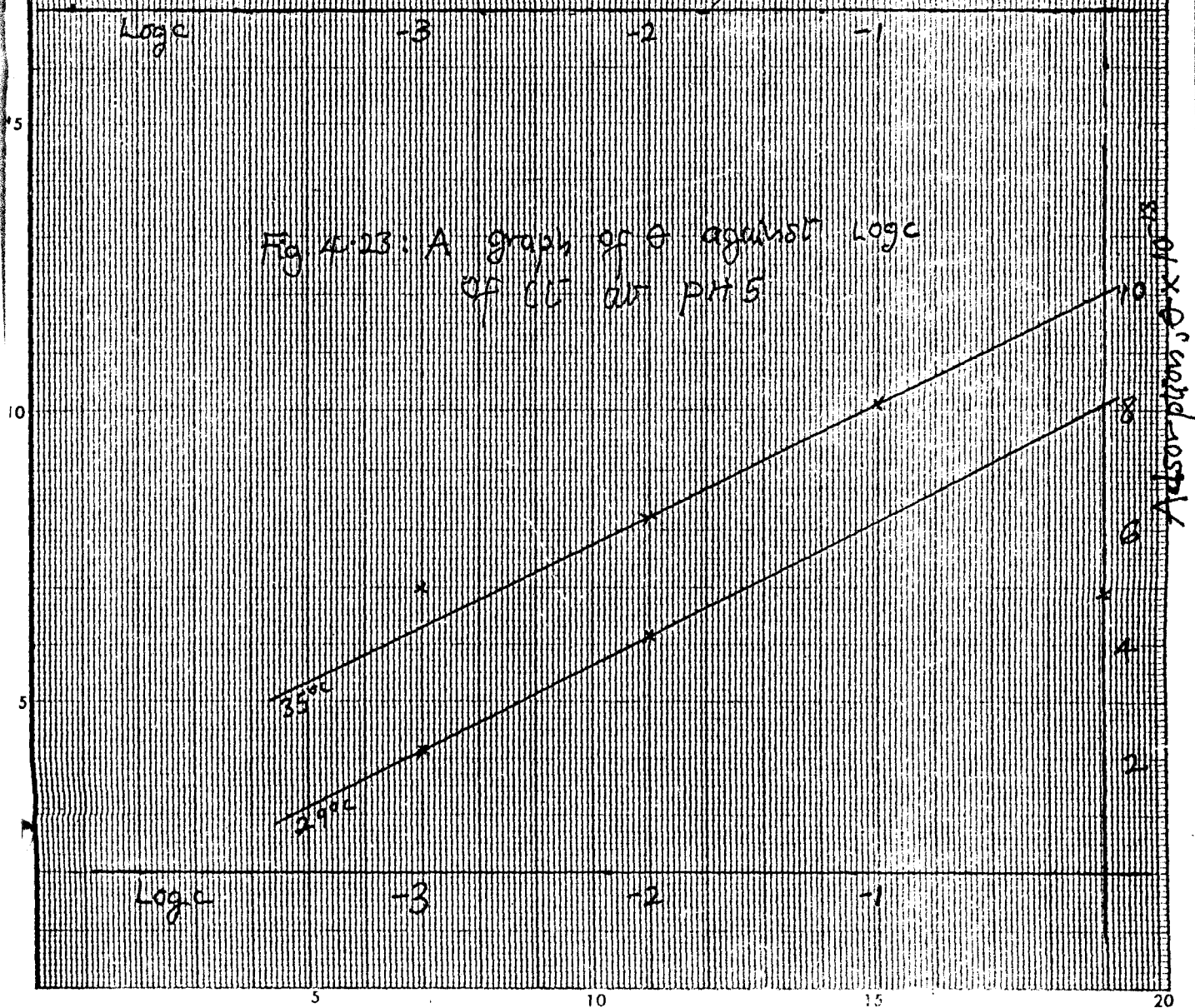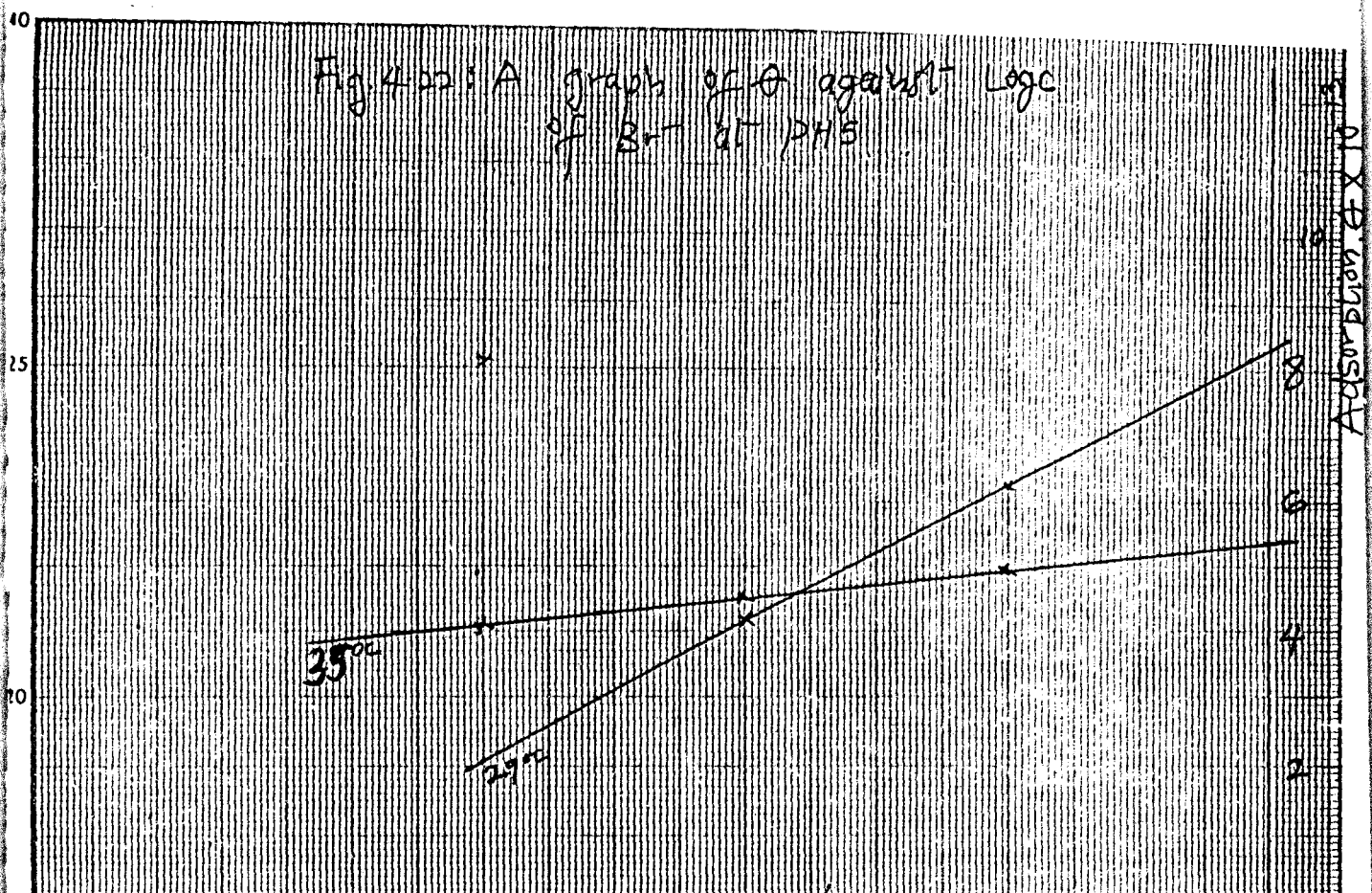
Fig 4.2c: A graph of θ against Log c of Br⁻ at pH6
Scale: 2cm to represent 2 units on y axis
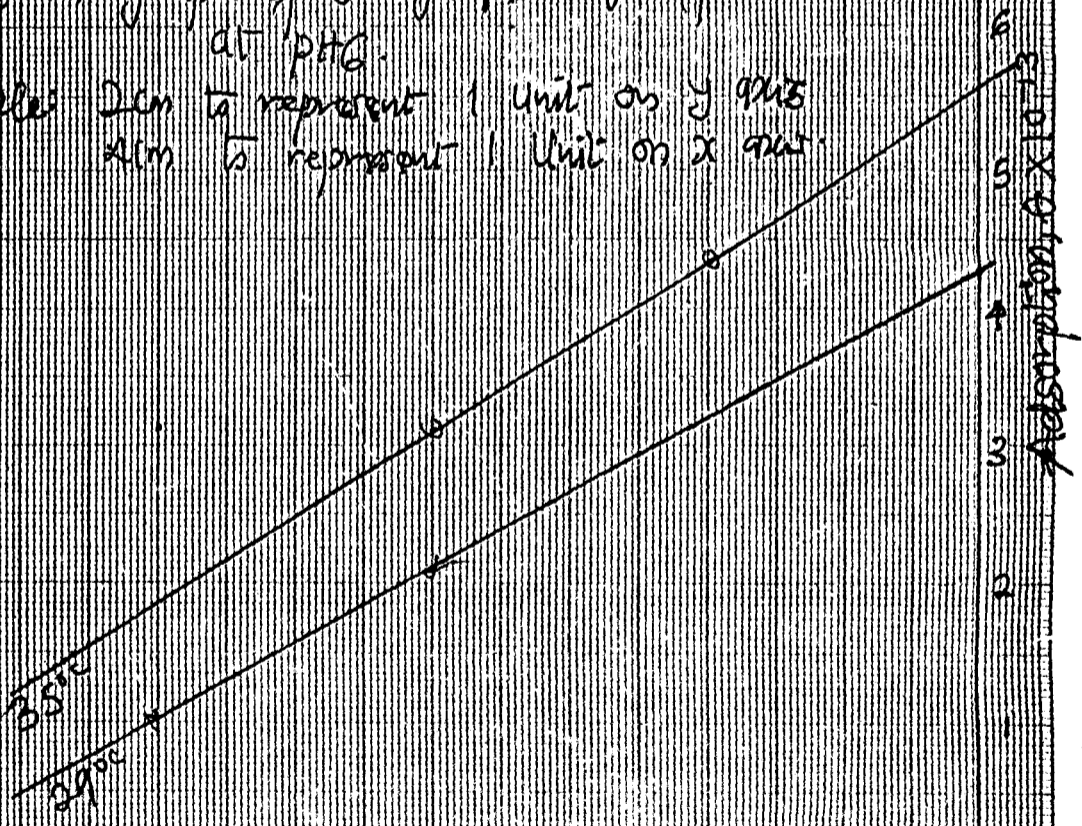4cm to represent 1 unit on x axis

29°C

Log c   -3   -2   -1

Adsorption θ × 10⁻³
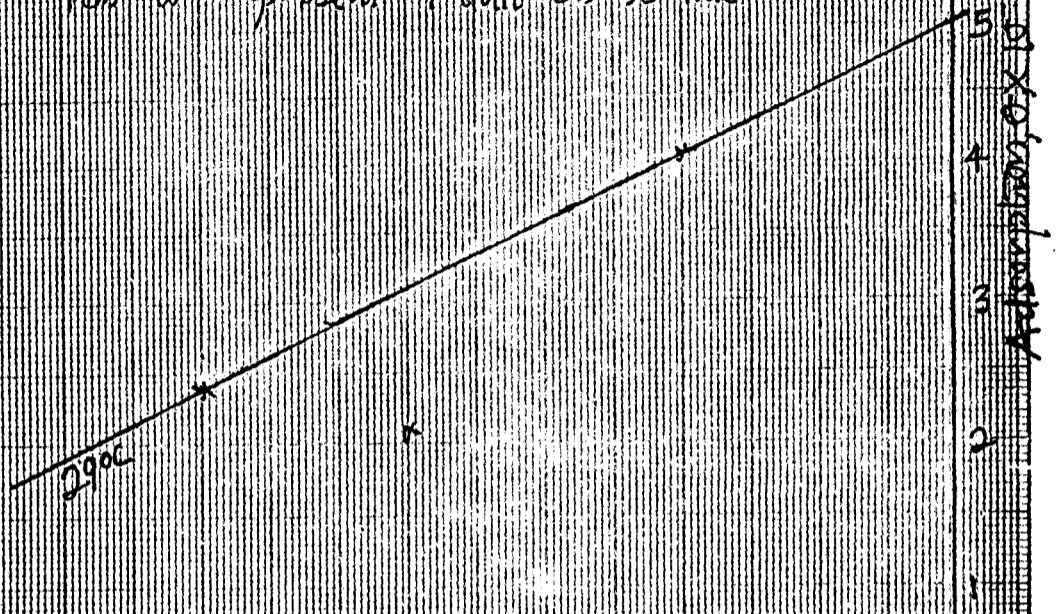
Fig 4.25: A graph of θ against Log c of Cl⁻ at pH6
Scale: 2cm to represent 1 unit on y axis
4cm to represent 1 unit on x axis

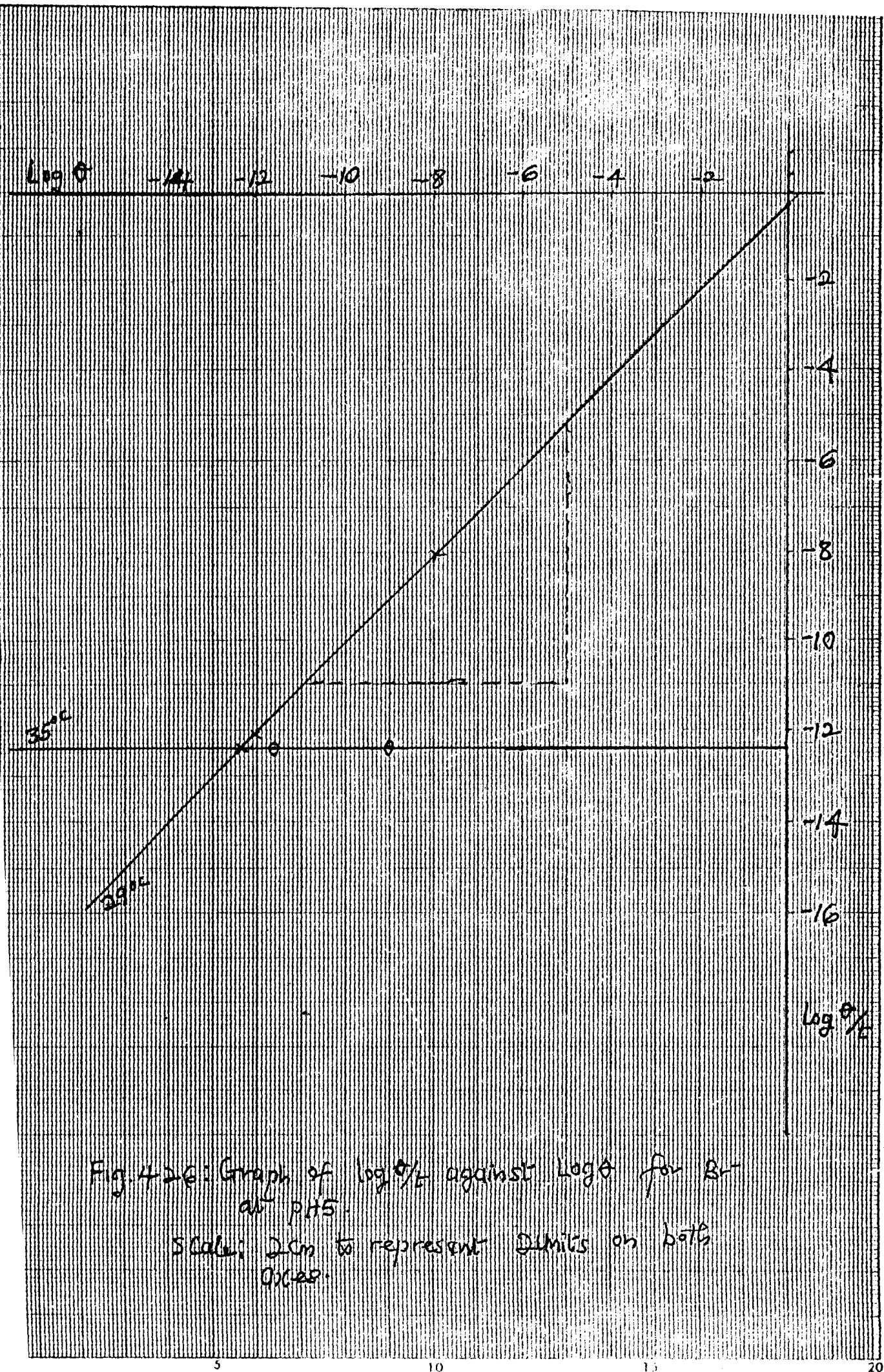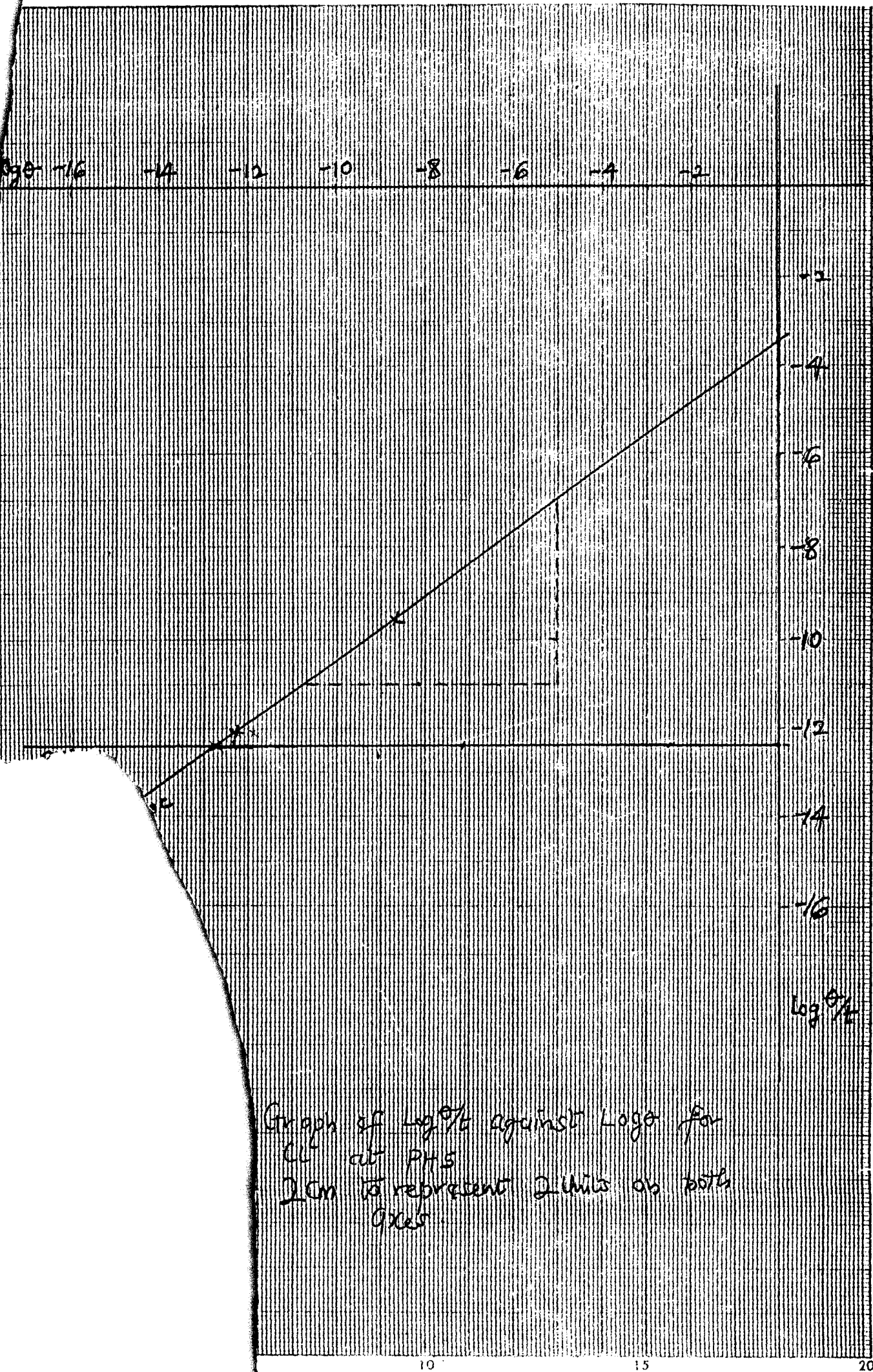35°C
29°C

Log c   -3   -2   -1

Adsorption θ × 10⁻³

Fig.4.26: Graph of log θ/t against Log θ for Br⁻ at PH5.

Scale: 2cm to represent 2units on both axes.

Graph of Log P/t against Log θ for Cu at PH5
2 cm to represent 2 units on both axes