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EXCHANGE ADSORPTION OF ELECTROLYTES ON TITANIUM DIOXIDE

BY

RICHARD A. SLEPETYS

A THESIS
SUBMITTED TO THE FACULTY OF
THE DEPARTMENT OF CHEMICAL ENGINEERING
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ABSTRACT

During the manufacture of titanium dioxide pigments many processing steps are carried out in solutions of electrolytes. Adsorption of these electrolytes strongly affects properties of the finished pigments.

Adsorption of electrolytes was studied on titania samples prepared by controlled neutralization of titanium tetrachloride solutions with ammonium hydroxide, and one sample of commercial sulfate process rutile titania. In analogy to zirconia--as reported by Kraus and Phillips--[22,23] titania also behaved as a weak anion exchanger in acid solutions and as a weak cation exchanger in basic solutions. Acid or base liberated was approximately equivalent to ions exchanged. On the best sample the exchange capacity was 0.8 milliequivalents per gram for sodium, 1.1 for barium, and 0.7 for sulfate. These values compare with the exchange of 1.4 millimoles of chromate ions per gram of zirconia, reported by Kraus and Phillips.[23]

The isotherm data were best correlated by the use of Langmuir's equation because it postulates conditions corresponding to ion exchange; i. e., monolayer adsorption on active sites. Since Freundlich's equation does not

take into account the saturation of adsorbent with adsorbate, it applied only at lower concentrations. The modified BET equation was good because only low relative saturations were reached.

Hofmeister series essentially applied to about 0.3 N solutions. At higher concentrations the order changed to $Ba^{++} > Na^{+} > Li^{+} > K^{+}$.

As it is typical of true ion exchange, temperature increase (25°C. to 70°C.) had no effect on the capacity of a laboratory-prepared sample. The capacity of the plant titania sample decreased with temperature, indicating weaker attraction for the ions.

The few articles dealing with adsorption of electrolyes on titanium dioxide disagree about the nature of this adsorption: some investigators have reported strong adsorption of anions with little or no adsorption of cations (Bhatia and Ghosh,[3] Kargin and Tolstaya [18]) while others have found the opposite to be true (Verkhovskii[36] and coworkers). These discrepancies in the literature can be explained now on the basis of amphoteric behavior of titania: cation exchange was reported in basic solutions and anion in acid ones.

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INTRODUCTION

It is a well-known fact in colloid chemistry that small amounts of materials adsorbed on a surface affect profoundly the properties of that surface.[37] Since pigmentary titanium dioxide has a comparatively large surface area (about 9 square meters per gram) and since many processing steps in its manufacture are carried out in solutions of electrolytes, appreciable adsorption of these electrolytes may take place. These adsorbed materials, in turn, affect dispersion and flocculation of the finished pigments in paint vehicles and their performance in other products where the hiding and whitening power of titanium dioxide is in some way utilized.

It is obvious, then, that knowledge of interaction between the surface of titanium dioxide and the surrounding electrolyte is of value to pigment manufacturers as well as users.

Adsorption of gases on titanium dioxide has been studied quite extensively, yet little has been reported in the literature on the adsorption of electrolytes. Furthermore, review of this literature disclosed a disagreement as to the nature of adsorption that takes place on titanium dioxide. Verkhovskii[36] and coworkers found strong exchange adsorption of cations with no anion adsorption. On the other hand, Bhatia and Ghosh[3] reported stronger adsorption of anions than cations. Similarly, Kargin and Tolstaya,[18] and Brusilovskii and Poshvina[7] found appreciable adsorption of anions.

An explanation of this disagreement suggests itself from the work of Kraus and Philliphs[22,23] with zirconium dioxide. They found that zirconium dioxide behaved as a cation exchanger in basic solutions and as an anion exchanger in acid solutions.

The thesis work, therefore, was designed to study the nature of adsorption of electrolytes on titanium dioxide and thereby explain the apparent disagreements in the literature. Effects of pH, solution concentration, valence of ion, sign of charge, temperature, and surface area were studied. From these effects the nature of adsorption was inferred.

LITERATURE

Adsorption from Aqueous Solutions

Bhatia and Ghosh[3] studied the adsorption of ions on freshly flocculated titania sols. The sols were prepared by careful addition of dilute titanium tetrachloride solution to water at 18°C. The resulting sols contained about 15 grams per liter titanium dioxide. These sols could be dialyzed to a maximum pH of 4.1 before coagulation took place. As the adsorbate (various sodium and potassium salts) was added, the sols gelled immediately. After 20 hrs. of equilibration with shaking, the supernatant liquid was analysed and the adsorption claculated. The adsorption of various anions in gram-moles per gram of adsorbent decreased in the following sequence: $Fe(CN)_6^{-3} > NO_2^- > SO_4^{-2} > Cl^- > S_2O_3^{-2} > Cr_2O_7^{-2} > Br^- > Fe(CN)_6^{-4} > IO_3^- > CrO_4^{-2} > OH^-$. The magnitude of adsorption ranged from 0.392 millimoles per gram for ferricyanide at 0.2082 molar equilibrium concentration to 0.0266 millimoles per gram at 0.0392 molar concentration. Anions were stronger adsorbed than cations since the pH of the equilibrium solution was found to increase due to liberation of OH^- ions.

A similar study was made by Verkhovskii [36] and coworkers. Titania gel was prepared by dilution of titanium tetrachloride with water followed by aging and evaporation until a jelly formed. This jelly was washed with water, dried at room temperature for several days, washed again with concentrated sulfuric acid, dried at 110°C, 4hrs., and finished in vacuo at 170-180°C. The gel was contacted with dilute solutions of alkali hydroxides, ammonium hydroxide, salts, and acids. Adsorption was determined by titration of hydrogen or hydroxyl ions liberated by the exchange. Bases were adsorbed strongly (up to 1.5 millimoles per gram), cations from salt solutions were adsorbed somewhat less by a postulated mechanism of hydrolytic decomposition, and no adsorption of acids was detected.

Kargin and Tolstaya[18] studied adsorption of sulfuric acid on freshly flocculated titania sols. The sols were prepared by the addition of titanium tetrachloride to hot water followed by dialysis to remove most HCl. Sodium sulfate was added to these sols, and the adsorption of hydrolytically formed sulfuric acid was determined. When the residual amount of HCl in the sol was low, adsorption of H_2SO_4 decreased linearly with pH to a zero value at neutral pH. As more HCl was left in the sols, the curve assumed an S shape.

Brusilovskii and Poshvina[7] measured the specific surface of titanic acids by the adsorption of phosphoric acid. The adsorption increased when the pH value at precipitation of titania was higher.

Gapon[12] used titanium dioxide and aluminum oxide as adsorbents in developing equations for the simultaneous adsorption of ammonium hydroxide and ammonium chloride.

Adsorption of Dyes and Surfactants

Morley and Wood[27] made a study of the adsorption of dyes on titanium dioxide. They found that only basic dyes were adsorbed if in the preparation of titanium dioxide the neutralization of titanium tetrachloride was carried over to a basic pH, and acid dyes were adsorbed when this neutralization was stopped slightly on the acid side. The authors theorized that this behavior was due to the formation of a basic chloride when the tetrachloride was not fully neutralized, and the formation of a titanate with overneutralization of titanium tetrachloride.

Ewing and Liu[10] studied the adsorption of dyes on commercial rutile, anatase, and zinc oxide pigments. The equilibrium technique using a 5 g. sample of a pigment and 25 ml. of adsorbate solution was employed. Nine days were required to obtain the equilibrium. Freundlich and Langmuir isotherm equations did not apply. The data could be correlated by the BET adsorption equation modified to apply for solutions: concentration value was substituted for pressure, and dye adsorbed per gram of adsorbent was substituted for the volume of gas adsorbed. On the basis of this correlation and the reversibility of adsorption physical bimolecular adsorption was postulated.

Ormanowski[31] conducted a similar study with titanium dioxide hydrolyzed from an ilmenite sulfate solution. This raw material was dried at temperatures ranging from 100°C. to 900°C. Five gram samples were equilibrated with 25 ml. of organic dye solutions (1.00 or 0.005 grams per liter concentration). Equilibrium was attained in five minutes. Acidic dyes were adsorbed 90% or better on samples dried up to 700°C. Samples dried at higher temperatures adsorbed only small amounts of acidic dyes. The reverse was found to be true about the basic dyes: they were little adsorbed on samples dried below 700°C., but adsorption increased above this drying temperature.

Adsorption of desulfonated lignosulfonate and sulfonated naphthalene-formaldehyde condensate surfactants on commercial anatase pigments was reported by Brown.[5] Isotherms reaching saturation at 0.02-0.04 g. per 100ml. adsorbate concentration were obtained.

Hydrous titania was found to be a good mordant adsorbing alizarin orange, coerulein, and alizarin blue dyes.[38]

Adsorption in Paint Systems

The adsorption of paint driers by titanium dioxide pigments has been of some concern to paint manufacturers. Adsorption of cobalt, lead, and manganese naphthenates on titanium dioxide pigment from a mineral spirits solution has been reported (0.0096 g. lead, 0.0020 g. manganese, and 0.004 g. cobalt per gram of titanium dioxide).[8]

A qualitative study of the adsorption of cobaltous ion from aqueous and acetic acid solutions on commercial titanium dioxide pigments was made by Nicholson.[30] Adsorption of simple cobaltous ions was found by the use of conductometric and spectrophotometric techniques. When cobalt was coordinated with ortho-phenantroline, however, this adsorption was practically eliminated.

Adsorption of Gases

Considerable work has been reported on the adsorption of gases on titanium dioxide. Since it does not pertain directly to the subject matter of the thesis, this literature will not be discussed. Several articles, however, are listed as references.[1,17,19,20,21,32,34]

Adsorption on Zirconium Dioxide

Adsorption of ions on zirconium dioxide was studied by Kraus and Phillips.[23] Zirconium hydroxide was prepared by the neutralization of zirconyl chloride with ammonium hydroxide and was subsequently dried at 25-800°C. This material adsorbed negative ions well in acid solutions and positive ions in basic solutions. Exchange capacity up to 1.4 millimoles per gram of adsorbent for chromate ion was obtained. The authors suggest that titanium dioxide may also exhibit similar properties.

Kraus[22] and coworkers reported recently an improvement of the capacity of zirconia exchangers when they were prepared as zirconium tungstate polymers.

Effect of Adsorption Conditions on the Adsorption Capacity

The adsorption capacity of a material depends not only on its previous history but also on the adsorption conditions. The temperature is known to exert little or no effect on a true ion exchange equilibrium because no covalent bonds are formed or broken; the ions only move from one environment to another.[28] In the case of physical adsorption increasing temperature decreases the amount adsorbed.[13,14] Since there is energy of activation involved in the process of chemisorption, increasing temperature increases the rate of adsorption.

The dependence of adsorption of electrolytes by zirconium dioxide on pH was pointed out by Kraus and Phillips,[23] as mentioned before. Similarly, Kargin and Tolstaya's[18] work on adsorption of sulfuric acid on flocculated titania sols shows a definite dependence of adsorption on pH of solution.

Evidently, this dependence is not limited to titanium dioxide and zirconium dioxide since an interesting relationship was derived by Plank[33] for the adsorption of acetate and phosphate ions on silica gel.

$$\frac{x/m}{c} = B\left[H^{+}\right]^{-q}$$

x/m--millimoles of adsorbate per gram of adsorbent

c--equilibrium concentration of adsorbate

$[H^+]$--hydrogen ion concentration

B, q--constants

Methods of Study

In general, three methods are used for studying adsorbents and ion exchangers: equilibration, column study, and titration. Equilibration is, probably, the most commonly used method in the laboratory. It consists simply of contacting a known amount of the adsorbent with a known volume of adsorbate solution of a given concentration until equilibrium is reached. Agitation of some kind is usually employed. At the end of the equilibration period the liquid is analyzed for the ions still remaining in solution, and the adsorption is calculated.[3,9,24,25,36] A modification of this method was used by Gregor[16] and coworkers. Instead of analyzing the final equilibrium solution, they eluted the ions adsorbed on the resin and analyzed the eluate.

In the column technique, a suitable column is packed with the adsorbent, and its properties are studied by passing adsorbate and eluent solutions through it.[24,29]

A cross between the column technique and the equilibration technique was developed by Fisher and Kunin[11] into a routine method for determining the capacities of exchange resins. The method consists of placing a weighed amount of resin into a funnel, converting it to the ionic form whose capacity has to be measured, and then eluting this ion and analyzing the eluate. This method was elaborated to differentiate between weak and strong acidic or basic exchangers.

The characterization of a resin as to its acidic or basic strength and the determination of the number of exchange sites belonging to these types is conveniently done by the titration curve technique.[15,25] In this technique a series of samples is equilibrated with a salt solution containing an excess of acid or base. The equilibrium pH is measured and plotted against the amount of free acid or base added. The characteristic curves obtained are very similar to those of regular acid-base titrations and are indicative of the strength of acid or base being titrated.

Adsorption Isotherm Correlations

There is a good number of correlations proposed in the literature for the adsorption of gases on solids. The adsorption phenomena in dilute solutions, however, are often quite adequately correlated by the use of the classical Freundlich adsorption isotherm.[13]

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

K and n are constants.

According to this equation, a straight line is obtained when a log-log plot is made of the amount of material adsorbed against its equilibrium concentration in solution.

There is one obvious weakness in the Freundlich equation. As the adsorbent becomes saturated the correlation breaks down since c continues to increase while x/m tends to level out at some saturation value.

A correlation which takes into account the saturation of the adsorbent as the concentration (or pressure, in the case of gases) of adsorbate is increased, was derived by Langmuir from equilibrium considerations between the adsorbent and the surrounding gas.[13]

$$\frac{p}{x/m} = \frac{1}{k_1 k_2} + \frac{p}{k_2}$$

p--gas pressure

In solutions, concentration of adsorbate is substituted for pressure.

$$\frac{c}{x/m} = \frac{1}{k_1 k_2} + \frac{c}{k_2}$$

Langmuir's equation is valid for the adsorption of a monomolecular layer, which is true about chemisorption, ion exchange, and most physical adsorption in solutions. Boyd and coworkers have applied this equation successfully in cation exchange.[4]

Brunauer, Emmett, and Teller[6] expanded Langmuir's correlation to apply for the adsorption of multiple layers.

$$\frac{p}{(p_s - p)\ (x/m)} = \frac{1}{(x/m)_m\ d} + \frac{(d - 1)\ p}{(x/m)_m\ dp_s}$$

p_s--condensation pressure

$(x/m)_m$--adsorption at monolayer coverage

d--a constant

Having substituted equilibrium concentration for the pressure term and solubility for the condensation pressure, Ewing and Liu[10] used this equation to correlate adsorption data of dyes from aqueous solutions on pigments.

EXPERIMENTAL PROCEDURES

Sample Preparation

Most adsorption studies of electrolytes on titanium dioxide reported in the literature were carried out on titania sol or gel samples prepared in some fixed fashion; i. e., none of the previous investigators (except Ormanowski) varied the conditions of sample preparation so as to have samples with different surface areas or adsorption capacities. Ormanowski[31] obtained samples with varying adsorption capacities by drying hydrous titania at increasingly higher temperatures (100-900°C.). This procedure, however, tends to inactivate titania surface in addition to inducing particle growth.

Three titania samples were prepared by controlled neutralization of aqueous solution of titanium tetrachloride with ammonium hydroxide. The precipitation conditions (given in Table I) were varied in such a manner as to yield titania samples with comparatively large surface area (for ease of adsorption study) and reasonable variation of this area between the samples. From the precipitation conditions sample 1 was expected to have the lowest surface area and sample 2 the highest. All samples were finished at the same drying temperature (375°C.).

Table I

Sample Preparation Data

Sample:	1	2	3
$TiCl_4$ concentration, gpl. TiO_2	200	200	200
Volume, ml.	3500	3500	3500
NH_4OH concentration, gpl.	300	100	200
Volume, ml.	2710	10130	4580
Addition time, min.	30	1	15
Temp. at the end of add'n. °C.	83	65	84
Cure temperature, °C.	100	80	90
Cure time, min.	60	30	45
Final HCl/TiO_2 weight ratio	0.64	0.44	0.53
Number of flasks used	2	3	2

Total neutralizeable HCl in the tetrachloride solution 361 gpl.

It is known that variations in the precipitation as well as drying conditions have an effect on the surface area or activity of titania. The particular set of conditions was chosen for convenience and other above-mentioned reasons.

It was also desirable to obtain the same crystalline structure as that of the well-known rutile pigment grades. In this manner the results of adsorption study on the laboratory-prepared samples could be compared better with similar phenomena on commercial titania. For the purpose of such a comparison, commercial pigment grade titania (National Lead Company, Titanium Division) of rutile crystalline modification without any surface treatment was taken as the fourth sample.

The precipitation of titania used in the adsorption study was carried out in five-liter three-neck flasks. An agitator made of bent glass rod (about 1.5 inches radial sweep) and running at 195 RPM was inserted through the middle neck. The opening was sealed with a rubber stopper equipped with a vapor-tight gland for the agitator. One of the side necks held a reflux condenser, and the other a thermometer. Titania hydrate was precipitated in such flasks by the controlled addition at a uniform rate of titanium tetrachloride to ammonium hydroxide. Titanium tetrachloride solution was added to ammonium hydroxide rather than ammonium hydroxide to the tetrachloride since titania hydrate obtained in this manner is less gelatinous and easier to handle than that prepared by the reversed neutralization procedure. The concentrations and amounts of reagents used, rates of addition, and curing temperatures are shown in Table I, p. 14. Since the hydrolysis of a single batch could not be carried out in one flask due to a large reaction volume, two or three such flasks were employed. The hydrate slurries then were blended in five-gallon bottles before further processing.

Titania sample No. 1 was prepared first. It was washed by decantation; i. e., the hydrate was allowed to settle in a five-gallon bottle for one day, supernatant liquid was siphoned off, and fresh wash water added.

The operation was repeated a number of times until slow settling rate indicated low electrolyte concentration in solution. The washing was finished by deliquoring on two 24 cm. Buchner funnels with suction.

An attempt was made to wash preparations 2 and 3 in a similar manner. Due to their finer particle size, however, these samples settled very slowly. In order to speed up the washing they were flocculated with ammonium hydroxide (to give approximately neutral pH) and were filtered and washed on a large vacuum filter (22.5 in. x 18.5 in.) using about 35 liters of demineralized wash water per sample.

The filter cakes were dried overnight at 120°C. in an oven and then in an electric muffle furnace at 375°C. for one hour. They were finished with a 6-inch Raymond mikro-pulverizer. The plant titania sample was also ground similarly.

The finished samples contained about 98 percent TiO_2. In addition, sample No. 1 had 0.38 percent of residual chloride (leachable in boiling 10 percent nitric acid), while no chloride could be detected in the other two preparations. The metallic impurities were determined spectrographically, and the crystalline form of the samples was established by X-ray diffraction. All these data are shown in Table II, p. 17.

High rutile content was found in samples 1 and 3.

Table II

Sample Compositions

Sample:	1	2	3	Plant Titania
Wet Analysis				
TiO_2, %	97.6	97.9	98.2	99.3
Cl^-, %	0.38	Not detected		0.0
X-Ray Analysis				
Rutile, %	100	40	80	95
Spectrographic Analysis				
SiO_2, %	------	0.1	------	0.1
Al_2O_3, %	------	0.004	------	0.06
Fe_2O_3, %	------	0.004	------	0.008
Pb, %	------	0.02	------	0.01
Nb, %	------	0.01	------	0.1
Surface Area				
Square meters per gram	73	268	151	9

Sample 2, however, had only 40 percent rutile, mainly, because of too low curing temperature (80°C.) used at the end of the hydrolysis reaction.

Determination of Surface Area

Surface area of the plant sample is known to be about 9 m^2/g. Area of laboratory-prepared samples was determined by comparing adsorption of water vapor with that of a sample whose area was known from BET measurements. All samples (2-3 grams) were dried at 300°C. for one hour in a muffle furnace, cooled to 200°C. in the furnace and then to room temperature in a desiccator. The samples were exposed to water vapor above 60 percent sulfuric acid (3.6 mm. Hg water vapor pressure at room temperature) at a total pressure of 5 mm. Hg for 16 hrs., and surface areas were estimated from amounts of water adsorbed.

Adsorption Rate Determinations

Adsorption rate was briefly studied by contacting a titania sample with 0.1 N HCl and NaOH for 5 min., 10 min., and 37 hrs. Conductivity of resulting solutions was measured.

Determination of Titration Curves

The titania samples were characterized as to their acidic or basic strength by the titration curves. The general procedure outlined by Kunin and Myers[25] was followed. According to this procedure, acid and base solutions of different strength were prepared in a corresponding salt solution and then equilibrated with the adsorbent. Table III lists the solutions used in establishing the titration curves.

Table III

Titration Curve Solutions

Solution No:	1	2	3	4	5	6	7
0.1N NaCl, ml.	0	10	20	0	10	20	25
0.1N HCl in 0.1N NaCl, ml.	25	15	5	0	0	0	0
0.1N NaOH in 0.1N NaCl, ml.	0	0	0	25	15	5	0

The presence of a neutral salt in the solutions is necessary for the determination of the nature of adsorption at neutral or near-neutral pH values.

The above-listed solutions (25 ml. per sample) were equilibrated with 5.00 g. of adsorbent. The sample and the respective solution were placed in a 2-ounce screw-cap jar, several of such jars were in turn set into a large wide-mouth bottle in a position perpendicular to the axis of the bottle, and the bottle was rolled on a ball mill rack for 15 min. at 105 RPM. The equilibrated mixtures were separated by centrifugation, 10.00 ml. of clear solution was pipetted off, and diluted to 100.0 ml. in a volumetric flask. The equilibrium pH was measured on the undiluted remainder with Beckman model H2 pH meter, using glass and calomel electrodes.

In addition to the measurement of equilibrium pH, the adsorption of anion and cation was determined by analyzing original and equilibrium solutions. These solutions were filtered through two No. 42 Whatman papers, if any turbidity still remained after centrifugation.

Determination of Adsorption Isotherms

The equilibration technique used in establishing the titration curves was also employed in the determination of adsorption isotherms at room temperature. At elevated temperature (70°C.) the setup had to be modified in order to heat the samples. Titania samples and adsorbate solutions were placed into 6-inch test tubes. The tubes were well stoppered, clamped in a Burrell, model BB, laboratory shaker, lowered into a water bath (70-75°C.), and shaken for 15 min. Bath temperature was reached in 1-2 minutes. The liquid from equilibrated mixtures was decanted into centrifuge tubes, centrifuged in order to separate the remainder of solids, and analyzed.

Isotherms were determined at room temperature for sodium, potassium, lithium, and barium in basic solutions, and for aluminum, chloride, and sulfate in acid solutions. In order to somewhat buffer these solutions, chloride-hydroxide mixtures in the approximate 5:2 molar ratio were used for sodium, potassium, lithium, and barium; sodium salt-acid solutions in 1:1 molar ratio were taken for chloride and sulfate; aluminum chloride alone was used for aluminum. Solution analyses are shown in Table IV, p. 21. Isotherms were also determined for sodium at 70°C. on two samples.

Analytical Methods

Adsorption was determined by analyzing the original and equilibrated solutions. Sodium, potassium, lithium, and barium were analyzed flame photometrically. Aluminum was precipitated and weighed as aluminum 8-quinolinate. Sulfate was also determined gravimetrically as barium sulfate. Chloride was titrated potentiometrically with silver nitrate using silver and glass electrodes.

Table IV

Composition of Electrolyte Solutions

Ion Studied	Mole Fraction of Salt	Mole Fraction of Base or Acid
Li^+	0.801	0.199
Na^+	0.717	0.283
K^+	0.745	0.255
Ba^{++}	0.646	0.354
Al^{+++}	1.000	0.000
Cl^-	0.496	0.504
SO_4^{--}	0.545	0.455

Equilibrium solutions of several isotherms were also analyzed by acid or base titration for hydrogen or hydroxyl ions liberated through ion exchange.

RESULTS

Rate Experiments

The few adsorption rate measurements which were made indicated that equilibrium was reached within 5 min. or less (Table V).

Table V

Adsorption Rate Measurements

	Equilibrium Solution Resistivity, ohm-cm	
Time	0.1 N HCl	0.1 N NaOH
Original Solution	274	420
5 min.	760	12000
10 min.	730	11900
37 hrs.	720	11800

Titration Curves

The titration curve data are given in Table VI, p. 23, and the curves are plotted in Fig. 1, p. 24. In addition, the dependence of sodium adsorption on pH is shown graphically in Fig. 2, p. 24.

Table VI

Titration Curve Data

Solution:	1	2	3	4	5	6	7
c_o for Cl^-	0.202	0.161	0.120	0.102	0.101	0.100	0.0994
c_o for Na^+	0.100	0.100	0.100	0.200	0.160	0.120	0.0994
Sample 1							
Acid or base added*	0.512	0.307	0.102	0.512	0.307	0.102	0.0
Equil. pH	1.18	1.28	1.70	12.10	11.67	7.93	2.69
c for Cl^-	0.211	0.172	0.131	0.125	0.130	0.123	0.114
x/m for Cl^-	-0.046	-0.056	-0.056	-0.118	-0.148	-0.118	-0.077
c for Na^+	0.100	0.100	0.100	0.173	0.136	0.116	0.0994
x/m for Na^+	0.0	0.0	0.0	0.14	0.12	0.02	0.00
Sample 2							
Acid or base added*	0.511	0.307	0.102	0.511	0.307	0.102	0.0
Equil. pH	1.56	2.36	6.20	11.49	10.32	9.00	7.92
c for Cl^-	0.170	0.135	0.120	0.103	0.102	0.103	0.102
x/m for Cl^-	0.16	0.13	0.0	0.0	0.0	0.0	0.0
c for Na^+	0.100	0.0968	0.096	0.117	0.103	0.099	0.0900
x/m for Na^+	0.0	0.015	0.02	0.42	0.29	0.102	0.048
Sample 3							
Acid or base added*	0.509	0.306	0.102	0.509	0.306	0.102	0.0
Equil. pH	1.27	1.68	4.38	12.03	11.33	9.33	7.65
c for Cl^-	0.185	0.141	0.118	0.103	0.102	0.103	0.103
x/m for Cl^-	0.087	0.102	0.010	0.0	0.0	0.0	0.0
c for Na^+	0.100	0.0947	0.0926	.147	0.112	0.099	0.0944
x/m for Na^+	0.0	0.02	0.04	0.27	0.24	0.107	0.025
Plant Sample							
Acid or base added*	0.504	0.302	0.101	0.504	0.302	0.101	0.0
Equil. pH	1.30	1.37	1.86	12.29	12.14	11.78	6.35
c for Cl^-	0.200	0.163	0.122	0.103	0.109	0.103	0.101
x/m for Cl^-	------------ Not detectable ------------------						
c for Na^+	0.100	0.0935	0.0985	.193	0.152	0.115	0.0961
x/m for Na^+	0.0	0.03	0.005	0.035	0.04	0.025	0.017

* Milliequivalents per gram of TiO_2; acid in solutions 1, 2, and 3, base in 4, 5, and 6.

For the definitions of symbols see Nomenclature, p. 55.

Fig. 1

Titration Curves

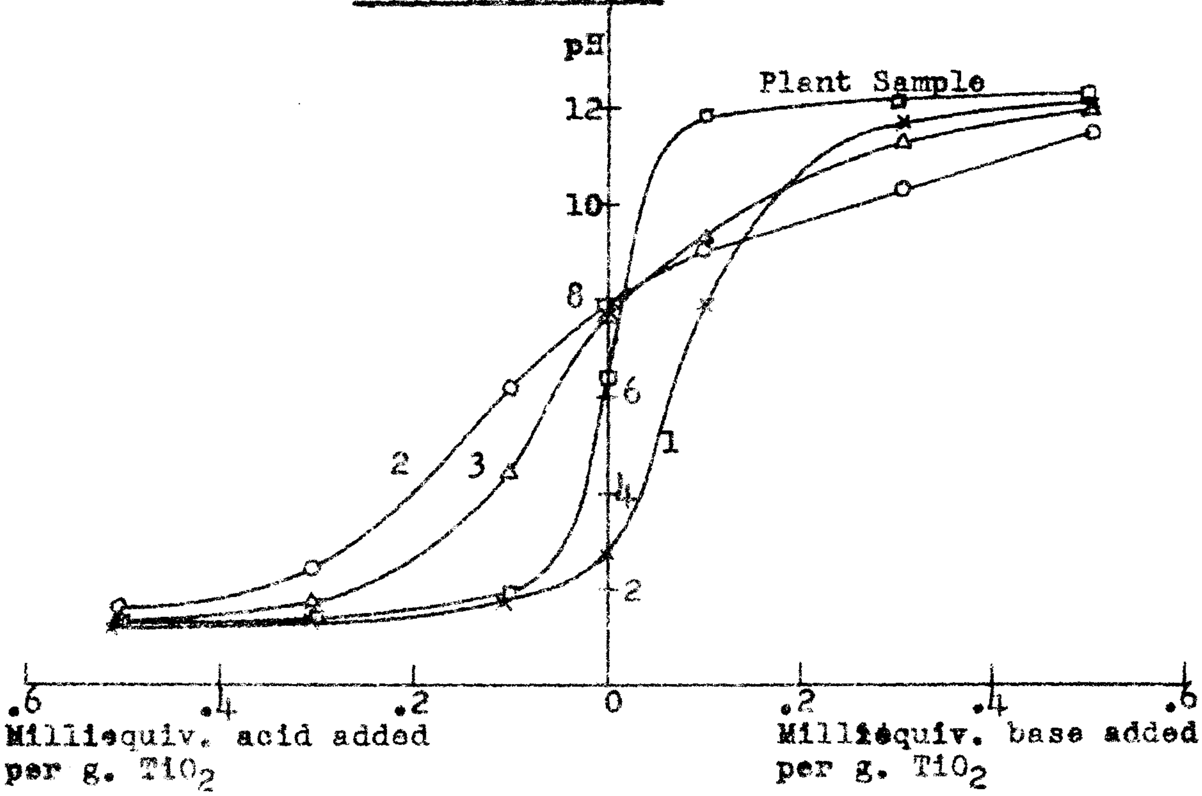
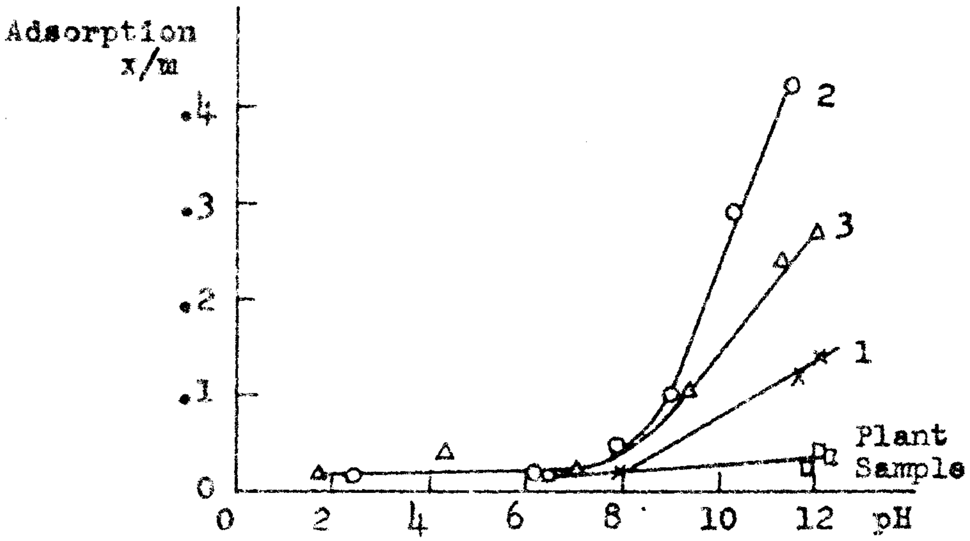


Fig. 2

Effect of pH on Na^+ Adsorption



Adsorption Isotherms

Adsorption isotherms for cations were determined in basic solutions because they were adsorbed much stronger at higher pH values. Adsorption of anions was studied for the same reason in acid solutions. Adsorption of aluminum, however, had to be studied in an acid solution since aluminate rather than trivalent aluminum ion exists in basic solutions. Data are given in Tables VII through XIII, pp. 27-33, and plotted in Figures 3 through 12, pp. 34-43.

Typical Langmuir adsorption isotherms were obtained for all ions studied. The modified BET equation also applied fairly well. Only the pattern of chloride adsorption was not quite clear due to low amounts adsorbed and some scatter of data. Freundlich's equation applied quite well for cations in basic solutions up to the point of adsorbent saturation. For sulfate Freundlich plot was curved due to the gradual saturation of adsorbent. The capacity was reached quickly with aluminum and chloride ions.

Residual HCl on sample 1 obscured the determination of chloride adsorption on this sample. Similarly, potassium adsorption could not be determined on the plant titania sample because of interference of potassium in the sample, which is commonly introduced as a calcination control agent.[2]

Liberation of hydrogen or hydroxyl ion by the exchange was determined in potassium, lithium, chloride, and sulfate isotherm experiments. This liberation was found to be closely equivalent to the respective ion adsorbed (Tables VIII, IX, XII, and XIII).

Elevating the temperature to 70°C. did not affect the adsorption of sodium on a laboratory-prepared sample (Table VII and Figure 3). It was decreased somewhat on the plant sample.

The effect of charge and hydrated ionic radius for several cations is illustrated in Figure 13, p. 47. Hofmeister series was followed up to about 0.3 N concentration. At higher concentrations the order of decreasing adsorption was $Ba^{++} > Na^{+} > Li^{+} > K^{+}$.

Adsorption on laboratory samples was found to be approximately proportional to their surfaces (Figure 14, p. 48, and Tables VII, X, XI, and XIII). Adsorption on plant sample, however, did not fit into this pattern. It was somewhat higher per unit area.

Table VII

Sodium Isotherm Data

c_o	c	Equil. pH	x/m	$\frac{c}{x/m}$	$\frac{c}{x/A}$	$\frac{c}{\frac{x}{m}(c_s - c)}$	c/c_s
Room Temperature Sample 1							
0.01000	0.01	2.7	0	---	---	---	---
0.1000	0.0980	8.9	.010	9.8	720	1.6	.0156
0.400	0.385	12.0	.077	5.0	360	0.85	.0615
1.000	0.939	12.0	.31	3.0	220	0.56	.150
1.400	1.36	12.0	.2	7	510	1.4	.217
2.00	1.97	12.0	.2	10	730	2.3	.317
Sample 2							
0.01000	0.00374	8.6	.0320	0.117	31.3	0.0187	.000596
0.1000	0.0688	9.3	.159	0.433	116	0.0798	.0110
0.400	0.327	11.4	.37	0.88	240	0.15	.0531
1.000	0.851	11.9	.762	1.12	300	0.207	.136
1.400	1.24	12.0	.82	1.5	400	0.30	.198
2.00	1.83	11.9	.87	2.1	560	0.47	.292
Sample 3							
0.01000	0.00503	8.5	.0253	0.199	30.0	0.0318	.000803
0.1000	0.0712	9.8	.148	0.481	72.7	0.0776	.0114
0.400	0.345	11.8	.28	1.2	180	0.020	.0550
1.000	0.900	12.0	.510	1.76	266	0.328	.143
1.400	1.27	12.1	.66	1.9	290	0.202	.206
2.00	1.90	11.9	.51	3.7	560	0.85	.303
Plant Sample							
0.01000	0.00810	9.5	.0146	0.555	5.0	0.0888	.00129
0.1000	0.0870	11.8	.116	0.750	6.8	0.121	.0139
0.400	0.373	12.1	.14	2.7	24	0.47	.0595
1.000	0.975	12.0	.13	7.5	68	1.4	.155
1.400	1.40	12.1	---	---	---	---	---
2.00	1.98	11.9	.1	20	180	4.7	.316

$c_s = 6.17$[35]

For the definition of symbols see Nomenclature, p. 55.

Table VII

(Continued)

c_o	c	x/m	$\frac{c}{x/m}$	$\frac{c}{x/m(c_s-c)}$	c/c_s
70°C. Sample 3					
0.01000	0.00595	.0206	0.289	0.0449	.000923
0.1000	0.0780	.112	0.697	0.109	.0108
0.400	0.337	.321	1.05	0.172	.0522
1.000	0.899	.514	1.75	0.315	.139
2.00	1.86	.71	2.62	0.550	.288
Plant Sample					
0.01000	0.00868	.00664	1.31	0.203	.00135
0.1000	0.0980	.010	9.8	1.5	.0152
0.400	0.388	.060	6.5	1.1	.0601
1.000	0.950	.25	3.8	0.69	.147

$c_s = 6.45^{35}$

Table VIII

Potassium Isotherm Data

c_o	c	Equil. pH	x/m	x/m'	$\frac{c}{x/m}$	$\frac{c}{x/m(c_s-c)}$	c/c_s
Sample 3							
.00953	.00421	8.6	.0271	.0124	0.155	0.0347	.000942
.0953	.0722	9.9	.118	.0937	0.612	0.139	.0162
.238	.198	12.2	.20	.19	0.99	0.23	.0443
.476	.425	13.0	.26	.24	1.6	0.40	.0952
.715	.661	13.5	.28	.27	2.4	0.63	.148
.953	.913	13.6	.20	.28	4.6	1.2	.204

$c_s = 4.47^{35}$ x/m' was calculated from base titration.

Table IX

Lithium Isotherm Data

c_o	c	Equil. pH	x/m	x/m'	$\frac{c}{x/m}$	$\frac{c}{x/m(c_s-c)}$	c/c_s
Sample 3							
.00792	.00573	8.6	.0111	.00806	0.517	.0370	.000410
.0792	.0688	9.0	.0530	.0699	1.30	.097	.00494
.1982	.169	9.6	.15	.120	1.1	.080	.0122
.396	.335	10.8	.31	.33	1.1	.081	.0245
.594	.505	11.7	.45	.44	1.1	.082	.0376
.792	.705	12.0	.44	.51	1.6	.12	.0531
Plant Sample							
.00792	.00701	8.5	.0046	.00796	1.5	.11	.000502
.0792	.0760	12.0	.016	.027	4.8	.34	.00545
.1982	.194	12.3	.02	.030	9.7	.70	.0140
.396	.391	12.3	.03	.035	13	.96	.0287
.594	.594	12.3	---	.04	---	---	---
.792	.792	12.3	---	.03	---	---	---

$c_s = 14.0^{35}$ x/m' was calculated from base titration.

Table X

Barium Isotherm Data

c_o	c	Equil. pH	x/m	$\frac{c}{x/m}$	$\frac{c}{x/A}$	$\frac{c}{x/m(c_s-c)}$	c/c_s
Sample 1							
.01169	.01169	4.0	0	---	---	---	---
.1169	.0875	7.4	0.151	0.580	42.3	0.433	.0612
.234	.163	11.1	0.36	0.45	33	0.354	.114
.390	.319	12.1	0.36	0.89	64	0.80	.223
.585	.521	12.3	0.33	1.6	120	1.7	.359
.780	.740	12.6	0.20	3.7	270	5.4	.518
Sample 2							
.01169	.00035	7.1	0.0579	.032	1.6	0.0042	.00025
.1169	.0444	7.5	0.370	0.177	32.1	0.0865	.0311
.234	.112	8.5	0.623	0.241	48.2	0.136	.0784
.390	.213	9.9	0.904	0.343	63.2	0.194	.149
.585	.361	11.8	1.14	0.596	85.0	0.297	.253
.780	.549	12.3	1.18	0.793	124	0.53	.382
Sample 3							
.01169	.00164	7.1	0.0512	.121	4.83	0.0224	.00115
.1169	.0555	7.9	0.313	1.0	26.7	0.128	.0389
.234	.129	9.6	0.535	1.9	36.4	0.186	.0902
.390	.248	11.9	0.723	4.1	51.8	0.281	.174
.585	.440	12.3	0.739	4.7	90.1	0.60	.308
.780	.625	12.5	0.789	3.7	120	0.99	.437
Plant Sample							
.01169	.00440	10.3	0.0365	.121	1.1	0.0848	.00308
.1169	.0979	12.0	0.096	1.0	9.0	0.75	.0685
.234	.213	12.3	0.11	1.9	17	1.6	.149
.390	.372	12.5	0.091	4.1	37	3.9	.260
.585	.561	12.6	0.12	4.7	42	5.4	.393
.780	.741	12.7	0.20	3.7	33	5.4	.519

$c_s = 1.43^{35}$

Table XI

Aluminum Isotherm Data

c_o	Equil. pH	For Chloride c	For Chloride x/m	For Aluminum c	For Aluminum x/m	For Aluminum $\overset{o}{x}/m$	For Aluminum $\overset{o}{x}/A$
Sample 2							
.00996	7.8	.00960	.0018	0	.0510	0	0
.0996	2.7	.0772	.114	.0480	.264	0.182	48.8
.249	2.5	.222	.14	.1931	.29	0.67	180
.498	2.4	.468	.15	.442	.29	1.5	400
.747	2.3	.725	.11	.688	.30	2.3	620
.996	2.2	.967	.15	.942	.28	3.4	910
Sample 3							
.00996	6.5	.0100	0	0	.0507	0	0
.0996	2.4	.0852	.0682	.0680	.161	0.42	63
.249	2.4	.232	.087	.213	.18	1.2	180
.498	2.3	.478	.102	.465	.17	2.8	420
.747	2.2	.735	.061	.712	.17	4.2	630
.996	2.1	.986	.051	.960	.18	5.3	800
Plant Sample							
.00996	2.9	.0100	0	---	---	---	---
.0996	2.5	.0992	0	---	---	---	---
.249	2.4	.0249	0	---	---	---	---
.498	2.3	.498	0	---	---	---	---

Table XII

Chloride Isotherm Data

c_o	c	Equil. pH	x/m	x/m'
Sample 1				
.0987	0.108	1.2	-.097	---
.246	0.260	0.3	-.072	---
.497	0.507	0.2	-.051	---
.740	0.756	0.2	-.082	---
.987	1.01	0.2	-.011	---
Sample 2				
.0987	0.0775	8.2	.108	.222
.246	0.214	2.4	.16	.31
.497	0.455	0.6	.21	.33
.740	0.698	0.5	.27	.35
.987	0.957	0.5	.15	.31
Sample 3				
.0987	0.0790	7.5	.100	.16
.246	0.228	1.4	.092	.18
.497	0.472	0.4	.13	.19
.740	0.718	0.4	.11	.20
.987	0.976	0.4	.056	.15
Plant Sample				
.0987	0.0986	1.2	0	.015
.246	0.252	0.3	0	.02
.497	0.501	0.3	0	.01
.740	0.746	0.3	0	---

x/m' was calculated from acid titration.

Table XIII

Sulfate Isotherm Data

c_o	c	Equil. pH	x/m	x/m'	$\frac{c}{x/m}$	$\frac{c}{x/A}$	$\frac{c}{x/m(c_s-c)}$	c/c_s
Sample 1								
0.01079	0.0017	1.6	.0545	.0252	0.068	5.0	.00622	.00016
0.1079	0.0722	1.1	.186	.051	0.388	28.3	.0359	.00662
0.270	0.230	0.9	.21	.067	1.1	80	.102	.0211
0.540	0.486	0.6	.28	.11	1.7	120	.16	.0446
0.810	0.740	0.4	.36	.12	2.1	150	.21	.0679
1.079	1.019	0.3	.31	.11	3.3	240	.33	.0934
Sample 2								
0.01079	0.0096	7.8	.0061	.0251	1.6	430	.15	.00088
0.1079	0.0643	4.6	.217	.251	0.286	76.6	.0265	.00590
0.270	0.177	1.6	.48	.49	0.37	99	.035	.0162
0.540	0.424	0.8	.593	.552	0.715	192	.0681	.0389
0.810	0.677	0.6	.680	.588	0.996	267	.0978	.0621
1.079	0.939	0.6	.715	.588	1.31	351	.131	.0861
Sample 3								
0.01079	0.010	7.1	.005	.0250	2.0	300	.18	.00092
0.1079	0.0735	2.4	.175	.23	0.420	63.5	.0389	.00674
0.270	0.205	1.2	.33	.298	0.622	94.1	.0582	.0188
0.540	0.463	0.7	.39	.35	1.2	180	.12	.0425
0.810	0.716	0.5	.48	.37	1.5	230	.15	.0657
1.079	0.983	0.7	.49	.38	2.0	300	.20	.0901
Plant Sample								
0.01079	0.015	2.2	0	.0247	---	---		
0.1079	0.106	1.4	.01	.03	10	90		
0.270	0.260	0.9	.050	.05	5.2	50	Points	
0.540	0.526	0.5	.071	.07	7.4	67		
0.810	0.771	0.4	.20	.08	3.9	35	Scattered	
1.079	1.050	0.6	.15	.08	7.0	63		

$c_s = 10.9^{35}$ x/m' was calculated from acid titration.

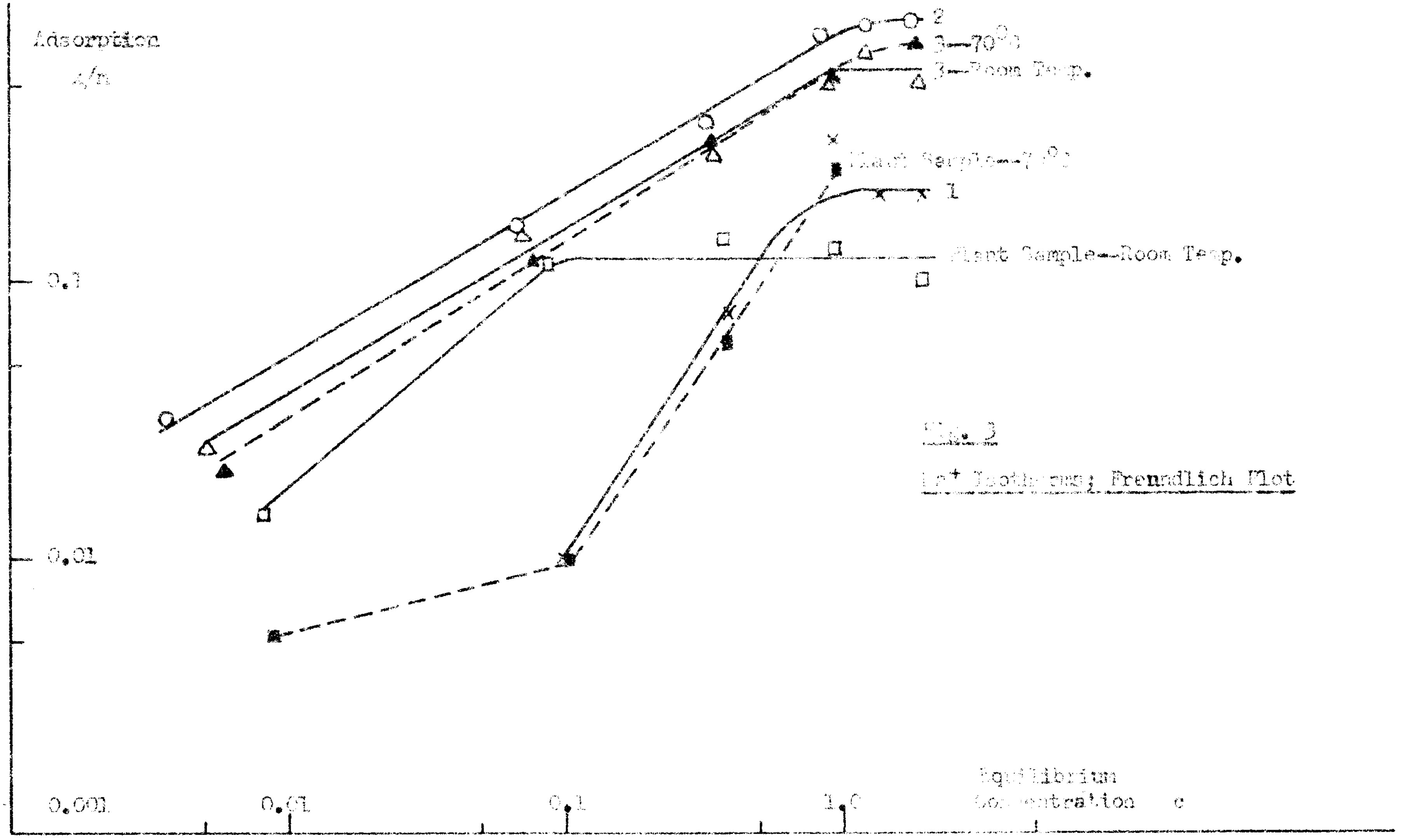
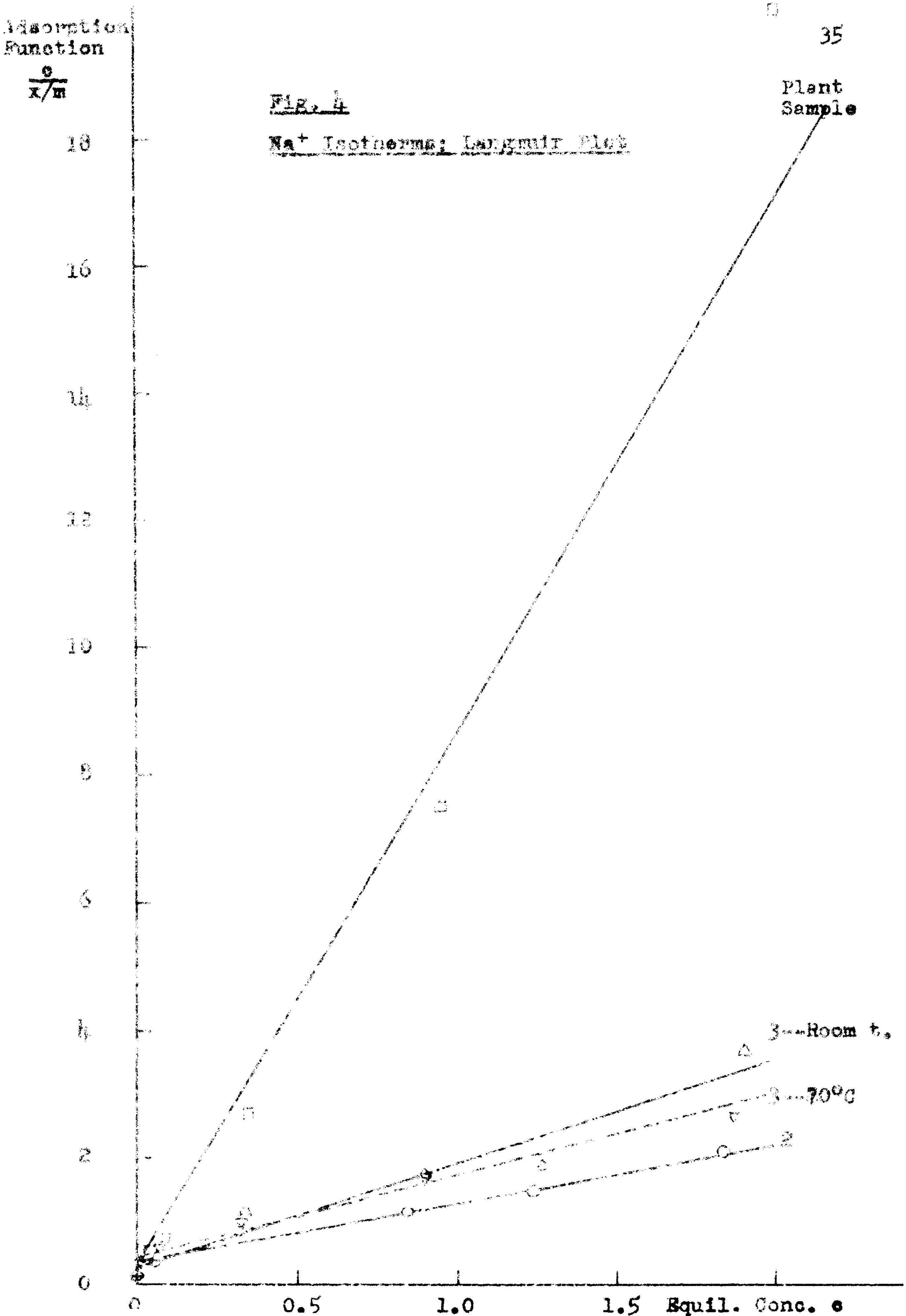


Fig. 3

Li^+ Isotherms; Freundlich Plot

Fig. 4

Na$^+$ Isotherms; Langmuir Plot



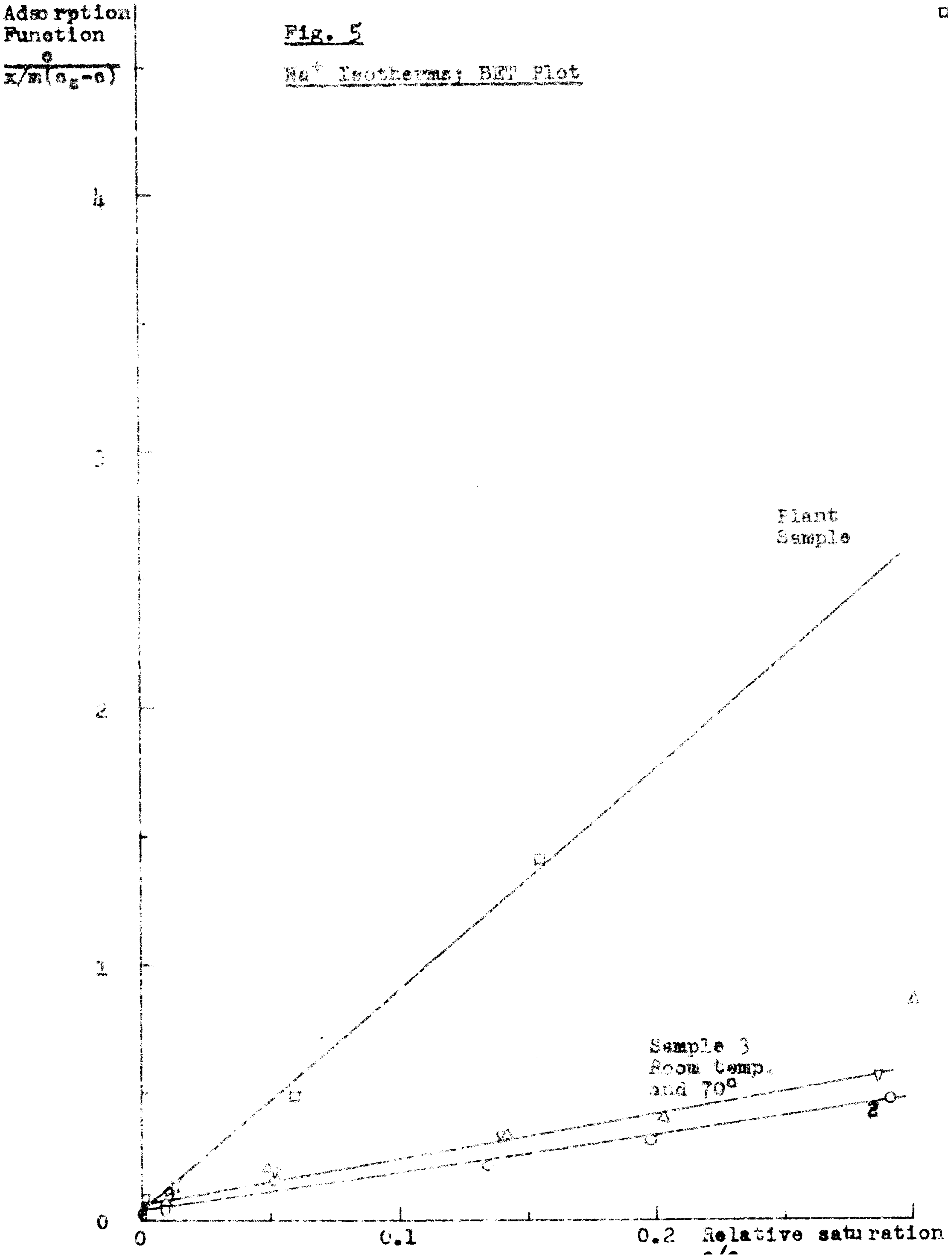
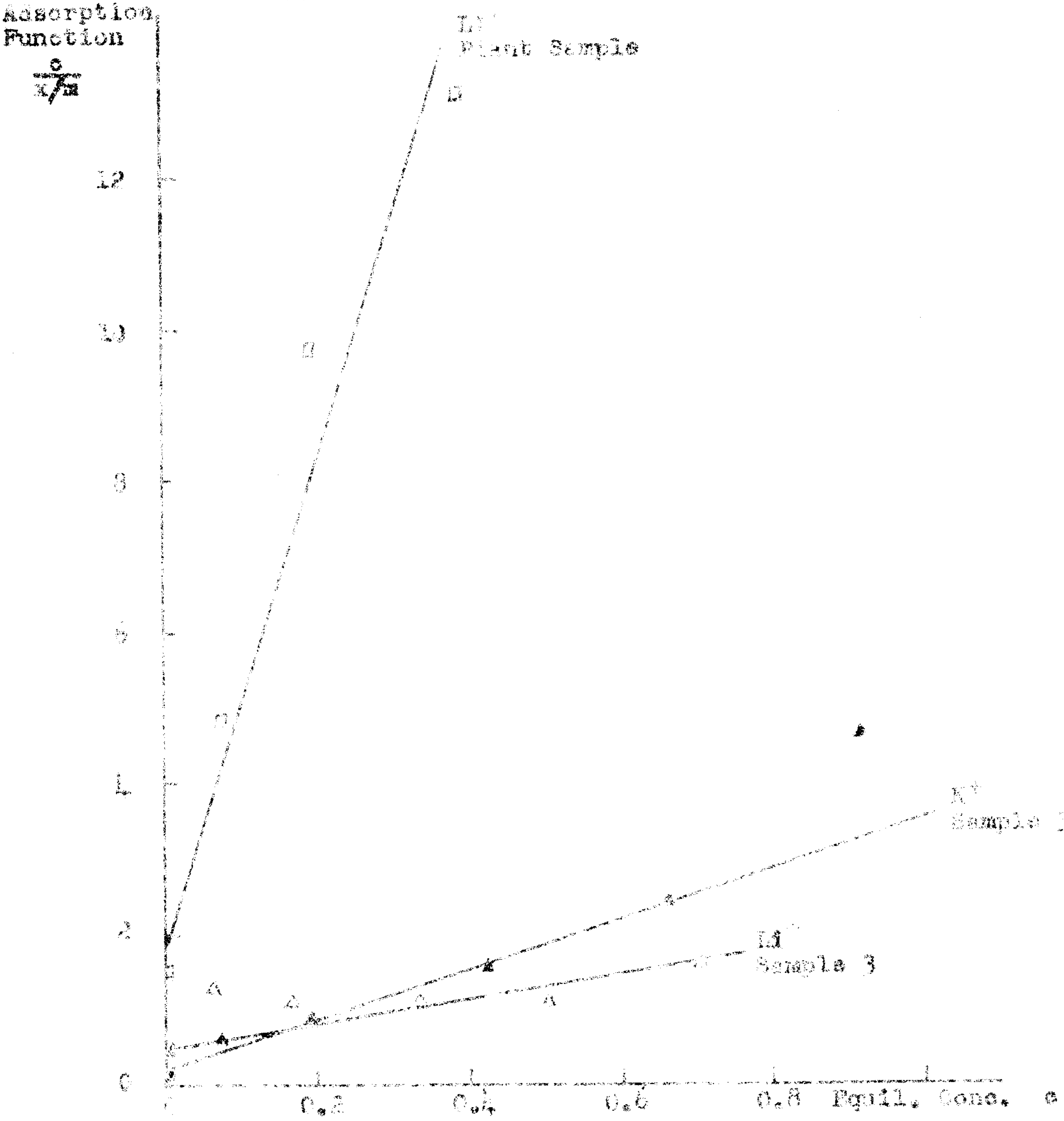


Fig. 5

Na^+ Isotherms; BET Plot

Fig. 6

K^+ and Li^+ Isotherms; Langmuir Plot



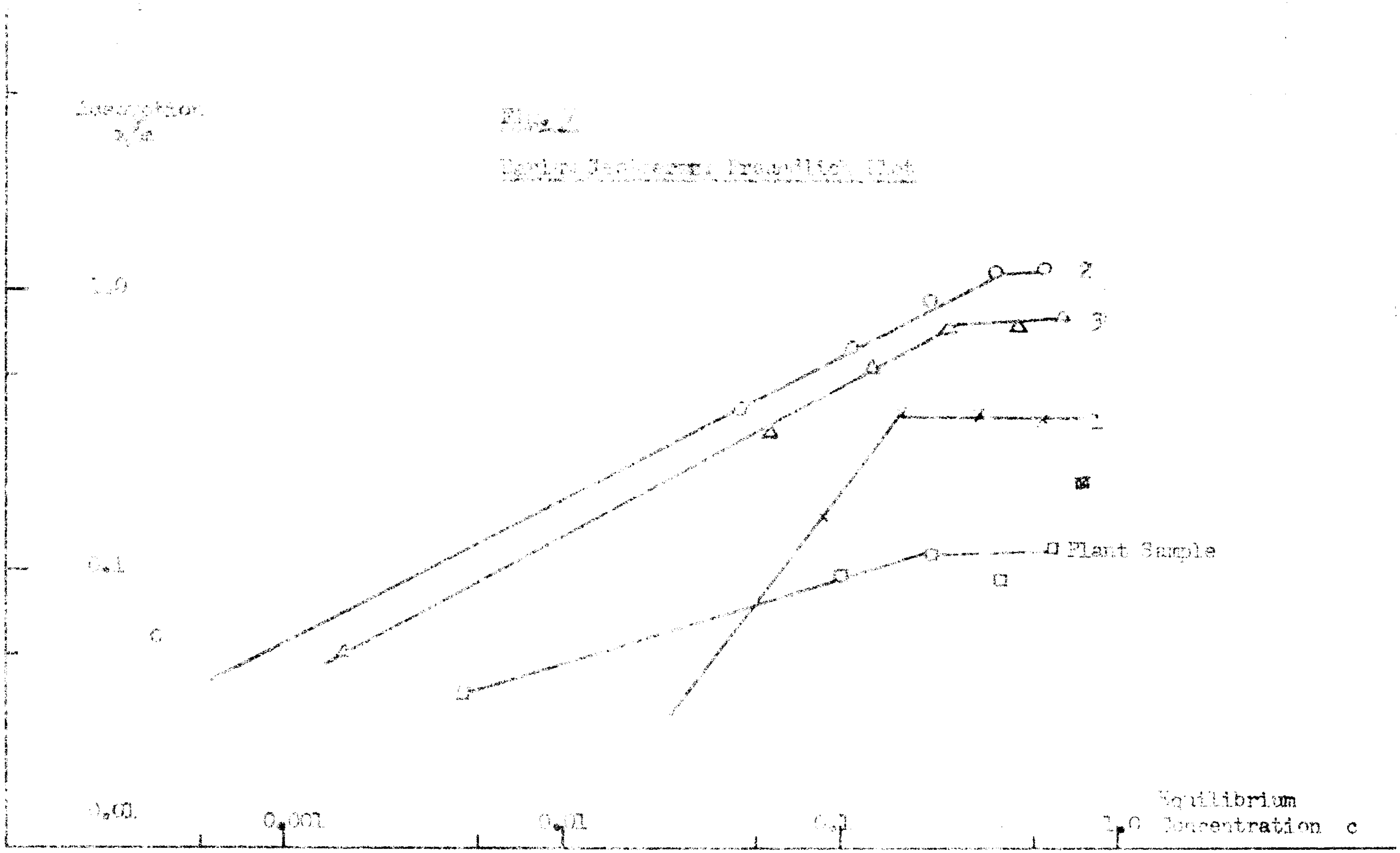


Fig. 7

Radium Isotherms, Freundlich Plot

Fig. 8

Ba^{++} Isotherms; Langmuir Plot

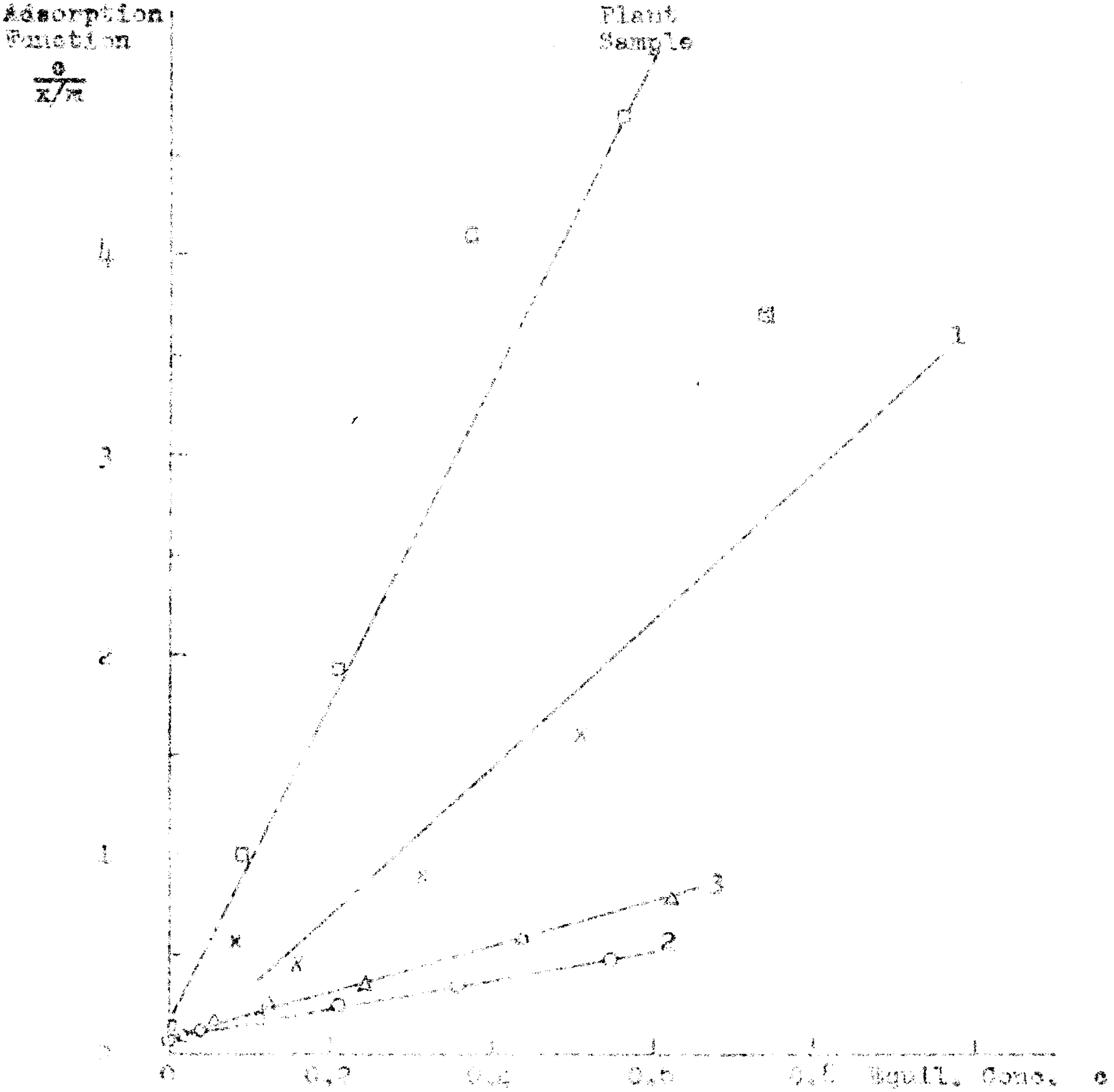
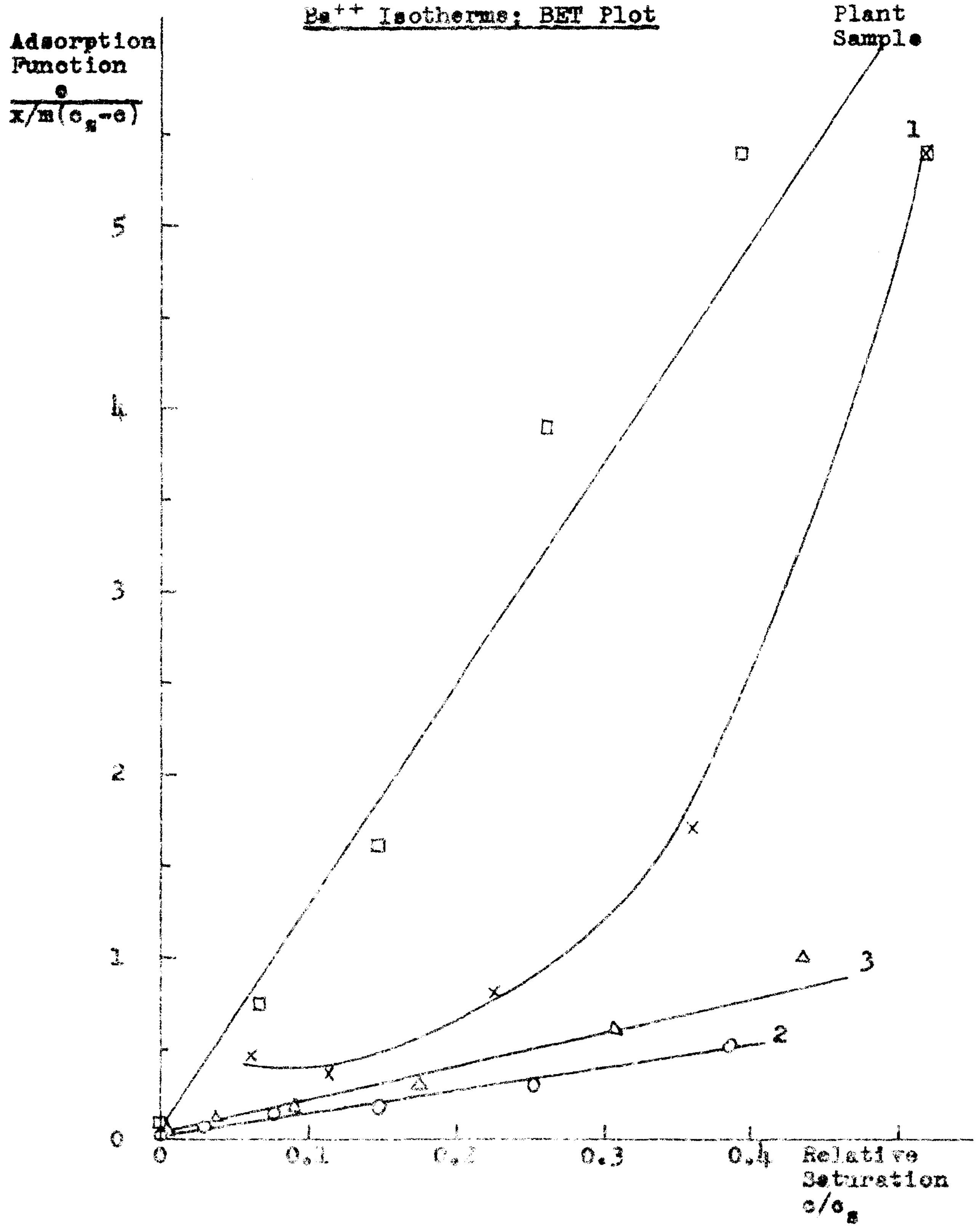


Fig. 9

Ba^{++} Isotherms; BET Plot



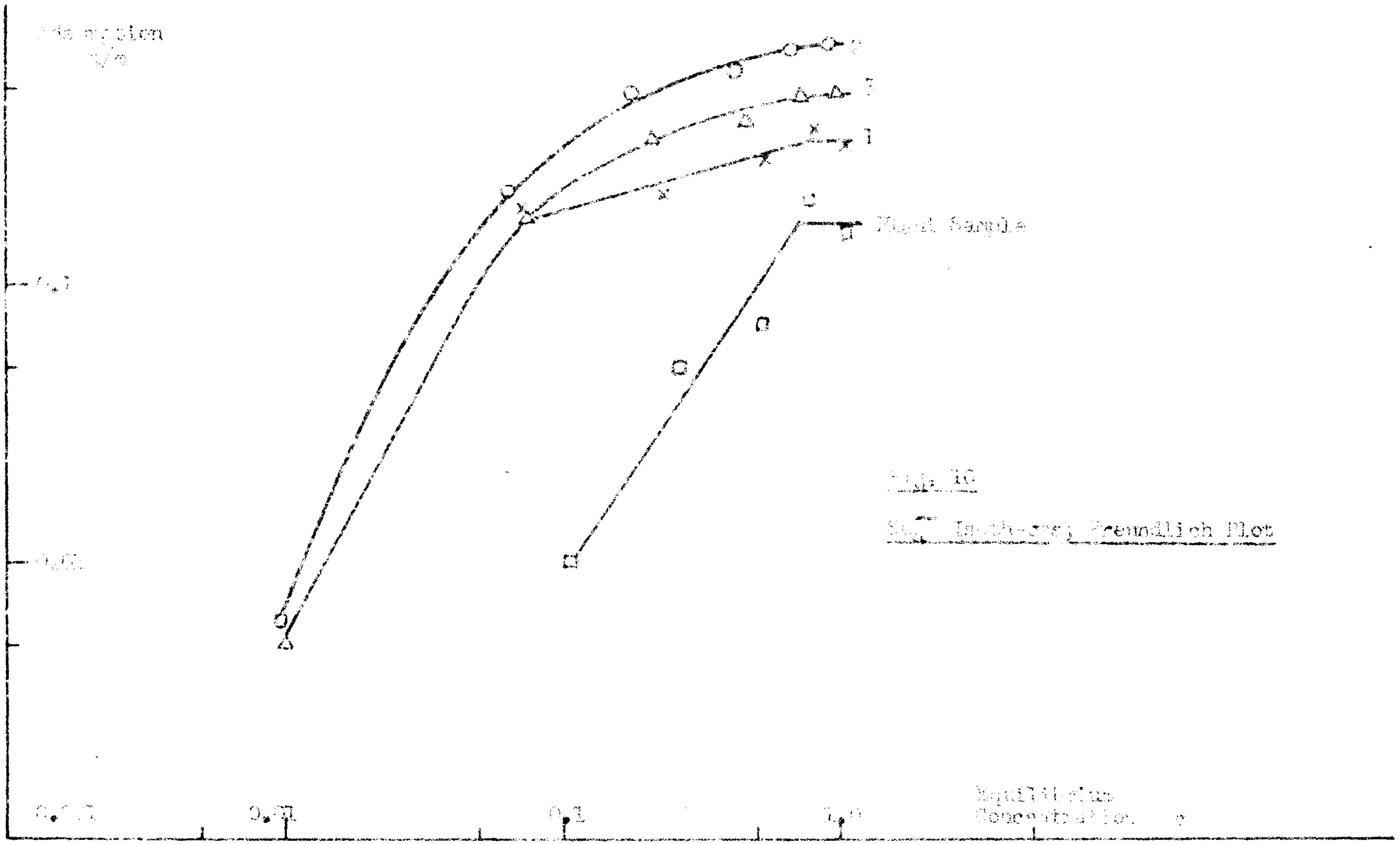
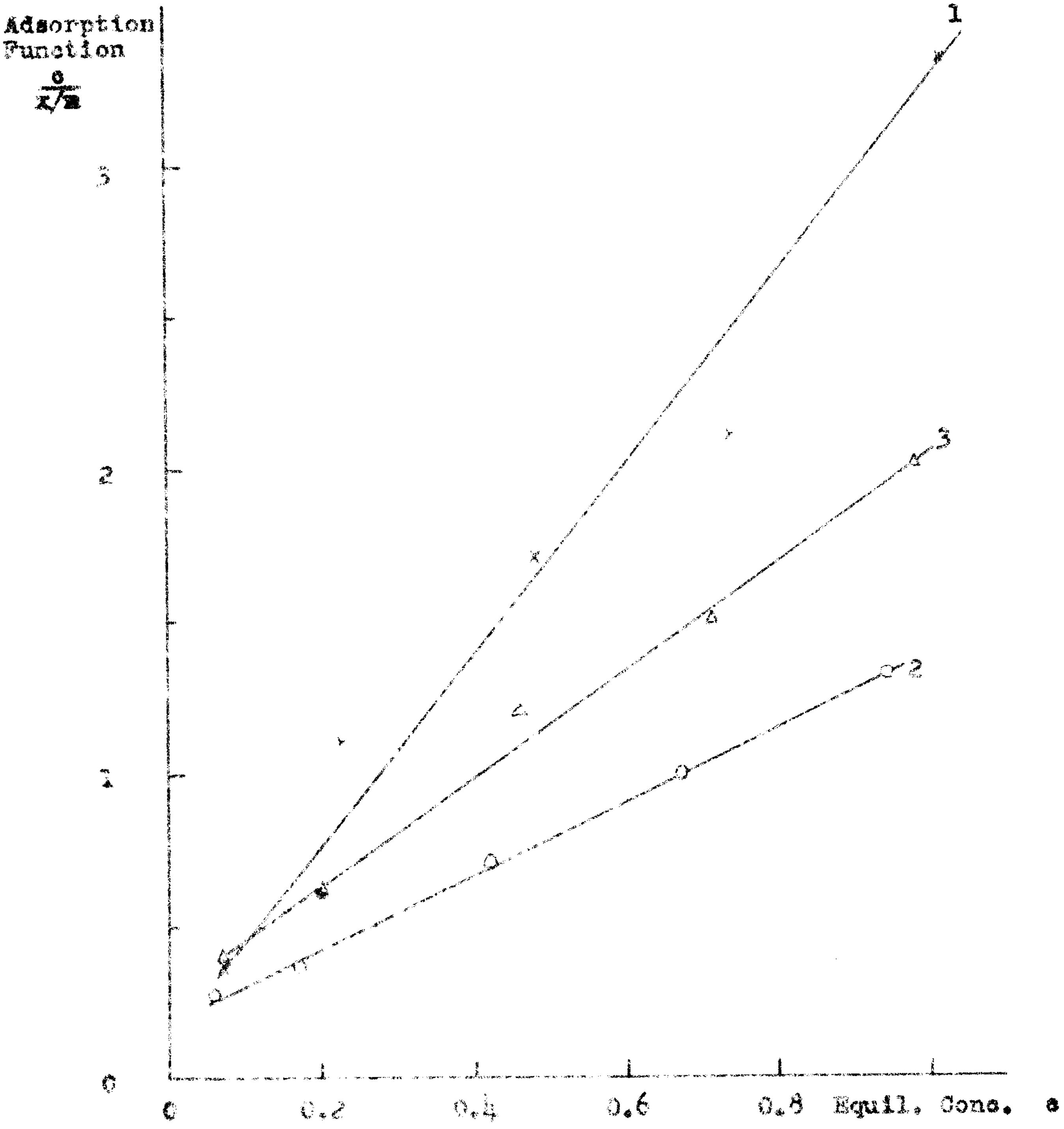


Fig. 10

Sr++ Isotherm; Freundlich Plot

Fig. 11

SO_4^{--} Isotherms; Langmuir Plot



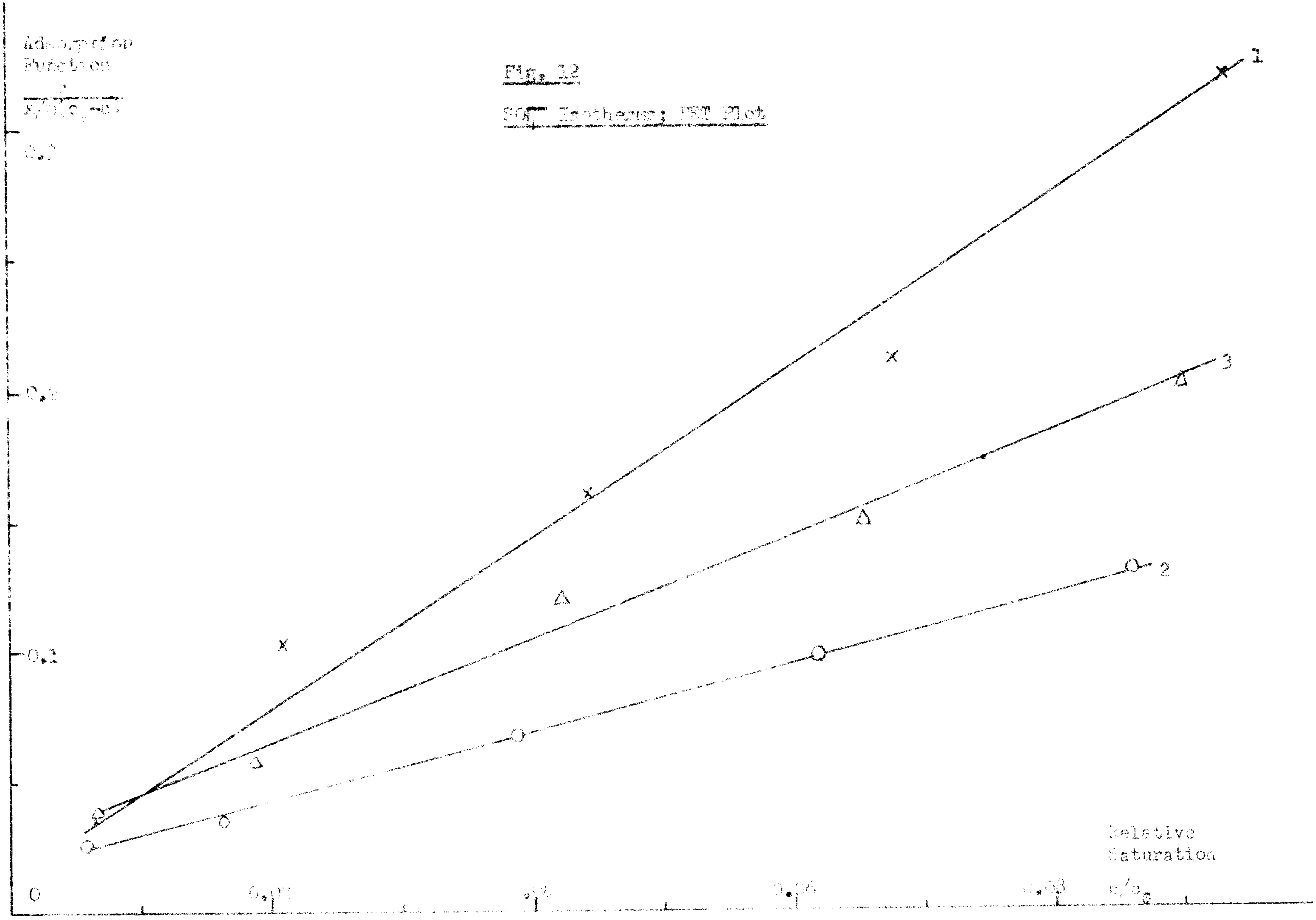


Fig. 12

SO₂ Isotherms; BET Plot

DISCUSSION

The data collected during this study indicate that titanium dioxide entered ion exchange reactions amphoterically. Depending on the pH of solutions, either cations or anions were exchanged.

Titration curves were characteristic of weak acid or base exchangers. Curves for samples 2 and 3 were flatter than those for sample 1 and the plant sample, indicating somewhat higher capacities.

Curve No. 1 was displaced on the graph to the right due to residual HCl in the sample from incomplete washing. Chloride content of this sample was 0.38 percent or 0.11 milliequivalents of chloride per gram. The displacement of this titration curve from the axis of zero base or acid addition was about 0.1 milliequivalent per gram at neutral pH. It is evident, that free acid in the sample had to be neutralized before pH of the equilibrium solution could increase. The presence of chloride in sample No. 1 was also responsible for negative chloride adsorption values; chloride ions were leached out rather than adsorbed on the sample.

The adsorptive power of titania samples was very strongly dependent on the pH of solution (see Table VI and Figure 2). Only very small amount, if any, of sodium ions was adsorbed below a pH of 8. From this point on, adsorption of sodium ions increased approximately in a linear fashion with pH. Figure 2 also shows that adsorption capacity of titania samples increased in accordance with the conditions of preparation: plant titania $<$ No. 1 $<$ No. 3 $<$ No. 2. Due to inactivation and decrease of surface of the plant titania sample at high calcination temperature (about 900°C), its adsorption capacity in both acid and basic solutions was appreciatly lower than that of laboratory preparations.

The adsorption of chloride ions in acid solutions was not as great as that of sodium ions in basic solutions (see Table VI). This also can be seen on the titration curves, especially, for samples 2 and 3. The "break" on the acid side was somewhat sharper and closer to the axis of zero addition than on the basic side, indicating higher capacity for the base than for the acid.

Isotherm data followed well the Langmuir's adsorption equation. This equation was successfully used by Boyd[4] and coworkers to correlated cation exchange by an organic exchange resin. Since the Langmuir equation postulates formation of an adsorbed monolayer on active sites of adsorbent surface in equilibrium with dissolved ions (or surrounding gas), and since these conditions also describe well ion exchange reactions, exchange adsorption on titania surface may be inferred. Data reported by Verkhovskii[36] and coworkers also correlated well using Langmuir's equation

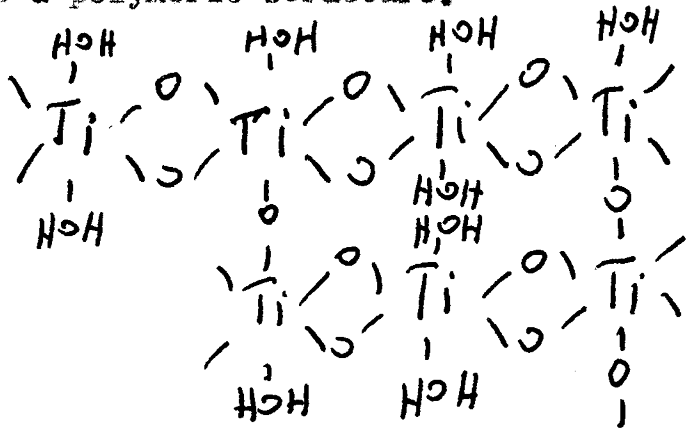
(Figure 15, p. 49).

The BET equation gave good correlations for the simple reason that only low relative saturation was reached in the adsorption experiments. In this region the equation is very similar to Langmuir equation, and describes the formation of a monolayer. This, of course, is true about ion exchange.

Due to saturation of the adsorbent, Freundlich isotherm applied only in more dilute solutions.

Liberation of acid or base in amounts equivalent to ions adsorbed offered additional indication of exchange reaction.

The following mechanism is postulated for the exchange reaction between the hydrated surface of TiO_2 and the surrounding electrolyte. Tetravalent titanium in solution is hexa-coordinated and forms during hydrolysis of sulfate solutions a polymeric structure.[2]



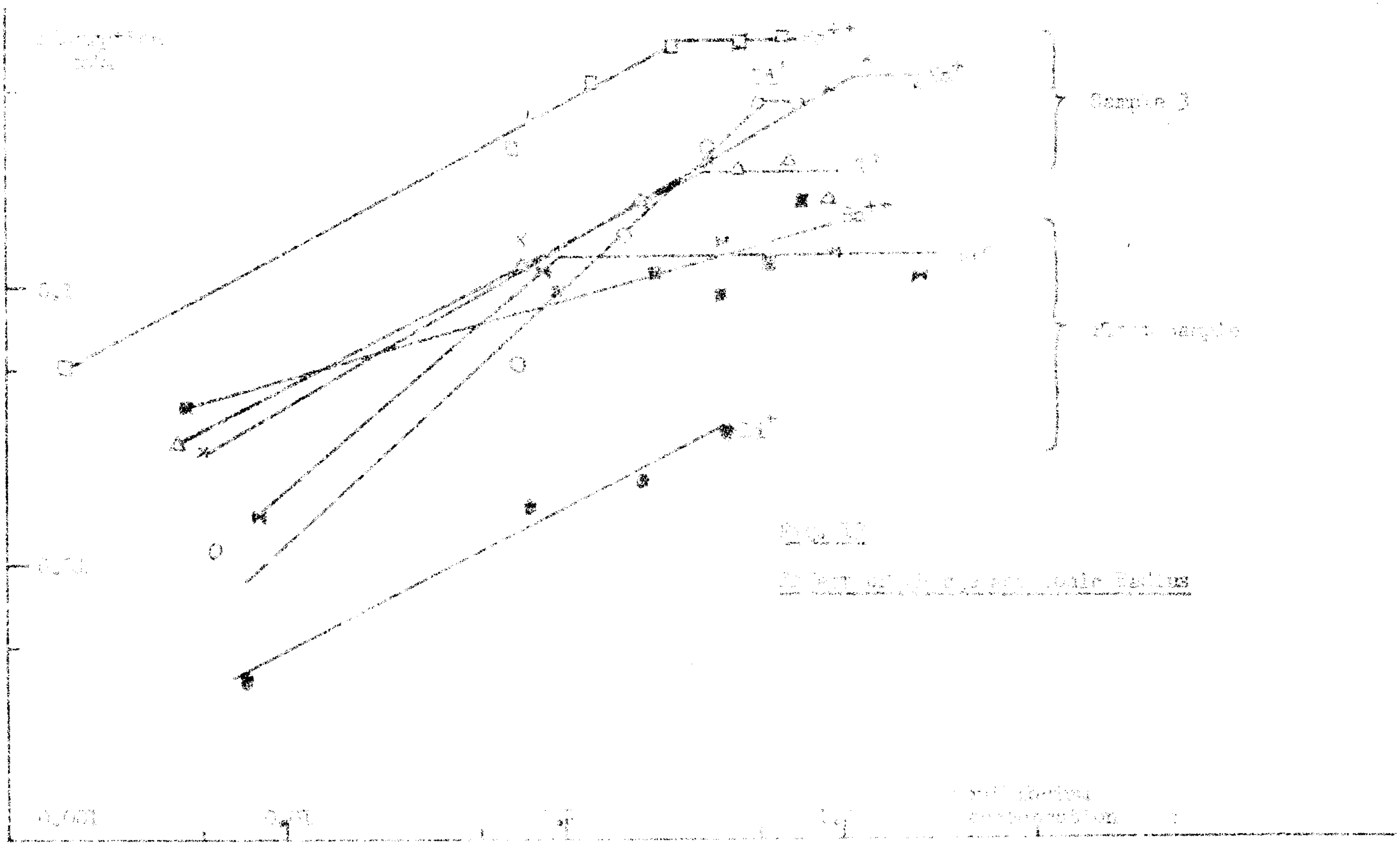


Fig. 17

[illegible]

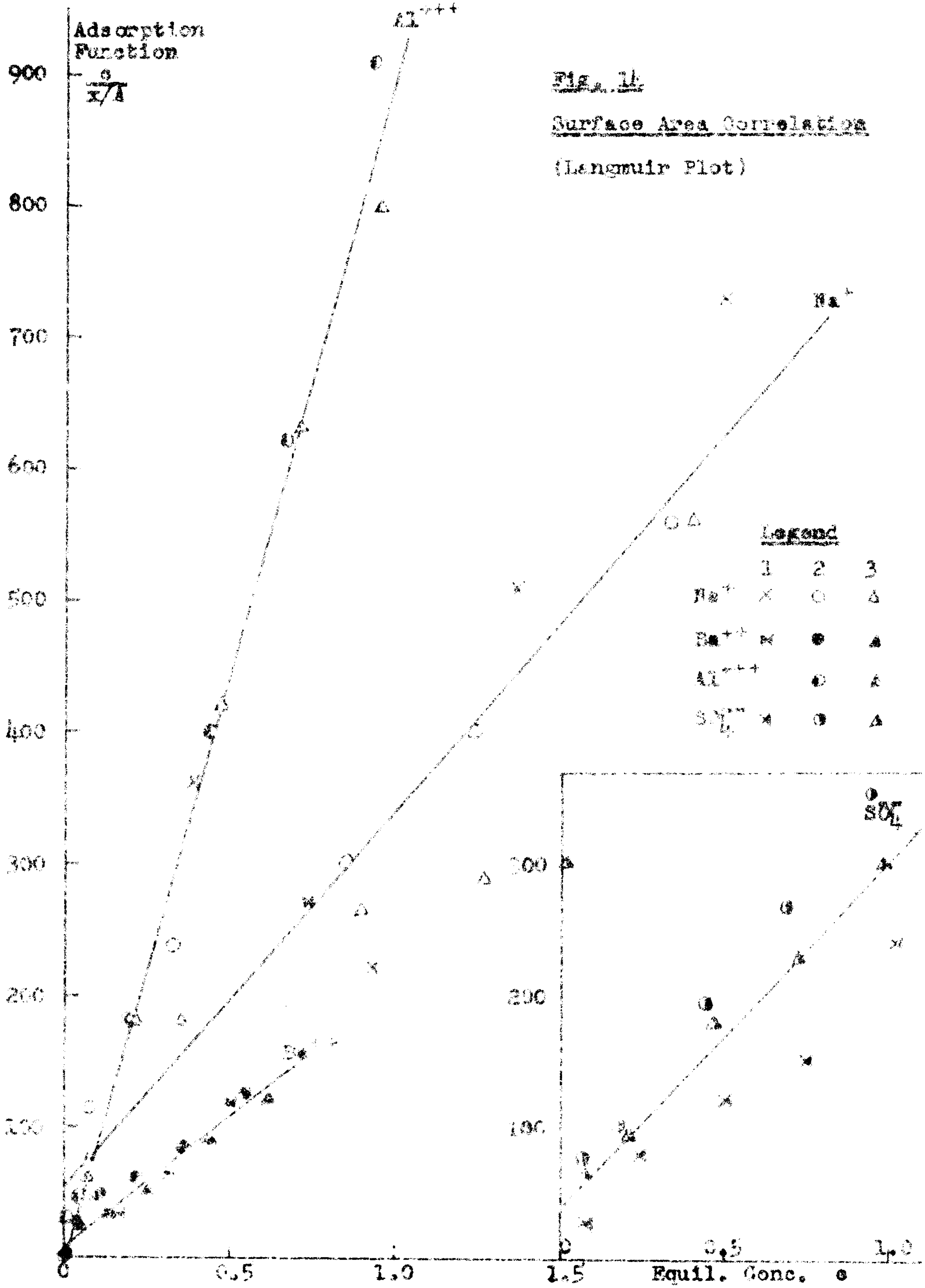


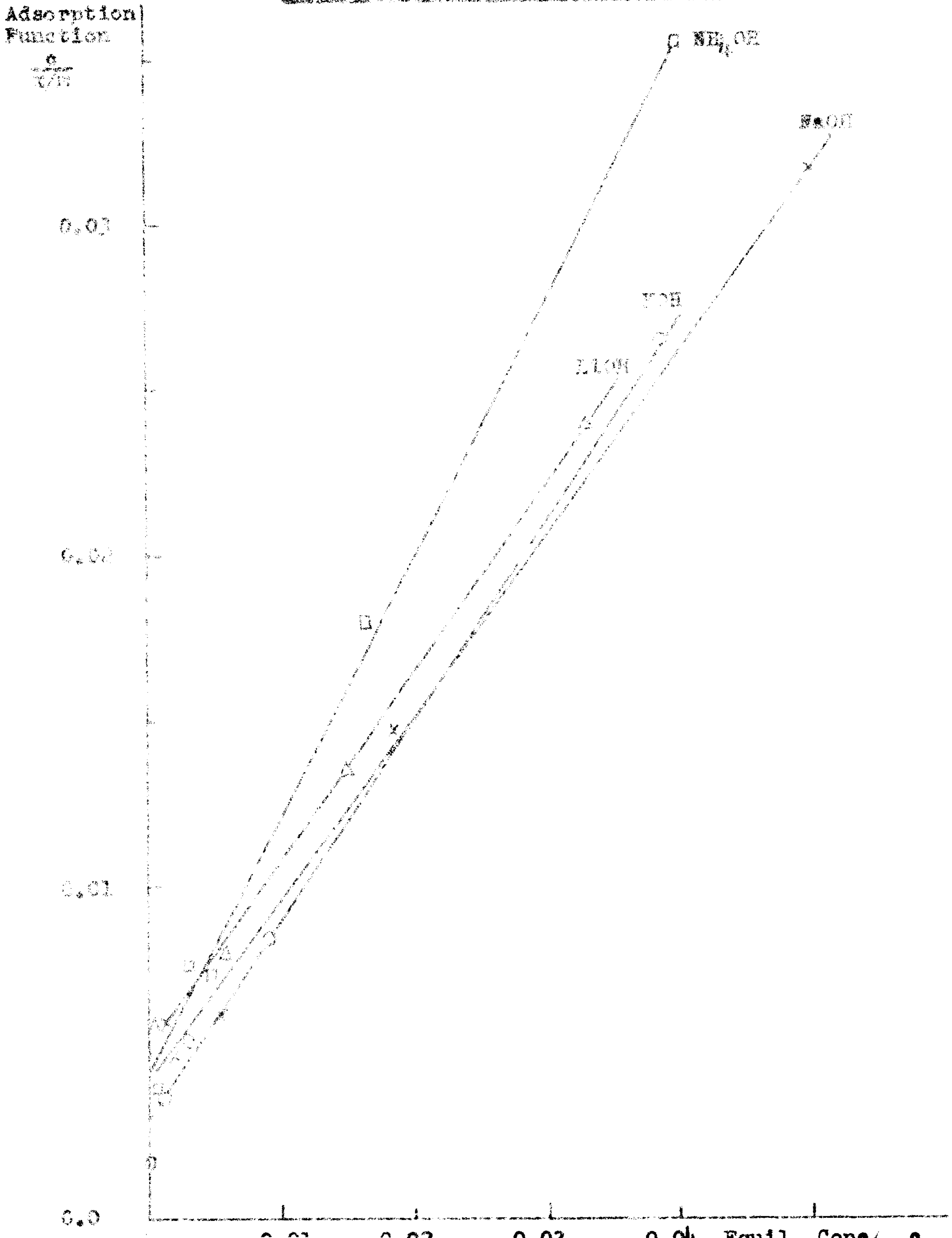
Fig. 14

Surface Area Correlation

(Langmuir Plot)

Fig. [illegible]

Terephthalic Data; Langmuir Plot



It is quite possible that a similar hydrated polymeric structure is formed when titanium tetrachloride is neutralized with a base. Water is an integral part of the structure and is not easily removed. Titania finished at high temperature still readsorbs some of this water from the atmosphere (0.6 millimoles per gram was adsorbed on the plant sample used in this study). Apparently, depending on the pH of solution, either hydrogen or hydroxyl ion can be replaced by an appropriate ion.

As it could be expected for true ion exchange, the temperature effect with the laboratory sample was negligible. The decrease in adsorption with increasing temperature on the plant sample indicated weaker attraction for the ions. This may be due to inactivation of the surface at higher finishing temperatures.

Equivalence of adsorption per unit surface area for three laboratory samples was indicative of equal number of exchange sites present per square meter of area. There was, of course, some scatter of data in the surface area correlation, but, generally, the correlation was reasonably good. Again, plant sample was out of line with laboratory samples due to different conditions of preparation. Varying amounts of rutile and anatase in the laboratory samples, apparently, had no effect on their surface activity.

The effect of charge and ionic radius in dilute solutions (up to about 0.3 N) can be explained by the hydrated ionic radius and the charge of ions. Due to the higher charge, barium was attracted strongest; it was followed by potassium, sodium and lithium, in the order of increasing ionic radius. At higher concentrations this order was upset. The reason for this may be the difference in the activities of the respective ions (Table XIV). No comparison could be made between the exchange adsorption of these ions and aluminum, since the latter was studied in acid solutions.

Table XIV

Ionic Radii and Activity Coefficients of Cations

Ion	Hydrated Ionic Radius, Å[25]	Activity Coefficient in 0.1N Cl^- Solution[26]
Li^+	10.1	0.775
Na^+	7.9	0.659
K^+	5.2	0.614
Ba^{++}	6.3	0.399

The literature about adsorption of electrolytes on titanium dioxide can be explained now on the basis of amphoteric exchange behavior of the material. The adsorption experiments of Bhatia and Ghosh,[3] Kargin and Tolstaya,[18] and Dmusilovskii and Poshvina[7] were done in acid solutions. Consequently, they reported predominant adsorption of anions. On the other hand, Verkhovskii[36] and coworkers concentrated more on basic solutions and found that cations were adsorbed. However, they also carried out some experiments in neutral and acid solutions, yet did not detect any exchange of anions. The reason for their inability to detect anion exchange in strongly acid solutions is believed to lie in their analytical method and sample treatment. Verkhovskii's titania was treated with concentrated sulfuric acid before final drying. Essentially, then, it was an exchanger in the sulfate form. Other anions could be exchanged for this sulfate under suitable conditions. However, this exchange was not detected by Verkhovskii and coworkers because they analyzed for hydrogen or hydroxyl ion liberated. In case of cation exchange there were hydrogen ions to be liberated, but in case of anion exchange sulfate was released instead of the hydroxyl ion.

Such inability to detect anion exchange by titration with a standard acid was observed with sulfate adsorption on sample 1. Since this sample contained some residual chloride, the sulfate adsorption value as determined by acid titration was appreciably lower than that obtained from sulfate analyses (Table XIII). Evidently, here, too, some chloride was released in exchange for sulfate ions.

CONCLUSIONS

Titanium dioxide was found to behave as an amphoteric ion exchanger: weakly acid in basic solutions and weakly basic an acid solutions.

Exchange capacities were primarily dependent on surface area of titania, pH and concentration of solutions. Under best conditions 0.8 milliequivalents of sodium, 1.1 of barium, and 0.7 of sulfate ions could be exchanged per gram of titania.

The isotherm data were best correlated by Langmuir equation since this equation was derived for adsorption conditions similar to ion exchange.

Hofmeister series applied essentially up to about 0.3 N solutions. At higher concentrations the order changed to $Ba^{++} > Na^{+} > Li^{+} > K^{+}$, probably, due to change in activity coefficients of the ions.

The increase in temperature from 25°C. to 70°C. had no noticeable effect on the exchange of electrolytes on comparatively active laboratory titania samples. The capacity of less active commercial pigmentary titania decreased with temperature.

RECOMMENDATIONS

The above-presented work suggests several topics for further study:

1. Reversibility of adsorption:
    a. At constant solution pH.
    b. At varying solution pH.
2. Evaluation of the performance of titania exchangers in a column.
3. Development of improved exchanger capacities by the use of "polymerization" technique such as employed by Kraus[22] and coworkers in the preparation of zirconium tungstate exchangers.

NOMENCLATURE

c--equilibrium concentration, gramequivalents per liter.

c_o--original concentration of electrolyte, gramequivalents per liter.

c_s--concentration of saturated electrolyte solution, gramequivalents per liter.

p--gas pressure.

p_s--condensation pressure at the given temperature.

x/m--adsorption, milligramequivalents of adsorbate per gram of titania.

x/A--adsorption, milligramequivalents of adsorbate per 1 square meter of titania surface.

$(x/m)_m$--adsorption at monolayer coverage.

a, b, d, k, K, n--constants.

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