

AN INVESTIGATION OF THE ADSORPTION OF  
SILVER FROM AQUEOUS SOLUTION.

A thesis presented for the degree of  
Doctor of Philosophy  
in the faculty of Science of Leicester University  
by  
William Allen

The University,  
Leicester.

August, 1981.

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STATEMENT

The accompanying thesis submitted for the degree of Doctor of Philosophy entitled "An investigation of the adsorption of silver from aqueous solution" is based on work conducted by the author in the Department of Science, Bolton Institute of Technology, mainly during the period between August, 1977, and August, 1981.

All the work recorded in this thesis is original unless otherwise acknowledged in the text or by references. None of the work has been submitted for another degree in this or any other university.

Signed ..... *W. Allen* .....

Date *22/8/81* .....

## ACKNOWLEDGEMENTS

The author would like to express his sincere thanks and gratitude to Dr. R. W. C. Broadbank, Dr. K. W. Morcom and Dr. R. W. Hayes, for their guidance and encouragement throughout the research programme, and during the preparation of this thesis.

I am also grateful to my employers, Messrs. W. & J. Leigh & Co., Bolton, for providing financial assistance and occasional leave of absence during this research.

I also wish to thank Miss Kathleen Bentley for her patience in typing this thesis.

Finally, I thank all my friends and colleagues, particularly Mr. M. Wharmby, for their invaluable support throughout a most enjoyable period of work.

....

## SUMMARY

### AN INVESTIGATION OF THE ADSORPTION OF SILVER FROM AQUEOUS SOLUTION

The work presented in this thesis is concerned with the adsorption of silver from aqueous solution, on soda-glass, polyethylene and polypropylene. The silver concentrations used, ranged from 0.5 to 100 mg dm<sup>-3</sup>, and were investigated at a series of temperatures.

The silver was present as AnalaR silver nitrate in doubly deionised water, and the adsorbed silver was detected as silver -110m using a NaI(Tl) well-type crystal to count the gamma activity.

The study indicates that silver adsorption on glass is extremely pH sensitive, increasing with increasing pH, and reaching a maximum value at pH 11.5. At pH values greater than 11.5 silver adsorption is significantly reduced. The pH dependence was shown to be important at silver concentrations ranging from 0.5 to 100 mg dm<sup>-3</sup>.

The presence of added cations, other than the hydrogen ion, also inhibit the adsorption of silver.

The pH work was extended to include desorption under acid conditions, and the results have been used to formulate a set of guidelines, in an attempt to improve existing analytical technique when handling trace concentrations of silver.

A contact-time study was carried out at various temperatures and concentrations of silver, to establish a tentative equilibrium time for the adsorption process. A kinetic analysis has been applied, from which specific rates for the forward and reverse processes have been assigned. The effect of pH and concentration on these rates has also been considered.

The temperature dependence of silver adsorption was investigated, and a series of isotherms were produced at 281, 293, 298 and 303 K. The isotherms indicate a positive temperature coefficient for the adsorption of silver on glass. A thermodynamic treatment was applied, and a heat of adsorption calculated.

A possible mechanism for the adsorption of silver on soda-glass has been proposed.

The work was extended to investigate the adsorption of silver on substrates apart from glass, namely, polyethylene and polypropylene. The results have been compared to those obtained for glass.

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## CHAPTER I

### INTRODUCTION

With the advent of more sensitive detection techniques it has been shown that ions in aqueous solution can be adsorbed on the walls of the vessel containing the solution. The extent of adsorption varies depending on the ions in solution and the conditions under which the solutions are stored. It is, therefore, probable that with dilution any such adsorption losses become more significant.

The term "adsorption" is used loosely within this thesis, to describe the process by which silver ions in solution become firmly held on the container walls. It could in fact be describing trace adsorption, or permeation into the glass, followed by ion exchange.

The present author's research, studies the adsorption of silver in aqueous solution at trace concentrations. Benes and Majer (32) have defined trace concentrations as follows:

If an aqueous solution is considered and if the relative molecular weight of the trace substance is close to 100, then the relationship  $1 \text{ ppm} = 10^{-4}\% \approx 10^{-5} \text{ M}$  is approximately valid, and more precisely a "trace" is defined as  $10^{-1}$  to  $10^{-3}\%$  and a "microtrace" as  $10^{-3}$  to  $10^{-6}\%$ .

The present author's work involves "traces" and "microtraces" of silver as defined above.

The primary aim of this work is to give guidance to the analyst seeking to determine trace concentrations of silver, on the practical conditions required to minimise losses due to adsorption on to the vessels used.

In addition to this, sufficient results were obtained to enable the author to suggest a model for the adsorption process.

The current work builds on the research carried out by previous workers (1, 2, 4, 19, 20, 22), and in particular that reported by Wharmby (1).

In the main, the present author has used soda-glass vials as the adsorbent, similar to those used by Wharmby, although some work was also carried out using polyethylene and polypropylene vials.

In the study carried out by Wharmby a suitable experimental technique for the detection and measurement of silver adsorption, was established. The indications were that silver adsorption is a chemisorption process, because of its dependence on concentration, and temperature, and the difficulty in removing adsorbed silver from the glass. Wharmby also indicated a possible pH effect.

To ensure continuity, and to consolidate previous work, the present author decided to investigate thoroughly the effect of pH on the silver adsorption process. This is of particular importance to the research because the radio-tracer used (silver -110m) to label stock solutions, is supplied in nitric acid solution.

The hydrogen ion is shown to have a very significant effect on the extent of adsorption, reducing it with increased concentration. In addition the effects of other cations on the silver adsorption process, have been compared with hydrogen ions, and a trend has been indicated.

After establishing the effect of pH, experiments were designed, using nitric acid solutions to study the desorption of silver ions from soda-glass and borosilicate glass. The results have provided reliable information to enable adsorption losses to be reduced to a minimum, and suggestions have been made to provide a set of guidelines for the analyst, when handling trace concentrations of silver.

In order to establish whether there was a limiting extent of silver adsorption, a series of contact time experiments was performed at a range of temperatures and silver concentrations. It was found that increasing temperature or concentration, or both, increased the amount of silver adsorbed. An atomic adsorption spectrophotometer was used in this section of work, as an alternative detection method, and although it was found to have limitations, the author was able to corroborate results determined by gamma counting of labelled silver. Using these data a tentative maximum capacity for silver adsorption on soda-glass is suggested.

In addition the effects of pH and of varying the anion, on silver adsorption, have been examined.

The temperature dependence of silver adsorption was investigated and a series of isotherms, at 281, 293, 298 and 303 K, have been produced. A positive temperature coefficient of adsorption for silver was evident from these isotherms. A speculative treatment has been applied to the results in an attempt to estimate a heat of adsorption for silver on soda-glass. Also the kinetics of the adsorption process are discussed in Chapter VI and a model is proposed for silver adsorption on soda-glass.

A study of other adsorbents found polyethylene and polypropylene, generally speaking, to adsorb less well than does soda-glass over short contact times; however, the results were more erratic than those observed for glass and a more detailed examination would be required to produce reliable data. Nevertheless, the author has made some indication as to the effect of pH on the adsorption of silver on polypropylene, and also for the removal of adsorbed silver from this substrate.

## CHAPTER II

### A CRITICAL REVIEW OF PREVIOUS STUDIES OF SILVER ADSORPTION ON GLASS, AND OF RELATED STUDIES.

In addition to the detailed review already presented by Wharmby, (1), this account presents a brief synopsis of other adsorption studies. Some of the papers discussed may not deal with silver adsorption directly. However, the writer felt that some of the arguments presented were relevant to this thesis.

Dyck, (2), some time ago had noted that West et al (3) reported a rather marked increase in the amount of silver adsorbed on glass at a pH of 4 compared to that at pH's of 7 and 8. This was contrary to his own findings. Dyck carried out adsorption experiments involving silver  $-110m$  and it became apparent almost immediately that the containers used for handling the solutions adsorbed appreciable quantities of silver at low concentrations (  $0.02 \text{ mg dm}^{-3} \text{ Ag}^+$ ). The results of experiments carried out in borosilicate glass beakers showed that a direct correspondence between pH and amount of  $\text{Ag}^+$  adsorbed was clearly evident. Using a  $0.01 \text{ mg dm}^{-3}$  silver solution it was shown that after 50-days contact at pH 3.8, 18% of the silver had been lost from solution, but at pH 1.5, only a 5% loss was observed. However, Dyck, reported that pH did not have any effect on silver adsorption from a  $0.1$  or a  $1.0 \text{ mg dm}^{-3}$  solution, in fact he observed zero adsorption losses from both these solutions at either pH 3.8 or 1.5, after 50-days contact.

Dyck gives virtually no detail of experimental technique in his paper, but in his graphs he plots fraction  $\text{Ag}^+$  in solution against contact time. The implication is that Dyck counted his solutions before and after adsorption and derived the "18%" and "5%" losses by subtracting count rates. This approach is also suggested by his carrying out experiments in borosilicate glass beakers.

An "18% loss" from an initial concentration of  $0.01 \text{ mg dm}^{-3}$  represents a difference in count rates of 18%, quite significant. However,

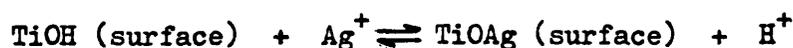
adsorption of the same amount of silver (i.e. a concentration of  $0.0018 \text{ mg dm}^{-3}$ ) from  $0.1 \text{ mg dm}^{-3}$  solution represents a difference in count rates of only 1.8%, it is doubtful that this is all that significant even in a well conducted experiment. This loss from a  $1.0 \text{ mg dm}^{-3}$  solution represents only a 0.18% difference in count rates, quite insignificant. It is quite possible that the amount of silver adsorbed did increase as silver concentration was increased, but not sufficiently to make the difference between "before" and "after" count rates significant.

Dyck also reports that a  $50^\circ\text{C}$ . temperature change (from  $0^\circ$  to  $50^\circ\text{C}$ .) had no effect on the adsorption of  $\text{Ag}^+$  on glass, although no evidence is presented to support this claim.

The present author has carried out extensive pH studies which are detailed in Chapter IV, and contrary to Dyck the results provide substantial evidence to show that silver adsorption increases markedly with an increase in pH, at silver concentrations ranging from 0.5 to  $100 \text{ mg dm}^{-3}$ .

It should also be pointed out that in figure 4.20 where four isotherms are plotted, we can clearly observe a temperature dependence over a 22 degree range. However, neither of Dyck's points can be disputed as the present author's work uses soda-glass whereas Dyck used borosilicate glass.

The work of Misra (4), deals with the adsorption of silver ions on titanium dioxide. This is a different adsorption system, but it is interesting to note that the isotherms plotted by Misra gave an excellent fit to the Langmuir equation which enabled a heat of adsorption of about  $7 \text{ kJ mol}^{-1}$  to be calculated. The present author calculated a heat of adsorption of approximately  $30 \text{ kJ mol}^{-1}$  for the adsorption of silver ions on to soda-glass, using a similar treatment to that of Langmuir. Misra also postulates the following equilibrium.



He then argues that when the adsorbed silver has reached a saturation value, the distance between the adsorbed silver ions on the basis of the B.E.T. surface areas, turns out to be  $5.38\text{\AA}$ . Furthermore, Parfitt (17), and

Dawson (18) have shown that about 50% of the  $\text{TiO}_2$  surface is occupied by hydroxyl groups. On the basis of the oxide ion radius ( $1.32\text{\AA}$ ), they then calculated the distance between the alternate hydroxyl groups as  $5.28\text{\AA}$ , which corresponds closely with the distance between adsorbed silver ions. This led Misra to believe that maximum coverage occurs when the silver ions are occupying all the hydroxyl group positions, after an exchange with the hydrogen ions. This conclusion is mentioned because the present author also postulates an  $-\text{O}-\text{Ag}$  bond in the discussion at the end of Chapter VI.

Ahmed and Cleave (16) studied the adsorption of  $\text{Ca}^{2+}$  on a quartz substrate, using  $\text{Ca}^{45}$  as a tracer. The writer has included this paper because Ahmed et al found that calcium adsorption increased with pH between pH 4 and 11.5, followed by a sharp drop in adsorption. This type of curve profile is similar to that observed for silver in figure 4.8. Ahmed et al also postulate a mechanism leading to the formation of

$-\text{Si}-\text{O}-\text{M}$  bonds, of the type described by the writer.

The experimental work of Benes and Garba (7), studied the adsorption of radio-manganese in tracer quantities on commercial glass ampoules. In particular, they looked at the adsorption and desorption of manganese traces as a function of concentration, pH value and contact time. The radioactivity of samples was measured using a well-type scintillation counter with  $\text{NaI}(\text{Tl})$  crystal. Manganese was used because of the interest of its different valency states and its colloid formation. Glass was selected as an adsorbent because its adsorbing properties were relatively well-known.

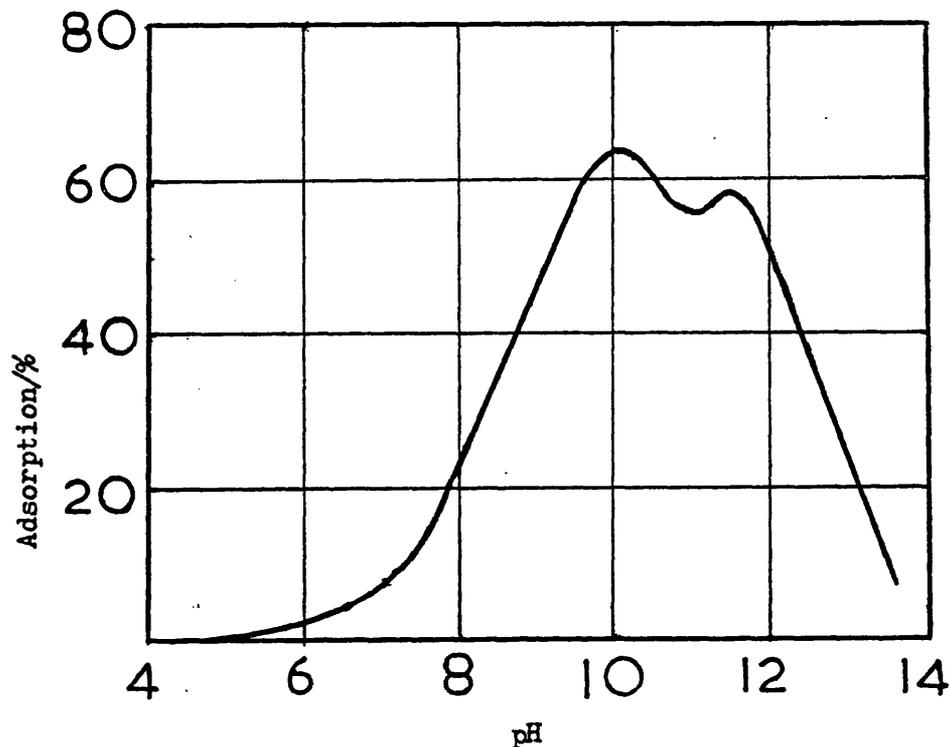
The present author feels that of the previous workers discussed, Benes et al (7) were outstanding in their approach to the problems involved. They devised a consistent experimental procedure and reduced the number of complicating factors to a minimum.

Surface area was accurately measured, solutions were prepared in the adsorption ampoules, and the pH of each solution was determined. A repeatable washing procedure was devised, using triply distilled water, and pH was controlled using isothermally distilled  $\text{HCl}$ , or  $\text{NaOH}$ , prepared by dissolving pure sodium metal. The solutions were prepared in a dry box, in

a dust and CO<sub>2</sub>-free atmosphere, keeping in mind that colloid impurities and carbonate in solution could affect the results.

The effect of varying pH is demonstrated in figure 2.1.

Figure 2.1 Benes and Garba (7) The pH dependence of Manganese Adsorption



Percentage of manganese adsorbed on glass from a solution with an original manganese concentration of less than  $5 \times 10^{-8}$  M, as a function of pH

This curve is explained by Benes and Garba as follows: At pH values above 9, oxygen dissolved in solution oxidises the manganese traces to the trivalent state i.e.  $Mn^{2+} \rightleftharpoons Mn^{3+}$ . This starts to form a colloidal hydroxide which is adsorbed less as pH increases and it becomes negatively charged. However, when the solubility product of  $Mn(OH)_2$  is exceeded, colloidal Mn(II) is formed preventing oxidation to Mn(III). This colloid formation causes an increase in adsorption up to pH 11.5, the zero point of charge, at greater pH's the colloid adsorbs  $OH^-$  ions and becomes negatively charged, the adsorption is then reduced. A similar explanation is used in Chapter VI to explain figure 4.8.

Ichikawa and Sato (8) studied the adsorption characteristics of carrier-free Europium at various pH values. The substrates used were small plates (1cm x 1cm x 2mm) of polythene, polypropylene, polystyrene, polycarbonate, polyvinylchloride, acrylic resin, Teflon, acetobutyrate, slide glass and borosilicate glass. The slides of various substrates were immersed in adsorbate solutions in an Erlenmeyer flask equipped with a stopper, the flask was sealed and shaken for the desired time at 25°C. The slides were then dried on filter paper and the beta-radioactivity of both sides was measured by a G-M counter. Their procedure was unusual, and probably resulted in both weakly, and strongly adsorbed material being counted. Also Ichikawa et al made no attempt to quantify adsorption other than as "c.p.m./cm<sup>2</sup>".

For all substrates equilibrium was reached after 2-hours, and maximum adsorption occurred at pH 4.5. Increasing the Europium concentration increased the amount of adsorption. It is interesting to note that these workers claim that ions of smaller charge are adsorbed less effectively, but they do not quote a source for this information.

In a recent study, Struempfer (19) monitored the adsorption of silver, lead, cadmium, zinc and nickel from aqueous solution, using flameless atomic absorption spectrometry and borosilicate glass, polyethylene and polypropylene containers. The concentrations of solutions under test were of the order of 0.001 mg dm<sup>-3</sup>; this level of silver is approximately a factor of 10<sup>3</sup> smaller than used by the present author and previous workers, making absolute comparisons difficult. The present author's experience of silver adsorption would tend to indicate that at such low concentrations, losses to pipettes, tubing etc., would be sufficient to introduce a variable experimental error, and that silver adsorption is probably independent of the surface area available. Nevertheless, Struempfer (19) has shown that reducing the pH reduces adsorption of silver on glass, and that polyethylene and polypropylene adsorbed about 50% less than borosilicate glass after a 24-day contact time. However, to put this into perspective all the silver

had completely adsorbed on to the glass after only 4-days contact. One new area looked at by Struempfer was the effect of daylight on the adsorption of silver. He found that it greatly enhanced the process. For all work carried out by the present author, daylight was excluded, except during washing cycles.

The work of Hensley, Long and Willard (20) was discussed in detail in the recent review by Wharmby (1). They carried out an adsorption study with radioactive sodium, silver and caesium on soft glass, pyrex and various metals. Their work showed that for soft glass within a sodium solution there is a fast initial rate of adsorption from solution, but that this rate falls off with time. Tests indicated that at room temperature, the silver ion behaved similarly to sodium.

The method employed was to use soft glass squares, one inch slides, immersing them in silver solutions in Coplin staining jars made of soft glass. The radioactive silver was silver -110, received as the nitrate, which was dissolved directly in distilled water to form the required solution, approximately  $3.9 \times 10^{-5}$  mol kg<sup>-1</sup>. The counting was carried out by mounting the glass slides near a bell shaped mica window Geiger counter tube, with conventional auxiliary equipment.

The most recent work on silver adsorption has been carried out by Wharmby (1) and presented in the form of a M.Phil. thesis. The present author's research was planned as a continuation of this work which was mainly concerned with establishing a consistent experimental technique for evaluating the adsorption of silver on soda-glass vials. The method entailed the use of silver -110m as a radiotracer, and the system used was a scintillation counter using a NaI(Tl) well-type crystal. With the exception of the electronic scaler the same equipment was used by the present author. This system was originally adapted from that used by Broadbank, Hayes and Morcom (22).

Most of Wharmby's work was carried out at a silver concentration of  $0.5 \text{ mg dm}^{-3}$ , and demonstrated that silver adsorption on to glass occurred via both a rapid initial process, with an equilibrium time of around 10

minutes, and a much slower process requiring up to 40-days to reach an equilibrium. Wharmby also showed that adsorption increases with concentration and temperature.

Conclusions:

1. The above review has indicated the need for a detailed study of the effect of pH on silver adsorption, over a wide range of concentrations.
2. Some pointers have been given as to a possible mechanism for cation adsorption on to glass.
3. There is a lack of precise kinetic and thermodynamic data for the silver adsorption process. Therefore, a series of isotherms need producing.
4. There is a requirement to produce a clear set of guidelines for the analyst when handling trace concentrations of silver ions.
5. Previous workers have not considered whether adsorption losses from solutions of higher concentration are significant. In fact, in Chapter IV the author demonstrates that a 3% loss is observed from a  $100 \text{ mg dm}^{-3}$  silver solution after 100-days at 298 K. (see Section 4.4.3).

### CHAPTER III

#### DEVELOPMENT OF EXPERIMENTAL TECHNIQUE, AND RELEVANT TECHNICAL DATA

##### 3.1 Description of the main detection method used

The experimental technique in this thesis uses silver solutions labelled with silver  $^{110}\text{m}$ . The gamma radiation is readily counted by scintillation with the aid of a NaI(Tl) well-type crystal.

The detection of small changes in concentration at trace levels can be achieved most efficiently by the use of radiotracers, in fact this method has been used extensively by previous workers (1, 3, 20, 22). The measurement of radiation when transferred between adsorbate and adsorbent offers a direct, rapid and quantitative method for the study of ion exchange during the adsorption process.

The particular counting system used in the present study was based on the one already used successfully by Broadbank et al, and later Wharmby (1, 22). The equipment consisted of an electronic scaler-timer (Nuclear Enterprises, type ST6), a scintillation counter head (I.D.L. 663C), fitted with a sodium iodide (Thallium activated) well-type crystal of diameter  $1\frac{3}{4}$ " , and thickness 2" , with a well size of  $1" \times \frac{25}{32}$ "

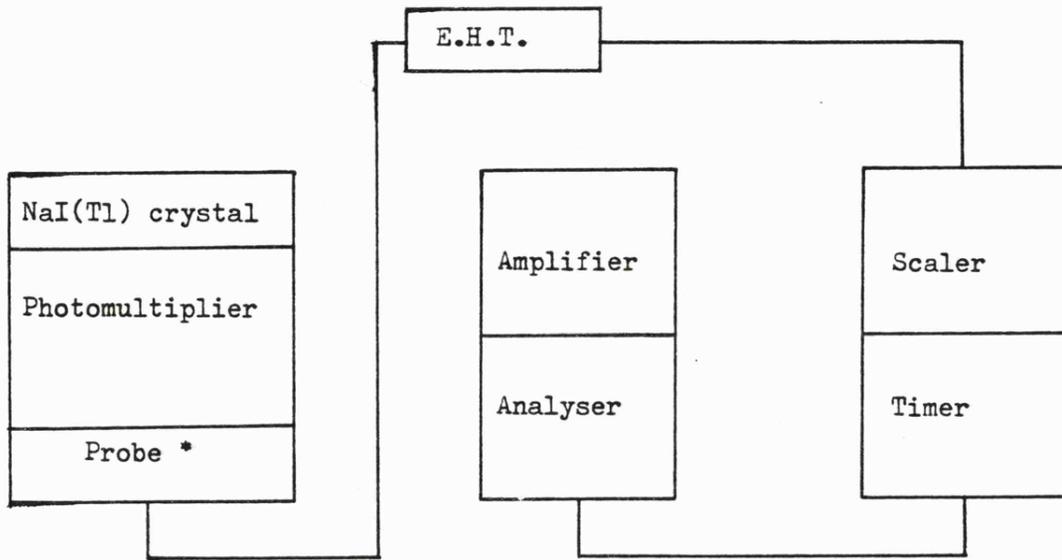
A block representation of the counting system is shown in figure 3.1, and the arrangement for mounting the sample is depicted by figure 3.2.

##### 3.1.1 Setting up the counting equipment

The counting system used by the present author was slightly more convenient than that used by Wharmby (1), in that the S.T.6. has automatic time-scaler facility. The E.H.T. and upper and lower discriminator bias settings were chosen to maximise the ratio of sample count rate squared to background count rate. The settings finally selected were as follows :-

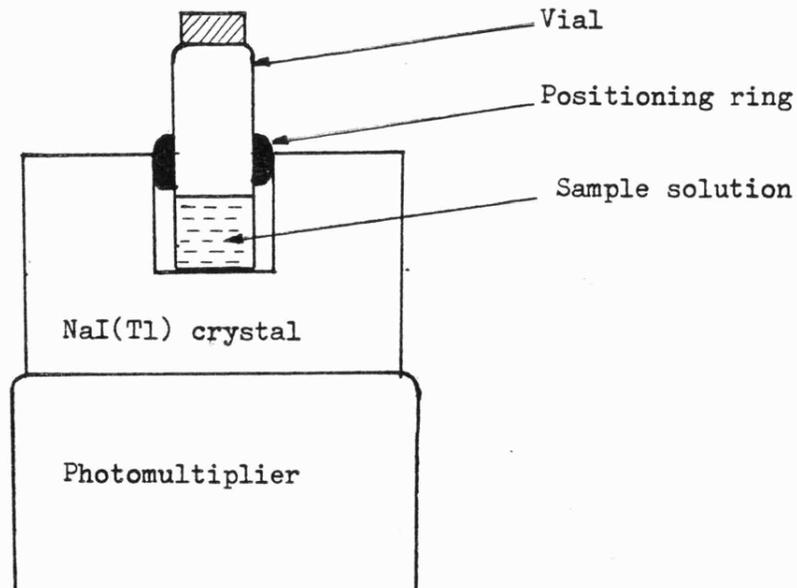
|            |             |
|------------|-------------|
| E.H.T.     | 710V        |
| Lower Disc | 0.2 (0.05V) |
| Upper Disc | 4.0 (1.05V) |

FIG. 3.1 The scintillation counting system



\* The probe contains a potential divider to provide appropriate voltages to the dynodes and also ensures sufficiently low impedance signal for the capacity of the cable.

FIG. 3.2 The sample mounting arrangement



As a cross-check 2 vials were counted on the present author's equipment and on alternative scintillation systems at Birmingham Polytechnic.\*

The results were as follows :-

Ratio of count rates from S.T.6. = 1.253

Ratio of count rates from Birmingham = 1.241

This proximity of results was deemed satisfactory.

### 3.2 Choice of Radionuclide

The programme of work carried out by the writer was designed as a logical extension to the groundwork of Wharmby (1), and it was decided to use the same radionuclide. The choice then, was silver -110m, the isotopic data is given in Table 3.1.

Table 3.1 Radioisotope Data for Silver -110m (29)

Half-life 253 days

| Type of decay and particle energies (MeV) $\beta$ | $\gamma$ Energies (MeV) |
|---|-------------------------|
| I.T. (2%)   | 0.116 (0%)              |
|   | 0.450 (1%)              |
| $E_{\max}$  |                         |
| 0.085 (65%)                                       | 0.620 (1%)              |
| 0.530 (33%)                                       | 0.660 (93%)             |
|   | 0.680 (13%)             |
|   | 0.690 (10%)             |
|   | 0.710 (17%)             |
|   | 0.740 (2%)              |
|   | 0.760 (23%)             |
|   | 0.820 (7%)              |
|   | 0.890 (72%)             |
|   | 0.940 (34%)             |
|   | 1.380 (24%)             |
|   | 1.480 (5%)              |
|   | 1.510 (12%)             |
|   | 1.560 (2%)              |

\* The author is indebted to Dr. R. Broadbank for his co-operation in making this exercise possible.

As can be seen in table 3.1, the decay scheme for silver  $^{110m}\text{Ag}$  is complex and involves both beta and gamma radiation. In this study only the gamma rays are counted, and a scintillation counter of the type described in 3.1 was used.

In general, scintillation counters are superior to G.M. counters for gamma radiation because of their greater efficiency. The shorter resolving time enables lost counts to be neglected. Counting gamma radiation avoids the problem of self adsorption which occurs with beta radiation. The scintillation counting of gamma rays, however, is against a higher background reading than with the Geiger counting of beta particles.

The silver isotope was supplied by the Radiochemical Centre, Amersham, as a 0.1M nitric acid solution containing  $0.61 \text{ mg Ag cm}^{-3}$ , with an activity of  $1 \text{ mCi cm}^{-3}$ . For convenience the isotope was diluted to  $5 \text{ cm}^3$  with doubly deionised water.

### 3.2.1 Radiochemical Purity of the silver $^{110m}\text{Ag}$

The present author used in part, the isotope acquired by Wharmby. A check was carried out on its radiochemical purity. \* One vial was used and the decay of the adsorbed silver was followed over a period of one year. The derived half-life was 252.6 days compared to a literature value of 253 days.

## 3.3 Sample preparation, extraction, washing and counting procedure

### 3.3.1 Labelled Silver Solutions

All labelled stock solutions used throughout this work were prepared in new grade A laboratory graduated flasks, by the following procedure :-

- (a) The flask and stopper were rinsed five times with doubly deionised water, and then half filled with the same.
- (b) An aliquot of unlabelled,  $1000 \text{ mg dm}^{-3}$  silver solution, as silver nitrate, was then added to the flask. (The  $1000 \text{ mg dm}^{-3}$  silver stock solution was stored in a black polypropylene bottle covered in foil, and the solution was made up freshly at 6-monthly intervals).

\* The author is indebted to Dr. R. W. C. Broadbank for carrying out this determination.

(c) An aliquot of silver -110m solution was added to the flask, which was then topped up to its graduation using doubly deionised water.

(d) The flask was stoppered, shaken vigorously, covered in foil, and left to equilibrate for at least 24-hours before use.

All transfers of solution were made using an auto-pipette with disposable polyethylene tips.

Example calculation for the preparation of 250 cm<sup>3</sup> of labelled 1 mg dm<sup>-3</sup> silver solution

250 cm<sup>3</sup> requires 0.25 mg Ag = 0.25 cm<sup>3</sup> of 1000 mg dm<sup>-3</sup> silver stock solution.

To this is added 0.1 cm<sup>3</sup> of radiotracer solution.

$$5 \text{ cm}^3 \text{ of tracer solution} = 0.61 \text{ mg Ag}$$

$$\therefore 0.1 \text{ cm}^3 = 0.0122 \text{ mg Ag}$$

$$\therefore \text{total silver in flask} = 0.2622 \text{ mg} = \underline{1.0488 \text{ mg dm}^{-3}}$$

The silver content of the added Ag -110m solution is then negligible in comparison with that contributed by the stock solution. Throughout this thesis, therefore, the silver concentration quoted for each experiment has not taken account of the silver contributed by the radiotracer. In any event the initial silver concentration can only be an estimate because the solution preparation must involve some adsorption losses, however small. The silver concentrations used in this work were mainly 0.5, 1.0 and 10 mg dm<sup>-3</sup>, so that valid comparisons could be made to the ground-work carried out by Wharmby, (1). However, a limited amount of work was carried out at 100 and 1000 mg Ag dm<sup>-3</sup> in some specific experiments where a higher silver concentration was desirable. (see expt.4.4.2).

The pH of all the labelled silver solutions used varied between 5.2 and 5.6, unless otherwise stated for a particular experiment.

### 3.3.2 Prewashing of Vials

All vials whether glass, polyethylene or polypropylene, were half

filled with doubly deionised water, capped and shaken for 30 seconds. The vials and caps were then allowed to drain, upturned on a tissue, for a minimum of 24 hours before use.

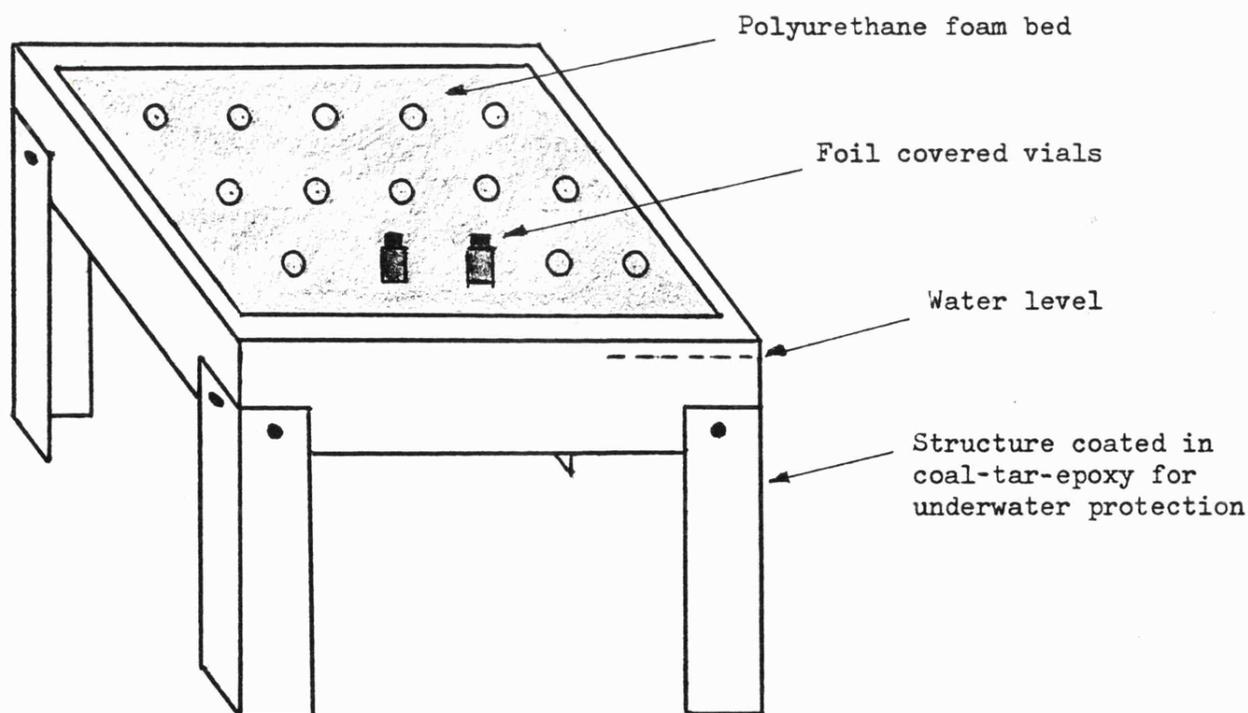
### 3.3.3 Sample preparation

A 3 cm<sup>3</sup> aliquot of labelled solution was added to a pre-washed vial using an auto-pipette. The vial was held vertical in a rack whilst the cap was fitted. It was then removed and held vertical while wrapped in foil, taking care to avoid agitation, so as not to increase the contact area.

Vials were then transferred to a thermostat-bath and kept at the prescribed temperature for the desired contact time.

A rack was designed and built to hold the vials conveniently in the thermostat bath, and to facilitate transfer to and from the bath.\* This rack is illustrated in figure 3.3.

Figure 3.3 Rack to support vials in the thermostat bath



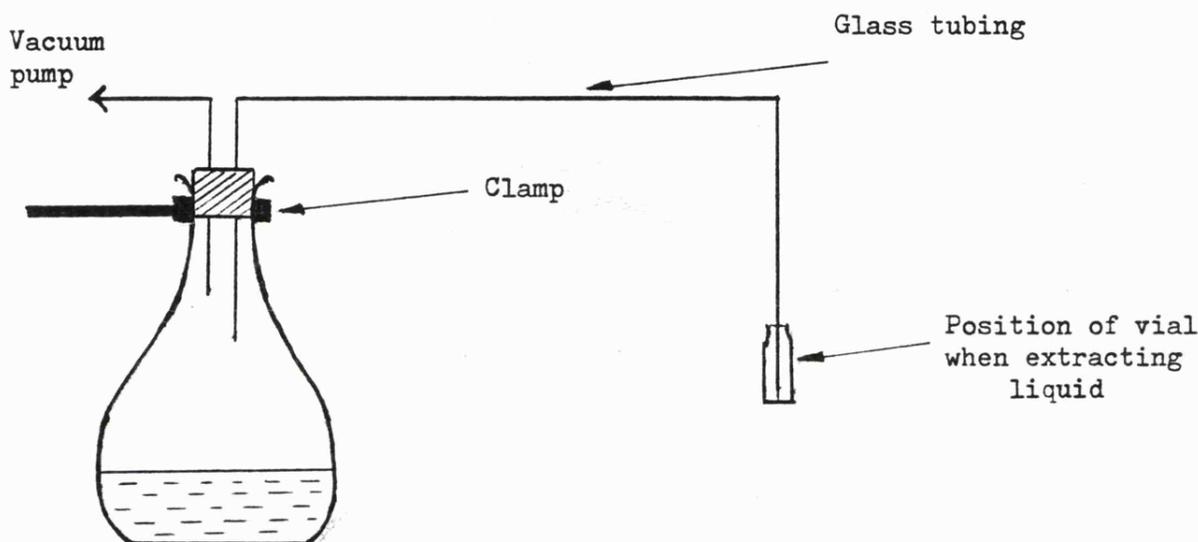
The foam support has a series of holes for water penetration

\* The author is grateful to his employers, W. & J. Leigh & Co., for the assistance given in building this rack.

### 3.3.4 Extraction and Washing Procedure

It was necessary to carry out the extraction and washing operations without allowing the labelled solution to come into contact with more than the desired surface area. To achieve this a suction technique was used to remove the silver solution, (the extraction system is illustrated in figure 3.4) and the doubly deionised water used in the washing cycle.

Figure 3.4 Extraction Apparatus



It is important that the washing cycle is both reproducible in operation, and effective enough so that further washings do not remove a significant amount of silver from the vial.

It is necessary to count the vial and solution before extraction, this initial count is referred to as the count rate "IN", throughout this work. After counting, the vial cap was removed and the vial held under the capillary tube. The labelled solution was removed by suction, the pump and a stopclock being started simultaneously. The extraction process required approximately 10 seconds. A  $3.2 \text{ cm}^3$  aliquot of doubly deionised water was then added by auto-pipette, to just cover the previous contact

area. The water was kept in contact with the glass for 5 seconds, without agitation, and then extracted over approximately 10 seconds.

This operation was repeated until ten washes had been carried out. The work carried out by Wharmby (1) has shown that under normal conditions 10 washes provide a satisfactory washing cycle. The present author has demonstrated that the washing procedure provides reproducible counting conditions after prolonged contact time, and at elevated temperatures (see sections 3.8 and 3.9). It has also been shown to be satisfactory for polyethylene and polypropylene (see sections 3.10 and 3.11). The temperature of the doubly deionised water used in the washing cycles varied between 290 and 293 K, during Winter and Summer months.

### 3.3.5 Counting Procedure

The count rate "IN" was determined before extraction and washing, a count duration of one minute was usually sufficient. The count rate "OUT", i.e. after extraction and washing was determined usually by a 5 to 30 minute count depending on the amount of activity on the vial, a count of  $10^4$  or greater was achieved for almost all the vials used, which yielded an estimated standard deviation of about 100 counts. Background counts were taken over minimum periods of 6 hours. The term "corrected c.p.m." means count per minute corrected for background.

All counts were taken with the vial mounted as illustrated in figure 3.2.

Radioactive decay is a random process and the results from the counting equipment were shown to follow a normal distribution (1).

In all the work carried out by the present author, duplicate experiments were performed. It was also verified from table 3.2, that dispensing the labelled solution using an automatic pipette, ensured delivery of a consistent volume.

Table 3.2 Corrected c.p.m. "IN" for 3 cm<sup>3</sup> aliquots of  
labelled 100 mg dm<sup>-3</sup> silver solution

| Vial No. | c.p.m. | Vial No. | c.p.m. |
|----------|--------|----------|--------|
| 1        | 121756 | 6        | 123440 |
| 2        | 125884 | 7        | 124434 |
| 3        | 121042 | 8        | 121969 |
| 4        | 130244 | 9        | 121668 |
| 5        | 121686 | 10       | 121178 |

mean = 123330, S.D. = 2891, i.e. a relative S.D. of about 2.3%

The fraction of silver adsorbed was calculated by dividing  
corrected c.p.m. "OUT" by corrected c.p.m. "IN", for each vial counted.

### 3.3.6 Statistical significance of recorded count rates

The adsorbed silver has sometimes been assessed from rather small 'OUT' count rates. In such cases the term "not significant" has been used to indicate that the relative standard deviation of the corrected 'OUT' count rate was greater than the arbitrarily chosen figure of 20%. In tables where count rates have not been quoted, the relative standard deviation of the corrected 'OUT' count rates was less than 10%.

Standard deviations have been assessed as :-

$$\sqrt{\frac{N}{t_1^2} + \frac{B}{t_2^2}} \dots\dots (28)$$

$t_1$  = time in minutes, to accumulate N counts of the sample plus background.

$t_2$  = time in minutes, to accumulate B background counts.

As an illustrative example the highest recorded corrected 'OUT' count rate in table 4.1 was from vial 1, 667 c.p.m.,  $N = 13180$

$$t_1 = 16.6$$

$$B = 45720$$

$$t_2 = 360$$

$$\therefore \text{corrected 'OUT' count rate} = 667 \pm \sqrt{\frac{13180}{275.56} + \frac{45720}{129600}}$$

$$= 667 \pm 7$$

and the relative S.D. is about  $\pm 1\%$

From the same table the relatively low count rate of 51 c.p.m. was recorded for vial 11, where  $N = 7000$

$$t_1 = 39.3$$

$$B = 45720$$

$$t_2 = 360$$

$$\begin{aligned} \therefore \text{corrected 'OUT' count rate} &= 51 \pm \sqrt{\frac{7000}{1544.5} + \frac{45720}{129600}} \\ &= 51 \pm 2.2 \end{aligned}$$

or a relative S.D. of  $\pm 4.3\%$

A similar treatment was applied to vials 1 and 7 from table 4.2; the following values were calculated :-

$$\text{Vial 1} \quad 317 \pm 5 \text{ or a relative S.D. of } \pm 1.6\%$$

$$\text{Vial 7} \quad 12 \pm 2 \text{ or a relative S.D. of } \pm 16\%$$

The 'IN' counts are recorded in solutions of higher activity - i.e. sample count rate is well above background, therefore, "statistical problems" do not generally arise.

The author has attempted to compare "detection limits" in atomic absorption spectrophotometry and "not significant" in counting, as follows :-

The detection limit of the A.A.S. is defined as that concentration of an element, in p.p.m., which gives a reading equal to twice the standard deviation of the background signal.\* If we now take something analogous in counting labelled silver - e.g., say that the "detection limit" is that amount of silver which gives a count-rate of twice the standard deviation of the background count rate, determined under the same counting conditions as the sample. Also assume the standard deviation to be approximately equal to the square root of counts recorded, and standard deviation of count rate to be  $\frac{\sqrt{B}}{t_2}$ . On this basis the "detection limit"

\* General performance data from the Pye-Unicam Users Handbook.

would be the amount of silver which gives a count rate of  $\frac{2\sqrt{B}}{t_2}$ ,

when counted under the same conditions - i.e. for  $t_2$  minutes.

Now taking the previous example, (vial 1, table 4.1) a background of 45720 counts, recorded in 360 minutes. Then the background count rate is 127 c.p.m. with a standard deviation of  $\frac{\sqrt{45720}}{360}$ , i.e.  $\sim 0.6$  c.p.m.

Thus the "detection limit" is twice this, i.e. the amount of silver which gives a count rate of 1.2 c.p.m. Therefore, a 360 minute count would give a total of 360 (127 + 1.2) counts, i.e. 46152 counts. The standard deviation for the sample alone would then be :-  $\sqrt{\frac{46152}{(360)^2} + \frac{45720}{(360)^2}} = 0.84$  counts.

The relative S.D. then is  $\frac{0.84}{1.2} \times 100$ , i.e. about 70%. It was, therefore,

probably more reasonable to use the arbitrarily chosen figure of 20% as a boundary between "significant" and "not significant" than simply taking twice the standard deviation of background. Nevertheless, continuing with the above example (vial 1, table 4.1), an 'IN' count rate of 156179 c.p.m. corresponds to 3 ml of solution of concentration  $100 \text{ mg dm}^{-3}$ . A count rate of 1.2 c.p.m. corresponds to a concentration  $\frac{1.2}{156179} \times 100 \text{ mg dm}^{-3}$ , i.e.

a concentration of  $7.68 \times 10^{-4} \text{ mg dm}^{-3}$ , compared to a quoted detection limit of  $2 \times 10^{-3} \text{ mg dm}^{-3}$  for the S.P. 192 atomic adsorption spectrophotometer.

The detection limit of the author's counting system could of course be improved by increasing the specific activity of the silver.

### 3.4 Choice of vials for experimental work

To ensure continuity and comparability to previous work, the glass vials used by the writer were from the same source as those used by Wharmby (1), and were identical in every aspect apart from the manufacturer's batch number. The technical data were as follows :-

Soda-glass Manufacturer - Chance Brothers Ltd., Smethwick.

|                  |                                |       |
|------------------|--------------------------------|-------|
| Typical analysis | - SiO <sub>2</sub>             | 71.4% |
|                  | CaO                            | 4.6   |
|                  | Na <sub>2</sub> O              | 15.0  |
|                  | K <sub>2</sub> O               | 1.7   |
|                  | MgO                            | 4.0   |
|                  | Al <sub>2</sub> O <sub>3</sub> | 2.2   |
|                  | BaO                            | 0.8   |
|                  | SO <sub>3</sub>                | 0.2   |
|                  | Sb <sub>2</sub> O <sub>3</sub> | Nil   |

Vial Manufacturer - F.B.G. - Trident Ltd., Bristol.

External Dimensions - 58 x 17 mm.

The vials were found to be geometrically convenient. The 17 mm diameter was slightly smaller than the internal diameter of the well crystal, and hence a collar was constructed from paper, to enable the vials to be positioned consistently for each count.

The 58 mm height was satisfactory, and a 3 cm<sup>3</sup> aliquot of solution provided a suitable volume, such that the liquid height in the vial was approximately three-quarters of the internal height of the well, and the entire contact area would be counted each time. Therefore, the problem of low count area related to total contact area, does not arise.

In all experiments new vials were used and no vial was used twice.

Stress tests showed that samples taken from the glass vials exhibited only very small levels of residual stress on the exterior surfaces, and the inner surfaces were effectively stress free. \* Outer surface stress

\* The author is grateful to Dr. E. J. Hearn of the City of Birmingham Polytechnic, for carrying out these tests.

levels of vials were effectively the same, and screwing on the caps had no effect at most parts of the vial. However, tight screwing of the cap did increase the stress level significantly at the shoulder circumference near the cap. Even so, the stress levels were not particularly high, and in any case the shoulder of the vial is remote from the contact area used.

In addition to soda-glass, polyethylene vials were also used. The type chosen were of similar dimensions to the glass vials, and the relevant technical data were as follows :-

Manufacturer - ICI, Welwyn Garden City.

Polyethylene low density 922 w.v.p.  $24\text{g/m}^2/24\text{ hr/1 thou thick}$   
at  $38^\circ\text{C}$ . and 90% relative humidity.

Melt index 20.

Vials manufactured by Initial Plastics, by injection moulding,  
no coatings or additives used.

Vial supplier - Baird & Tatlock (Type 275/0450 size 02)

External Dimensions - height 50 mm.  
diameter 16 mm.

Also two types of polypropylene vial were used, and for convenience they are referred to as, type 1 propathene, and type 2 propathene, in the experiments discussed in Chapter V. The technical data for type 1 propathene is as follows :-

Manufacturer - ICI, Welwyn Garden City

Supplier - Hopkin & Williams (Type 034986722)

External dimensions - height 55 mm.  
diameter 16 mm.

W.v.p. - no manufacturer's data.

The technical data for type 2 propathene is given below :-

Supplier - Gordon Keeble (Type GK16)

External dimensions - height 54 mm.  
diameter 15.7 mm.

W.v.p. - no manufacturer's data.

### 3.5 Contact Area

The internal diameters of the glass vials used were found to be very consistent when measured using a travelling microscope. The meniscus height was also measured by travelling microscope, and for a set of 10 vials containing  $3 \text{ cm}^3$  of water the average contact area was found to be  $9 \text{ cm}^2$  using the formula Total Contact Area =  $\pi r^2 + 2\pi rh$ , where  $r$  is the internal radius and  $h$  the liquid height. The spread of results was 8.9 to  $9.1 \text{ cm}^2$ . This variation was considered to be acceptable, and thus for all experimental work the contact area for  $3 \text{ cm}^3$  of solution in the glass vials was taken as  $9 \text{ cm}^2$ . The internal liquid height was also measured at zero and 14 days contact and evaporation losses were not detected.

In a similar manner the contact areas for  $3 \text{ cm}^3$  of solution in the polythene and polypropylene vials were found to be as follows :-

|                   |                       |
|-------------------|-----------------------|
| Polyethylene      | - $11.0 \text{ cm}^2$ |
| Type 1 propathene | - $10.7 \text{ cm}^2$ |
| Type 2 propathene | - $10.9 \text{ cm}^2$ |

A knowledge of contact area was required so that adsorption results could be expressed as a total amount of silver adsorbed per square centimetre. However, the actual micro surface area of glass can be many times greater than the geometric area, depending on the surface treatments and cleansing agents used on the glass surface during manufacture. For example, the surface area of flat glass has been measured by a gas adsorption technique and found to be at least 10 times the geometric value.\*

### 3.6 Counting Geometry

The evaluation of silver adsorbed is made on the assumption that similar activities will give the same c.p.m. whether they arise from silver adsorbed on the vial, or from silver in the solution bulk. To confirm this assumption three vials containing  $3 \text{ cm}^3$  of  $1 \text{ mg dm}^{-3}$  labelled silver solution were stored in a thermostat-bath for 45 days at 298 K. After this contact period the corrected c.p.m. "IN" was determined for each vial. The vials

\*The author is grateful to Dr. B. Evans of Messrs. Pilkington Brothers Ltd., St. Helens, for this information.

were then extracted and washed as described in 3.3.4, and the corrected c.p.m. "OUT" was determined. A  $3 \text{ cm}^3$  aliquot of 50% nitric acid solution (at 363 K) was then added to each vial and the vials were left to soak for 40 minutes. After this time the vials were counted again, i.e. with a large proportion of the adsorbed silver now in the acid solution bulk. The acid solution was extracted and the vials were counted a fourth time to show how much silver had desorbed into the solution bulk. The results are given in table 3.3.

Table 3.3 Counting Geometry Check

| Vial No. | Corrected c.p.m. "IN" | Corrected c.p.m. "OUT" | Corrected c.p.m. "OUT" after acid soak | Corrected c.p.m. after removing acid |
|----------|-----------------------|------------------------|--|--------------------------------------|
| 1        | 58873                 | 6731                   | 6824                                   | 2636                                 |
| 2        | 58920                 | 5232                   | 5250                                   | 1555                                 |
| 3        | 58802                 | 5728                   | 5748                                   | 2272                                 |

Table 3.3 shows that silver was adsorbed, and that at least 60% of the adsorbed silver was transferred to the solution bulk after soaking in the nitric acid solution.

These results therefore demonstrate that the activity counted was not significantly different whether all on the glass, or when one third on glass and two thirds in solution.

As a further check the writer studied the effect of varying the contact area for a given activity. This was achieved by adding a  $0.04 \text{ cm}^3$  aliquot of labelled silver solution to a glass vial, then determining the corrected c.p.m. "IN". A  $3 \text{ cm}^3$  aliquot of water was then added to the vial and the corrected c.p.m. "IN" was again determined, and the results were as follows :-

| <u>Volume (<math>\text{cm}^3</math>)</u> | <u>Corrected c.p.m. "IN"</u> |
|--|------------------------------|
| 0.04                                     | 899                          |
| 3.04                                     | 836                          |

The difference observed was not significant.

In view of these results the counting procedure and subsequent quantitative adsorption calculations were deemed satisfactory.

### 3.7 Distribution of silver on the adsorbent

It was considered that errors may arise due to non-uniform adsorption of silver onto either glass or polymers, in particular at the liquid/air interface within the vials. Therefore, experiments were carried out to determine whether the distribution of silver over the adsorbent was uniform.

#### 3.7.1 Polythene Vials

Two vials containing adsorbed, labelled silver, were dissected horizontally, across the contact area and the subsequent halves were counted.

|        | Surface Area Ratio | Count Ratio  |
|--------|--------------------|--------------|
|        | Top : Bottom       | Top : Bottom |
| Vial 1 | 1 : 2.7            | 1 : 2.5      |
| Vial 2 | 1 : 1.8            | 1 : 1.9      |

The results show that excess silver at the liquid/air interface was not observed, and considering the crude nature of this experiment the silver adsorbed was found to be very uniformly dispersed, although the writer accepts that there may be areas of "concentrated adsorption" on a micro scale.

#### 3.7.2 Glass Vials

In view of the technical difficulties arising from the glass cutting of tubes of this diameter, with the added problem of radioactivity, another technique was devised to enable the writer to look at the distribution of adsorbed silver on the glass vials. The following experiment was designed to determine whether the bulk of silver is adsorbed at the liquid/air interface, or uniformly distributed over the glass. To accelerate adsorption 2 vials each containing  $3 \text{ cm}^3$  of  $100 \text{ mg dm}^{-3}$  labelled silver solution was stored in a thermostat-bath for 15 days at 298 K, then treated as follows :-

Vial 1 The corrected c.p.m. "IN" and "OUT" was determined in the standard manner, and the amount of silver adsorbed was calculated.  
A  $2.5 \text{ cm}^3$  aliquot of 10 molar nitric acid

solution was then added, and the vial was soaked for 10 minutes. The acid was then extracted and three washes of  $2.5 \text{ cm}^3$  of doubly deionised water were performed. The vial was then re-counted.  $2.5 \text{ cm}^3$  of water was found to occupy a surface area of  $7.5 \text{ cm}^2$  in the vial.

Vial 2 As for Vial 1 but a  $3.2 \text{ cm}^3$  aliquot of acid was used, followed by  $3.2 \text{ cm}^3$  aliquots of doubly deionised water for the washes. This volume was chosen to ensure that the entire silver contact area for  $3 \text{ cm}^3$  ( $9 \text{ cm}^2$ ) of silver solution would be covered by the acid. The results are summarised in table 3.4, below.

Table 3.4 Acid Soaking of vials to determine silver distribution

| Vial No. | Initial Adsorption<br>/mg Ag $\text{cm}^{-2} \cdot 10^6$ | After acid soak<br>/mg Ag $\text{cm}^{-2} \cdot 10^6$ | Percentage removed. | Silver Contact Area soaked/ $\text{cm}^2$ |
|----------|--|---|---------------------|---|
| 1        | 126  | 83  | 34                  | 7.5                                       |
| 2        | 110  | 59  | 46                  | 9.0                                       |

Thus the percentage of adsorbed silver removed was roughly proportional to the area exposed to nitric acid. It, therefore, seems reasonable to assume that the silver is roughly uniformly distributed throughout the contact area.

### 3.8 Washing cycles after prolonged contact time

In order to establish that the assumptions made regarding the washing procedure described in 3.3.4, were valid after prolonged contact time the following experiment was carried out.

A  $3 \text{ cm}^3$  aliquot of  $1 \text{ mg dm}^{-3}$  labelled silver solution was added to

two vials, the vials were sealed, covered in foil and placed in a thermostat-bath for 60 days at 298 K. After this time the vials were removed and the corrected c.p.m. "IN" were determined as described in 3.3.5. Then the normal washing procedure was carried out, but the vials were counted after each wash, and the amount of remaining adsorption calculated at each stage.

The results are given in table 3.5.

The washing cycles, represented in figure 3.5 are not significantly different from those observed by Wharmby (1) for the 4 day contact of  $0.5 \text{ mg dm}^{-3}$  labelled silver solution; after 10 washes no further significant amounts of silver appear to be removed by this technique.

### 3.9 Comparison of washing cycles at 292 and 373 K

This experiment was carried out to see whether a quicker more efficient washing procedure could be perfected by raising the temperature of the doubly deionised water used in the standard washing procedure. To observe this comparison, a  $3 \text{ cm}^3$  aliquot of  $0.5 \text{ mg dm}^{-3}$  labelled silver solution was added to 2 vials, the vials were sealed, covered in foil and placed in a thermostat-bath for 4 days at 298 K. After this time the vials were removed and the corrected c.p.m. "IN" were determined as described in 3.3.5. Then, on one vial a washing cycle was carried out at 292 K, and on the other a washing cycle using doubly deionised water at 373 K. For both vials the corrected c.p.m. "OUT" was determined after each wash and the results are given in table 3.6.

Table 3.5 Washing cycles at 298 K after 60 days contact

| No. of washes                          | Corrected c.p.m. "OUT" | Fraction Adsorbed | Amount Adsorbed /mg Ag cm <sup>-2</sup> .10 <sup>6</sup> |
|--|------------------------|-------------------|--|
| Vial 1 - Corrected c.p.m. "IN" = 25128 |                        |                   |  |
| 1                                      | 2608                   | 0.1038            | 34.5   |
| 2                                      | 2352                   | 0.0936            | 31.2   |
| 3                                      | 2178                   | 0.0867            | 28.8   |
| 4                                      | 2157                   | 0.0858            | 28.6   |
| 5                                      | 2126                   | 0.0846            | 28.2   |
| 6                                      | 2028                   | 0.0807            | 26.9   |
| 7                                      | 2028                   | 0.0807            | 26.9   |
| 8                                      | 1982                   | 0.0789            | 26.2   |
| 9                                      | 1953                   | 0.0777            | 25.9   |
| 10                                     | 1908                   | 0.0759            | 25.3   |
| Vial 2 - Corrected c.p.m. "IN" = 24998 |                        |                   |  |
| 1                                      | 3006                   | 0.1202            | 40.0   |
| 2                                      | 2975                   | 0.1190            | 39.6   |
| 3                                      | 2700                   | 0.1080            | 36.0   |
| 4                                      | 2698                   | 0.1079            | 35.9   |
| 5                                      | 2585                   | 0.1034            | 34.4   |
| 6                                      | 2574                   | 0.1030            | 34.3   |
| 7                                      | 2485                   | 0.0994            | 33.1   |
| 8                                      | 2426                   | 0.0970            | 32.3   |
| 9                                      | 2373                   | 0.0949            | 31.6   |
| 10                                     | 2381                   | 0.0952            | 31.7   |

The results in table 3.5, are plotted in figure 3.5

FIG. 3.5 Graphs of silver adsorption against number of washes, after 60 days contact at 298 K

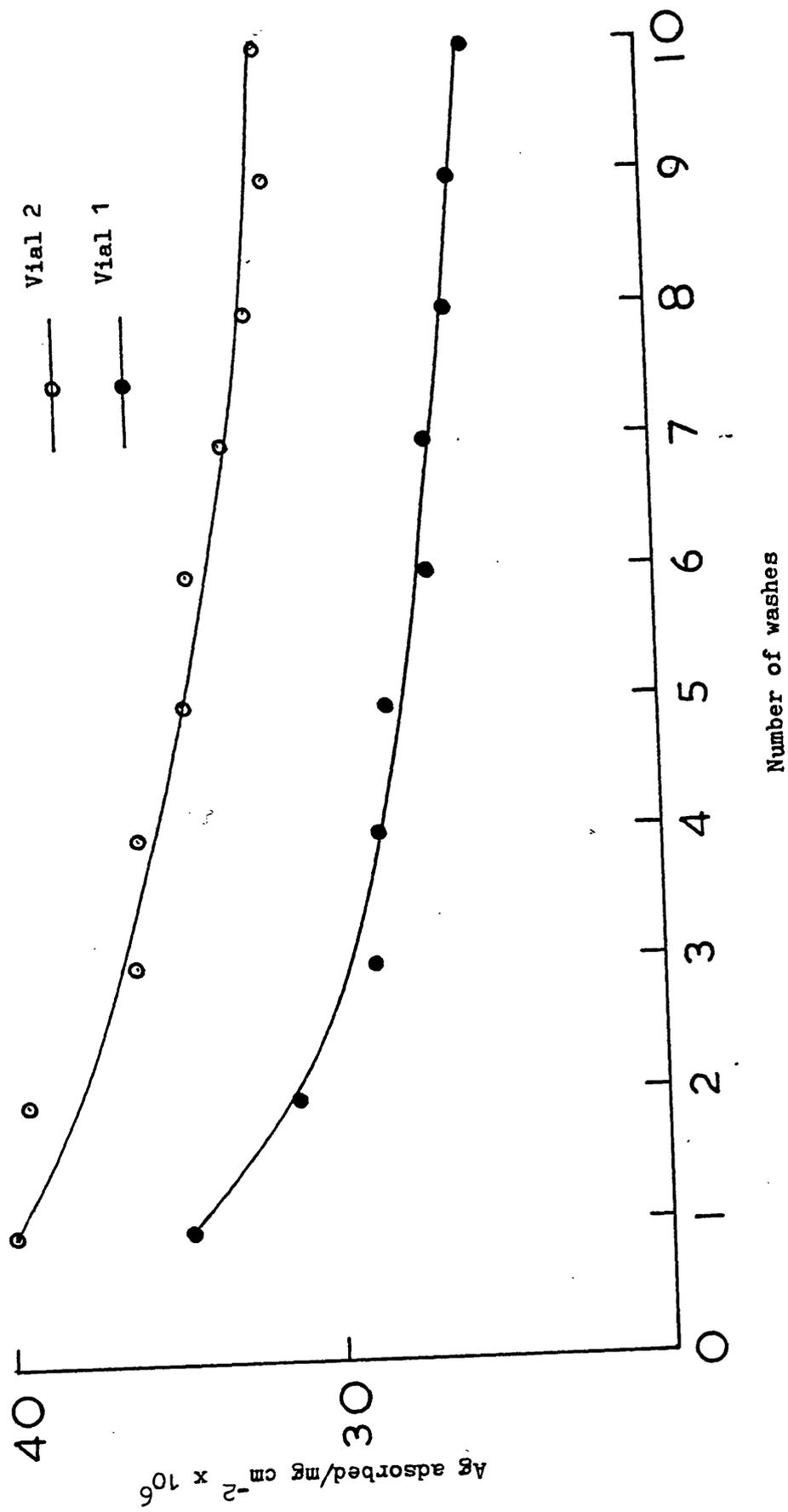
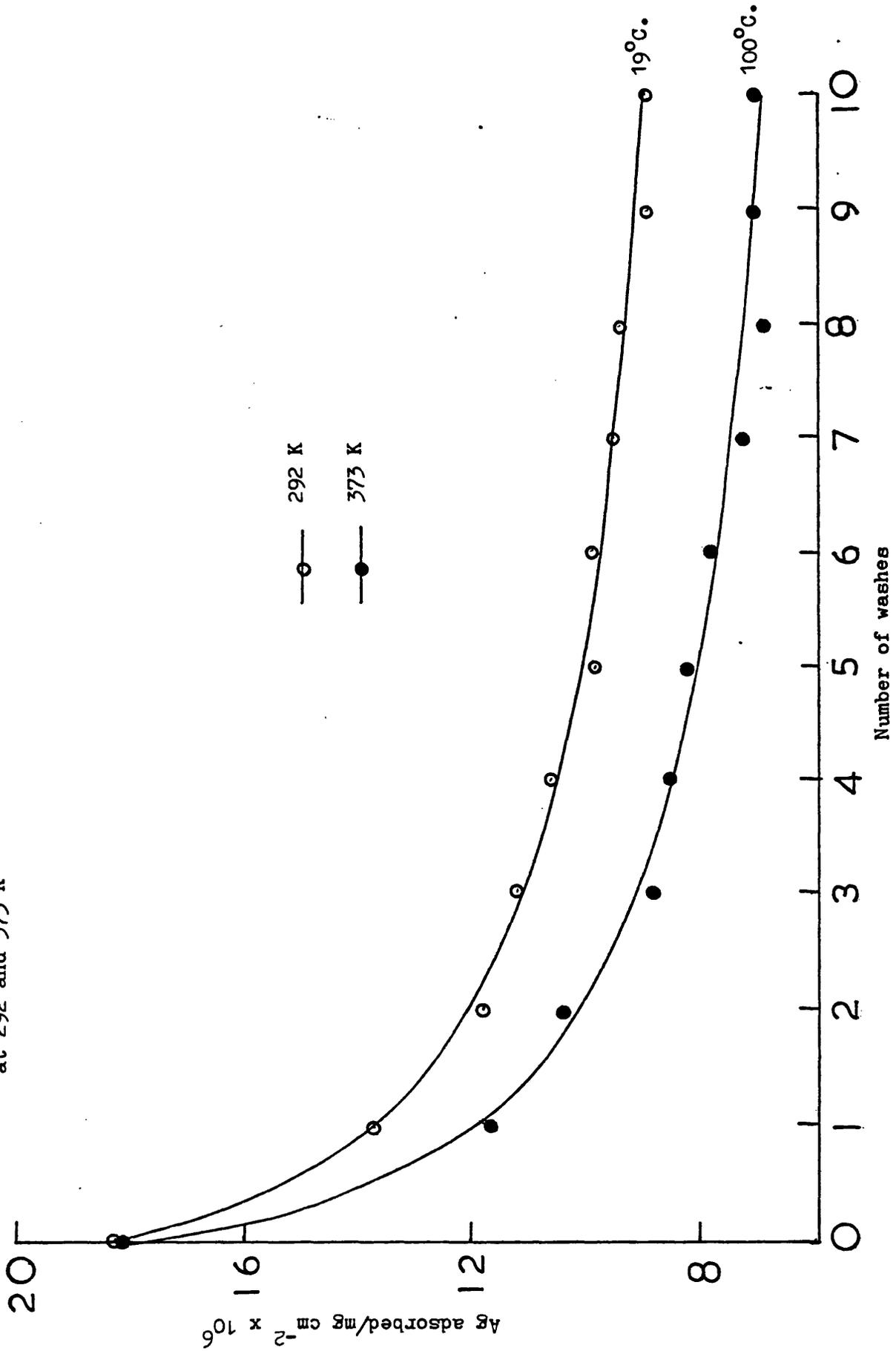


Table 3.6 Washing cycle comparison at 292 and 373 K

| No. of washes   | Corrected c.p.m. "OUT" | Fraction adsorbed. | Amount Adsorbed /mg Ag cm <sup>-2</sup> ,10 <sup>6</sup> |
|---|------------------------|--------------------|--|
| Vial 1 - washed at 292 K, corrected c.p.m. "IN" = 12738 |                        |                    |  |
| 1   | 1040                   | 0.0816             | 13.6   |
| 2   | 905                    | 0.0711             | 11.8   |
| 3   | 857                    | 0.0673             | 11.2   |
| 4   | 811                    | 0.0637             | 10.6   |
| 5   | 756                    | 0.0593             | 9.8  |
| 6   | 758                    | 0.0595             | 9.9  |
| 7   | 730                    | 0.0573             | 9.5  |
| 8   | 720                    | 0.0566             | 9.4  |
| 9   | 683                    | 0.0536             | 8.9  |
| 10  | 685                    | 0.0538             | 8.9  |
| Vial 2 - washed at 373 K, corrected c.p.m. "IN" = 12675 |                        |                    |  |
| 1   | 886                    | 0.0699             | 11.6   |
| 2   | 794                    | 0.0626             | 10.4   |
| 3   | 670                    | 0.0528             | 8.8  |
| 4   | 649                    | 0.0512             | 8.5  |
| 5   | 627                    | 0.0495             | 8.2  |
| 6   | 596                    | 0.0470             | 7.8  |
| 7   | 554                    | 0.0437             | 7.2  |
| 8   | 522                    | 0.0411             | 6.8  |
| 9   | 537                    | 0.0424             | 7.0  |
| 10  | 534                    | 0.0421             | 7.0  |

The results in table 3.6, are plotted in figure 3.6

FIG. 3.6 Graphs of silver adsorption against number of washes for washing cycles at 292 K and 373 K



The graphs in figure 3.6 show that the washing cycle at 373 K was slightly more effective than at 292 K, however, the advantage was not sufficient to justify the inconvenience of using the higher temperature wash cycle in the remainder of this work.

### 3.10 Washing cycles for polyethylene vials

The polyethylene vials used were of the type described in 3.4 and this preliminary experiment was carried out to establish whether the washing cycle used for glass vials would be suitable also for polyethylene.

A  $3 \text{ cm}^3$  aliquot of  $1 \text{ mg dm}^{-3}$  labelled silver solution was added to two vials, the vials were sealed, wrapped in foil and placed in a thermostat-bath at 298 K for seven days.

After this time the vials were removed and the corrected c.p.m. "IN" was determined for each vial as described in 3.3.5. The vials were then extracted and washed as described in 3.3.4, but the corrected c.p.m. "OUT" was measured after each wash. The results are given in table 3.7.

The curves in figure 3.7 suggest that less washes may be required to remove the loosely held silver from polyethylene, than from glass. Vial 1 reaches a limiting value after extraction and 1 wash. Vial 2, is slightly different requiring about 5 washes. These results give the first indication of the erratic nature of silver adsorption on polyethylene, which is discussed in more detail in Chapter VI. However, for consistency it was decided to use a 10 wash cycle for all further polyethylene work carried out in Chapter V.

### 3.11 Washing cycles for polypropylene vials

The vials used in this experiment were type 1 propathene as described in section 3.4. The aim was to study the effect of the standard 10 wash cycle on polypropylene vials containing adsorbed silver.

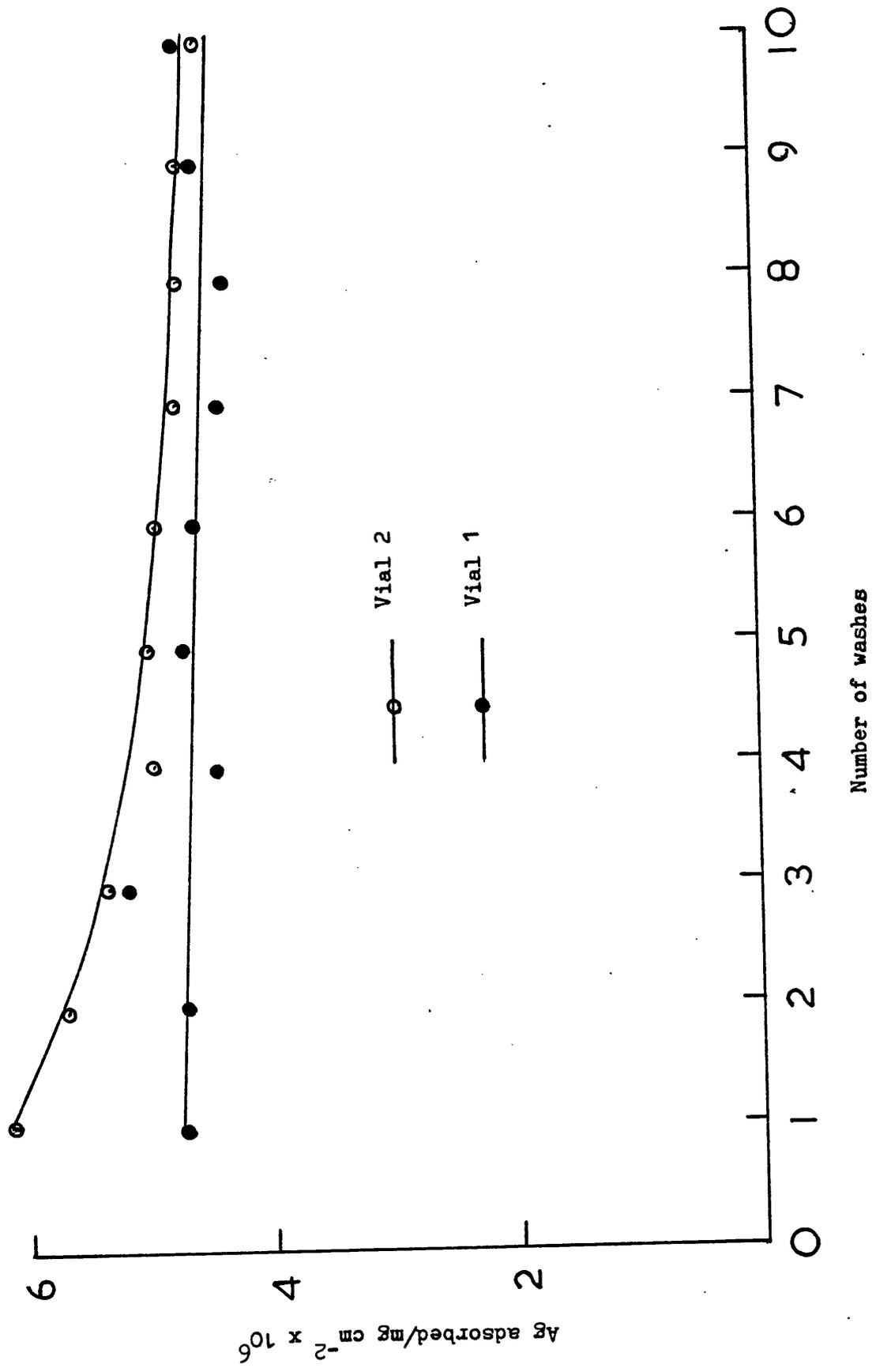
A  $3 \text{ cm}^3$  aliquot of  $1 \text{ mg dm}^{-3}$  labelled silver solution was added to two vials, the vials were sealed, wrapped in foil and placed in a thermostat-bath at 298 K for 42 days. After this time the vials were removed and the corrected c.p.m. "IN" was determined for each vial as described in section 3.3.5. The vials were then extracted and washed as described in section

Table 3.7 Washing cycles for polyethylene vials

| No. of washes.                        | Corrected c.p.m. "OUT" | Fraction adsorbed | Amount adsorbed /mg Ag cm <sup>-2</sup> .10 <sup>6</sup> |
|---------------------------------------|------------------------|-------------------|--|
| Vial 1 - corrected c.p.m. "IN" = 9567 |                        |                   |  |
| 1                                     | 165                    | 0.0172            | 4.7  |
| 2                                     | 166                    | 0.0174            | 4.7  |
| 3                                     | 165                    | 0.0172            | 5.2  |
| 4                                     | 156                    | 0.0163            | 4.4  |
| 5                                     | 165                    | 0.0172            | 4.7  |
| 6                                     | 163                    | 0.0170            | 4.6  |
| 7                                     | 156                    | 0.0163            | 4.4  |
| 8                                     | 154                    | 0.0161            | 4.3  |
| 9                                     | 162                    | 0.0169            | 4.6  |
| 10                                    | 167                    | 0.0175            | 4.7  |
| Vial 2 - corrected c.p.m. "IN" - 9282 |                        |                   |  |
| 1                                     | 212                    | 0.0228            | 6.2  |
| 2                                     | 195                    | 0.0210            | 5.7  |
| 3                                     | 181                    | 0.0195            | 5.3  |
| 4                                     | 168                    | 0.0181            | 4.9  |
| 5                                     | 171                    | 0.0184            | 5.0  |
| 6                                     | 167                    | 0.0180            | 4.9  |
| 7                                     | 162                    | 0.0185            | 4.7  |
| 8                                     | 163                    | 0.0176            | 4.7  |
| 9                                     | 160                    | 0.0172            | 4.7  |
| 10                                    | 154                    | 0.0166            | 4.5  |

The results in table 3.7, are plotted in figure 3.7

FIG. 3.7 Graphs of silver adsorption against number of washes on polyethylene vials



3.3.4, but the corrected c.p.m. "OUT" was measured after each wash. The results are given in table 3.8.

It can be seen from figure 3.8 that 2 washes is sufficient to reach a limiting value of silver adsorption on both polypropylene vials. Again, there is an indication of erratic behaviour; the silver adsorption for vial 2 was almost double that for vial 1. This poor reproducibility was subsequently found to be due to striations imparted in the surface of some vials due to imperfections in the injection mould used in the manufacturing process.\* In the meantime it was concluded that this washing procedure would be adequate for further adsorption studies using polypropylene vials.

### 3.12 Assessment of atomic absorption spectrophotometry as an alternative detection method

During this research a new atomic absorption spectrophotometer (Pye-Unicam SP 192) became available, this was an improvement over the model available to Wharmby (1), and meant that smaller detection limits were now possible. A small programme of work was therefore carried out to evaluate the potential of this instrument as a detection device for trace concentrations of silver.

The working conditions and detection limits are outlined below.

|                 |   |                                     |
|-----------------|---|-------------------------------------|
| Air Flow        | - | 5 dm <sup>3</sup> min <sup>-1</sup> |
| Acetylene Flow  | - | 1 dm <sup>3</sup> min <sup>-1</sup> |
| Wavelength      | - | 328.1 nm                            |
| Bandpass        | - | 0.3 nm                              |
| Lamp Current    | - | 4 mA                                |
| Sensitivity     | - | 0.03 mg dm <sup>-3</sup>            |
| Detection Limit | - | 0.002 mg dm <sup>-3</sup>           |

Initially (see experiment 4.4.5) the AAS was calibrated using silver standards in neutral solution (as recommended in the Pye-Unicam Users Handbook). However, in all subsequent AAS work calibration standards were prepared in acid solution of pH < 0.1 to reduce adsorption losses to the graduated flasks. A sample calibration curve is shown in figure 3.10.

N.B. All silver solutions used in the AAS work are unlabelled.

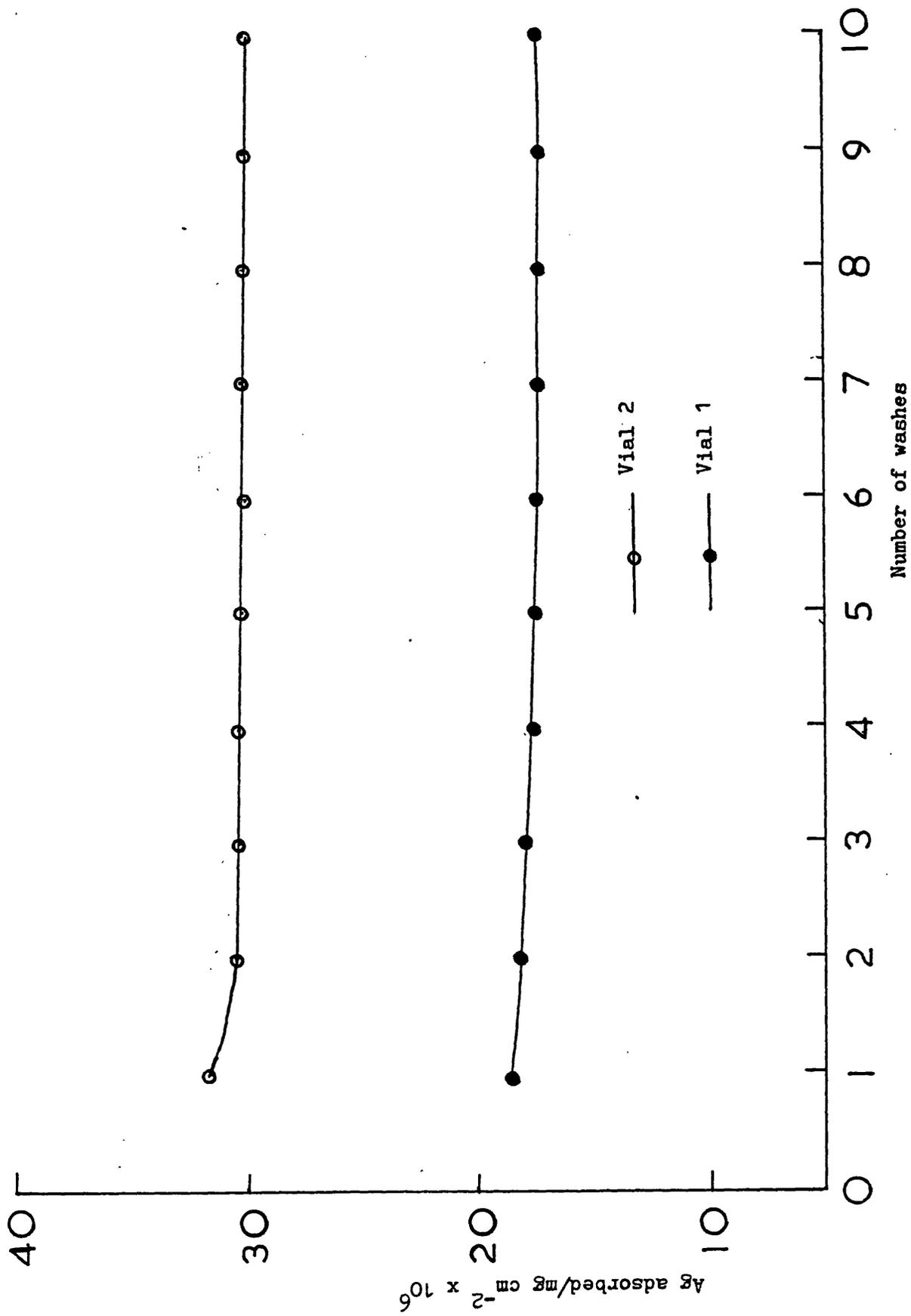
\* The author is indebted to Mr. M. Toogood of Messrs. Hopkin and Williams for his co-operation in alleviating this problem.

Table 3.8 Washing cycles for polypropylene vials

| No. of washes                        | Corrected c.p.m. OUT | Fraction adsorbed | Amount adsorbed /mg Ag cm <sup>-2</sup> .10 <sup>6</sup> |
|--------------------------------------|----------------------|-------------------|--|
| Vial 1 - corrected c.p.m. IN = 90258 |                      |                   |  |
| 1                                    | 5930                 | 0.0657            | 18.4   |
| 2                                    | 5877                 | 0.0651            | 18.2   |
| 3                                    | 5796                 | 0.0642            | 18.0   |
| 4                                    | 5654                 | 0.0626            | 17.5   |
| 5                                    | 5615                 | 0.0622            | 17.4   |
| 6                                    | 5661                 | 0.0627            | 17.5   |
| 7                                    | 5585                 | 0.0619            | 17.3   |
| 8                                    | 5618                 | 0.0622            | 17.4   |
| 9                                    | 5579                 | 0.0618            | 17.3   |
| 10                                   | 5650                 | 0.0626            | 17.5   |
| Vial 2 - corrected c.p.m. IN = 90419 |                      |                   |  |
| 1                                    | 10224                | 0.1131            | 31.7   |
| 2                                    | 9859                 | 0.1090            | 30.5   |
| 3                                    | 9837                 | 0.1088            | 30.4   |
| 4                                    | 9797                 | 0.1084            | 30.3   |
| 5                                    | 9749                 | 0.1078            | 30.2   |
| 6                                    | 9702                 | 0.1073            | 30.0   |
| 7                                    | 9770                 | 0.1081            | 30.2   |
| 8                                    | 9681                 | 0.1071            | 30.0   |
| 9                                    | 9770                 | 0.1081            | 30.2   |
| 10                                   | 9712                 | 0.1074            | 30.1   |

The results from table 3.8, are plotted in figure 3.8

FIG. 3.8 Graphs of silver adsorption against number of washes, on polypropylene vials



### 3.12.1 Observation of a washing cycle using the A.A.S. as the detector

A 5 cm<sup>3</sup> aliquot of 10 mg dm<sup>-3</sup> silver solution was added to each of two glass vials, (a 5 cm<sup>3</sup> aliquot was used to provide the maximum volume for A.A. analysis), the vials were sealed, wrapped in foil and placed in a thermostat-bath for 4-days at 298 K.

After this contact time the A.A.S. was calibrated using standards, the vials were removed and the silver concentrations were determined. After all the solution had been extracted a 5 cm<sup>3</sup> aliquot of doubly deionised water was added to each vial, the vials were capped and shaken for 10 seconds, this operation was designated 1 wash. A number of washes were carried out, and the washings were measured on the A.A.S. The results are shown in table 3.9.

Table 3.9 Washing cycle monitored by A.A.S.

| No. of washes | Silver concentration /mg dm <sup>-3</sup> |        |
|---------------|---|--------|
|               | Vial 1                                    | Vial 2 |
| 0             | 9.000                                     | 9.100  |
| 1             | 0.150                                     | 0.040  |
| 2             | 0.012                                     | 0.012  |
| 3             | 0.000                                     | 0.000  |

It can be seen from table 3.9 that the silver removed by the third wash, is at, or below the instruments' detection limit. Previous experiments (see section 3.9) had shown that amounts of silver less than 0.001 mg dm<sup>-3</sup> are removed by further washing. The instrument is, therefore, not suitable for monitoring washing cycle experiments. However, as is reported in section 4.4.5 A.A.S. can be used to measure larger changes in concentration of the adsorbate in solution.

### 3.12.2 Silver losses on graduated glassware, as detected by A.A.S.

The work reported in section 4.3 demonstrates that acid may be used to remove a large proportion of adsorbed silver from glass. It was,

therefore, decided to prepare a stock solution in a graduated flask, and measure the concentration by A.A.S. before and after the addition of acid, as an alternative to measuring the amount of silver retained by the adsorbent using radiotracer technique.

The A.A.S. was calibrated using acid standards, and a new 250 cm<sup>3</sup> graduated flask was thoroughly washed with doubly deionised water. Then a 2 mg dm<sup>-3</sup> silver solution was prepared in the graduated flask, using 0.5 cm<sup>3</sup> of 1000 mg dm<sup>-3</sup> silver solution, diluted to 250 cm<sup>3</sup>. The flask was shaken for 15 seconds and immediately the concentration was measured on the A.A.S. The instrument was then set to give an integrated reading every 4 seconds. After 60 seconds had elapsed 2 cm<sup>3</sup> of concentrated nitric acid solution was added with shaking, and the readings were continued for a further 60 seconds, when another 1 cm<sup>3</sup> of concentrated nitric acid solution was added.

N.B. The contact surface area to volume ratio inside the graduated flask remained relatively unchanged, because the A.A.S. consumed only 4 cm<sup>3</sup> of solution per minute.

The results are listed in table 3.10.

The results seemed to imply that about two thirds of the silver was adsorbed on to the graduated flask in a matter of seconds, only to be desorbed back into solution on addition of nitric acid. This initially caused surprise, as adsorption of this speed and magnitude had not been experienced previously. However, it was suspected that the results could perhaps be due to the use of a calibration curve produced from acidified silver standards. The experiment was therefore repeated with two calibration curves, one using acidified standards, and the other, neutral standards.

The results in table 3.11, show the absorbance values for both sets of calibration standards, and the curves are plotted in figure 3.10.

Table 3.10 Measurement of adsorbate concentration in neutral  
and acid conditions

| Age of 2 mg dm <sup>-3</sup> silver solution<br>including 15 sec. shake (secs.) | Absorbance<br>Reading | Silver Concentration<br>/mg dm <sup>-3</sup> |
|---|-----------------------|--|
| 19  | 0.114                 | 0.7  |
| 23  | 0.115                 | 0.7  |
| 27  | 0.115                 | 0.7  |
| 31  | 0.116                 | 0.7  |
| 35  | 0.118                 | 0.7  |
| 39  | 0.117                 | 0.7  |
| 43  | 0.116                 | 0.7  |
| 47  | 0.115                 | 0.7  |
| 51  | 0.117                 | 0.7  |
| 55  | 0.118                 | 0.7  |
| 59  | 0.117                 | 0.7  |
| 63  | 0.118                 | 0.7  |
| 67  | 0.119                 | 0.7  |
| 71  | 0.118                 | 0.7  |
| 75 (+ 2 cm <sup>3</sup> acid)   | 0.118                 | 0.7  |
| 79  | 0.235                 | 2.0  |
| 83  | 0.235                 | 2.0  |
| 87  | 0.235                 | 2.0  |
| 91  | 0.245                 | 2.0  |
| 95  | 0.242                 | 2.0  |
| 99  | 0.235                 | 2.0  |
| 103   | 0.228                 | 1.9  |
| 107   | 0.223                 | 1.8  |
| 111   | 0.218                 | 1.8  |
| 115   | 0.214                 | 1.7  |
| 119   | 0.213                 | 1.7  |
| 123   | 0.210                 | 1.7  |
| 127   | 0.210                 | 1.7  |
| 131   | 0.207                 | 1.6  |
| 135 (+ 1 cm <sup>3</sup> acid)  | 0.207                 | 1.6  |
| 139   | 0.212                 | 1.7  |
| 143   | 0.212                 | 1.7  |
| 147   | 0.211                 | 1.7  |
| 151   | 0.210                 | 1.7  |
| 155   | 0.210                 | 1.7  |
| 159   | 0.208                 | 1.6  |
| 163   | 0.208                 | 1.6  |

The results from table 3.10 are plotted in figure 3.9

FIG. 3.9 Graph of silver concentration against contact time, monitored by AAS, calibrated with acidified standards

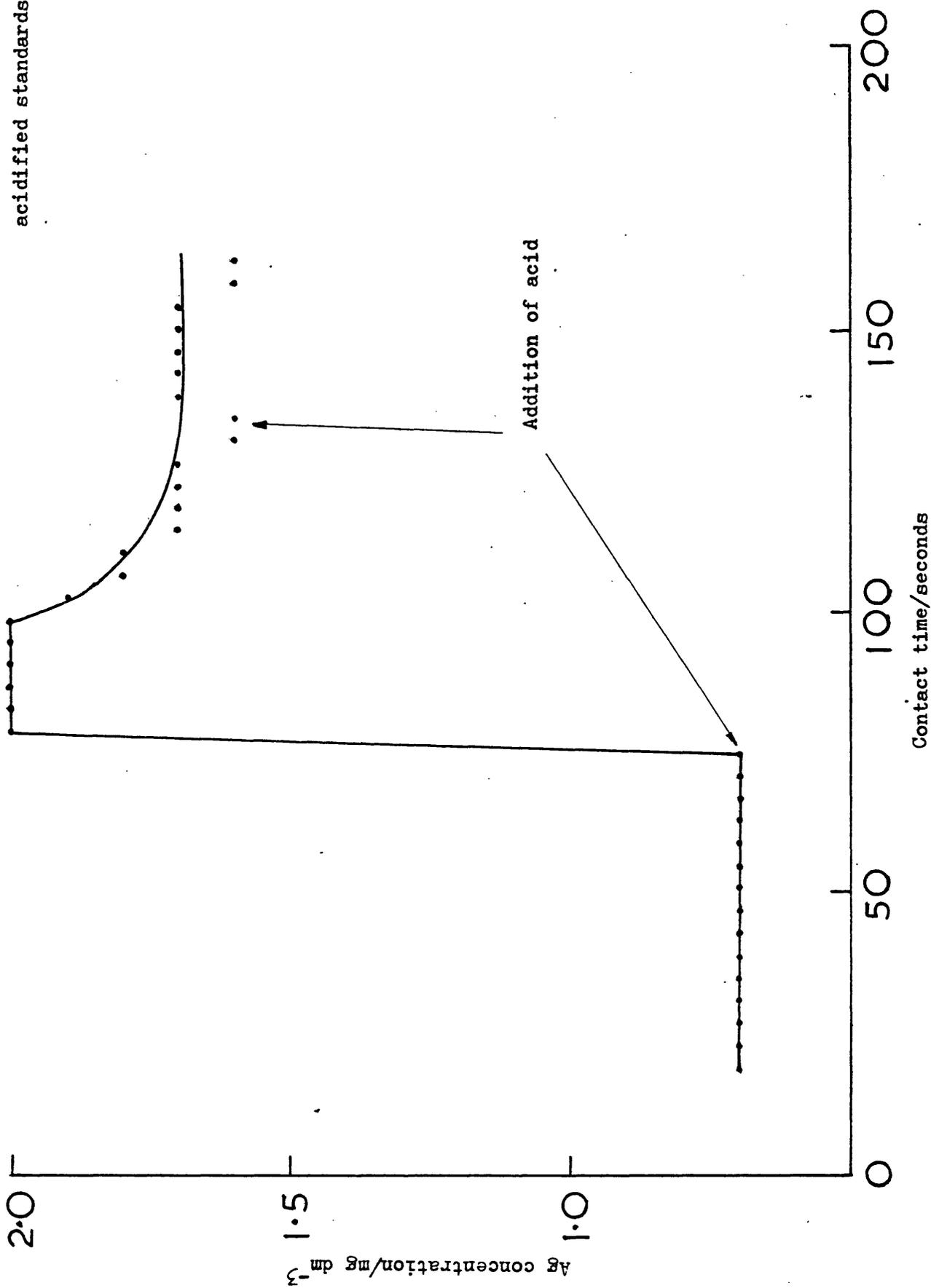


Table 3.11 Calibration of A.A.S. using acidic and neutral standard solutions

| Silver Concentration<br>/mg dm <sup>-3</sup> | Absorbance of Standard Solutions |         |
|--|----------------------------------|---------|
|  | Acidic                           | Neutral |
| 10   | 0.569                            | 0.480   |
| 8  | 0.500                            | 0.414   |
| 4  | 0.312                            | 0.205   |
| 2  | 0.180                            | 0.093   |
| 1  | 0.103                            | 0.039   |

The results in table 3.12 show absorbance and 2 silver concentrations determined from both calibration curves.

FIG. 3.10 Calibration curves for the AAS using both acidic and neutral, standard silver solutions

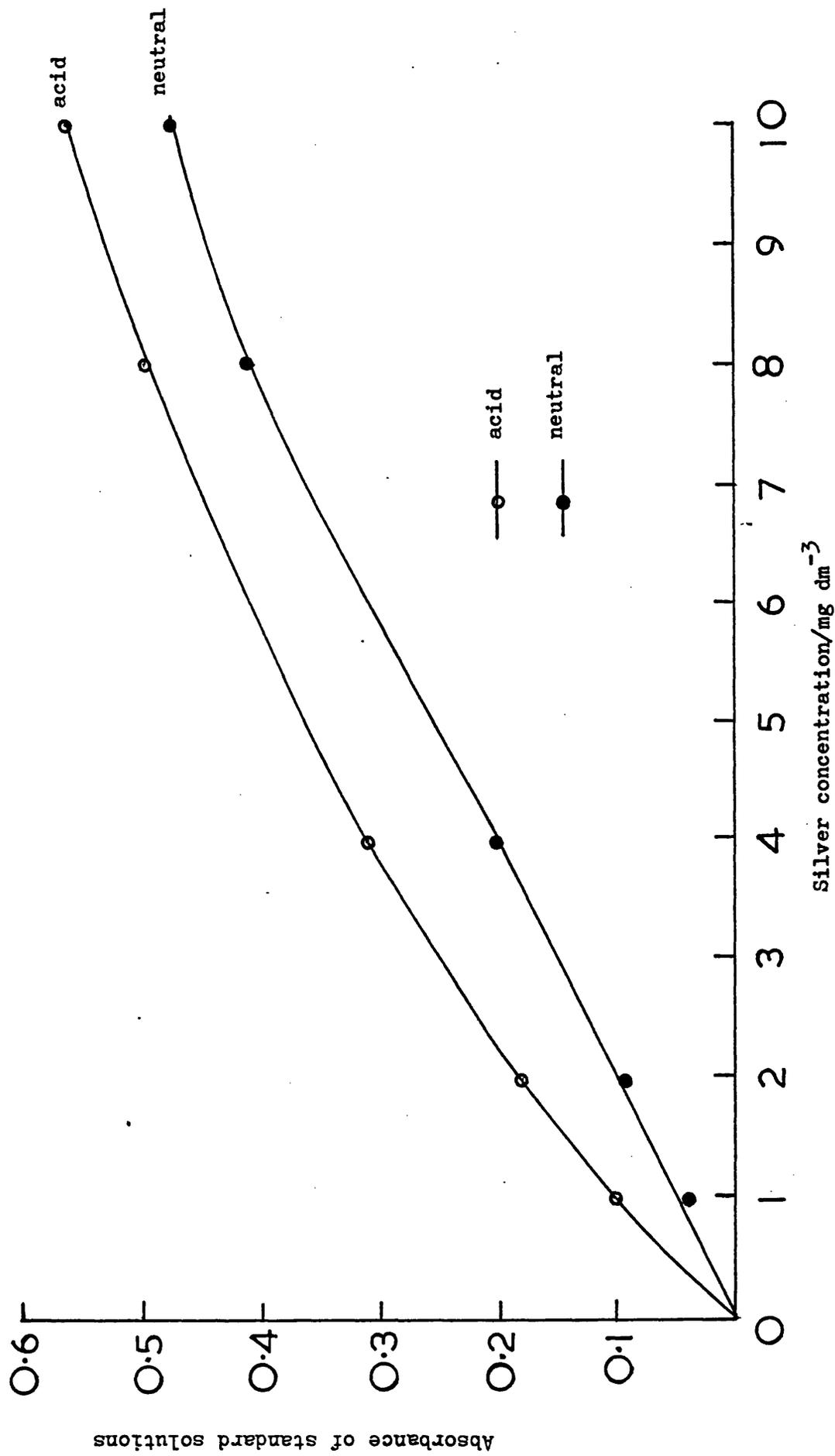


Table 3.12 Measurement of adsorbate concentration in

neutral and acid conditions

| Age of 2 mg dm <sup>-3</sup><br>silver solution<br>including 15 sec.<br>shake (secs.) | Absorbance<br>Reading | Silver Concentration /mg dm <sup>-3</sup> |                             |
|---|-----------------------|---|-----------------------------|
|   |                       | From acid<br>calibration                  | From neutral<br>calibration |
| 19  | 0.088                 | 0.9                                       | 1.8                         |
| 23  | 0.088                 | 0.9                                       | 1.8                         |
| 27  | 0.091                 | 0.9                                       | 1.8                         |
| 31  | 0.089                 | 0.9                                       | 1.8                         |
| 35  | 0.090                 | 0.9                                       | 1.8                         |
| 39  | 0.090                 | 0.9                                       | 1.8                         |
| 43  | 0.089                 | 0.9                                       | 1.8                         |
| 47  | 0.090                 | 0.9                                       | 1.8                         |
| 51  | 0.091                 | 0.9                                       | 1.8                         |
| 55  | 0.092                 | 0.9                                       | 1.8                         |
| 59  | 0.091                 | 0.9                                       | 1.8                         |
| 63  | 0.092                 | 0.9                                       | 1.8                         |
| 67  | 0.093                 | 0.9                                       | 1.8                         |
| 71 (+ 2cm <sup>3</sup> acid)  | 0.093                 | 0.9                                       | 1.8                         |
| 75  | 0.204                 | 2.2                                       | 4.0                         |
| 79  | 0.190                 | 2.0                                       | 3.8                         |
| 83  | 0.184                 | 2.0                                       | 3.7                         |
| 87  | 0.181                 | 1.9                                       | 3.6                         |
| 91  | 0.178                 | 1.9                                       | 3.6                         |
| 95  | 0.180                 | 1.9                                       | 3.6                         |
| 99  | 0.179                 | 1.9                                       | 3.6                         |
| 103   | 0.178                 | 1.9                                       | 3.6                         |
| 107   | 0.177                 | 1.9                                       | 3.6                         |
| 111   | 0.178                 | 1.9                                       | 3.6                         |
| 115   | 0.178                 | 1.9                                       | 3.6                         |
| 119 (+ 1cm <sup>3</sup> acid)   | 0.177                 | 1.9                                       | 3.6                         |
| 123   | 0.178                 | 1.9                                       | 3.6                         |
| 127   | 0.179                 | 1.9                                       | 3.6                         |
| 131   | 0.178                 | 1.9                                       | 3.6                         |
| 135   | 0.178                 | 1.9                                       | 3.6                         |
| 139   | 0.178                 | 1.9                                       | 3.6                         |
| 143   | 0.178                 | 1.9                                       | 3.6                         |

The results above are plotted in figure 3.11

FIG. 3.11 Graphs of silver concentration against contact time, using both acid and neutral AAS calibration standards

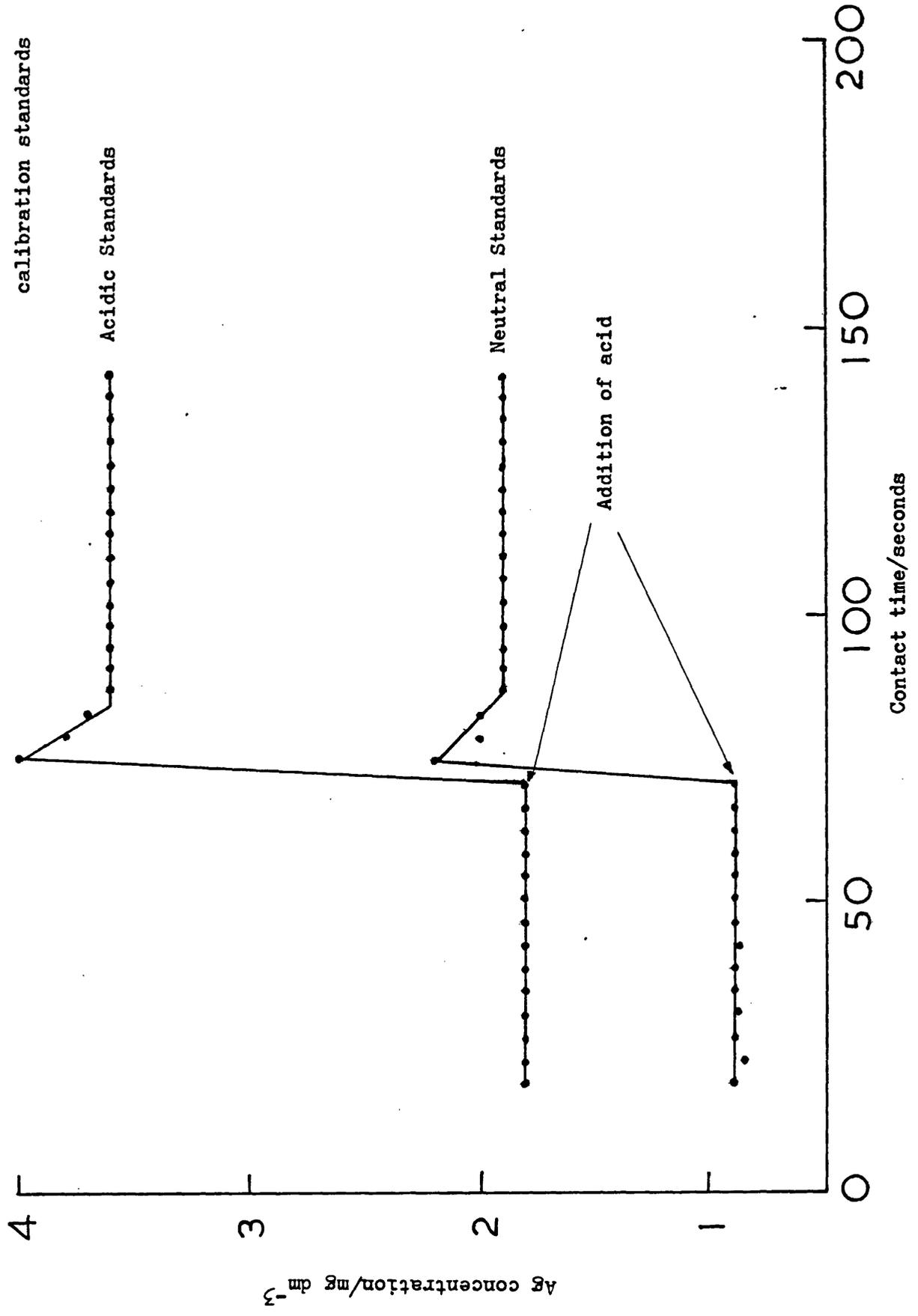


Figure 3.11 then does not reflect adsorption, but simply changes in the sensitivity of the A.A.S. when measuring silver solutions at different pH values. The effect is quite marked, the sensitivity of the instrument to silver, being almost exactly doubled in going from a pH of about 6 to a pH value of less than 1.

Consultations with the instrument manufacturer revealed that the acid effect is known for most cations and is well documented in the case of iron, where, although the mechanism is not fully understood, it is thought ferrous ions may form stable complexes in the A.A. flame, thus giving a reduced absorbance figure. The effect can be overcome by using a chelating agent, or indeed acid solution. The alternative is to use a hotter, nitrous oxide, flame.\*

It was concluded then, that the use of a radiotracer was indeed the most reliable and sensitive method available to the present author for the study of silver adsorption from aqueous solution. However, the results obtained by A.A.S. in experiment 4.4.5. are still valid, as both calibration and measurement of solutions under test were carried out at the same pH, although the sensitivity would not have been at its optimum.

\* The author is grateful to Messrs. Pye-Unicam Ltd. of Cambridge for this information.

## CHAPTER IV

### EXPERIMENTAL WORK AND RESULTS FOR SILVER ADSORPTION ON GLASS

This section of work deals with the adsorption of silver ions on glass, and in particular the influence of pH on this process.

Previous adsorption studies of cations on glass have indicated a pH effect and in some work the specific activity of the labelled solution appears to be important.

The pH study involves a series of experiments designed to explore all aspects of pH with respect to its effect on the adsorption and desorption of silver ions in contact with soda-glass.

It was felt necessary to carry out this particular work in some depth in order to establish some general rules concerning adsorption, before proceeding further with the investigation.

In addition to the pH dependence, the effect of other added cations on the adsorption of silver is also described in this Chapter.

A study of silver adsorption was carried out over prolonged contact times, at varying pH values, silver concentrations, and temperatures. The resulting data is discussed in Chapter VI, where a simple kinetic treatment has been applied, and a possible model for the adsorption of silver on glass has been proposed.

On establishing the time necessary for the adsorption process to reach equilibrium, a series of adsorption isotherms were produced at 281, 293, 298 and 303 K, and a speculative treatment has been applied to the data from these isotherms, in an attempt to estimate an enthalpy value for the adsorption process.

#### 4.1 Adsorption of silver ions from solutions at pH values less than 6

The following experiments deal with the adsorption of silver from 100, 10 and 0.5 mg dm<sup>-3</sup> silver solutions with pH values less than six. The experiments were carried out at 298 K using a 7 day contact time.

##### 4.1.1 The effect of pH on the adsorption of silver from a 100 mg dm<sup>-3</sup> silver solution on soda-glass at 298 K

The glass vials were pre-washed as described in 3.3.2, an aliquot of nitric acid was added to each vial followed by 3 cm<sup>3</sup> of the 100 mg dm<sup>-3</sup> labelled silver nitrate solution. In order to ensure identical contact areas for all the vials, the volume of nitric acid solution added was kept constant at 0.1 cm<sup>3</sup>.

The pH was increased from 0.1 to 4.8 by decreasing the concentration of the 0.1 cm<sup>3</sup> aliquot of acid solution.

The pH calculations, include the hydrogen ion concentration of the doubly deionised water, and that of the labelled silver nitrate solution. The concentration of labelled silver nitrate was such that the highest pH attainable without addition of nitric acid was 4.8.

The vials were sealed, wrapped in foil to exclude light, and immersed in a thermostat-bath for 7 days at 298 K. At the end of this contact period the vials were removed and washed as described in 3.3.4, and counted as described in 3.3.5.

Table 4.1 The pH dependence of adsorption for 100 mg dm<sup>-3</sup>silver solution at 298 K

| Vial No | pH  | [H <sup>+</sup> ]<br>mol dm <sup>-3</sup> | Corrected Count<br>Rate 'IN'/c.p.m. | Corrected Count<br>Rate 'OUT'/c.p.m. | Ag adsorbed<br>/mg cm <sup>-2</sup> x 10 <sup>6</sup> |
|---------|-----|---|-------------------------------------|--------------------------------------|---|
| 1       | 4.8 | 0.000017                                  | 156179                              | 667                                  | 115.4   |
| 2       | 4.8 | 0.000017                                  | 158589                              | 628                                  | 107.0   |
| 3       | 3.5 | 0.000493                                  | 156737                              | 215                                  | 37.0  |
| 4       | 3.5 | 0.000493                                  | 155857                              | 249                                  | 43.1  |
| 5       | 2.3 | 0.004779                                  | 156811                              | 90                                   | 15.5  |
| 6       | 2.3 | 0.004779                                  | 156749                              | 108                                  | 18.6  |
| 7       | 1.3 | 0.047637                                  | 156214                              | 83                                   | 14.3  |
| 8       | 1.3 | 0.047637                                  | 157034                              | 65                                   | 11.1  |
| 9       | 0.3 | 0.476217                                  | 157464                              | 77                                   | 13.2  |
| 10      | 0.3 | 0.476217                                  | 157131                              | 70                                   | 12.0  |
| 11      | 0.1 | 0.761917                                  | 156012                              | 51                                   | 8.8   |
| 12      | 0.1 | 0.761917                                  | 156142                              | 61                                   | 10.5  |

The results are plotted in Figure 4.1

4.1.2 The effect of pH on the adsorption of silver from a  
10 mg dm<sup>-3</sup> silver solution on soda-glass at 298 K

The experimental procedure was identical to that described in 4.1.1 except that the labelled silver nitrate solution was at a concentration of 10 mg dm<sup>-3</sup> which allowed a maximum pH of 5.6 to be used.

FIG. 4.1. Graph of silver adsorption from  $100 \text{ mg dm}^{-3}$  silver solution, against pH after 7-days contact at 298 K.

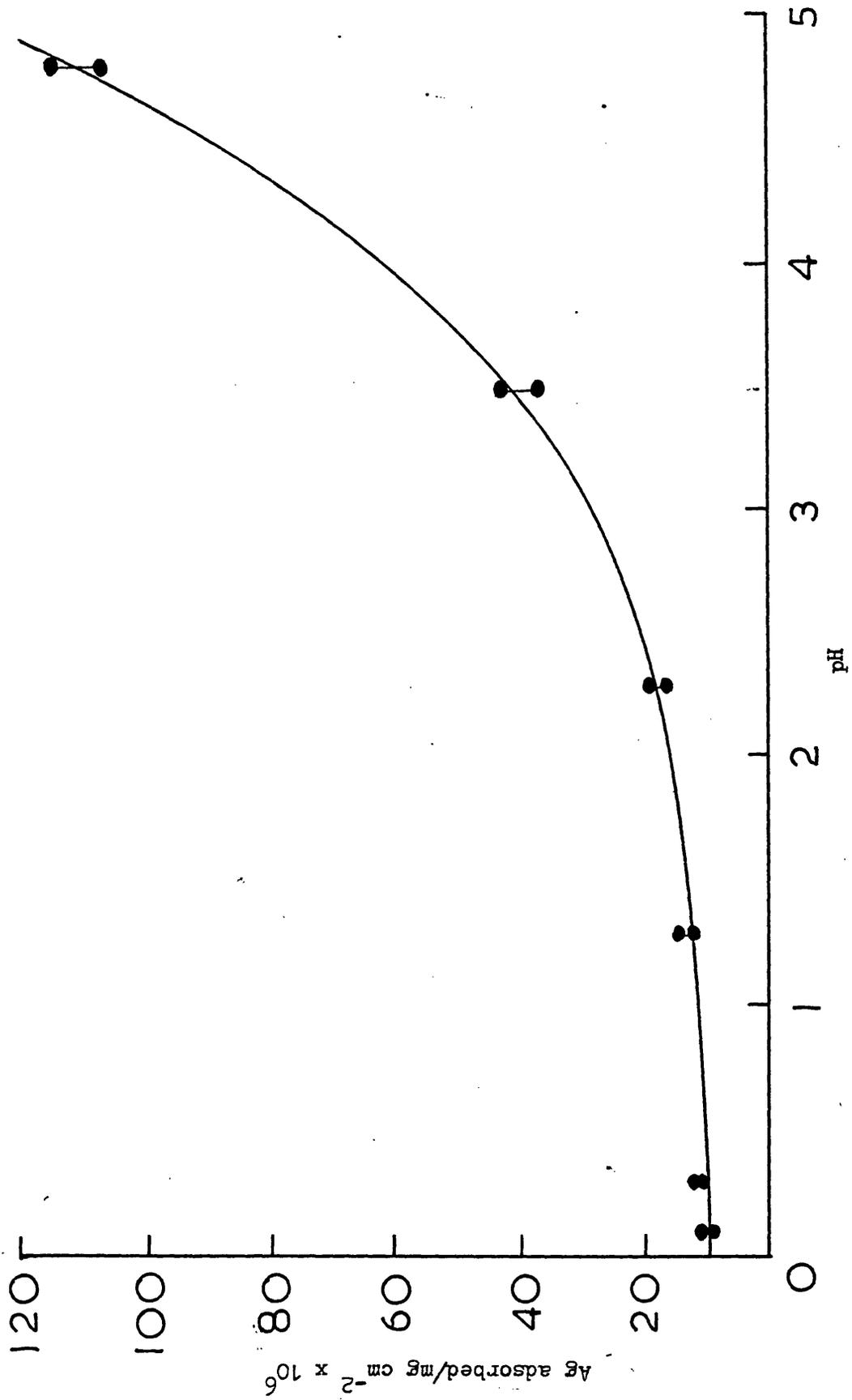


Table 4.2 The pH dependence of adsorption from a 10 mg dm<sup>-3</sup> silver solution at 298 K

| Vial No | pH  | [H <sup>+</sup> ]<br>mol dm <sup>-3</sup> | Corrected Count Rate<br>'IN'/c.p.m. | Corrected Count Rate<br>'OUT'/c.p.m. | Ag Adsorbed/<br>mg cm <sup>-2</sup> x 10 <sup>6</sup> |
|---------|-----|---|-------------------------------------|--------------------------------------|---|
| 1       | 5.6 | 0.000003                                  | 13008                               | 317                                  | 65.8  |
| 2       | 5.6 | 0.000003                                  | 12971                               | 303                                  | 63.1  |
| 3       | 3.3 | 0.000478                                  | 13152                               | 42                                   | 8.6   |
| 4       | 3.3 | 0.000478                                  | 12793                               | 42                                   | 8.8   |
| 5       | 2.3 | 0.004764                                  | 13055                               | 24                                   | 4.9   |
| 6       | 2.3 | 0.004764                                  | 12909                               | 14                                   | 2.9   |
| 7       | 1.3 | 0.047622                                  | 13162                               | 12                                   | 2.4   |
| 8       | 1.3 | 0.047622                                  | RESULTS NOT SIGNIFICANT             |                                      |   |
| 9       | 0.3 | 0.476200                                  |                                     |                                      |   |
| 10      | 0.3 | 0.476200                                  |                                     |                                      |   |
| 11      | 0.1 | 0.761919                                  |                                     |                                      |   |
| 12      | 0.1 | 0.761919                                  |                                     |                                      |   |

The results are plotted in Figure 4.2

4.1.3 The effect of pH on the adsorption of silver from a 0.5 mg dm<sup>-3</sup> silver solution on soda-glass at 298 K

The experimental procedure was identical to that described in 4.1.1 except that the labelled silver nitrate solution was at a concentration of 0.5 mg dm<sup>-3</sup>, which allowed a maximum pH of 5.6 to be used.

FIG. 4.2. Graph of silver adsorption from  $10 \text{ mg dm}^{-3}$  silver solution, against pH after 7-days contact at 298 K.

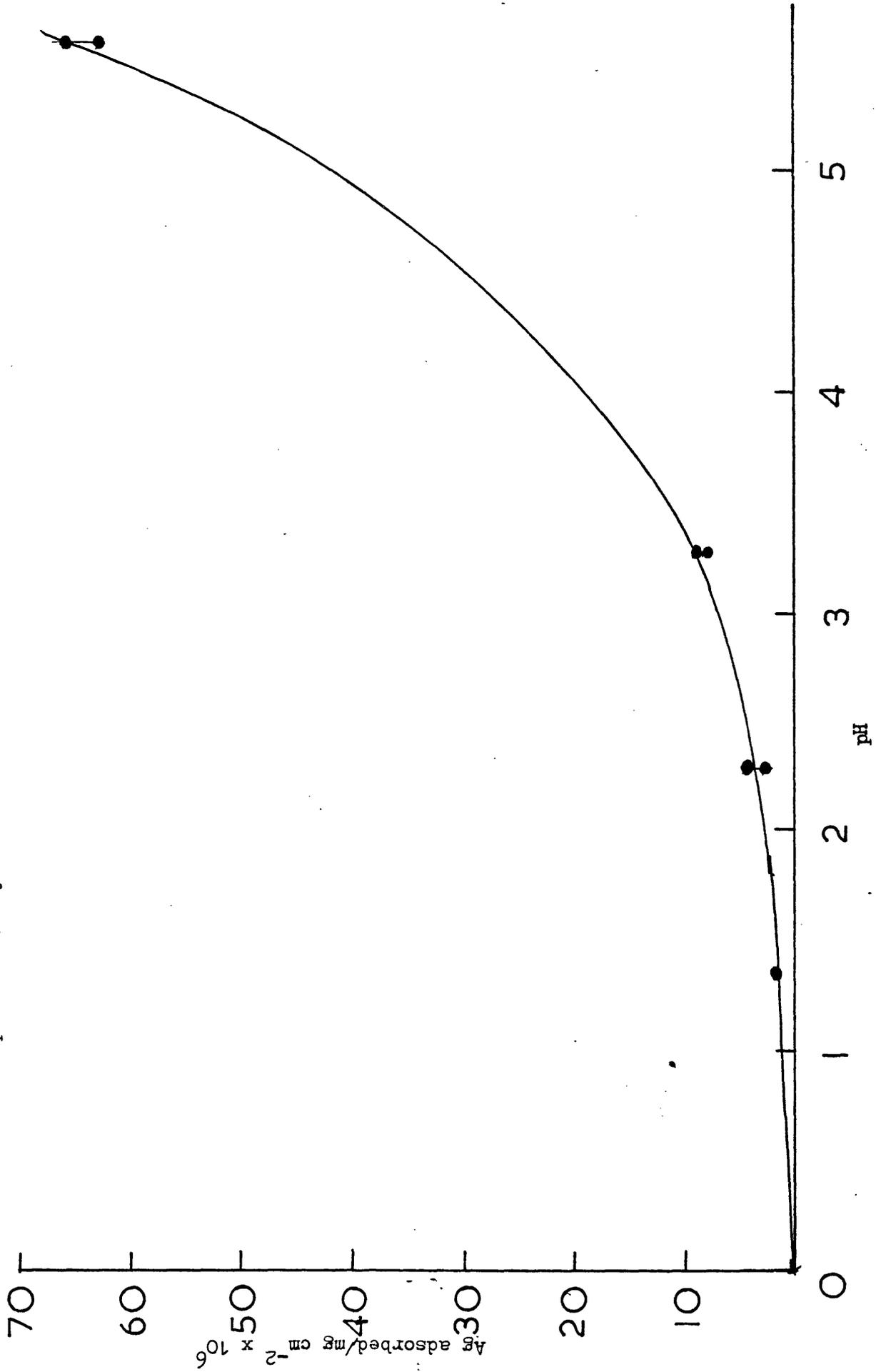


Table 4.3 The pH dependence of adsorption from a  $0.5 \text{ mg dm}^{-3}$  silver solution at 298 K

| Vial No | pH  | $[\text{H}^+]$<br>mol $\text{dm}^{-3}$ | Corrected<br>Count Rate<br>'IN'/c.p.m. | Corrected<br>Count Rate<br>'OUT'/c.p.m. | Fraction<br>Ag<br>adsorbed | Ag<br>adsorbed<br>/mg $\text{cm}^{-2} \times 10^6$ |  |
|---------|-----|--|--|---|----------------------------|--|--|
| 1       | 5.6 | 0.000003                               | 11621                                  | 759                                     | 0.0653                     | 10.8   |  |
| 2       | 5.6 | 0.000003                               | 11544                                  | 804                                     | 0.0696                     | 11.6   |  |
| 3       | 3.3 | 0.000478                               | 12180                                  | 123                                     | 0.0101                     | 1.6  |  |
| 4       | 3.3 | 0.000478                               | 12112                                  | 261                                     | 0.0215                     | 3.5  |  |
| 5       | 2.3 | 0.004764                               | 11755                                  | 54                                      | 0.0046                     | 0.7  |  |
| 6       | 2.3 | 0.004764                               | 11686                                  | 97                                      | 0.0083                     | 1.3  |  |
| 7       | 1.3 | 0.047622                               | RESULTS NOT SIGNIFICANT                |   |                            |  |  |
| 8       | 1.3 | 0.047622                               |  |   |                            |  |  |
| 9       | 0.3 | 0.476200                               |  |   |                            |  |  |
| 10      | 0.3 | 0.476200                               |  |   |                            |  |  |
| 11      | 0.1 | 0.761919                               |  |   |                            |  |  |
| 12      | 0.1 | 0.761919                               |  |   |                            |  |  |

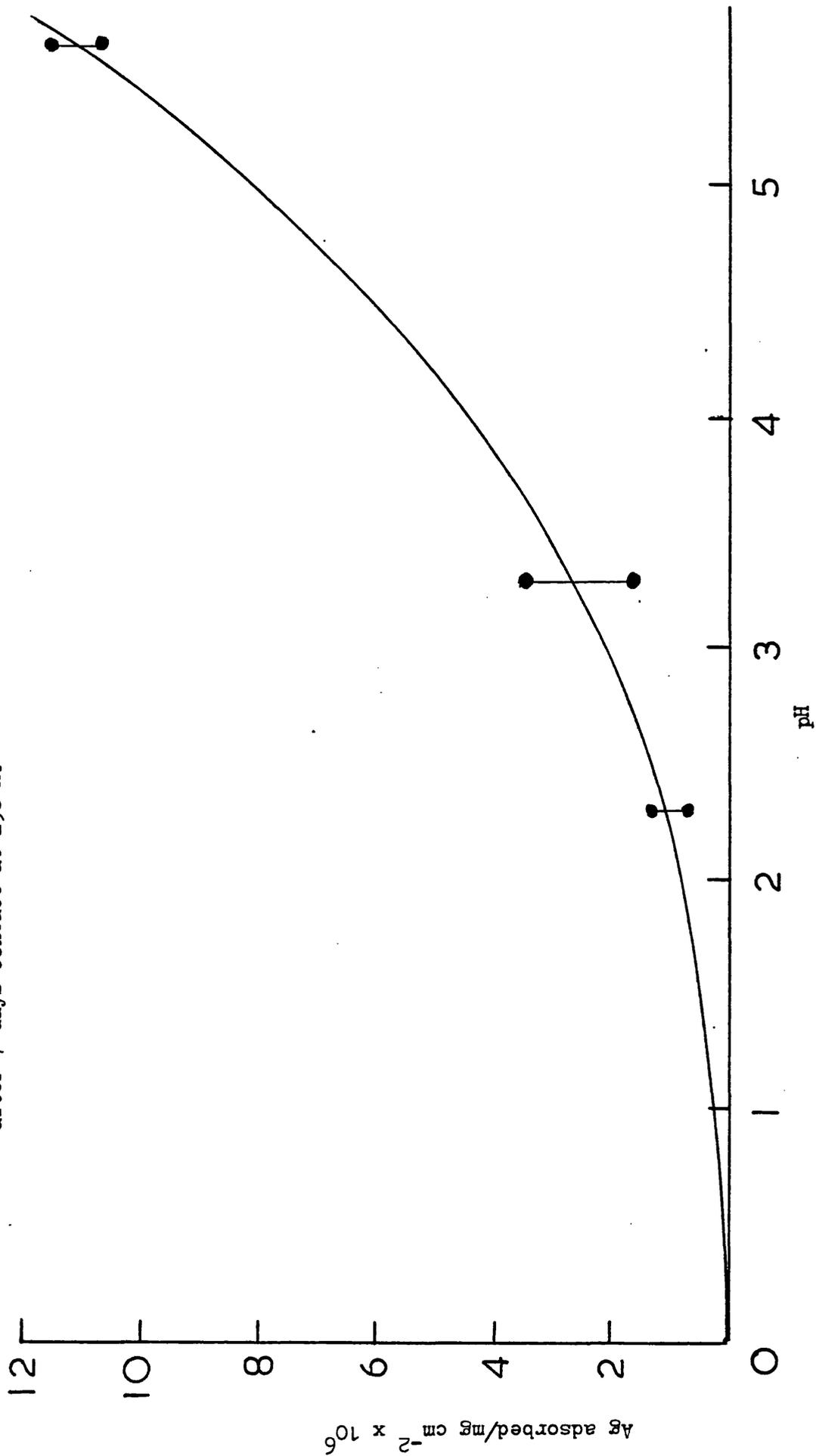
The results are plotted in Figure 4.3

It can be seen from tables 4.1, 4.2 and 4.3 that duplication of results at the various pH values is reasonable, indicating that the observed dependence of adsorption on pH, is significant.

It can also be seen that the adsorption of silver is greatly reduced at low pH values, in fact when the pH is lowered from 5.0 to 2.5, the total silver adsorbed is reduced by 90%, below pH 2.5 the effect appears to be less pronounced. However, at the same pH, silver adsorption increases with silver concentration.

The inference of this work is that there is preferential adsorption of the  $\text{H}_3\text{O}^+$ , thus reducing the sites available for adsorption of the  $\text{Ag}^+$ .

FIG. 4.3. Graph of silver adsorption from a  $0.5 \text{ mg dm}^{-3}$  silver solution, after 7-days contact at 298 K.



The results also indicate that the previously observed specific activity effect (1) was probably due to the pH variation of the labelled silver nitrate solutions.

The immediate practical implication of these experiments is that analytical errors due to adsorption losses can be minimised by sampling into acid, and by carrying out analysis at a pH below 2.5.

4.1.4 Long contact time study for a  $10 \text{ mg dm}^{-3}$  silver solution at pH 2.3 and 298 K

The results from the previous experiments indicated a reduction in the amount of silver adsorbed, due to lowering the pH, after 7 days contact. They did not, however, indicate whether this was due to a reduction in the rate of adsorption of silver, or simply a selected adsorption of hydrogen ions preventing any further uptake of silver. The following experiment was designed to clarify the situation.

A  $10 \text{ mg dm}^{-3}$  silver solution was selected in order to improve the sensitivity of the technique when using solutions of low pH values.

In order to be consistent with the previous experiment a pH of 2.3 was chosen. The vials were prepared in the manner described in section 3.3.2. In all, six vials were prepared, and duplicates were removed for washing and counting after 4, 7 and 14 days.

Table 4.4 Adsorption at pH 2.3 and 298 K from a  $10 \text{ mg dm}^{-3}$  silver solution

| Vial No | Contact Time/ days | Corrected Count Rate 'IN'/c.p.m. | Corrected Count Rate 'OUT'/c.p.m. | Ag Adsorbed/<br>$\text{mg cm}^{-2} \times 10^6$ | Relative Standard Deviation/% |
|---------|--------------------|----------------------------------|-----------------------------------|---|-------------------------------|
| 1       | 4                  | 6348                             | 9.4                               | 4.9   | 13.2                          |
| 2       | 4                  | 6295                             | 6.7                               | 3.5   | 18.4                          |
| 3       | 7                  | 6779                             | 15.5                              | 7.6   | 8.2                           |
| 4       | 7                  | 6458                             | 8.2                               | 4.2   | 14.9                          |
| 5       | 14                 | 5524                             | 5.6                               | 3.3   | 27.0                          |
| 6       | 14                 | 5293                             | 8.0                               | 5.0   | 19.1                          |

In all probability these results show that no further adsorption of silver occurs between 4 and 14 days at pH 2.3, thus indicating that the rate of adsorption of silver has not simply been reduced. However, the reliability of the results may be in doubt due to the standard deviation associated with the count rates 'OUT'.

It is interesting to note that the 7 day contact results were in good agreement with those reported in 4.1.2.

#### 4.2 Adsorption of silver ions from solutions at pH values greater than 6

In order to adjust the pH of the solutions to 6 and above a sodium hydroxide solution was used. It was realised that the addition of another cation, namely  $\text{Na}^+$ , could affect the adsorption process, therefore, preliminary experiments concerning the effect of  $\text{Na}^+$  were carried out.

##### 4.2.1 The effect of sodium ions on the adsorption of silver from a $10 \text{ mg dm}^{-3}$ silver solution on soda-glass at 298 K and a pH of 5.6

The glass vials were pre-washed as described in 3.3.2, an aliquot of sodium nitrate solution was added to each vial, followed by  $3 \text{ cm}^3$  of  $10 \text{ mg dm}^{-3}$  labelled silver nitrate solution. The concentrations of sodium nitrate used were of the same order as the hydrogen ion concentrations used in 4.1.2, so that a direct comparison between the relative effects of  $\text{H}^+$  and  $\text{Na}^+$  on the adsorption process could be made. In order to ensure identical contact areas in all vials, the aliquot of sodium nitrate was kept

constant at  $0.1 \text{ cm}^3$ .

The vials were sealed, wrapped in foil to exclude light, and immersed in a water-bath for 7 days contact at 298 K. At the end of this period the vials were removed and washed as described in 3.3.4, and counted as described in 3.3.5.

Table 4.5 Adsorption from a  $10 \text{ mg dm}^{-3}$  silver solution in the presence of sodium ions at 298 K

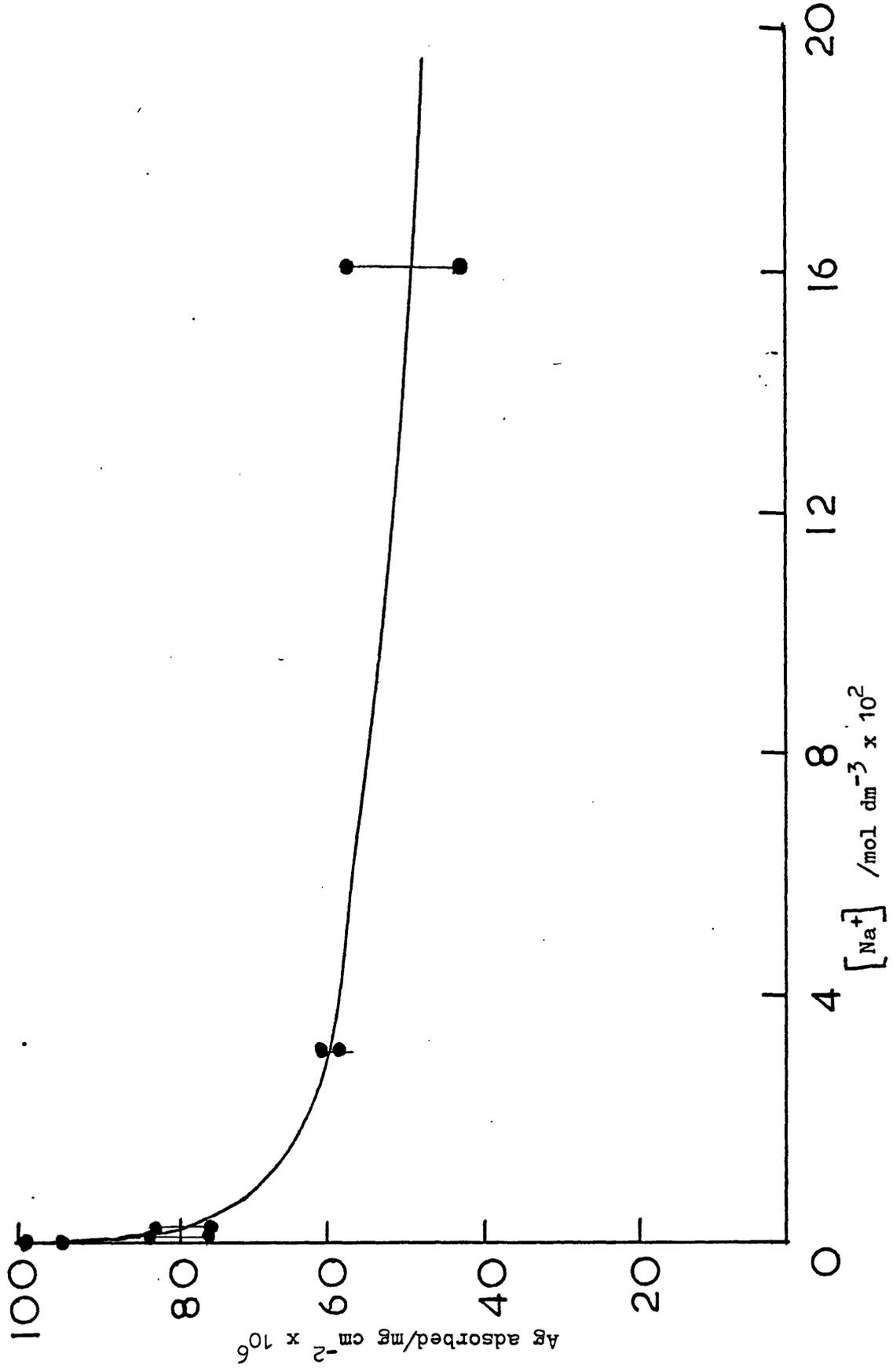
| Vial No | $[\text{Na}^+]$<br>$\text{mol dm}^{-3}$ | Corrected<br>Count Rate<br>'IN'/c.p.m. | Corrected<br>Count Rate<br>'OUT'/c.p.m. | Fraction<br>Ag<br>adsorbed | Ag<br>adsorbed/<br>$\text{mg cm}^{-2} \times 10^6$ |
|---------|---|--|---|----------------------------|--|
| 1       | 0                                       | 12637                                  | 377                                     | 0.0298                     | 99.4   |
| 2       | 0                                       | 12432                                  | 349                                     | 0.0281                     | 94.8   |
| 3       | 0.000323                                | 12450                                  | 283                                     | 0.0227                     | 75.7   |
| 4       | 0.000323                                | 11950                                  | 299                                     | 0.0250                     | 83.3   |
| 5       | 0.001613                                | 11974                                  | 297                                     | 0.0248                     | 82.5   |
| 6       | 0.001613                                | 12271                                  | 281                                     | 0.0229                     | 75.3   |
| 7       | 0.003226                                | 12270                                  | 309                                     | 0.0252                     | 83.8   |
| 8       | 0.003226                                | 12487                                  | 298                                     | 0.0239                     | 79.4   |
| 9       | 0.032258                                | 12402                                  | 227                                     | 0.0183                     | 60.9   |
| 10      | 0.032258                                | 12507                                  | 221                                     | 0.0177                     | 58.9   |
| 11      | 0.161290                                | 12851                                  | 223                                     | 0.0174                     | 57.7   |
| 12      | 0.161290                                | 12239                                  | 156                                     | 0.0127                     | 42.5   |

The results are plotted in Figure 4.4

Figure 4.4 shows that there is an initial rapid drop in the silver adsorption with an increase in the  $\text{Na}^+$  concentration. However, once a sodium ion concentration of  $400 \times 10^{-4} \text{ mol dm}^{-3}$  is exceeded, any further increase has no significant effect on the amount of silver adsorbed.

These results confirm that nitric acid is a much more effective inhibitor of silver adsorption than sodium nitrate. However, it was felt that this experiment should be repeated at a different initial silver concentration to confirm this general behaviour.

FIG. 4.4. Graph of silver adsorption from a  $10 \text{ mg dm}^{-3}$  silver solution, against sodium ion concentration after 7-days contact at 298 K.



4.2.2. The effect of sodium ions on the adsorption of silver from a  $0.5 \text{ mg dm}^{-3}$  solution at 298 K and a pH of 5.6

The experimental procedure was identical to that described in 4.2.1 except for the different silver concentration. The results are given in table 4.6.

Table 4.6

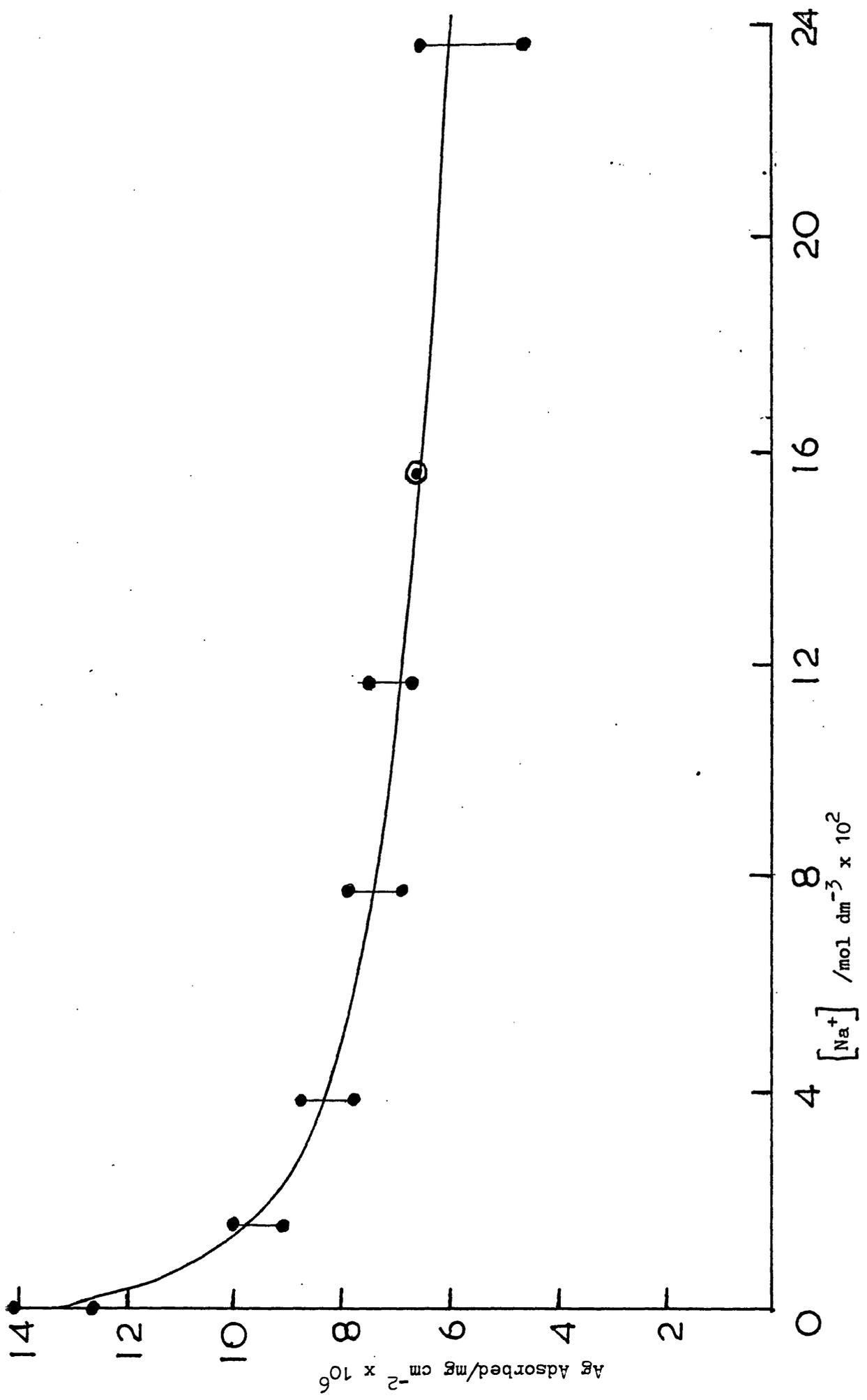
| Vial No | $[\text{Na}^+]$<br>$/\text{mol dm}^{-3}$ | Corrected<br>Count Rate<br>'IN'/c.p.m. | Corrected<br>Count Rate<br>'OUT'/c.p.m. | Fraction<br>Ag<br>adsorbed | Ag<br>adsorbed<br>$/\text{mg cm}^{-2} \times 10^6$ |
|---------|--|--|---|----------------------------|--|
| 1       | 0  | 11066                                  | 895                                     | 0.0809                     | 12.6   |
| 2       | 0  | 11234                                  | 1010                                    | 0.0899                     | 14.0   |
| 3       | 0.015625                                 | 11210                                  | 723                                     | 0.0645                     | 10.0   |
| 4       | 0.015625                                 | 11234                                  | 659                                     | 0.0587                     | 9.1  |
| 5       | 0.039063                                 | 11270                                  | 568                                     | 0.0504                     | 7.8  |
| 6       | 0.039063                                 | 11231                                  | 635                                     | 0.0565                     | 8.8  |
| 7       | 0.078125                                 | 11337                                  | 506                                     | 0.0446                     | 6.9  |
| 8       | 0.078125                                 | 10994                                  | 566                                     | 0.0515                     | 8.0  |
| 9       | 0.117188                                 | 11285                                  | 485                                     | 0.0430                     | 6.7  |
| 10      | 0.117188                                 | 11165                                  | 545                                     | 0.0488                     | 7.6  |
| 11      | 0.156250                                 | 11953                                  | 507                                     | 0.0424                     | 6.6  |
| 12      | 0.156250                                 | 11344                                  | 477                                     | 0.0420                     | 6.5  |
| 13      | 0.234375                                 | 11958                                  | 512                                     | 0.0428                     | 6.6  |
| 14      | 0.234375                                 | 11133                                  | 334                                     | 0.0300                     | 4.6  |

The results are plotted in Figure 4.5.

The curve in Figure 4.5 shows the same profile as that observed in Figure 4.4, thus confirming that sodium ions do not reduce the silver adsorption as effectively as hydrogen ions.

Furthermore the curves in Figures 4.4 and 4.5 indicate that the effect of sodium ions became constant at the same concentration of sodium, namely  $400 \times 10^{-4} \text{ mol dm}^{-3}$ . Hence the effect of added sodium ions is

FIG. 4.5. Graph of silver adsorption from a  $0.5 \text{ mg dm}^{-3}$  silver solution, against sodium ion concentration after 7-days contact at 298 K.



independent of the silver concentration. A similar conclusion was indicated for nitric acid by assessment of the curves in Figures 4.1, 4.2 and 4.3.

For both  $10 \text{ mg dm}^{-3}$  and  $0.5 \text{ mg dm}^{-3}$  silver solutions, sodium nitrate only reduced the silver adsorbed by a maximum of 50% whereas nitric acid reduced the adsorption by 90%.

Having evaluated the effect of added sodium ions it was now possible to carry out a meaningful study of silver adsorption at high pH values.

#### 4.2.3 Adsorption of silver from a $10 \text{ mg dm}^{-3}$ solution for a range of pH values greater than 5.6 at 298 K.

The glass vials were pre-washed as described in 3.3.2, a  $0.1 \text{ cm}^3$  aliquot of sodium hydroxide was added to each vial, followed by  $3 \text{ cm}^3$  of the  $10 \text{ mg dm}^{-3}$  labelled silver nitrate solution. The concentration of the sodium hydroxide solution was varied to produce a set of vials with a pH range from 5.6 to 13.5. The vials were sealed, wrapped in foil and transferred to a thermostat-bath at 298 K for a period of 7 days. They were then removed and counted as described in 3.3.4 and 3.3.5.

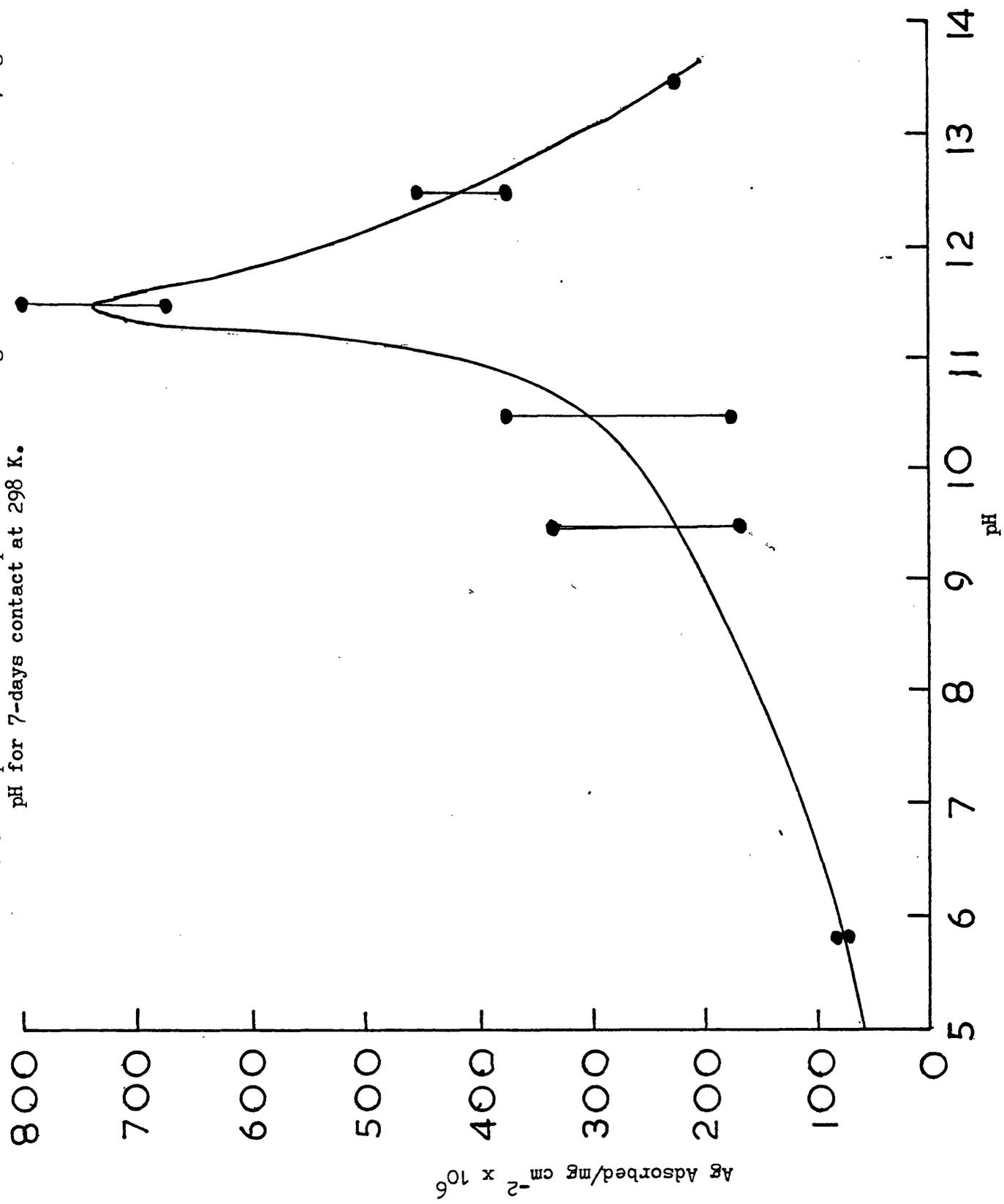
Table 4.7 The pH dependence of adsorption from a  $10 \text{ mg dm}^{-3}$  silver solution at 298 K

| Vial No | pH   | $[\text{OH}^-]$<br>/mol $\text{dm}^{-3}$ | Corrected<br>Count Rate<br>'IN'/c.p.m. | Corrected<br>Count Rate<br>'OUT'/c.p.m. | Fraction<br>Ag<br>adsorbed | Ag<br>adsorbed<br>/mg $\text{cm}^{-2} \times 10^6$ |
|---------|------|--|--|---|----------------------------|--|
| 1       | 5.6  | negligible                               | 6912                                   | 143                                     | 0.0207                     | 68.9   |
| 2       | 5.6  | "  | 6893                                   | 168                                     | 0.0244                     | 75.8   |
| 3       | 9.5  | 0.00003226                               | 7025                                   | 706                                     | 0.1005                     | 334.8  |
| 4       | 9.5  | 0.00003226                               | 6867                                   | 342                                     | 0.0498                     | 166.1  |
| 5       | 10.5 | 0.0003226                                | 6879                                   | 352                                     | 0.0512                     | 170.3  |
| 6       | 10.5 | 0.0003226                                | 6706                                   | 757                                     | 0.1129                     | 376.4  |
| 7       | 11.5 | 0.0032260                                | 7681                                   | 1552                                    | 0.2021                     | 673.4  |
| 8       | 11.5 | 0.0032260                                | 6993                                   | 1675                                    | 0.2395                     | 798.2  |
| 9       | 12.5 | 0.0322600                                | 6990                                   | 785                                     | 0.1123                     | 374.3  |
| 10      | 12.5 | 0.0322600                                | 7325                                   | 988                                     | 0.1349                     | 449.6  |
| 11      | 13.5 | 0.322600                                 | 7167                                   | 484                                     | 0.0675                     | 225.1  |

A slight cloudiness was observed in vials 7 to 11, the cloudiness had disappeared on standing overnight.

The results are plotted in Figure 4.6.

FIG. 4.6. Graph of silver adsorption from a  $10 \text{ mg dm}^{-3}$  silver solution, against pH for 7-days contact at 298 K.



The curve in Figure 4.6 shows that the amount of silver adsorbed, increases slowly as the pH value is raised from 5.6 to 10.5, then there is a sharp increase showing a maximum at pH value 11.5. On further increasing the pH there is a rapid decrease in the amount of silver adsorbed. This adsorption maximum has been observed in previous adsorption studies carried out by Benes and Garba (7) on the manganese ion.

It was shown in 4.2.2 that sodium ions significantly reduced the amount of silver adsorbed. However, increasing the pH by addition of sodium hydroxide has greatly increased the amount of silver adsorbed, this indicates that the adsorption process is influenced more by the hydroxide ions, than the sodium ions.

Following are three possible mechanisms which could explain this behaviour.

- (a) The hydroxide ions may be adsorbed by the glass thus providing negatively charged sites that would increase the silver adsorption by coulombic attraction.
- (b) The hydroxide ions may react with the glass surface to increase the micro surface area by a factor many times greater than the geometric surface area available, or
- (c) The hydroxide ion may react with the silver solution to produce a number of silver species which adsorb to different degrees.

#### 4.2.4 The effect of pre-soaking glass vials in sodium hydroxide solutions

The following experiment was designed to test mechanism (b) for enhanced adsorption, and involves soaking the glass vials in a series of sodium hydroxide solutions.

The glass vials were pre-soaked in sodium hydroxide solutions ranging from pH 7 to 14 for 7 days at 298 K. The vials were then washed five times using doubly deionised water, until the washings did not discolour pH paper.

Then 3 cm<sup>3</sup> of the 10 mg dm<sup>-3</sup> labelled silver solution at pH 5.6, was added to each vial. The vials were sealed, wrapped in foil and placed in a

thermostat-bath at 298 K for 7 days. After this contact time the vials were removed and counted as described in 3.3.4 and 3.3.5.

Table 4.8 Adsorption from a  $10 \text{ mg dm}^{-3}$  silver solution on to vials pre-soaked in sodium hydroxide solutions

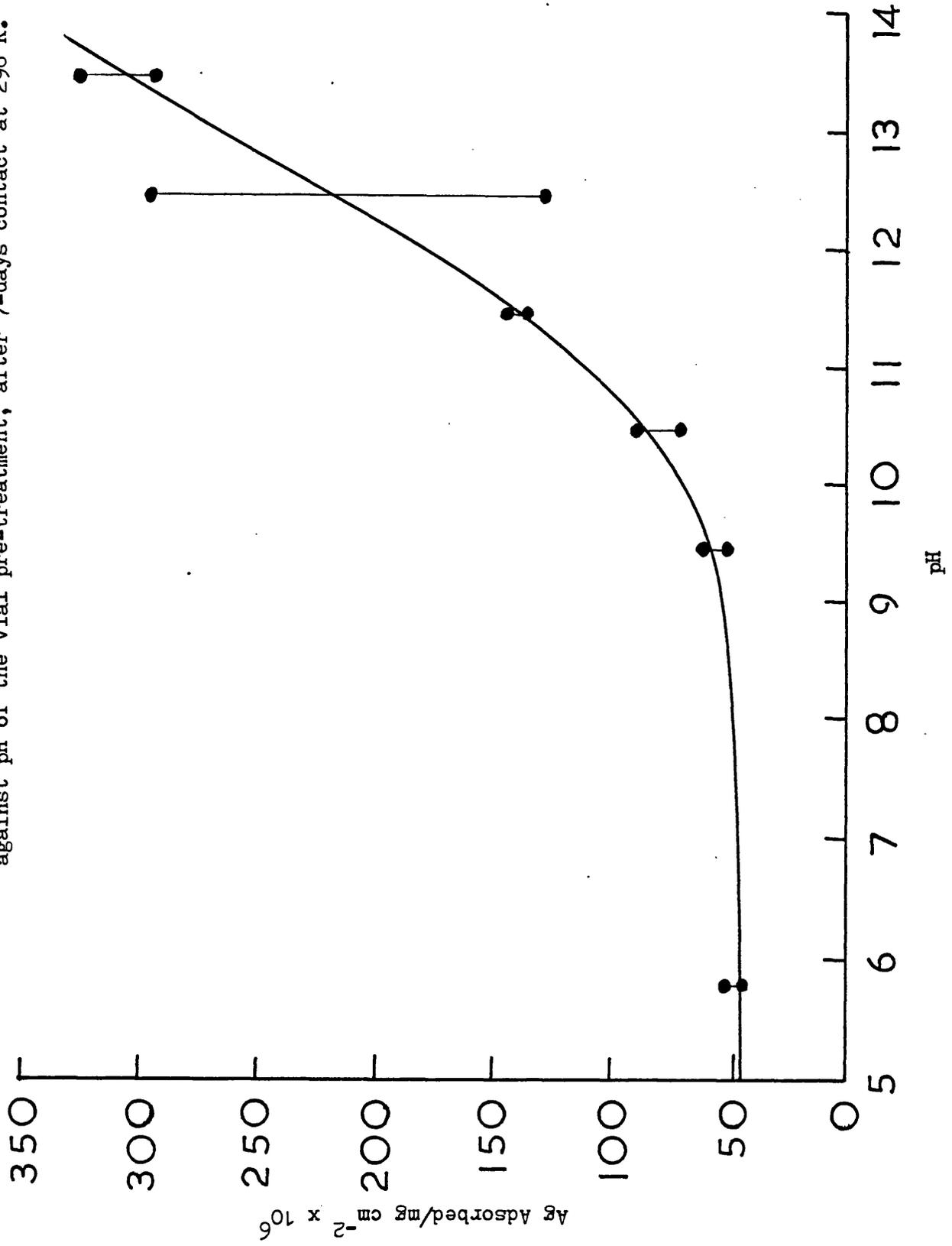
| Vial No | Pre-treatment pH | Corrected Count Rate 'IN'/c.p.m. | Corrected Count Rate 'OUT'/c.p.m. | Fraction Ag adsorbed | Ag adsorbed /mg cm <sup>-2</sup> x 10 <sup>6</sup> |
|---------|------------------|----------------------------------|-----------------------------------|----------------------|--|
| 1       | 5.6              | 4384                             | 66                                | 0.0151               | 50.1   |
| 2       | 5.6              | 4571                             | 66                                | 0.0144               | 48.1   |
| 3       | 9.5              | 4505                             | 81                                | 0.0180               | 59.9   |
| 4       | 9.5              | 4505                             | 68                                | 0.0151               | 50.3   |
| 5       | 10.5             | 4393                             | 115                               | 0.0262               | 87.2   |
| 6       | 10.5             | 4443                             | 94                                | 0.0212               | 70.5   |
| 7       | 11.5             | 4358                             | 185                               | 0.0425               | 141.5  |
| 8       | 11.5             | 4490                             | 195                               | 0.0434               | 144.7  |
| 9       | 12.5             | 4446                             | 171                               | 0.0385               | 128.2  |
| 10      | 12.5             | 4419                             | 393                               | 0.0889               | 296.4  |
| 11      | 13.5             | 4302                             | 421                               | 0.0979               | 326.2  |
| 12      | 13.5             | 4377                             | 387                               | 0.0884               | 294.7  |

The results are plotted in Figure 4.7

The profile of Figure 4.7 is very similar to that of Figure 4.6, in that there is a steep rise in the amount of silver adsorbed on the vials pre-treated with sodium hydroxide solutions of pH greater than 9.5. The amount of silver adsorbed does not, however, reach a peak and then fall as in Figure 4.6, instead the amount adsorbed continues to rise but the maximum reached is only half that observed in Figure 4.6.

The results from experiments 4.2.3 and 4.2.4 are evidence for the observed increase in silver adsorption between pH 5.6 and 11.5 being due to

FIG. 4.7. Graph of silver adsorption from a  $10 \text{ mg dm}^{-3}$  silver solution against pH of the vial pre-treatment, after 7-days contact at 298 K.



the effect of hydroxide ions etching the glass surface. At pH values greater than 11.5 other silver species may well be formed which could greatly reduce the amount of silver adsorbed. Some of these species could be colloidal, as in fact turbidity was observed at high pH values. (Table 4.7 vials 7-11).

This possibility is discussed in more detail in a later chapter.

The following curve in Figure 4.8 is a composite of Figures 4.2 and 4.6, to show the pH dependence over the whole pH range. It is interesting to note that figure 4.8 produces a smooth curve where both experiments overlap.

#### 4.2.5 The adsorption of silver in the presence of other cation species

In previous sections we have observed and commented on the effect of  $H^+$  and  $Na^+$  on the silver adsorption process. This work proved to be most interesting, and it was therefore decided to expand this somewhat to look at the effect of a divalent, and a trivalent cation. The cations chosen were  $Cd^{2+}$  and  $Al^{3+}$ , these ions were convenient as both their nitrate salts were very soluble in D.D.  $H_2O$ . The effects of  $H^+$ ,  $Na^+$ ,  $Cd^{2+}$  and  $Al^{3+}$  are compared to see whether any obvious trends emerge.

Twelve vials were washed as described in section 3.3.2. A  $3\text{ cm}^3$  aliquot of  $0.5\text{ mg dm}^{-3}$  labelled silver solution was added to each. Then a  $0.1\text{ cm}^3$  aliquot of cadmium nitrate solution was added to each vial. The concentration of the cadmium aliquot was varied to produce a set of vials containing a range of cadmium to silver ratios. The vials were then sealed, wrapped in foil and immersed in a thermostat-bath at 298 K. After 7 days the vials were removed from the thermostat-bath for washing and counting in the usual manner.

A similar set of vials were prepared but substituting the cadmium solutions by  $0.2\text{ cm}^3$  aliquots of aluminium nitrate solutions. The results in Table 4.9. show the dependence of silver adsorption on the concentration of additional cations competing for adsorption sites. In this table there are also included results from Tables 4.3 and 4.6, so that we can also discuss

FIG. 4.8. Graph of silver adsorption from a  $10 \text{ mg dm}^{-3}$  silver solution, against pH, for 7-days contact at 298 K.

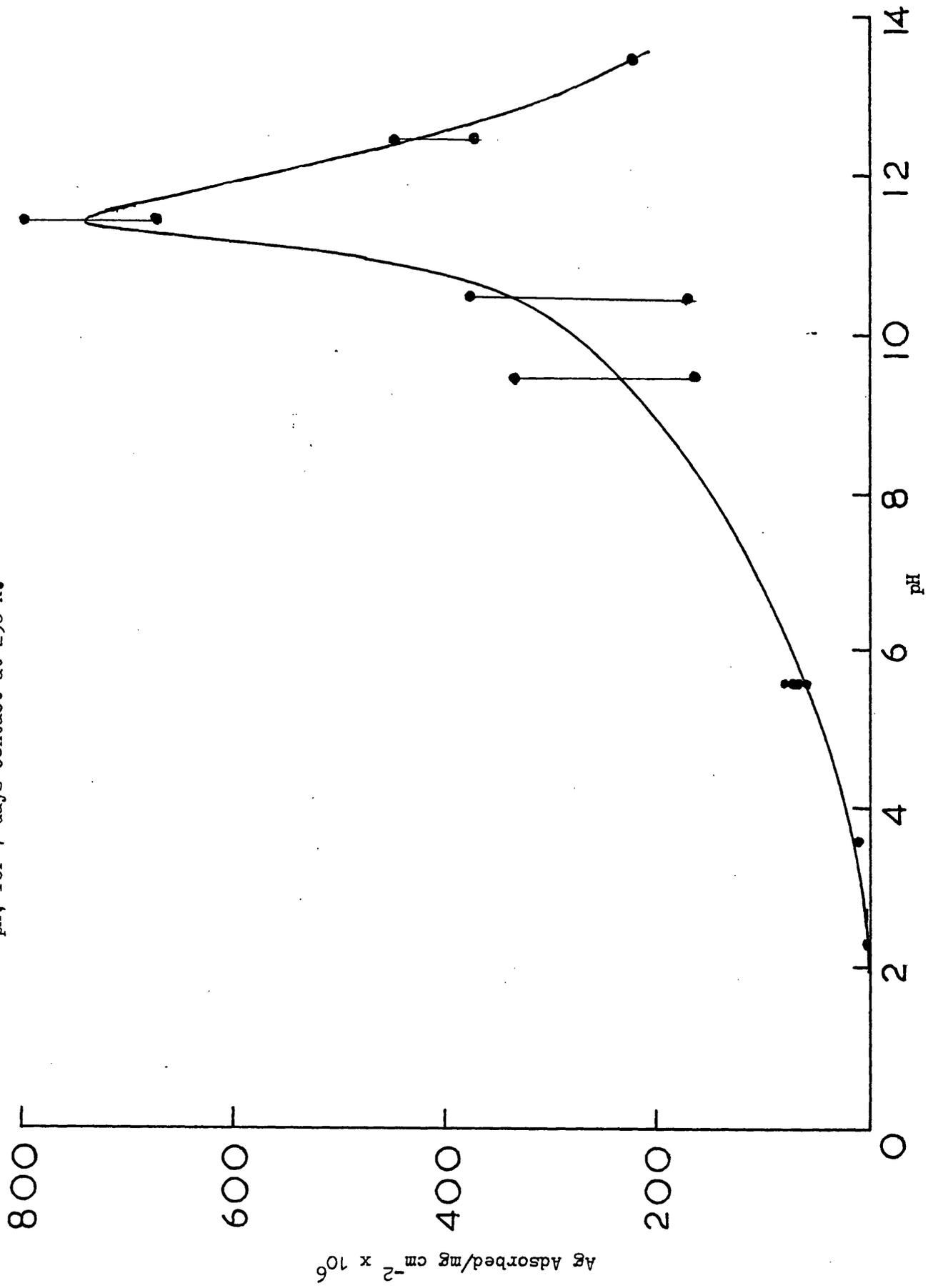
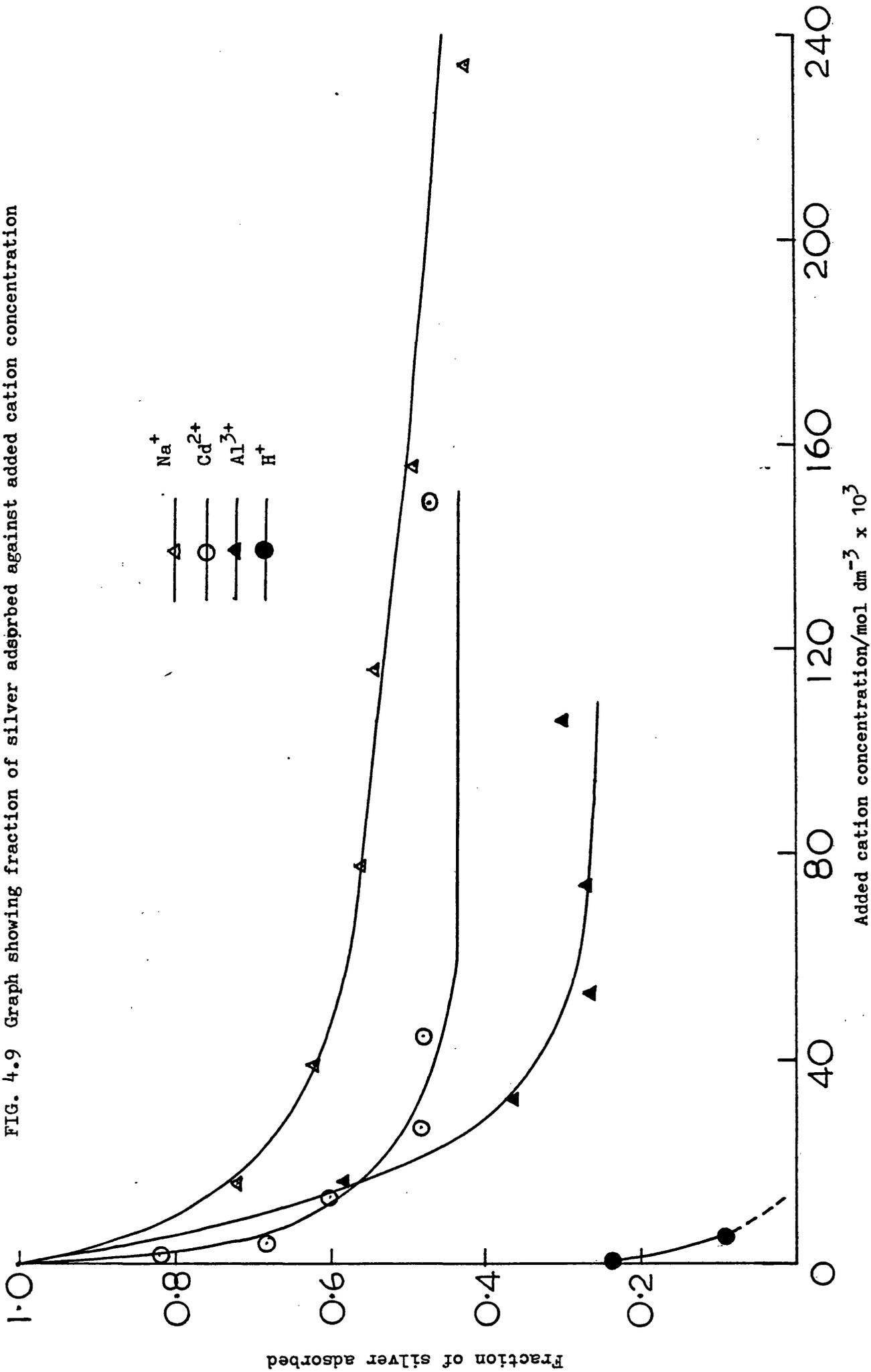


Table 4.9 The effect of added cations on the adsorption of silver

| $[Cd^{2+}]$<br>/mol dm <sup>-3</sup> x 10 <sup>3</sup> | Fraction<br>Ag<br>adsorbed | $[Al^{3+}]$<br>/mol dm <sup>-3</sup> x 10 <sup>3</sup> | Fraction<br>Ag<br>adsorbed | $[Na^+]$<br>/mol dm <sup>-3</sup> x 10 <sup>3</sup> | Fraction<br>Ag<br>adsorbed | $[H^+]$<br>/mol dm <sup>-3</sup> x 10 <sup>3</sup> | Fraction<br>Ag<br>adsorbed |
|--|----------------------------|--|----------------------------|---|----------------------------|--|----------------------------|
| -  | 1.00                       | -  | 1.00                       | -   | 1.0                        | negligible   | 1.0                        |
| -  | 1.00                       | -  | 1.00                       | -   | 1.0                        | "  | 1.0                        |
| 2.234  | 0.82                       | 15.872   | 0.58                       | 15.617  | 0.72                       | 0.48   | 0.23                       |
| 2.234  | 0.82                       | 15.872   | 0.58                       | 15.617  | 0.72                       | 0.48   | 0.23                       |
| 4.459  | 0.68                       | 31.781   | 0.36                       | 39.063  | 0.62                       | 4.76   | 0.09                       |
| 4.459  | 0.68                       | 31.781   | 0.36                       | 39.063  | 0.62                       | 4.76   | 0.09                       |
| 13.386   | 0.60                       | 52.951   | 0.26                       | 78.170  | 0.56                       | 47.62  | -                          |
| 13.386   | 0.60                       | 52.951   | 0.26                       | 78.170  | 0.56                       | 47.62  | -                          |
| 26.780   | 0.48                       | 74.149   | 0.27                       | 117.233   | 0.54                       | 476.20   | -                          |
| 26.780   | 0.48                       | 74.149   | 0.27                       | 117.233   | 0.54                       | 476.20   | -                          |
| 44.634   | 0.48                       | 105.937  | 0.30                       | 156.339   | 0.49                       | 761.90   | -                          |
| 44.634   | 0.48                       | 105.937  | 0.30                       | 156.339   | 0.49                       | 761.90   | -                          |
| 148.774  | 0.48                       | -  | -                          | 234.509   | 0.42                       | -  | -                          |
| -  | -                          | -  | -                          | 234.509   | 0.42                       | -  | -                          |

The results in the above table are represented by the curves in Figure 4.9

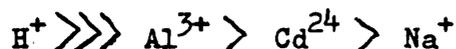
FIG. 4.9 Graph showing fraction of silver adsorbed against added cation concentration



the comparative effects of  $H^+$  and  $Na^+$  with those for  $Cd^{2+}$  and  $Al^{3+}$ .

The results are shown in Table 4.9, taking zero added cations as unity then expressing the adsorption as the fraction of silver adsorbed for each added cation concentration. Each experiment was carried out in duplicate and the fraction adsorbed was calculated from the average of the two adsorption values.

It can be seen from Figure 4.9 that the addition of other cations has reduced the amount of silver adsorbed, and the following trend showing their effectiveness as silver adsorption inhibitors can be seen :-



It is interesting to note that the ionic mobilities of these elements are as follows (21).

| Cation    | $m^2 S^{-1} V^{-1} \times 10^8$ |   |
|-----------|---------------------------------|---|
| $Ag^+$    | 6.41658                         | Calculated from $\lambda = FzU$                           |
| $H^+$     | 36.25380                        | Where $\lambda$ = ionic conductivity at infinite dilution |
| $Al^{3+}$ | 6.52849                         | F = Faradays' number                                      |
| $Cd^{2+}$ | 5.59585                         | Z = ion charge  |
| $Na^+$    | 5.19689                         | U = ionic mobility  |

If we assume that the additional cations are competing with silver for adsorption sites, then it is also reasonable to propose that their competitiveness is partially dependent upon their respective ionic mobilities. This is verified to some extent by the table above, which shows that the ionic mobility values decrease in the same order as their effectiveness as silver adsorption inhibitors. It is also interesting to note that their effectiveness also decreases with ionic charge, which agrees with Ichikawa and Sato's (8) claim that ions of smaller charge are adsorbed less effectively.

#### 4.3 The desorption of silver from soda-glass

The following section is concerned with the removal of adsorbed silver from soda-glass, this is of particular importance in the cleaning of laboratory glassware, and also the improvement of analytical technique.

The experiments described in 4.1 have shown that silver adsorption is greatly reduced at low pH values, it was therefore concluded that the use of nitric acid solution for the removal of adsorbed silver should be investigated.

#### 4.3.1 Removal of adsorbed silver by nitric acid solution

The vials were pre-washed as described in 3.3.2, then  $3 \text{ cm}^3$  of labelled  $1 \text{ mg dm}^{-3}$  silver nitrate solution was added to each vial. The vials were sealed, wrapped in foil and immersed in a thermostat-bath at 298 K for 7 days.

At the end of the 7 day contact period the vials were removed and two of them were counted as described in 3.3.4 and 3.3.5, to establish how much silver had been adsorbed. A  $0.1 \text{ cm}^3$  aliquot of concentrated nitric acid was added to the remaining vials, to reduce the pH to less than 1.

The vials were re-sealed and returned to the thermostat-bath, then removed at increasing contact times and counted as described in 3.3.4 and 3.3.5.

The results are shown in Table 4.10.

It can be seen from Figure 4.10 that the desorption of silver is rapid up to one hour contact, after this time 50% of the adsorbed silver has been removed. However, after one day contact with the acid, 30% of the adsorbed silver was still attached to the glass, and after eight days there was 15% of the adsorbed silver remaining.

It is suggested that desorption takes place because of an exchange between silver ions, and hydrogen ions in solution. However, this experiment does not show true desorption, but competitive adsorption and desorption because both silver and hydrogen ions were simultaneously present in the solution. Hence it was decided to repeat the experiment, but to remove the labelled silver nitrate solution prior to the addition of the nitric acid.

#### 4.3.2 A study of silver desorption from soda-glass in contact with nitric acid at 298 K

The vials were pre-washed as described in 3.3.2, then  $3 \text{ cm}^3$  of  $1 \text{ mg dm}^{-3}$  labelled silver nitrate solution was added to each vial. The vials

Table 4.10 Competitive adsorption and desorption of silver under acid conditions using  $1 \text{ mg dm}^{-3}$

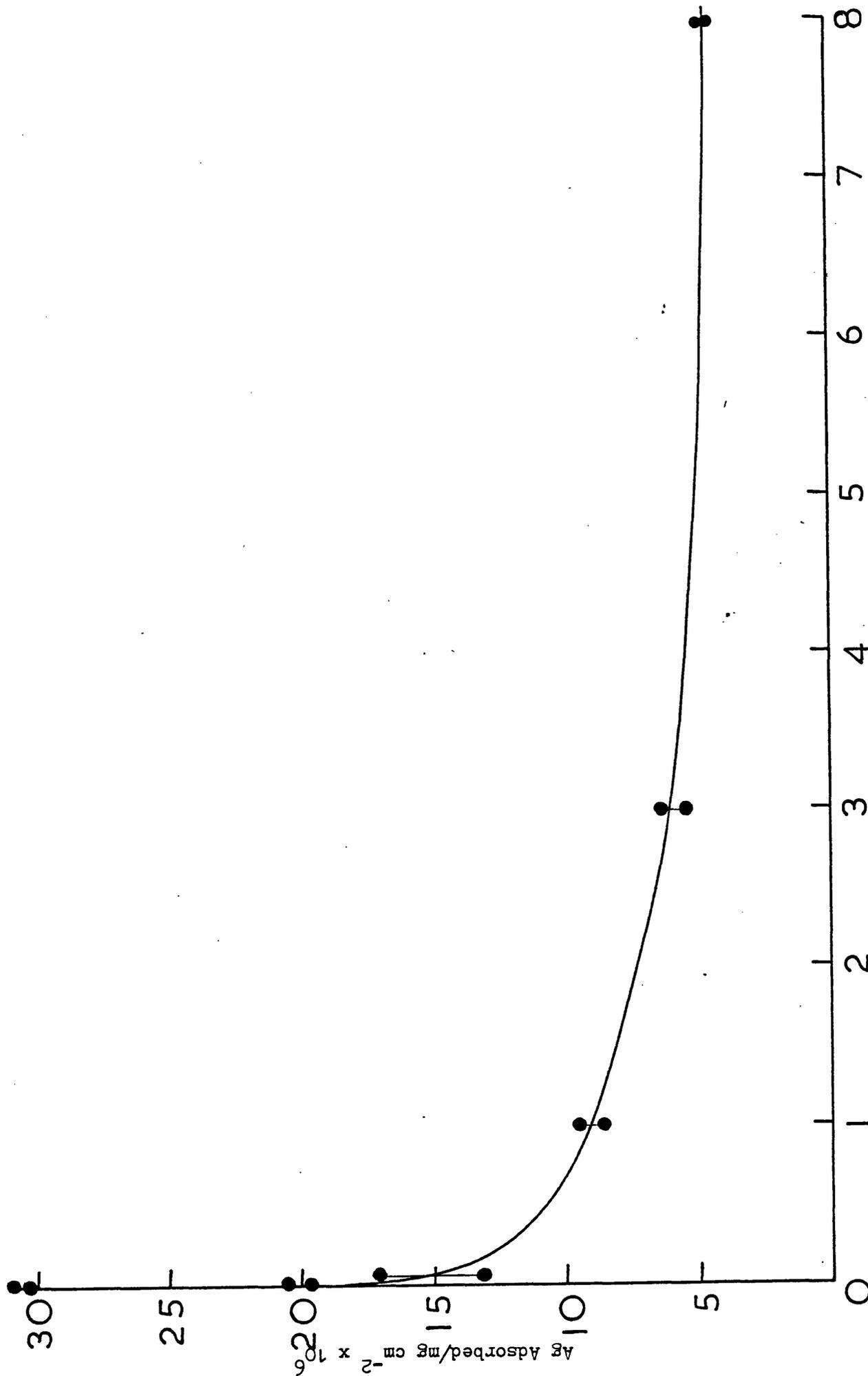
silver solution at 298 K, after 7 days contact

| Vial No. | Acid Contact Time /hours | Corrected Count IN/c.p.m. | Corrected Count OUT/c.p.m. | Fraction Ag adsorbed | Ag adsorbed /mg $\text{cm}^{-2} \times 10^6$ | Ag desorbed /mg $\text{cm}^{-2} \times 10^6$ | % Ag desorbed |
|----------|--------------------------|---------------------------|----------------------------|----------------------|--|--|---------------|
| 1        | Zero                     | 89336                     | 8301                       | 0.0929               | 30.9   | -  | 0             |
| 2        | Zero                     | 88944                     | 8106                       | 0.0911               | 30.3   | -  | 0             |
| 3        | $3.336 \times 10^{-2}$   | 89090                     | 5470                       | 0.0614               | 20.4   | 10.2   | 33            |
| 4        | $3.336 \times 10^{-2}$   | 89191                     | 5242                       | 0.0588               | 19.5   | 11.1   | 36            |
| 5        | 1.0                      | 87685                     | 3451                       | 0.0394               | 13.1   | 17.5   | 57            |
| 6        | 1.0                      | 88193                     | 4532                       | 0.0514               | 17.1   | 13.5   | 44            |
| 7        | 24.0                     | 83646                     | 2183                       | 0.0261               | 8.6  | 22.0   | 72            |
| 8        | 24.0                     | 82046                     | 2319                       | 0.0283               | 9.4  | 21.2   | 69            |
| 9        | 72.0                     | 82274                     | 1347                       | 0.0164               | 5.4  | 25.2   | 82            |
| 10       | 72.0                     | 83913                     | 1565                       | 0.0187               | 6.2  | 24.4   | 80            |
| 11       | 192.0                    | 81093                     | 1151                       | 0.0142               | 4.7  | 25.9   | 85            |
| 12       | 192.0                    | 82569                     | 1129                       | 0.0137               | 4.5  | 26.1   | 85            |

The amount of silver desorbed was calculated assuming an average initial adsorption of  $30.6 \text{ mg cm}^{-2} \times 10^6$ .

The results are plotted in Figure 4.10

FIG.4.10 Graph showing the competitive adsorption and desorption of silver under acid conditions, from vials containing adsorbed silver.



were sealed, wrapped in foil and immersed in a thermostat-bath for 7 days at 298 K.

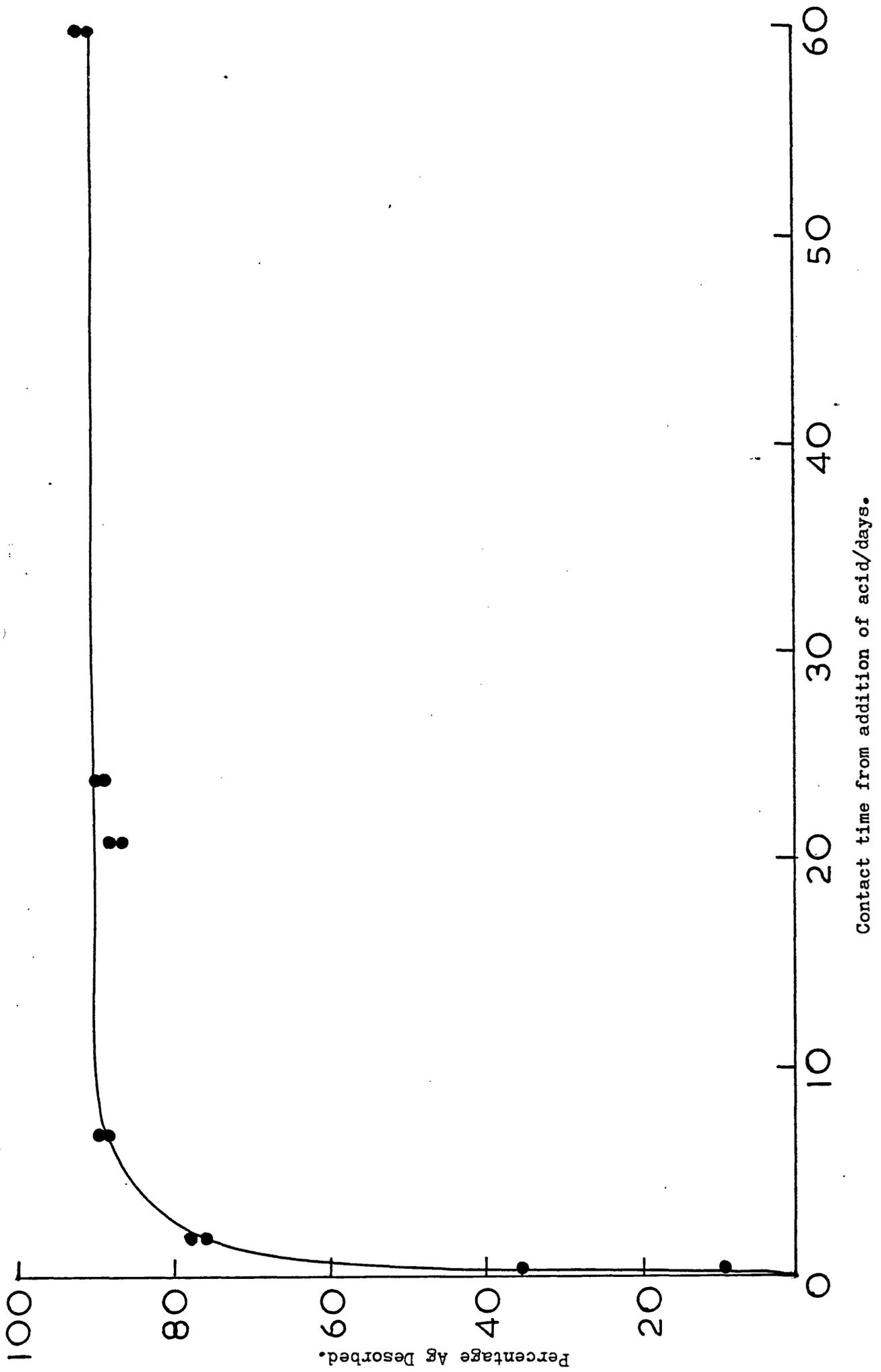
After this contact period the vials were removed from the thermostat-bath, washed, and counted as described in 3.3.4 and 3.3.5. A  $3.2 \text{ cm}^3$  aliquot of 1.0 molar nitric acid was added to each vial to provide a pH of less than 0.1 as in 4.3.1, and to effect complete coverage of the surface previously in contact with the labelled silver nitrate solution. The vials were re-sealed, wrapped in foil and returned to the thermostat-bath at 298 K. The vials were then removed from the thermostat-bath at a series of contact times, washed and counted in the usual manner.

Table 4.11 The desorption of silver under acid conditions after 7 days contact with a  $1 \text{ mg dm}^{-3}$  silver solution at 298 K

| Vial No | Initial Ag adsorbed / $\text{mg cm}^{-2} \times 10^6$ | Acid Contact Time/days | Final Ag adsorbed / $\text{mg cm}^{-2} \times 10^6$ | Ag desorbed % |
|---------|---|------------------------|---|---------------|
| 1       | 22.0  | $4.167 \times 10^{-2}$ | 20.0  | 9.1           |
| 2       | 27.1  | $4.167 \times 10^{-2}$ | 17.5  | 35.4          |
| 3       | 27.6  | 2.000                  | 6.6   | 76.1          |
| 4       | 28.4  | 2.000                  | 6.3   | 77.8          |
| 5       | 27.4  | 7.000                  | 2.9   | 89.4          |
| 6       | 32.7  | 7.000                  | 3.8   | 88.4          |
| 7       | 26.1  | 21.000                 | 3.5   | 86.6          |
| 8       | 20.5  | 21.000                 | 2.5   | 87.8          |
| 9       | 21.0  | 24.000                 | 2.3   | 89.0          |
| 10      | 19.9  | 24.000                 | 2.1   | 89.5          |
| 11      | 20.5  | 60.000                 | 1.9   | 90.7          |
| 12      | 20.8  | 60.000                 | 1.6   | 92.3          |

The vials removed after 24 days contact time were washed and counted then further soaked in 1.0 molar nitric acid for 5 minutes. Then the vials were washed and counted as described previously, no significant amounts of

FIG. 4.11 Graph of silver desorption against contact time under acid conditions at 298 K.



silver were removed after this additional treatment. This was carried out to establish whether fresh nitric acid solution, containing no desorbed silver ions, would remove any more adsorbed silver.

The results above are plotted in Figure 4.11.

These results confirm the rapid initial desorption observed in 4.3.1 and also the slower desorption process up to 7 days and longer. The percentage desorption observed after 7 days is almost identical to that shown in 4.3.1. This indicates that the displacement of silver ions by hydrogen ions is not affected by small amounts of silver ions in solution.

This desorption process shows that prolonged soaking of glassware in nitric acid may still leave it containing adsorbed silver, and possibly, other cations on the glass surface. If this glassware is then used for other analytical work, the solutions could become contaminated if the remaining silver continues to desorb.

It would also appear that if water samples are taken into glassware on site, for subsequent analysis in the laboratory, then all the adsorbed silver would not be removed from the glass by subsequent additions of acid. It is, therefore, suggested that any samples should be taken into glassware already containing acid solution, thus minimising adsorption losses, shown in 4.1.1, 2 and 3.

The experiments carried out in this section have been concerned with soda-glass vials, it was, therefore, decided to design an experiment to study adsorption losses on graduated laboratory glassware, which is predominantly borosilicate glass. This experiment has been included in this section because the adsorption losses were detected using a nitric acid desorption technique.

#### 4.3.3 A study of silver adsorption on a borosilicate graduated flask at 298 K

A previously unused 250 cm<sup>3</sup> graduated flask was washed three times in doubly deionised water. The flask was drained and then filled with a 0.5 mg dm<sup>-3</sup> labelled silver nitrate solution. The flask was then covered with foil and immersed in a thermostat-bath at 298 K for a period of 40 days.

$3 \text{ cm}^3$  aliquots of labelled silver nitrate solution were withdrawn and placed in duplicate glass vials of the type described in 3.4. The vials were then counted as described in 3.3.4 and 3.3.5. A  $6 \text{ cm}^3$  aliquot of concentrated nitric acid was then added to the flask, the flask was shaken and allowed to stand for 10 minutes. A  $3 \text{ cm}^3$  aliquot of acidified silver solution was then transferred to duplicate vials, and the vials were counted in the usual manner.

Table 4.12

| Vial No | Corrected Count Rate of $3 \text{ cm}^3$ labelled Ag solution c.p.m. | Vial No | Corrected Count Rate of $3 \text{ cm}^3$ acidified silver solution. c.p.m. |
|---------|--|---------|--|
| 1       | 1261   | 3       | 1498   |
| 2       | 1264   | 4       | 1496   |

This experiment has shown that the nitric acid removed some adsorbed silver from the flask, indicated by the increased count rate in Table 4.12. The nitric acid may not have removed all the adsorbed silver, but we can now calculate the minimum amount of silver adsorbed on borosilicate glass after 40 days in contact with  $0.5 \text{ mg dm}^{-3}$  silver solution.

$$\begin{aligned}
 \text{Final Count Rate (Mean)} &= 1497 \text{ c.p.m.} \\
 \text{Final Count Rate Corrected for withdrawal of } 6 \text{ cm}^3 &= 1534 \text{ c.p.m.} \\
 \text{Initial Count Rate (Mean)} &= 1263 \text{ c.p.m.} \\
 \text{Fraction of silver desorbed by Nitric Acid} &= \frac{1534 - 1263}{1534} \\
 \text{Amount of silver in flask} &= 0.125 \text{ mg} \\
 \text{Approximate surface contact area} &= 707 \text{ cm}^2 \\
 \text{Amount of silver adsorbed after 40 days} &= \frac{1534 - 1263 \times 0.125}{1534 \times 707} \\
 &= \underline{\underline{31.2 \times 10^{-6} \text{ mg Ag cm}^{-2}}}
 \end{aligned}$$

Although the above value is an approximation, nevertheless its importance cannot be overlooked. The amount of silver adsorbed on borosilicate-

glass has been shown to be at least as great as that on soda-glass.

It has also been shown that nitric acid is an effective desorbing agent for borosilicate glass.

In addition to experiments 4.3.1, 2 and 3, it was decided to investigate the desorption of silver using nitric acid solutions of different concentrations and temperatures. One of the objects of the experiment being to design a method for quick and effective cleaning of laboratory glassware.

#### 4.3.4 Desorption of silver by acid washing cycles

A number of vials were washed as described in 3.3.2, 3 cm<sup>3</sup> of 1 mg dm<sup>-3</sup> labelled silver nitrate solution was then added to each vial. The vials were sealed, covered in foil and immersed in a thermostat-bath at 298 K. After 5 days, three of the vials were removed from the thermostat-bath, washed and counted as described in 3.3.4 and 3.3.5. The washing reagent for vial 1 was doubly deionised water, for vial 2, 0.1 mol dm<sup>-3</sup> nitric acid, and for vial 3, 8.0 mol dm<sup>-3</sup> nitric acid, all at a temperature of 293 K. After this each vial was soaked for a further 48 hours in its respective washing agent. The reagent was then extracted and the vials were washed three times with doubly deionised water, and counted in the usual manner.

After 16 days the remaining vials were removed from the thermostat-bath. Vials 4, 5 and 6 were washed as described above, at a temperature of 293 K. The same washing cycles were also applied to vials 7, 8 and 9, but the temperature of the washing reagent was increased to 333 K. The remaining vial No. 10 was washed as above but using sodium hydroxide solution at 293 K.

In addition vials 4, 5 and 6 were soaked for a further 5 days in their respective washing reagents. The reagent was then extracted and the vials were washed three times in doubly deionised water, and then counted in the usual manner.

Table 4.13 Acid desorption treatments

| Vial No. | Contact Time/Days | Wash Reagent                                    | Amount Ag adsorbed /mg cm <sup>-2</sup> x 10 <sup>6</sup> | Amount Ag adsorbed after a further soak /mg cm <sup>-2</sup> x 10 <sup>6</sup> |
|----------|-------------------|---|---|--|
| 1        | 5                 | DDH <sub>20</sub>                               | 34.6  | 21.7   |
| 2        | 5                 | 0.1 mol dm <sup>-3</sup> HNO <sub>3</sub>       | 22.4  | 8.3  |
| 3        | 5                 | 8.0 mol dm <sup>-3</sup> HNO <sub>3</sub>       | 17.1  | 6.8  |
| 4        | 16                | DDH <sub>20</sub>                               | 32.5  | 17.6   |
| 5        | 16                | 0.1 mol dm <sup>-3</sup> HNO <sub>3</sub>       | 18.1  | 6.3  |
| 6        | 16                | 8.0 mol dm <sup>-3</sup> HNO <sub>3</sub>       | 15.7  | 3.7  |
| 7        | 16                | DDH <sub>20</sub> (HOT)                         | 13.5  | -  |
| 8        | 16                | 0.1 mol dm <sup>-3</sup> HNO <sub>3</sub> (HOT) | 13.8  | -  |
| 9        | 16                | 8.0 mol dm <sup>-3</sup> HNO <sub>3</sub> (HOT) | 8.7   | -  |
| 10       | 16                | 10% NaOH  | 28.4  | -  |

It can be seen from table 4.13, that after the acid washing and soaking of vials 2, 3, 5 and 6, about 30% of the adsorbed silver remained, based on the mean adsorption value for control vials 1 and 4. It has also been shown that there is only a small advantage to be gained using the more concentrated acid solution. Prolonged soaking in nitric acid solution seemed to be a much more effective means of removing adsorbed silver than soaking in doubly deionised water, as would be expected from the results of the desorption experiment in section 4.3.2.

The hot washes proved to be the most efficient cleaning method, in fact hot doubly deionised water was as effective as hot dilute nitric acid, and hot 8.0 mol dm<sup>-3</sup> nitric acid was the most effective. However, the disadvantage of hot washing is the effect it can have on the accuracy of calibrated glassware, /

by effecting permanent volumetric distortions within the glass vessel.

In addition to acid washing, sodium hydroxide solution was used in vial 10, as we can see it is only marginally better than doubly deionised water.

#### 4.4 A contact time study of silver adsorption on soda-glass

In previous contact time work very little evidence has been presented to establish a time for maximum adsorption of silver, i.e. when the system has attained equilibrium. Previous workers attempted to establish this by studying the adsorption process at elevated temperatures (1), but the results were inconclusive due to discolouration of the solutions. Hence a series of experiments were designed in an attempt to explain this discolouration.

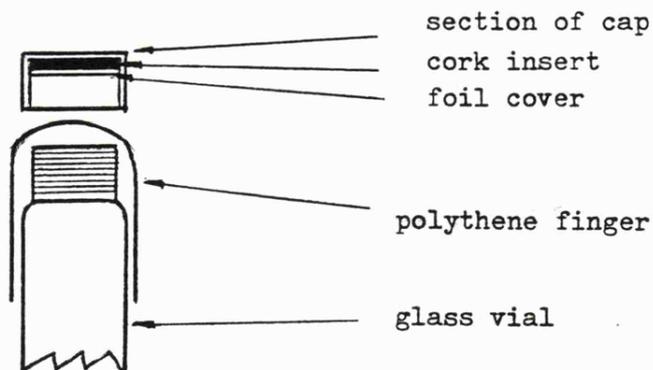
The effect of pH has been shown to be important for the adsorption of silver, hence a series of contact time experiments were carried out at different pH values.

The role of the anion is uncertain, therefore, a series of silver solutions were investigated to ascertain its importance. The results from these experiments have been used to assess an equilibrium contact time for silver adsorption, so that meaningful adsorption isotherms could be produced.

##### 4.4.1 The adsorption of silver at elevated temperatures and extended contact times

As previously described, other researchers have observed discolouration of the labelled silver solution when high temperature contact time experiments have been carried out (1). It was thought that the discolouration may have been due to contaminants from the screw cap used to seal the vial. These caps contain a cork pad with a foil cover glued on to form a seal at the neck of the vial. In order to eliminate the possibility of contaminants being leached from the caps at elevated temperatures an experiment was carried out using a polythene finger over the top of the vial, before screwing on the cap, see figure 4.12.

Figure 4.12



In this experiment a number of vials were set up in the normal manner, containing a  $10 \text{ mg dm}^{-3}$  labelled silver solution. The vials were then placed in a thermostat-bath at  $328 \text{ K}$ , and removed at various time intervals for counting in the prescribed manner.

After a 4 day contact the contents of all the vials were cloudy, and in some cases a yellow colouration was observed. The experiment was subsequently abandoned.

The above experiment was then repeated using P.T.F.E. tape as a secondary seal, instead of the polythene, this experiment was also abandoned for the same reasons.

It was concluded that contaminant from the vial caps was permeating through the secondary seals, assuming that the discolouration originated from the caps.

The following tests were carried out to try to ascertain the cause of colouration in the above experiments :-

- (a) Both dilute and concentrated silver nitrate solutions were boiled for 5-minutes - no changes were observed.
- (b) Vial caps were placed in the solutions from (a), the solutions were then boiled for a further 5 minutes. The dilute solution produced a turbid yellow/brown colouration and some black particles. The concentrated solution contained a higher proportion of black particles.
- (c) A similar boiling method was used, but substituting the vial caps for strips of P.T.F.E. tape - no changes were observed.
- (d) Test (b) was repeated but the cork/foil inserts were removed from the vial caps before boiling - no changes were observed.

(e) Two sets of vials were placed in an oven at 333 K for 7 days, one set contained deionised water, and the other  $10 \text{ mg dm}^{-3}$  silver nitrate solution, the latter set was wrapped in foil. The following methods were used to seal the 4 vials in each set.

- i) Standard cap.
- ii) Cap without cork/foil insert, but sealed with P.T.F.E. tape.
- iii) Cork stopper.
- iv) Rubber stopper.

The vials containing deionised water remained clear after 7 days, however, the vials containing silver nitrate solution gave the following results:-

- i) Straw coloured and black specks.
- ii) White/yellow turbid solution.
- iii) Pale yellow turbid solution.
- iv) Clear, but contained black specks.

In all the vials containing silver nitrate solution, a black rim was observed at the liquid/air interface within the vial.

It was concluded from these results that the best method of overcoming the contamination problem may be to use a vial cap made entirely of P.T.F.E., unfortunately no convenient source could be found. In view of this difficulty it was decided to approach the problem in a different manner. The next experiment was subsequently carried out at a lower temperature, but a higher silver nitrate concentration was used. The object of the experiment being the same as 4.4.1, that is to determine an equilibrium time and a maximum value for silver adsorption.

#### 4.4.2 Contact time at 318 K using $100 \text{ mg dm}^{-3}$ silver solution

Twelve vials were washed as described in 3.3.2, then  $3 \text{ cm}^3$  of  $100 \text{ mg dm}^{-3}$  labelled silver nitrate solution was added to each vial. The vials were sealed, covered in foil and placed in a thermostat-bath at 318 K. The

vials were removed from the bath at various time intervals for counting in the prescribed manner.

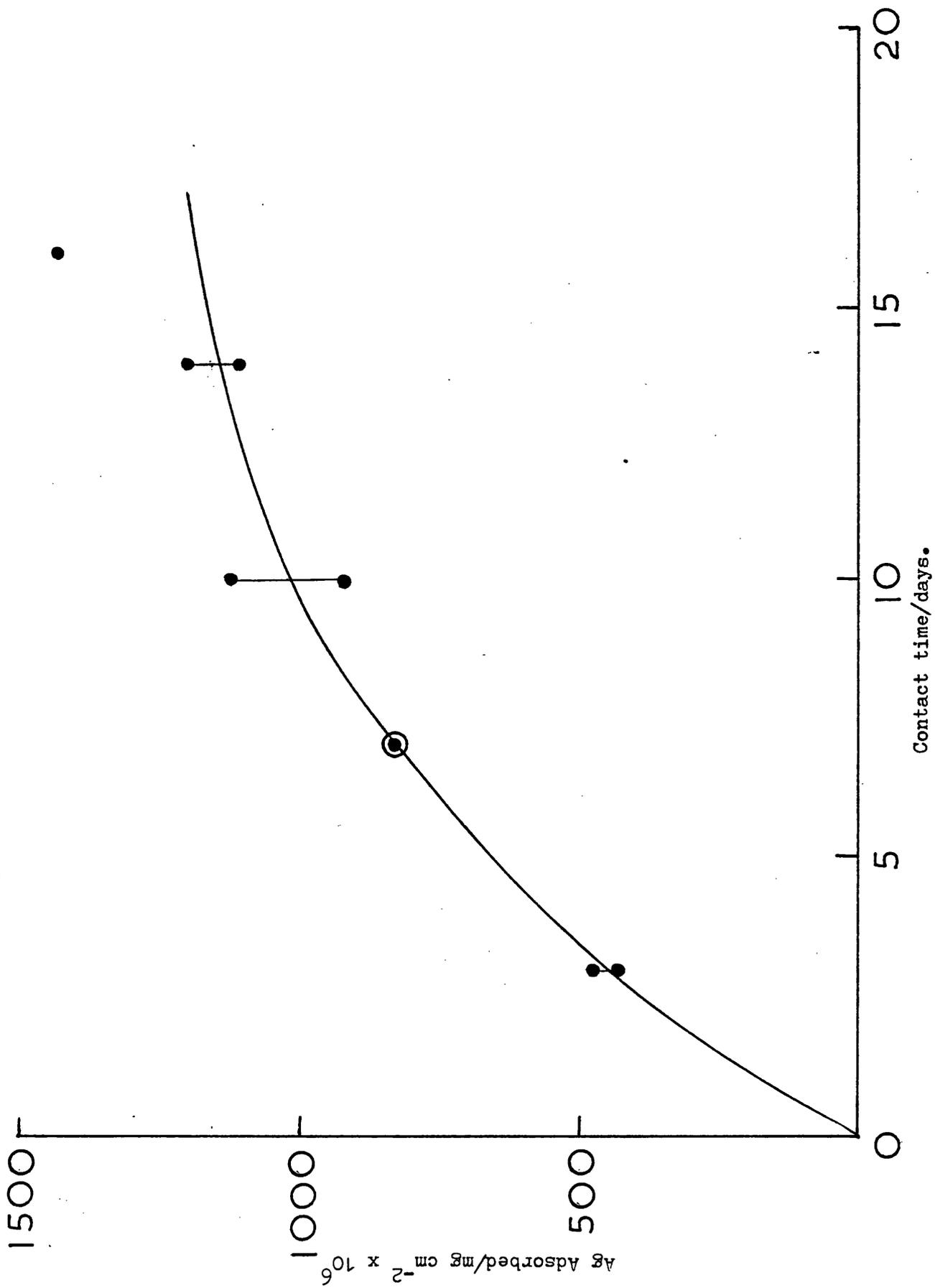
Table 4.14 Contact time study for 100 mg dm<sup>-3</sup> silver solution at 318 K

| Vial No | Contact Time /days | Corrected Count Rate 'IN'/c.p.m.  | Corrected Count Rate 'OUT'/c.p.m. | Ag adsorbed /mg cm <sup>-2</sup> x 10 <sup>6</sup> | Comments on condition of vial |
|---------|--------------------|---|-----------------------------------|--|-------------------------------|
| 1       | 3                  | 121756  | 2145                              | 476.1  | Clear                         |
| 2       | 3                  | 125884  | 1998                              | 428.9  | Clear                         |
| 3       | 7                  | 121042  | 3744                              | 835.9  | Clear                         |
| 4       | 7                  | 130244  | 4023                              | 834.8  | Clear                         |
| 5       | 10                 | 121686  | 7667                              | 16702.8  | Black deposit result ignored  |
| 6       | 10                 | 123440  | 5114                              | 1119.7   | Clear                         |
| 7       | 10                 | 124434  | 4212                              | 914.8  | Clear                         |
| 8       | 14                 | 121969  | 4996                              | 1107.0   | Clear                         |
| 9       | 14                 | 121668  | 5393                              | 1197.9   | Faint brown rim at liquid/    |
| 10      | 14                 | 121178  | 6478                              | 1437.5   | air interface                 |
| 11      | 21                 | Thermostat-bath burned out in interim period,   |                                   |  |                               |
| 12      | 21                 | the vials were not counted, however, a black rim was observed at the liquid/air interface |                                   |  |                               |

The above results are plotted in Figure 4.13

It can be seen from Figure 4.13, that the adsorption of silver would appear to be levelling off at about  $1000 \times 10^{-6}$  mg cm<sup>-2</sup>. However, the results are inconclusive probably due to the deposition of a black material at the liquid/air interface. In view of this problem it was decided to repeat the experiment using 100 mg dm<sup>-3</sup> silver nitrate solution at a further reduced temperature of 298 K.

FIG. 4.13 Graph of silver adsorption from a  $100 \text{ mg dm}^{-3}$  solution, against contact time at 318 K.



#### 4.4.3 Contact time at 298 K using 100 mg dm<sup>-3</sup> silver solution

Fourteen vials were washed in the usual manner, and a 3 cm<sup>3</sup> aliquot of 100 mg dm<sup>-3</sup> labelled silver nitrate solution was added to each. The vials were sealed, covered in foil and placed in a thermostat-bath at 298 K, and removed at various time intervals for counting in the prescribed manner.

Table 4.15 Contact time study for 100 mg dm<sup>-3</sup> silver solution at 298 K

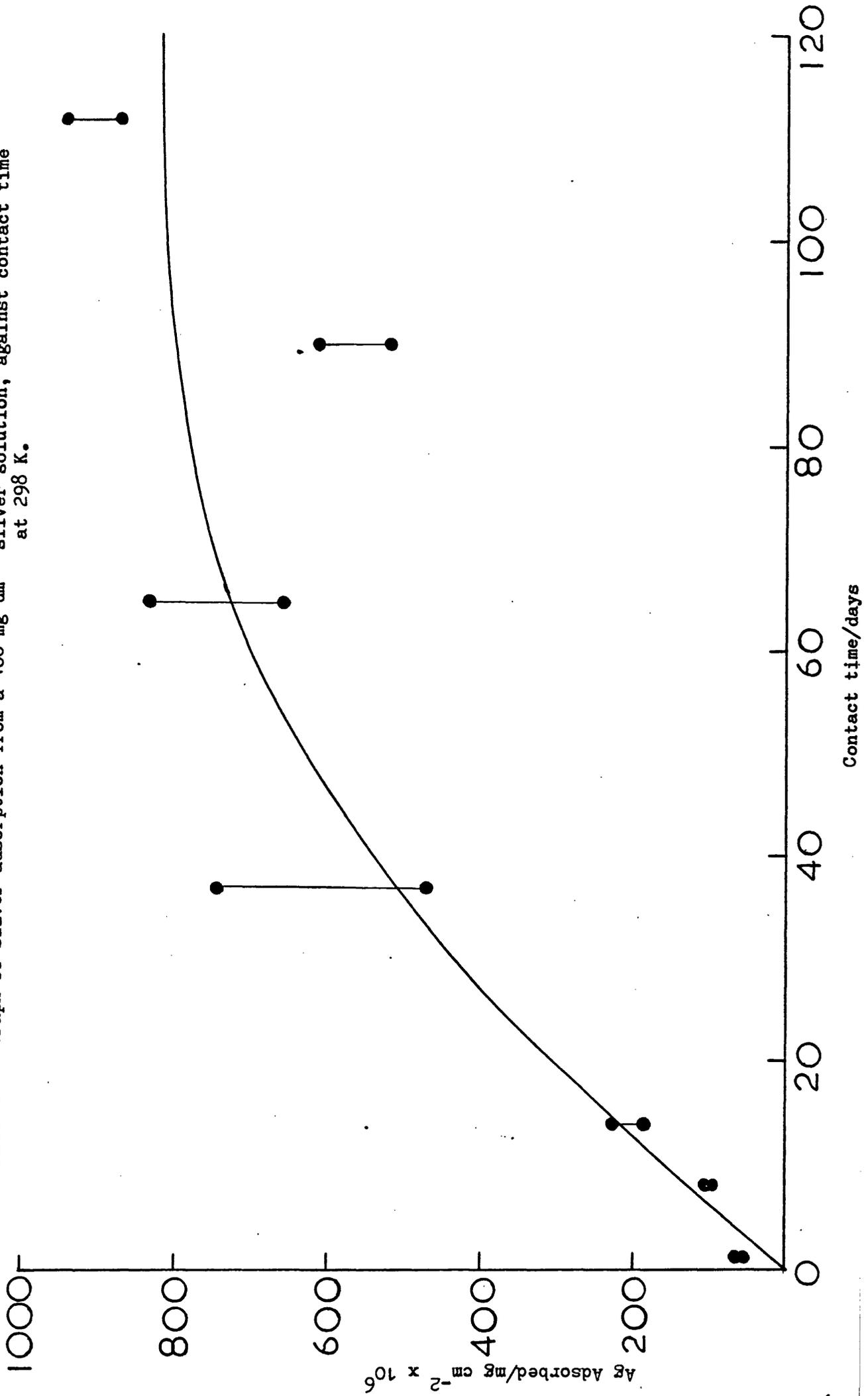
| Vial No | Contact Time/days | Corrected Count Rate 'IN'/c.p.m. | Corrected Count Rate 'OUT'/c.p.m. | Fraction Ag adsorbed | Total Ag adsorbed /mg cm <sup>-2</sup> x 10 <sup>6</sup> |
|---------|-------------------|----------------------------------|-----------------------------------|----------------------|--|
| 1       | 1                 | 101811                           | 195                               | 0.0019               | 63.3   |
| 2       | 1                 | 101733                           | 183                               | 0.0018               | 60.0   |
| 3       | 8                 | 96994                            | 286                               | 0.0029               | 96.6   |
| 4       | 8                 | 96788                            | 296                               | 0.0031               | 103.3  |
| 5       | 14                | 86385                            | 478                               | 0.0055               | 184.2  |
| 6       | 14                | 89985                            | 613                               | 0.0068               | 227.0  |
| 7       | 37                | 64678                            | 1441                              | 0.0223               | 742.6  |
| 8       | 37                | 64901                            | 911                               | 0.0140               | 467.8  |
| 9       | 65                | 54388                            | 1073                              | 0.0197               | 657.6  |
| 10      | 65                | 55611                            | 1394                              | 0.0251               | 835.5  |
| 11      | 90                | 49515                            | 773                               | 0.0156               | 520.4  |
| 12      | 90                | 50392                            | 921                               | 0.0183               | 609.2  |
| 13      | 112               | 48159                            | 1362                              | 0.0283               | 942.4  |
| 14      | 112               | 47734                            | 1255                              | 0.0263               | 876.1  |

The above results are plotted in Figure 4.14.

It can be seen from Figure 4.14 that the amount of silver adsorbed reaches a limiting value at about  $800 \times 10^{-6}$  mg cm<sup>-2</sup>. Assuming this to be representative we can say that silver adsorption on soda-glass at 100 mg dm<sup>-3</sup> and 298 K, attains equilibrium after about 80-days.

A further contact time experiment was carried out at a silver concentration of 1000 mg dm<sup>-3</sup> at 298 K. This additional work was to establish

FIG. 4.14 Graph of silver adsorption from a  $100 \text{ mg dm}^{-3}$  silver solution, against contact time at 298 K.



whether the silver adsorption is increased at higher silver nitrate concentrations, or is there a limiting concentration, outside which the adsorption process is independent of silver ion concentration.

#### 4.4.4 Contact time at 298 K using 1000 mg dm<sup>-3</sup> silver solution

Twelve vials were washed in the usual manner, then a 3 cm<sup>3</sup> aliquot of 1000 mg dm<sup>-3</sup> labelled silver solution was added to each. The vials were sealed, covered in foil and placed in a thermostat-bath at 298 K. They were then removed at various time intervals for counting in the usual manner.

Table 4.16 1000 mg dm<sup>-3</sup>/298 K

| Vial No | Contact time/days | Corrected Count Rate 'IN' /c.p.m. | Corrected Count Rate 'OUT' /c.p.m. | Fraction Ag adsorbed | Total Ag adsorbed /mg cm <sup>-2</sup> x 10 <sup>6</sup> |
|---------|-------------------|-----------------------------------|------------------------------------|----------------------|--|
| 1       | 3                 | 100614                            | 227                                | 0.0023               | 751  |
| 2       | 3                 | 100002                            | 95                                 | 0.0009               | 317  |
| 3       | 7                 | 95078                             | 46                                 | 0.0005               | 160  |
| 4       | 7                 | 95515                             | 25                                 | 0.0003               | 87   |
| 5       | 14                | 92865                             | 61                                 | 0.0007               | 220  |
| 6       | 14                | 94327                             | 133                                | 0.0014               | 469  |

The above experiment was abandoned because of the extremely erratic results, and their poor reproducibility. However, it is felt that we can tentatively say that the order of magnitude of adsorption is similar to that obtained in experiment 4.4.3. We may, therefore, be able to say that the adsorption of silver ions on soda-glass is independent of the silver concentration if that concentration exceeds 100 mg dm<sup>-3</sup>.

#### 4.4.5 Contact time at 333K using 10 mg dm<sup>-3</sup> silver nitrate

solution, determined by Atomic Absorption Spectrophotometry

It was decided to try to confirm that silver adsorption reaches a limiting value of approximately 800 x 10<sup>-6</sup> mg cm<sup>-2</sup> by using an independent technique, namely atomic absorption spectrophotometry. A contact time

experiment was carried out using a different silver ion concentration at a higher temperature than that used in 4.4.3. The amount of silver adsorbed was calculated by measuring the silver ion concentration in the adsorbate solution after various contact times.

The use of atomic absorption spectrophotometry is discussed in more detail in section 3.12.

Six vials were washed in the usual manner and 5 cm<sup>3</sup> of 10 mg dm<sup>-3</sup>, unlabelled, silver nitrate solution was added to each. The vials were covered in foil and placed in a thermostat-oven at 333 K, they were then removed for measurement on the A.A.S. after various time intervals.

These conditions were chosen to be in direct contrast to the 100 mg dm<sup>-3</sup> and 298 K in experiment 4.4.3 in order to establish whether the limiting amount of silver adsorbed is the same.

A volume of 5 cm<sup>3</sup> was chosen for the following reasons - a larger amount of solution is required for A.A.S. work and the very small air space remaining in the vial might help to eliminate the rim formed at the air/liquid interface.

A fresh set of non-acid calibration standards were prepared at each contact time, before carrying out measurement by atomic absorption. A sample calibration curve has been included, the calibration standards were prepared in doubly deionised water with no additions of acid solution. (see Figure 4.15).

The vials were allowed to cool to room temperature before the silver ion concentration was determined, because the instruments' digital display panel gave fluctuating readings when the solutions were hot.

The values obtained were subtracted from the initial concentration, then the adsorption per unit area was calculated. (see Figure 4.16).

#### Conditions and Detection Limit

Pye-Unicam SP 192 Atomic Absorption Spectrophotometer

Wavelength - 328.1 nm

Flame type - Air/Acetylene

Detection Limit - 0.002 mg dm<sup>-3</sup>

Table 4.17 Typical calibration results for the SP 192 A.A.S.

| Standard Concentration<br>/mg dm <sup>-3</sup> | Absorption Reading<br>from A.A.S. |
|--|-----------------------------------|
| 1  | 1.1                               |
| 2  | 2.2                               |
| 5  | 4.8                               |
| 8  | 7.5                               |
| 10   | 8.8                               |
| 11   | 9.3                               |

The above results are plotted in Figure 4.15.

Table 4.18 Contact time study for a 10 mg dm<sup>-3</sup> silver solution at 333 K

| Vial No | Contact Time<br>/days | Silver Concentration<br>/mg dm <sup>-3</sup> | Ag adsorbed<br>/mg cm <sup>-2</sup> x 10 <sup>6</sup> |
|---------|-----------------------|--|---|
| Control | 0                     | 9.87   | 0   |
| 1       | 1                     | 8.63   | 484   |
| 2       | 3                     | 7.82   | 800   |
| 3       | 6                     | 7.66   | 863   |
| 4       | 8                     | 7.74   | 832   |
| 5       | 13                    | 7.90   | 770   |
| 6       | 50                    | 7.40   | 960   |

The results above are plotted in Figure 4.16.

The above results indicate a levelling off of the amount of silver adsorbed after about seven days, and the limiting value can be seen to be approximately  $800 \times 10^{-6} \text{ mg cm}^{-2}$ , which is of the same order as that observed in 4.4.3. The rate of attainment of equilibrium was faster at the higher temperature, although the silver concentration was lower. The solution in vial 6 was slightly turbid otherwise no discolouration was observed in the vials.

FIG. 4.15 A.A.S. Calibration Curve for Silver.

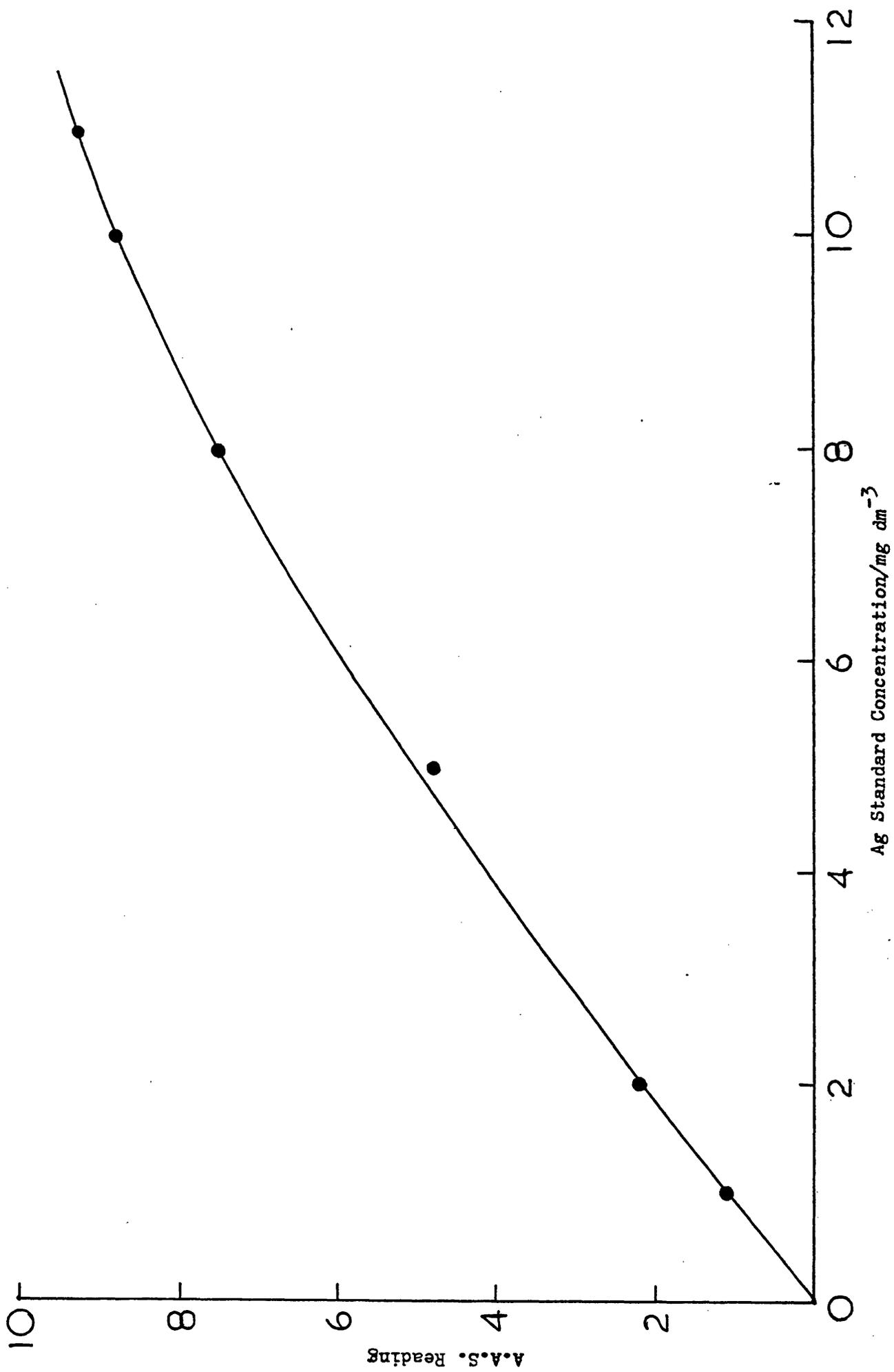
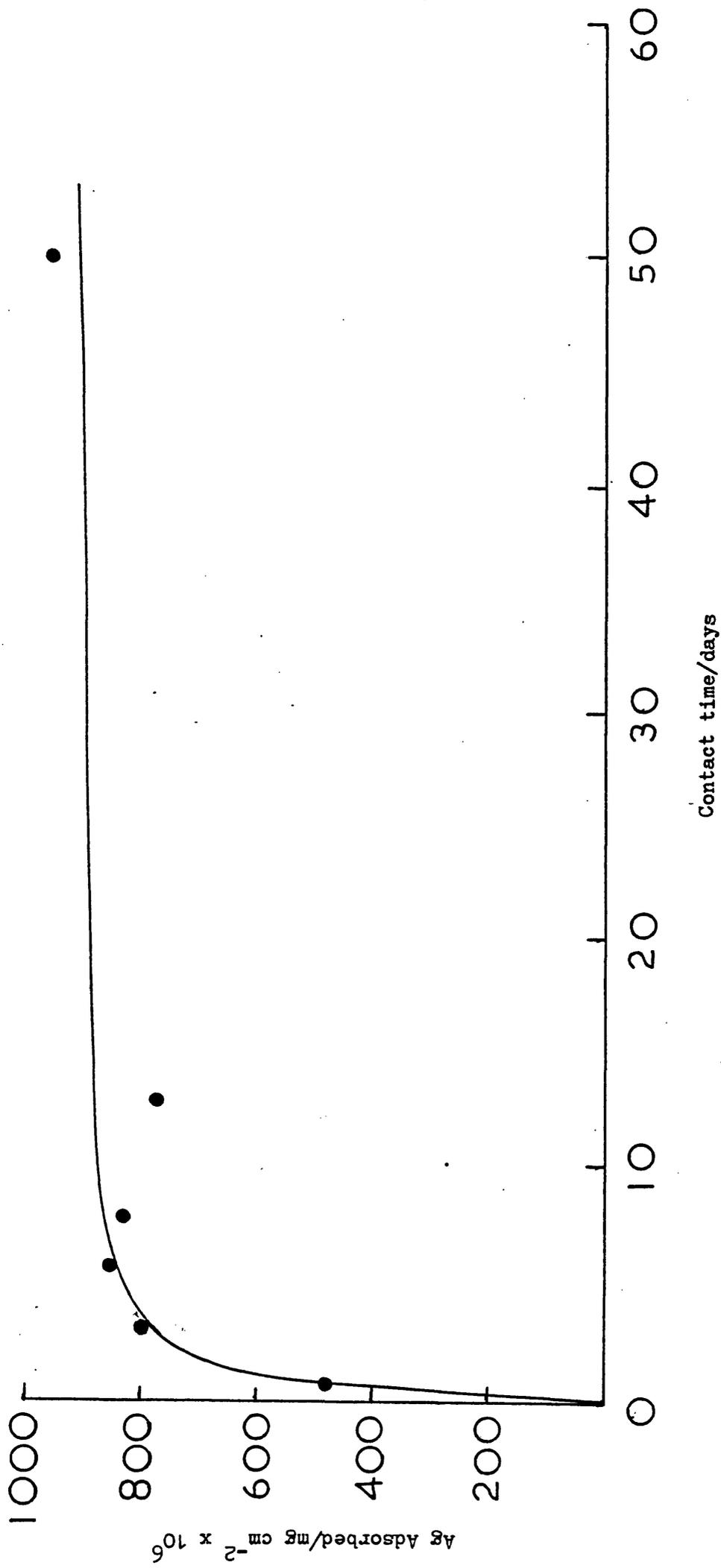


FIG. 4.16, Graph of silver adsorption from a  $10 \text{ mg dm}^{-3}$  silver solution, against contact time at 333 K.



4.4.6 The effect of anion change on contact time for  $1 \text{ mg dm}^{-3}$  silver solution at 298 K, and a pH of 5.6

The adsorption work carried out so far has involved the use of silver nitrate solutions. The following experiment was performed to establish whether the amount of silver adsorbed is independent of the anion. Two labelled  $1 \text{ mg dm}^{-3}$  silver solutions were prepared, using silver acetate and silver nitrate. The amount of silver adsorbed at a series of contact times was determined at 298 K.

A series of 48 vials were washed and prepared in the usual manner. A  $3 \text{ cm}^3$  aliquot of  $1 \text{ mg dm}^{-3}$  silver as silver nitrate solution was added to half of the vials, and  $3 \text{ cm}^3$  of  $1 \text{ mg dm}^{-3}$  of silver as silver acetate solution was added to the other half. The vials were then covered in foil and immersed in a thermostat-bath at 298 K. The vials were removed from the bath at various time intervals for washing and counting in the usual manner. At each contact time, duplicate vials containing each anion were removed for counting.

It can be seen from Figure 4.17 that the initial uptake of silver is rapid up to 30 minutes and then the rate of adsorption becomes slower. It can also be seen from Figure 4.18 that after 24 hours the uptake of silver has reached a limiting value of approximately  $33 \times 10^{-6} \text{ mg cm}^{-2}$ . The graphs indicate that the anion has had little or no effect on the amount of silver adsorbed. Although the graph profiles appear slightly different, the difference is not statistically significant.

The inference is that silver adsorption is similar for nitrate and acetate. It has also been shown that silver adsorption from saturated silver chloride solution is similar to that from nitrate and acetate.\*

4.4.7 The effect of pH at various contact times

In experiment 4.1.4 we have looked at prolonged contact time for a silver solution at pH 2.3. At such low pH values the amount of adsorption is small, it was, therefore, decided to look at contact time over a narrow pH

\* The author is indebted to Mr. D. P. Green of the City of Birmingham Polytechnic, for providing this information.

Table 4.19 The effect of anion change on silver adsorption at 298 K

| Nitrate<br>Vial No | Acetate<br>Vial No | Contact Time<br>/days    | Ag adsorbed/(mg Ag cm <sup>-2</sup> x 10 <sup>6</sup> ) |                      |
|--------------------|--------------------|--------------------------|---|----------------------|
|                    |                    |                          | From silver nitrate.                                    | From silver acetate. |
| 1                  | 25                 | 3.472 x 10 <sup>-4</sup> | 8.9   | 8.6                  |
| 2                  | 26                 | 3.472 x 10 <sup>-4</sup> | 9.2   | 9.5                  |
| 3                  | 27                 | 2.083 x 10 <sup>-2</sup> | 24.0  | 25.3                 |
| 4                  | 28                 | 2.083 x 10 <sup>-2</sup> | 20.5  | 22.2                 |
| 5                  | 29                 | 1.250 x 10 <sup>-1</sup> | 21.9  | 26.0                 |
| 6                  | 30                 | 1.250 x 10 <sup>-1</sup> | 27.4  | 33.0                 |
| 7                  | 31                 | 2.500 x 10 <sup>-1</sup> | 27.6  | 32.6                 |
| 8                  | 32                 | 2.500 x 10 <sup>-1</sup> | 32.9  | 26.2                 |
| 9                  | 33                 | 1                        | 33.7  | 36.1                 |
| 10                 | 34                 | 1                        | 25.6  | 36.5                 |
| 11                 | 35                 | 3                        | 39.3  | 34.1                 |
| 12                 | 36                 | 3                        | 28.4  | 34.2                 |
| 13                 | 37                 | 8                        | 28.9  | 35.1                 |
| 14                 | 38                 | 8                        | 31.2  | 31.5                 |
| 15                 | 39                 | 14                       | 32.0  | 32.9                 |
| 16                 | 40                 | 14                       | 33.5  | 33.0                 |
| 17                 | 41                 | 21                       | 41.4  | 42.8                 |
| 18                 | 42                 | 21                       | 35.6  | 44.0                 |
| 19                 | 43                 | 31                       | 34.1  | 36.7                 |
| 20                 | 44                 | 31                       | 33.8  | 38.7                 |
| 21                 | 45                 | 43                       | 35.9  | 29.6                 |
| 22                 | 46                 | 43                       | 30.3  | 28.3                 |
| 23                 | 47                 | 57                       | 36.7  | 31.6                 |
| 24                 | 48                 | 57                       | 32.6  | 37.8                 |

For vials 1, 2, 25 and 26 the contact time was too short to allow a count rate 'IN' to be taken, instead a blank containing 3 cm<sup>3</sup> of each active solution was counted and used for calculation purposes.

The above results are plotted in Figs. 4.17 and 4.18.

FIG. 4.17. Graphs of silver adsorption against short contact time at 298 K.

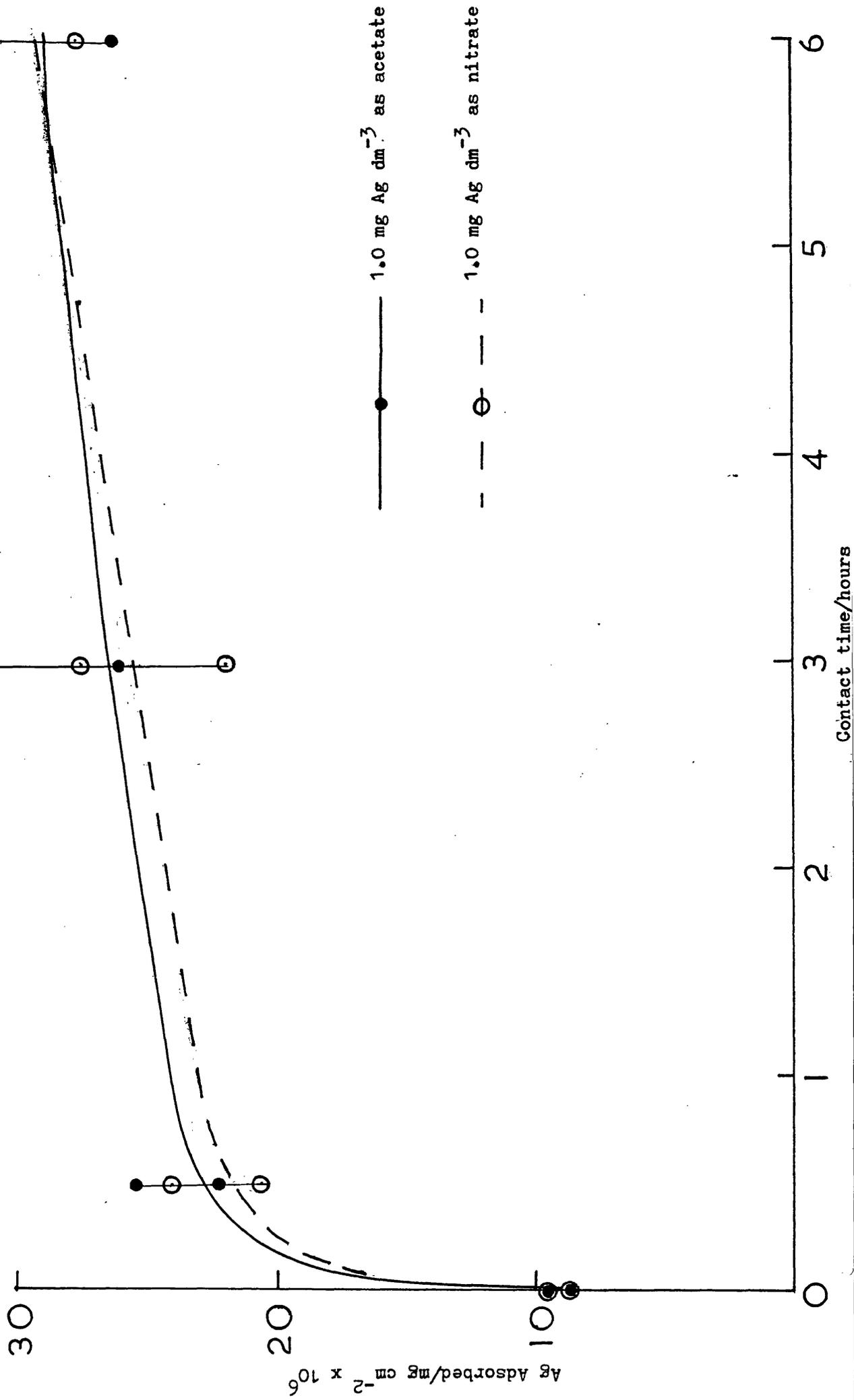
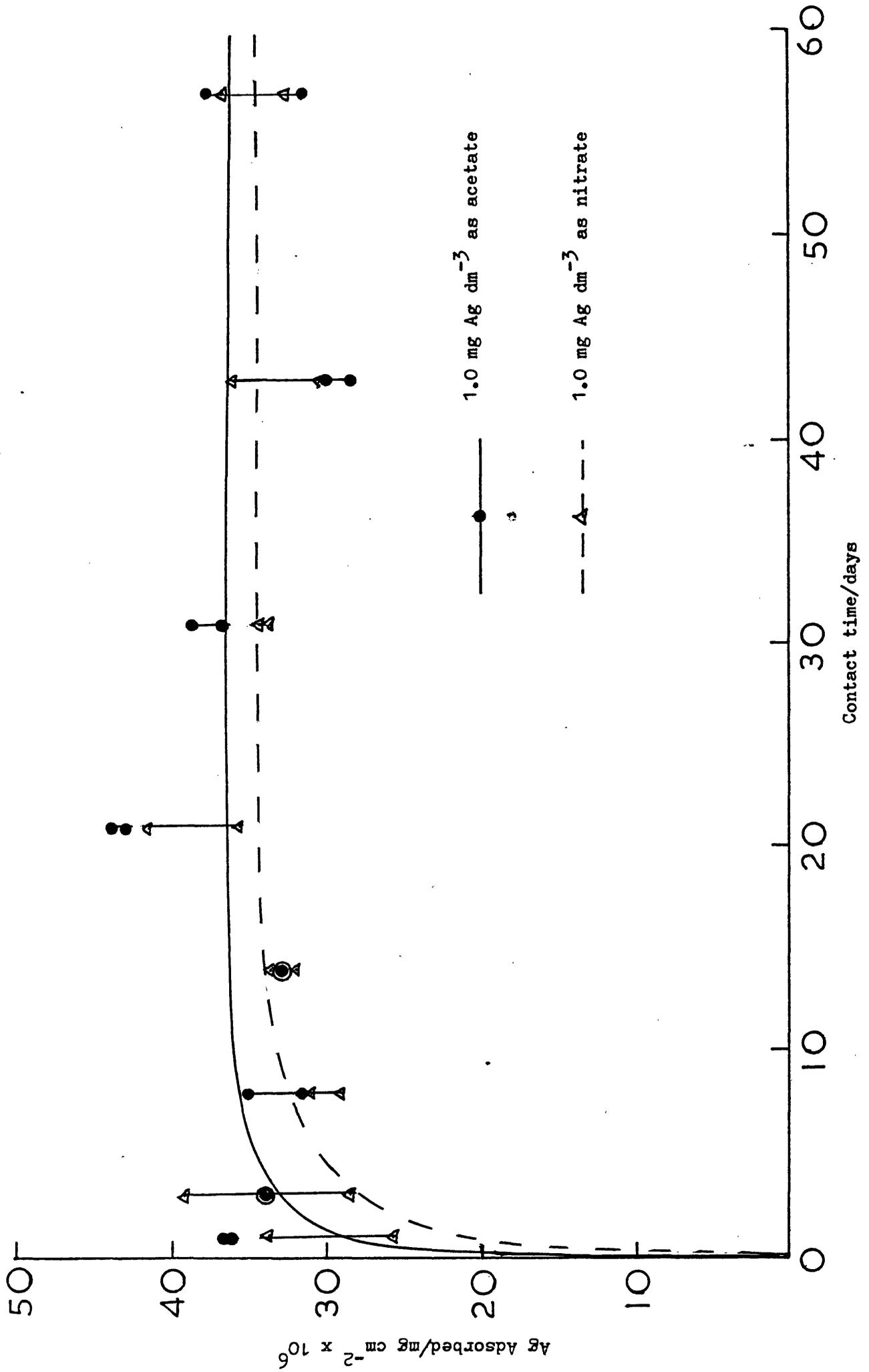


FIG. 4.18 Graphs of silver adsorption against extended contact time at 298 K.



range within the working pH values used throughout this work. It was also decided to compare the results with those obtained by Wharmby (1) at pH 5.3, using a  $0.5 \text{ mg dm}^{-3}$  silver nitrate solution.

A set of glass vials were washed as described in section 3.3.2 and  $3 \text{ cm}^3$  of  $0.5 \text{ mg dm}^{-3}$  labelled silver solution was added to each. In half of the vials the silver solution was adjusted to pH 5.0 and the remainder pH 4.6, using nitric acid solution, as previously described in 4.1.1.

The vials were covered in foil and placed in a thermostat-bath at 298 K, and then removed for washing and counting in the prescribed manner after various contact times. (see table 4.20 and figure 4.19).

As we would have expected the curves show definite trends, both the rate of adsorption and the amount adsorbed increase with pH. This means that in any adsorption studies undertaken, it is vital to state the pH at which the work is carried out. Also this may well explain discrepancies observed between work done by other researchers.

#### 4.5 Temperature dependence of silver adsorption

Previous experiments described in Section 4.4 indicated that a minimum of 40 day contact time was necessary before it could be assumed the adsorbed silver was in equilibrium with the silver in solution. If equilibrium is not attained then a thermodynamic treatment to calculate a heat of adsorption, is not applicable. It was, therefore, decided to set up three isotherm experiments, at 298, 308 and 318 K respectively, using 1, 2, 4, 8 and  $10 \text{ mg dm}^{-3}$  silver concentrations.

After the 40 days contact all the vials at 308 and 318 K were cloudy and a black rim had formed at the solution/air interface. In view of these results a repeat experiment was performed at lower temperatures.

##### 4.5.1 Adsorption isotherms at 281, 293, 298 and 303 K

Ten vials were washed in the usual manner and  $3 \text{ cm}^3$  of labelled silver nitrate solution was added to each. The silver ion concentrations were 1, 2, 4, 8 and  $10 \text{ mg dm}^{-3}$ , i.e. two vials of each concentration. The vials were

Table 4.20 The effect of pH on adsorption from  $0.5 \text{ mg dm}^{-3}$  silver solution at 298 K

| Contact Time<br>/Days | Amount Ag adsorbed/ $\text{mg cm}^{-2} \times 10^6$ |      |      |
|-----------------------|---|------|------|
|                       | pH 5.3  | 5.0  | 4.6  |
| $4.17 \times 10^{-3}$ | -   | 10.3 | 7.0  |
| $4.17 \times 10^{-3}$ | -   | 8.8  | 8.1  |
| $4.17 \times 10^{-2}$ | 10.1  | 9.7  | 9.0  |
| $4.17 \times 10^{-2}$ | 8.9   | 9.9  | 9.0  |
| 1                     | -   | 11.2 | 9.0  |
| 1                     | -   | 10.3 | 10.1 |
| 4                     | 12.6  | 15.0 | -    |
| 4                     | 14.6  | 15.5 | -    |
| 5                     | -   | -    | 12.2 |
| 5                     | -   | -    | 11.9 |
| 7                     | 20.9  | 16.3 | -    |
| 7                     | 15.6  | 16.6 | -    |
| 11                    | 22.9  | 21.3 | -    |
| 11                    | 27.7  | 19.4 | -    |
| 12                    | -   | -    | 14.0 |
| 12                    | -   | -    | 16.8 |
| 14                    | 19.3  | -    | -    |
| 14                    | 30.5  | -    | -    |
| 17                    | 44.5  | -    | -    |
| 17                    | 28.5  | -    | -    |
| 18                    | 30.4  | -    | -    |
| 18                    | 38.6  | -    | -    |
| 27                    | -   | 24.1 | 17.1 |
| 27                    | -   | 21.2 | 19.7 |
| 31                    | 55.3  | -    | -    |
| 31                    | 40.1  | -    | -    |
| 41                    | -   | -    | 18.7 |
| 41                    | -   | -    | 21.2 |
| 42                    | 42.5  | 29.9 | -    |
| 42                    | 63.0  | 22.0 | -    |
| 63                    | -   | 28.1 | 22.0 |
| 63                    | -   | 32.2 | 17.5 |
| 84                    | 33.6  | -    | -    |
| 84                    | 36.8  | -    | -    |

The above results are plotted in Figure 4.19

FIG. 4.19 Graphs of silver adsorption from  $0.5 \text{ mg dm}^{-3}$  silver solutions at pH's 5.3, 5.0 and 4.6, against contact time at 298 K

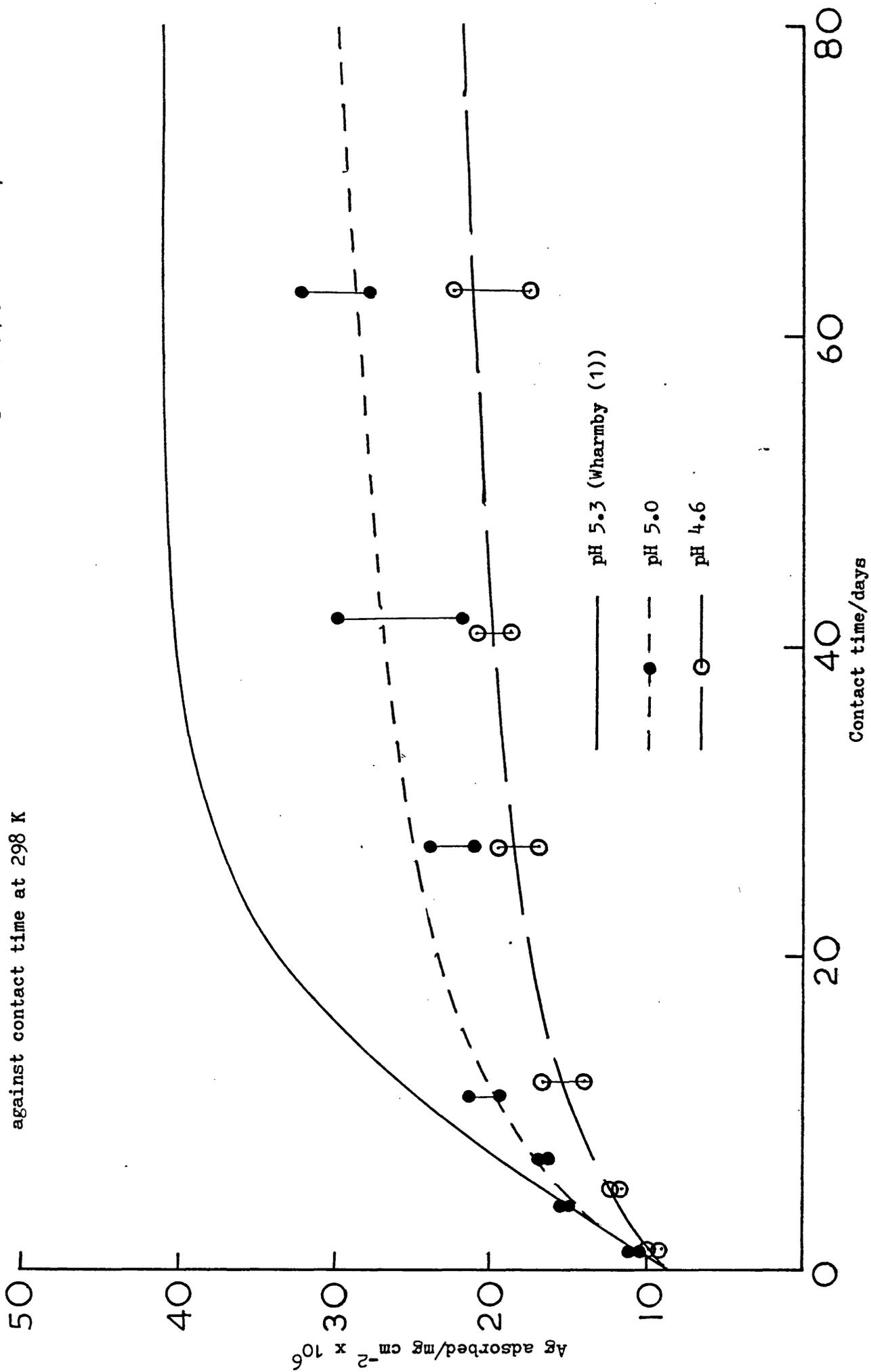


FIG. 4.20 Adsorption isotherms, showing silver adsorption against equilibrium concentration at 281, 293, 298 and 303 K

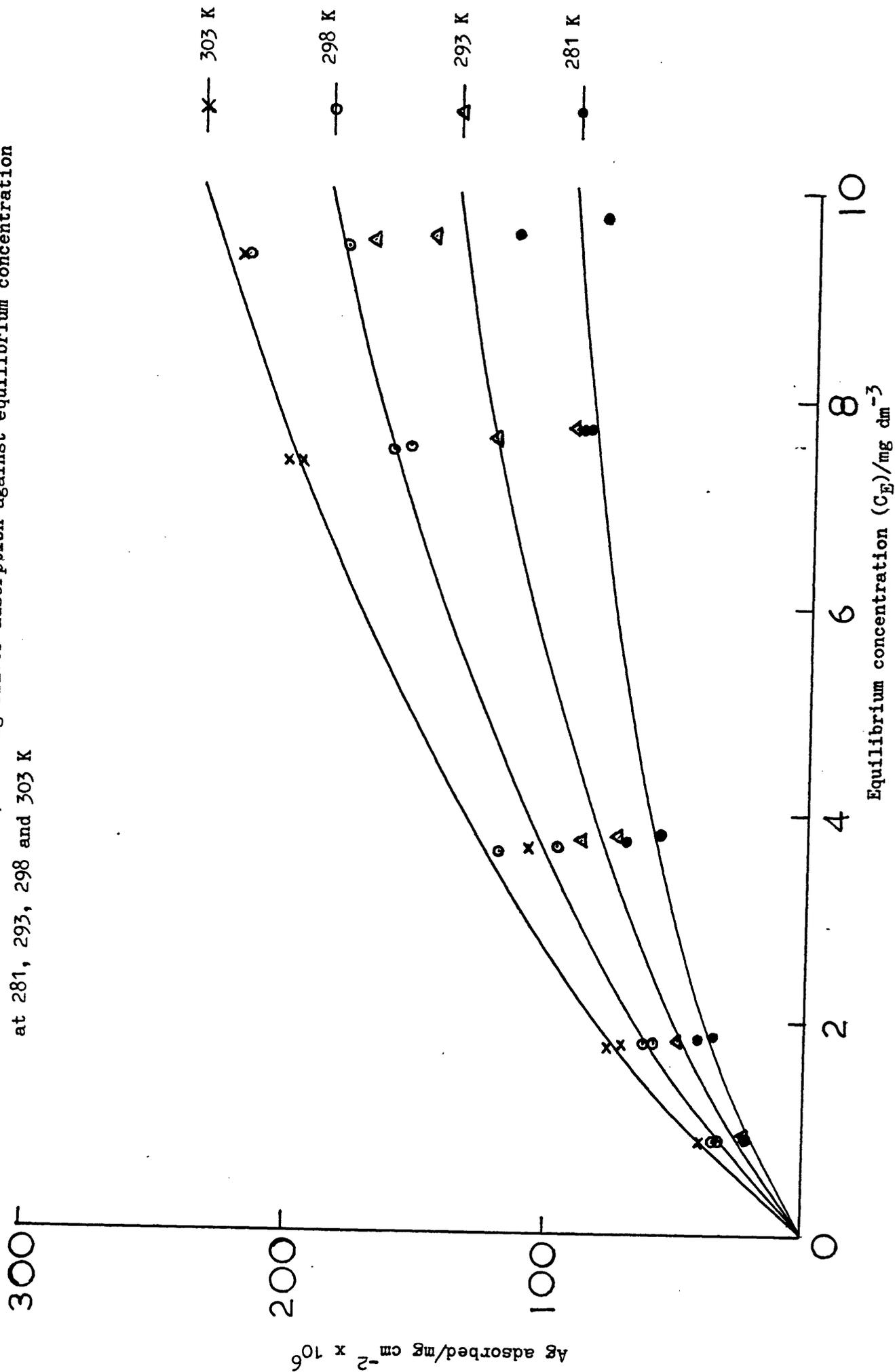


Table 4.21 40 day Isotherms

| Initial Ag concentration (C)/mg dm <sup>-3</sup> | Equilibrium Concentration (C <sub>E</sub> )/mg dm <sup>-3</sup> |       |       |       | Amount Adsorbed (x)/mg cm <sup>-2</sup> x 10 <sup>6</sup> |       |       |                 |
|--|---|-------|-------|-------|---|-------|-------|-----------------|
|  | 281 K   | 293 K | 298 K | 303 K | 281 K   | 293 K | 298 K | 303 K           |
| 1  | 0.919   | 0.932 | 0.897 | 0.879 | 27.0  | 22.6  | 34.3  | 40.3            |
| 1  | 0.925   | 0.923 | 0.888 | 0.879 | 25.0  | 25.7  | 37.4  | 40.4            |
| 2  | 1.892   | 1.854 | 1.816 | 1.789 | 36.0  | 48.8  | 61.2  | 70.4            |
| 2  | 1.874   | 1.852 | 1.825 | 1.771 | 42.0  | 49.4  | 58.4  | 76.5            |
| 4  | 3.829   | 3.783 | 3.664 | -     | 57.0  | 72.5  | 118.8 | Pale Yellow     |
| 4  | 3.790   | 3.736 | 3.712 | 3.769 | 70.0  | 87.9  | 96.1  | 107.1           |
| 8  | 7.733   | 7.724 | 7.535 | 7.393 | 89.0  | 92.0  | 155.1 | 202.2           |
| 8  | 7.739   | 7.628 | 7.518 | 7.408 | 87.0  | 124.0 | 160.7 | 197.3           |
| 10   | 9.652   | 9.556 | 9.341 | 9.340 | 116.0   | 148.1 | 219.7 | 219.9           |
| 10   | 9.757   | 9.486 | 9.457 | -     | 81.0  | 171.4 | 181.0 | Slightly turbid |

N.B. The equilibrium concentration is the initial concentration corrected for the amount of silver adsorbed after 40 days.

The results are plotted in Figure 4.20

The curves in figure 4.20 demonstrate clearly that silver adsorption increases significantly with temperature. These curves have been used to calculate an isosteric heat of adsorption for silver on glass, and are discussed in detail in Chapter VI.

covered in foil and placed in a refrigerator at 281 K. Similar sets of vials were prepared as described above and placed in thermostat-baths at 293, 298 and 303 K. After a contact time of 40 days the vials were washed and counted in the usual manner. The results are given in table 4.21.

N.B. Special precautions were taken when preparing the vials for the 281 K isotherm, i.e. all the glassware and solutions were cooled in an ice-bath during preparation.

#### 4.6 Pretreatment of Glass Vials

It has already been established in experiment 4.2.4 that pre-soaking glass vials in sodium hydroxide solution, increases the amount of silver adsorbed. Also the effect of hydrogen ions on the adsorption of silver has been thoroughly investigated in section 4.1. To supplement this work it was decided that a more detailed study of glass pre-treatment may provide the author with an alternative method for reducing the adsorption of silver, and thus improve analytical technique.

##### 4.6.1 The effect of pre-soaking in a selection of reagents

In the following experiment, glass vials were pre-soaked in various reagents, and then used in a contact time experiment to determine the effect of pre-treatment on the quantity of silver adsorbed. The vials were washed in the standard manner and dried for 2 days and then treated as follows :-

| Vial No | Pre-treatment Conditions  |
|---------|---|
| 1       | Control vial left to dry for 17 days.   |
| 2       | Control vial left to dry for 17 days.   |
| 3       | Soaked in D.D. H <sub>2</sub> O for 17 days.  |
| 4       | Soaked in D.D. H <sub>2</sub> O for 17 days.  |
| 5       | Soaked in 10% HNO <sub>3</sub> for 17 days, then washed 10 times in D.D. H <sub>2</sub> O.                                |
| 6       | Soaked in 10% HNO <sub>3</sub> for 17 days, then washed 10 times in D.D. H <sub>2</sub> O.                                |
| 7       | Soaked in 10% NaNO <sub>3</sub> for 17 days, then washed 10 times in D.D. H <sub>2</sub> O.                               |
| 8       | Soaked in 10% NaNO <sub>3</sub> for 17 days, then washed 10 times in D.D. H <sub>2</sub> O.                               |
| 9       | Soaked in 1000 mg dm <sup>-3</sup> AgNO <sub>3</sub> solution for 17 days, then washed 10 times in D.D. H <sub>2</sub> O. |

| Vial No | Pre-treatment Conditions   |
|---------|--|
| 10      | Soaked in $1000 \text{ mg dm}^{-3}$ $\text{Ag NO}_3$ solution for 17 days, then washed 10 times in D.D. $\text{H}_2\text{O}$ . |
| 11      | Soaked in 10% NaOH for 17 days, then washed 10 times in D.D. $\text{H}_2\text{O}$ .  |
| 12      | Soaked in 10% NaOH for 17 days, then washed 10 times in D.D. $\text{H}_2\text{O}$ .  |
| 13      | These vials were not pre-soaked, but washed with D.D. $\text{H}_2\text{O}$   |
| 14      | immediately prior to adding labelled silver nitrate solution, they were not allowed to dry.                                    |

After pre-treatment vials 1 to 12 were allowed to dry overnight.

A  $3 \text{ cm}^3$  aliquot of  $1 \text{ mg dm}^{-3}$  labelled silver solution was then added to each vial. The vials were wrapped in foil and placed in a thermostat-bath at 298 K. After a contact time of 7 days the vials were removed from the thermostat-bath for washing and counting in the prescribed manner. The results are shown in Table 4.22.

It can be seen from the results in Figure 4.21 that pre-soaking in doubly deionised water, nitric acid or sodium nitrate solution, reduces the amount of silver adsorbed by approximately 50%, nitric acid being marginally more effective than the other two reagents. Also vials 13 and 14 showed similar adsorption results to the control vials 1 and 2, we can conclude from this that our careful vial preparation procedure is probably unnecessary, in fact, a quick rinse in D.D.  $\text{H}_2\text{O}$  produces adequate results.

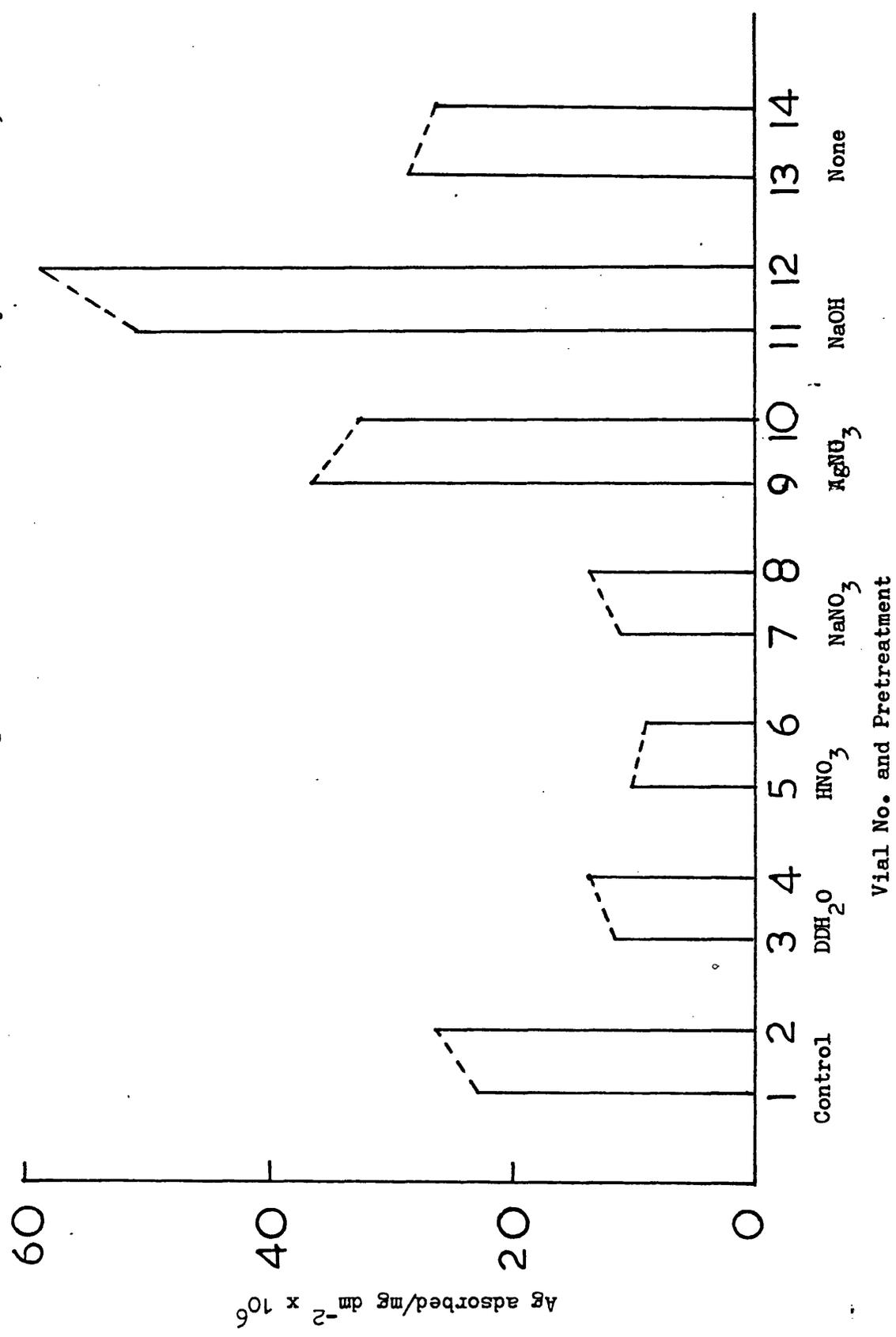
It can be seen from vials 11 and 12 that pre-soaking in sodium hydroxide solution produces a considerable increase in the amount of silver adsorbed, as we have already demonstrated in experiment 4.2.4. It can also be seen from vials 9 and 10 that pre-soaking in silver nitrate solution gives rise to approximately a 50% increase in the amount of silver adsorbed. However, this can be explained by ion exchange or isotopic dilution between the labelled silver in solution, and the glass surface which would already have adsorbed a considerable amount of silver from pre-soaking in "non-active"  $1000 \text{ mg dm}^{-3}$  silver solution.

Table 4.22 Pre-treatment of glass vials

| Vial No | Soaking Reagent      | Fraction Adsorbed | Amount Ag adsorbed /mg cm <sup>-2</sup> x 10 <sup>6</sup> |
|---------|----------------------|-------------------|---|
| 1       | Control              | 0.0688            | 22.9  |
| 2       | Control              | 0.0790            | 26.3  |
| 3       | D.D.H <sub>2</sub> O | 0.0352            | 11.7  |
| 4       | D.D.H <sub>2</sub> O | 0.0406            | 13.5  |
| 5       | HNO <sub>3</sub>     | 0.0304            | 10.1  |
| 6       | HNO <sub>3</sub>     | 0.0269            | 8.9   |
| 7       | NaNO <sub>3</sub>    | 0.0347            | 11.5  |
| 8       | NaNO <sub>3</sub>    | 0.0408            | 13.5  |
| 9       | AgNO <sub>3</sub>    | 0.1096            | 36.5  |
| 10      | AgNO <sub>3</sub>    | 0.0979            | 32.6  |
| 11      | NaOH                 | 0.1538            | 51.2  |
| 12      | NaOH                 | 0.1773            | 59.0  |
| 13      | -                    | 0.0850            | 28.3  |
| 14      | -                    | 0.0799            | 26.6  |

The results are depicted in Figure 4.21

FIG. 4.21 A visual representation of the effect of pretreatment on the adsorption of silver from a  $1.0 \text{ mg dm}^{-3}$  silver solution after 7 days contact at 298 K



#### 4.6.2 A study of acid and alkali pre-soaking

In an attempt to evaluate the mechanism by which pre-soaking in acid or alkali solutions, affects the amount of silver adsorbed, the following pre-treatments were carried out on a number of glass vials.

| Vial No | Pre-treatment Conditions   |
|---------|--|
| 1       | Control vial washed in the standard manner.  |
| 2       | Control vial washed in the standard manner.  |
| 3 )     | Soaked for 7 days in 10% $\text{HNO}_3$ , then washed 10 times with D.D. $\text{H}_2\text{O}$ , followed by a 7 day soak in 10% $\text{NaOH}$ , and finally 10 D.D. $\text{H}_2\text{O}$ washes. |
| 4 )     |  |
| 5 )     | As for vials 3 and 4 but soaked in $\text{NaOH}$ first, followed by $\text{HNO}_3$ second.   |
| 6 )     |  |

A  $3 \text{ cm}^3$  aliquot of  $1 \text{ mg dm}^{-3}$  labelled silver solution was then added to each vial. The vials were wrapped in foil and placed in a thermostat-bath at 298 K. After 7 days the vials were removed from the thermostat-bath for washing and counting in the prescribed manner. The following results were obtained.

Table 4.23 The effect of acid and alkali pre-treatment on silver adsorption

| Vial No | Soaking Reagent                   | Fraction Adsorbed | Amount Ag adsorbed<br>$/\text{mg cm}^{-2} \times 10^6$ |
|---------|-----------------------------------|-------------------|--|
| 1       | Control                           | 0.0640            | 21.3   |
| 2       | Control                           | 0.0698            | 23.3   |
| 3       | $\text{HNO}_3$ then $\text{NaOH}$ | 0.2973            | 99.1   |
| 4       | "                                 | 0.3721            | 124.0  |
| 5       | $\text{NaOH}$ then $\text{HNO}_3$ | 0.0551            | 18.4   |
| 6       | "                                 | 0.0531            | 17.7   |

The results in table 4.23 show that vials 3 and 4 produced a very high adsorption figure compared to control. If this had simply been the effect of the sodium hydroxide soak increasing the glass contact area, then we would have expected a higher adsorption figure for vials 5 and 6. It seems more likely that the sodium hydroxide is reacting with the glass to increase the micro-surface area, and then  $\text{OH}^-$  ions are adsorbing on the surface, the combined effect on silver adsorption would then be synergistic. If this is true we can then explain the reduced adsorption figures of vials 5 and 6, by a neutralisation effect of the nitric acid solution following by adsorption of  $\text{H}^+$  ions. It is postulated that the processes described above are taking place within a gel like structure at the glass surface. This theory is discussed in more detail at the end of Chapter VI.

#### 4.6.3 Isotopic dilution at the glass surface

As a follow-up to experiment 4.6.1 it was decided to look more closely at the effect of pre-soaking glass vials in active and non-active silver solutions, in order to provide more information regarding the adsorption mechanism. A number of vials were, therefore, pre-treated in the following manner.

Six vials were washed in the standard manner, then a  $3 \text{ cm}^3$  aliquot of labelled  $1 \text{ mg dm}^{-3}$  silver solution was added to vials 1 and 2. The vials were then treated in the standard manner to determine the amount of silver adsorbed after 7-days at 298 K.

A  $3 \text{ cm}^3$  aliquot of  $1 \text{ mg dm}^{-3}$  unlabelled silver solution was added to vials 3 and 4. The vials were wrapped in foil and placed in a thermostat-bath for 7 days at 298 K. The unlabelled silver solution was then extracted from the vials and they were washed 10 times with D.D.  $\text{H}_2\text{O}$ . A  $3 \text{ cm}^3$  aliquot of  $1 \text{ mg dm}^{-3}$  labelled silver solution was then added to vials 3 and 4, the vials were re-sealed and returned to the thermostat-bath for a further 7 days at 298 K. After this time the vials were removed for washing and counting, in the standard manner.

Vials 5 and 6 were treated in the same manner as vials 3 and 4 except that the labelled silver solution was added first, then the amount adsorbed after 7 days was determined. The unlabelled silver solution was added for the second 7 day soak, after which the amount of adsorbed silver was again determined. In each case it is assumed that negligible adsorption takes place after the first soak, merely isotopic or ionic exchange, because after 7 days the adsorbed silver is approaching equilibrium with that in solution (see figure 4.18).

Control vials 1 and 2 adsorbed on average  $21 \times 10^{-6} \text{ mg Ag cm}^{-2}$

Vials 3 and 4 for 1st soak the amount adsorbed was assessed

to be as above,

for 2nd soak the amount of activity was

equivalent to only  $16 \times 10^{-6} \text{ mg Ag cm}^{-2}$

Vials 5 and 6 for 1st soak the amount adsorbed was

$18.6 \times 10^{-6} \text{ mg Ag cm}^{-2}$

for 2nd soak the amount of activity was

equivalent to  $5.1 \times 10^{-6} \text{ mg Ag cm}^{-2}$

Some isotopic exchange has taken place, however, the results indicate that only around 75% of the adsorbed silver has undergone isotopic exchange, demonstrating that isotopic equilibrium between adsorbed silver and silver in solution is achieved slowly. This statement is discussed further in chapter VI.

CHAPTER VSILVER ADSORPTION ON POLYETHYLENE AND POLYPROPYLENE

In addition to the work already reported in Chapter IV, it was decided to extend the study to include two other container substrates. The most common laboratory alternatives to glass being polyethylene and polypropylene. Some research has been carried out by earlier workers (3), however, the results have been both erratic and inconclusive. It was therefore decided to approach the situation as a direct comparison to the work already carried out and reported in Chapter IV. The same experimental procedures were used as those for glass vials, described in Chapter III, only a slight modification in the size of the vial positioning ring was necessary before counting, as the polymeric vials were slightly narrower than the glass vials.

5.1 Assessment of polyethylene as an adsorbent

The vials selected for study are described in section 3.4. The first experiment is a contact time observation of a  $1 \text{ mg dm}^{-3}$  labelled silver solution at 298 K.

5.1.1 Contact time comparison for  $1 \text{ mg dm}^{-3}$  silver solution on polyethylene and glass

Eight polyethylene, and eight glass vials were pre-washed in the usual manner. A  $3 \text{ cm}^3$  aliquot of  $1 \text{ mg dm}^{-3}$  labelled silver solution was then added to each vial. The vials were sealed, wrapped in foil and placed in a thermostat-bath at 298 K. Duplicate vials of each material type were then removed after 0.5, 1.0, 2.0 and 168 hours, for extraction, washing and counting in the manner described in 3.3.4 and 3.3.5.

N.B. Poor duplication of results on PE was observed over the short contact time, the last 4 vials were therefore left for an extended period (168 hours) to see if a more stable pattern had been established. The results are shown in table 5.1.

Table 5.1 A contact time comparison for silver adsorption on PE and glass

| Contact Time<br>/hours | Ag adsorbed/mg cm <sup>-2</sup> x 10 <sup>6</sup> |              |          |       |
|------------------------|---|--------------|----------|-------|
|                        | Vial No.  | Polyethylene | Vial No. | Glass |
| 0.5                    | 1   | 0.3          | 9        | 17.1  |
| 0.5                    | 2   | 0.2          | 10       | 12.4  |
| 1.0                    | 3   | 4.1          | 11       | 18.2  |
| 1.0                    | 4   | 0.3          | 12       | 20.0  |
| 2.0                    | 5   | 0.2          | 13       | 21.7  |
| 2.0                    | 6   | 0.4          | 14       | 25.6  |
| 168.0                  | 7   | 2.9          | 15       | 31.6  |
| 168.0                  | 8   | 13.3         | 16       | 33.1  |

The results in table 5.1 show poor duplication on polyethylene after both short and extended contact times. However, generally the amount adsorbed on PE is far less than that on glass, but adsorption on the former material continues to rise steadily unlike glass whose adsorption rate decreases steadily until a limiting value is reached.

A number of experiments were then designed to investigate the erratic nature of polyethylene as an adsorbent.

#### 5.1.2 Reproducibility study for PE using 1 mg dm<sup>-3</sup> silver solution and 8 days contact time

It was thought possible that the standard washing procedure followed by overnight drying, may not be sufficient to produce a uniformly dried out surface, due to the water vapour permeability property of polyethylene. It was, therefore, decided to wash eight vials in the standard manner, but then to leave them for 3 weeks to dry out thoroughly. A 3 cm<sup>3</sup> aliquot of labelled, 1 mg dm<sup>-3</sup> silver solution was then added to each vial. The vials were sealed, wrapped in foil and placed in a thermostat-bath for 8 days at 298 K. The vials were then removed, extracted, washed and counted as described in 3.3.4 and 3.3.5. The results are shown in table 5.2.

Table 5.2 Silver adsorption on polyethylene from  $1 \text{ mg dm}^{-3}$  silver solution at 298 K after 8 days contact

| Vial No | Fraction adsorbed | Ag adsorbed / $\text{mg cm}^{-2} \times 10^6$ |
|---------|-------------------|---|
| 1       | 0.4578            | 124.8   |
| 2       | 0.0660            | 18.0  |
| 3       | 0.1996            | 54.4  |
| 4       | 0.1899            | 51.7  |
| 5       | 0.0882            | 24.0  |
| 6       | 0.3556            | 96.9  |
| 7       | 0.0804            | 21.9  |
| 8       | 0.3949            | 107.7   |

It can be seen from the results in table 5.2 that the reproducibility of adsorption has not been improved by the extended drying period. However, this experiment shows that the amount of silver adsorbed can be increased by at least a factor of ten by following this procedure.

5.1.3 Reproducibility study for PE using  $1 \text{ mg dm}^{-3}$  silver solution and 28 days contact

This experiment using all the standard vial preparation techniques but an extended contact time is used to see whether the polyethylene vials will eventually reach a more consistent silver adsorption level.

Eight vials were pre-washed and dried as described in section 3.3.2. A  $3 \text{ cm}^3$  aliquot of  $1 \text{ mg dm}^{-3}$  labelled silver solution was then added to each vial. The vials were sealed, wrapped in foil and immersed in a thermostat-bath for 28 days at 298 K. After this time the vials were removed for extraction, washing and counting as described in sections 3.3.4 and 3.3.5. The results are reported in table 5.3. Two glass vials were also included in this experiment as controls.

Table 5.3 Silver adsorption on polyethylene from  $1 \text{ mg dm}^{-3}$  silver solution at 298 K after 28 days contact

| Vial No    | Fraction adsorbed | Ag adsorbed / $\text{mg cm}^{-2} \times 10^6$ |
|------------|-------------------|---|
| 1          | 0.0288            | 7.8   |
| 2          | 0.0317            | 8.6   |
| 3          | 0.2251            | 61.2  |
| 4          | 0.0321            | 8.6   |
| 5          | 0.0631            | 17.2  |
| 6          | 0.1402            | 38.2  |
| 7          | 0.0119            | 3.2   |
| 8          | 0.0367            | 9.8   |
| 9 (glass)  | 0.1161            | 38.7  |
| 10 (glass) | 0.1092            | 36.4  |

The results in table 5.3 still show that polyethylene shows erratic adsorption properties after 28 days contact, although it is true to say that a larger percentage of this sample are consistent with each other. If we eliminate vial numbers 3, 5 and 6 as high results, and vial 7 as a low result, then the average adsorption value of the remaining vials is  $8.7 \times 10^{-6} \text{ mg cm}^{-2}$  which is only 25% as much as on glass.

#### 5.1.4 Effect of pre-treatment of the polyethylene on adsorption from a $1 \text{ mg dm}^{-3}$ silver solution

In view of the erratic results observed in 5.1.2 and 5.1.3 it was decided to investigate the effect of various pre-washing reagents on the amount of silver adsorption.

A set of vials were prepared using the standard pre-washing procedure described in section 3.3.2, but using a selection of washing solutions followed by doubly deionised water. A  $3 \text{ cm}^3$  aliquot of  $1 \text{ mg dm}^{-3}$  labelled silver solution was then added to each vial. The vials were sealed, wrapped in foil and immersed in a thermostat-bath for 7 days at 298 K. The vials were then

extracted., washed and counted as described in sections 3.3.4 and 3.3.5. The observations are reported in table 5.4.

Table 5.4 The effects of pre-treatment of polyethylene

| Vial No | Pre-Wash Reagent     | Fraction adsorbed | Ag adsorbed /mg cm <sup>-2</sup> x 10 <sup>6</sup> |
|---------|----------------------|-------------------|--|
| 1       | 10% HNO <sub>3</sub> | 0.0156            | 4.2  |
| 2       | "                    | 0.0154            | 4.0  |
| 3       | "                    | 0.0163            | 4.4  |
| 4       | 10% NaOH             | 0.0336            | 9.0  |
| 5       | "                    | 0.0262            | 7.0  |
| 6       | "                    | 0.0268            | 7.2  |
| 7       | "                    | 0.0279            | 7.6  |
| 8       | Solvent *            | 0.0212            | 5.6  |
| 9       | Mixture              | 0.0266            | 7.2  |

\* Solvent mixture 1:1:1 Acetone:Xylene:Methts, by volume.

The results above are more promising, the acid washed vials produced three consistent results which were also quite low adsorption levels. However, three vials were not considered a large enough sample to be confident that the results were representative. Therefore, another eight vials were treated exactly as described in 5.1.4 using 10% nitric acid solution to pre-wash them all, the adsorption results are shown in table 5.5.

Table 5.5 The effect of a nitric acid pre-wash on polyethylene vials

| Vial No | Fraction adsorbed | Ag adsorbed /mg cm <sup>-2</sup> x 10 <sup>6</sup> |
|---------|-------------------|--|
| 1       | 0.0173            | 4.7  |
| 2       | 0.0242            | 6.5  |
| 3       | 0.0312            | 8.5  |
| 4       | 0.0244            | 6.6  |
| 5       | 0.0164            | 4.4  |
| 6       | 0.0149            | 4.0  |
| 7       | 0.0254            | 6.9  |
| 8       | 0.0192            | 5.2  |

The results above show that the adsorption values are all of the same order, i.e. no gross discrepancies as observed in tables 5.2 and 5.3, however, vial 3 shows more than double the adsorption of vial 6. Also on reflection it was the present author's opinion that pre-washing with nitric acid solution would invalidate any comparisons with the adsorption work carried out on glass, reported in Chapter IV. A true picture of the adsorption properties of silver on polyethylene could easily be inhibited by the initial adsorption of hydrogen ions from the pre-washing procedure. However, before abandoning further work on polyethylene it was decided to try to improve reproducibility by shortening the contact period, and comparing both hot and cold pre-treatment using doubly deionised water.

5.1.5 Comparison of hot and cold pre-washing, on the adsorption of silver on polyethylene, from a  $1 \text{ mg dm}^{-3}$  labelled solution after a 4 day contact time

Twelve vials were prepared as follows. Vials 1 to 6 were pre-washed in the standard manner described in section 3.3.2, using doubly deionised water at 291 K, vials 7 to 12 were treated similarly but using doubly deionised water at a temperature of 363 K. A  $3 \text{ cm}^3$  aliquot of labelled  $1 \text{ mg dm}^{-3}$  silver solution was then added to each vial. The vials were sealed, covered in foil and placed in a thermostat-bath at 298 K for 4 days. After this time period the vials were removed for washing and counting as described in sections 3.3.4 and 3.3.5. The results are summarised in table 5.6.

The results for both sets of vials in table 5.6 are generally reproducible apart from vials 4 and 8, however, the contact time is relatively short. It may be that hot washing has increased adsorption due to the water vapour permeability of the polyethylene increasing with temperature. However, it was decided that a long term study of polyethylene as an adsorbent for silver ions, would probably provide unreliable data, and thus make it extremely difficult

Table 5.6 Comparison of hot and cold pre-washing on the adsorption characteristics of polyethylene

| Vial No | Fraction adsorbed | Ag adsorbed /mg cm <sup>-2</sup> x 10 <sup>6</sup> |                 |
|---------|-------------------|--|-----------------|
| 1       | 0.0047            | 1.2  | )               |
| 2       | 0.0028            | 0.7  | )               |
| 3       | 0.0036            | 0.9  | ) Cold pre-wash |
| 4       | 0.1745            | 47.5   | )               |
| 5       | 0.0045            | 1.2  | )               |
| 6       | 0.0043            | 1.1  | )               |
| 7       | 0.0500            | 13.6   | )               |
| 8       | 0.0106            | 2.8  | )               |
| 9       | 0.0448            | 12.2   | ) Hot pre-wash  |
| 10      | 0.0510            | 13.9   | )               |
| 11      | 0.0537            | 14.6   | )               |
| 12      | 0.0571            | 15.5   | )               |

to obtain enough useful data for comparison with glass, and that the remaining time available should be used to study polypropylene as an alternative. The writer did, however, contact ICI and was able to establish that the grade of polyethylene used for the manufacture of these vials was free from additives and that no release agents were used during the injection moulding process.

As a general statement it can be said that the erratic behaviour of polyethylene as an adsorbent, renders it an unreliable material for storage vessels containing trace solutions of silver, especially as the erratic behaviour could well be more unpredictable in vessels of greater surface area. West, West and Iddings (3), also found that adsorption work on polyethylene produced extremely erratic results.

#### 5.2 Assessment of polypropylene as an adsorbent

Two types of polypropylene vials were tested, these are referred to

from now on as PP type 1 and PP type 2, and are fully described in section 3.4.

#### 5.2.1 Reproducibility study for PP type 1 using $1 \text{ mg dm}^{-3}$ silver solution

A sample set of twelve vials were pre-washed and dried in the standard manner described in section 3.3.2. A  $3 \text{ cm}^3$  aliquot of  $1 \text{ mg dm}^{-3}$  labelled silver solution was then added to each vial. The vials were sealed, wrapped in foil and placed in a thermostat-bath for 7 days at 298 K. After this contact time the vials were removed for extraction, washing and counting by the methods described in section 3.3.4 and 3.3.5. The results are shown in table 5.7.

Table 5.7 Reproducibility study on polypropylene (type 1) using  $1 \text{ mg dm}^{-3}$  silver solution and 7 days contact time

| Vial No    | Fraction adsorbed | Ag adsorbed<br>$/\text{mg cm}^{-2} \times 10^6$ |
|------------|-------------------|---|
| 1          | 0.0134            | 3.7   |
| 2          | 0.0131            | 3.6   |
| 3          | 0.0105            | 2.9   |
| 4          | 0.0106            | 2.9   |
| 5          | 0.0161            | 4.5   |
| 6          | 0.0109            | 3.0   |
| 7          | 0.0118            | 3.2   |
| 8          | 0.0112            | 3.1   |
| 9          | 0.0084            | 2.3   |
| 10         | 0.0080            | 2.2   |
| 11         | 0.0135            | 3.7   |
| 12         | 0.0114            | 3.1   |
| Glass      | -                 | 31.6 (See table)                                |
| Comparison | -                 | 33.1 ( 5.1 )                                    |

It can be seen from the results in table 5.7 that the vials tested gave reasonably consistent adsorption values. It was therefore decided to continue work on this sample batch of vials. It is also interesting to note

that the adsorption values are of the order of 10% of those for glass.

### 5.2.2 Contact time study for PP type 1 vials using $1 \text{ mg dm}^{-3}$

#### silver solution

The remaining vials from the original sample were pre-washed and dried in the standard manner described in section 3.3.2. A  $3 \text{ cm}^3$  aliquot of  $1 \text{ mg dm}^{-3}$  labelled silver solution was then added to each vial. The vials were sealed, wrapped in foil and placed in a thermostat-bath at 298 K. After various contact times, duplicate vials were removed for extraction and counting as described in sections 3.3.4 and 3.3.5.

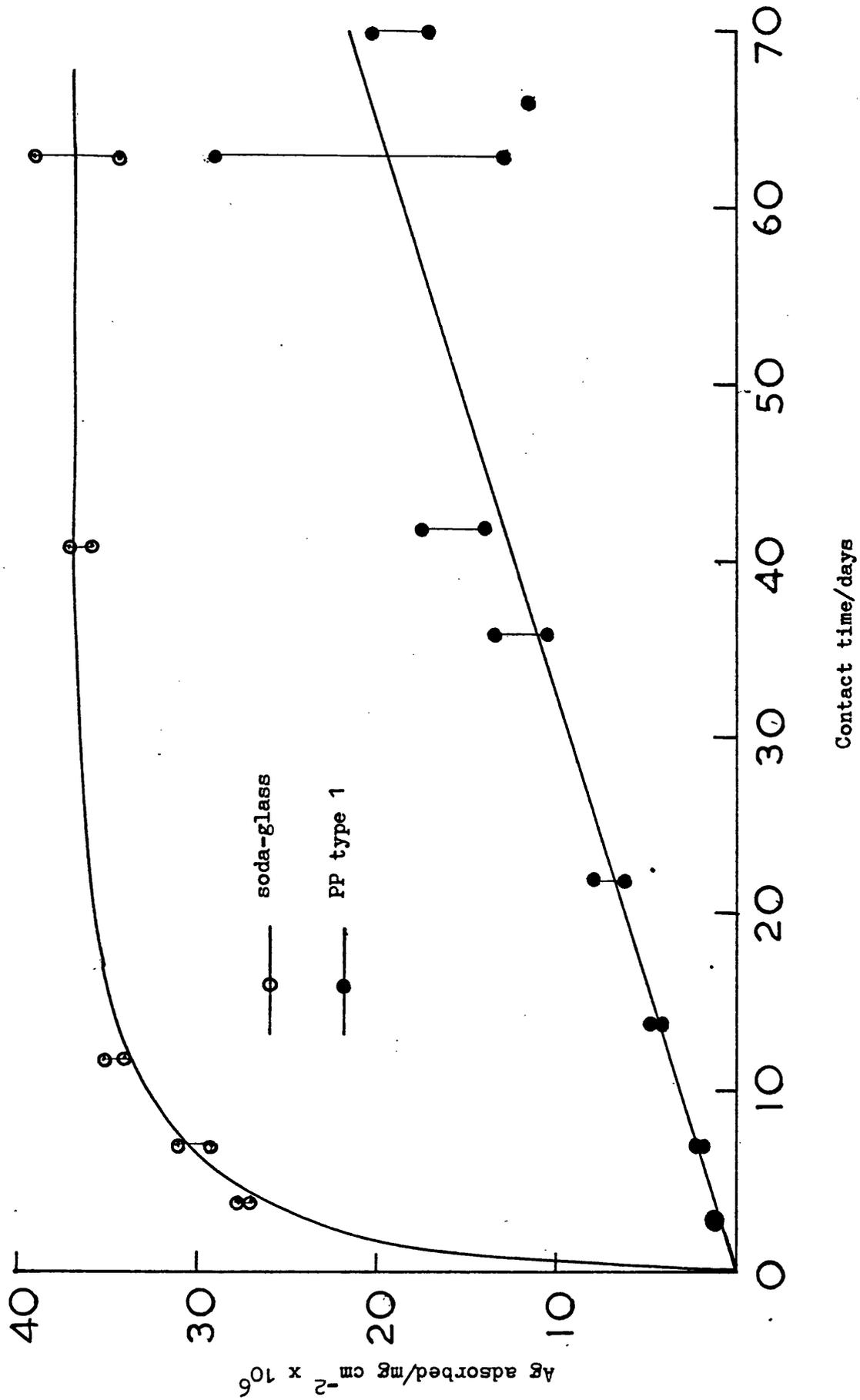
The results are given in table 5.8, glass controls are also included.

Table 5.8 Contact time study for PP type 1 using  $1 \text{ mg dm}^{-3}$  silver solution at 298 K

| Vial No | Contact time /days | Fraction adsorbed | Ag adsorbed / $\text{mg cm}^{-2} \times 10^6$ | Glass comparisons / $\text{mg cm}^{-2} \times 10^6$ |
|---------|--------------------|-------------------|---|---|
| 1       | 3                  | 0.0045            | 1.2   | 27.6 (4 days)                                       |
| 2       | 3                  | 0.0046            | 1.2   | 27.2 (4 days)                                       |
| 3       | 7                  | 0.0073            | 2.0   | 29.2 (7 days)                                       |
| 4       | 7                  | 0.0067            | 1.8   | 31.0 (7 days)                                       |
| 5       | 14                 | 0.0168            | 4.7   | 34.0 (12 days)                                      |
| 6       | 14                 | 0.0157            | 4.3   | 35.1 (12 days)                                      |
| 7       | 22                 | 0.0216            | 6.0   | 36.1 (41 days)                                      |
| 8       | 22                 | 0.0281            | 7.8   | 37.3 (41 days)                                      |
| 9       | 36                 | 0.0480            | 13.4  | 39.2 (63 days)                                      |
| 10      | 36                 | 0.0380            | 10.6  | 34.4 (63 days)                                      |
| 11      | 42                 | 0.0626            | 17.5  | Adsorbed  |
| 12      | 42                 | 0.0500            | 14.0  | silver determined                                   |
| 13      | 63                 | 0.0471            | 13.1  | at 298 K, from                                      |
| 14      | 63                 | 0.0683            | 19.1  | a $1 \text{ mg dm}^{-3}$                            |
| 15      | 66                 | 0.0416            | 11.6  | silver  |
| 16      | 70                 | 0.0616            | 17.2  | solution.   |
| 17      | 70                 | 0.0727            | 20.3  |   |

The above results have been plotted in figure 5.1

FIG. 5.1 Graphs of silver adsorption from  $1.0 \text{ mg dm}^{-3}$  silver solutions, on soda-glass and polypropylene type 1 against contact time at 298 K



It can be shown from figure 5.1 that the adsorption on polypropylene increases linearly with contact time.

It can also be shown that short term contact, i.e. up to 14-days, gives rise to adsorption levels of approximately 10% of those for glass vials, although extrapolation of figure 5.1 shows that the amount of adsorption on PP type 1 would eventually exceed that where glass levels off.

Some of the vials from 5.2.2 were subjected to additional washing cycles to see whether reagent other than  $\text{DDH}_2\text{O}$  would remove any further adsorbed silver.

### 5.2.3 Desorption of silver from PP type 1 using a selection of reagents

In addition to the standard washing cycles the following treatments were carried out on vials from 5.2.2.

#### (a) Vial 11, - 42-day contact

The amount of silver adsorbed after standard washing procedure was  $17.5 \times 10^{-6} \text{ mg cm}^{-2}$ . After an additional 60 second soak in 10% nitric acid solution and 3 standard  $\text{DDH}_2\text{O}$  washes, the amount of silver adsorbed was found to be  $16.7 \times 10^{-6} \text{ mg cm}^{-2}$ .

#### (b) Vial 12, - 42-day contact

The amount of silver adsorbed after standard washing procedure was  $14.0 \times 10^{-6} \text{ mg cm}^{-2}$ . After an additional 60 second soak in 10% sodium hydroxide solution and 3 standard  $\text{DDH}_2\text{O}$  washes, the amount of silver adsorbed was found to be  $12.6 \times 10^{-6} \text{ mg cm}^{-2}$ .

#### (c) Vial 13, - 63-day contact

The amount of silver adsorbed after standard washing procedure was  $13.1 \times 10^{-6} \text{ mg cm}^{-2}$ . After an additional 60 second soak in 1000  $\text{mg dm}^{-3}$  unlabelled silver solution and 3 standard  $\text{DDH}_2\text{O}$  washes, the apparent amount of silver adsorbed was found to be  $6.6 \times 10^{-6} \text{ mg cm}^{-2}$ .

#### (d) Vial 14, - 63-day contact

The amount of silver adsorbed after standard washing procedure was  $19.1 \times 10^{-6} \text{ mg cm}^{-2}$ . After an additional 60 second soak in a 1:1:1, acetone:meths:xylene, solvent mixture, and 3 standard  $\text{DDH}_2\text{O}$  washes, the amount of

silver adsorbed was found to be  $10.5 \times 10^{-6} \text{ mg cm}^{-2}$ .

The acid and alkali soaks removed virtually no further adsorbed silver, this suggests that the adsorption and desorption processes are not sensitive to  $\text{H}^+$  or  $\text{OH}^-$  ions.

The effect of soaking in silver nitrate solution was pronounced, and the recorded figure suggests a rapid ion exchange has taken place.

The solvent soak removed almost 50% of the adsorbed silver. The Xylene present in the mixture is probably responsible for this removal of silver, because Xylene rapidly permeates into polypropylene, in fact polypropylene containers are found to be suitable for applications where only intermittent contact occurs. \* Also ketones will dissolve trace amounts of atactic material within the polymer.

When the initial sample of vials had been exhausted the author experienced supply difficulties with PP type 1 vials, and a secondary source had to be found, therefore, subsequent work was carried out using PP Type 2 vials, as described in section 3.4.

#### 5.2.4 Reproducibility study for PP type 2 using $1 \text{ mg dm}^{-3}$ silver solution

A sample of five vials was pre-washed and dried as described in section 3.3.2. A  $3 \text{ cm}^3$  aliquot of  $1 \text{ mg dm}^{-3}$  labelled silver solution was then added to each vial. The vials were sealed, wrapped in foil and placed in a thermostat-bath for 7 days at 298 K. After this contact time the vials were removed for extraction, washing and counting as described in sections 3.3.4 and 3.3.5. The results are summarised in table 5.9.

\* The author is grateful to Mr. Hanson of ICI Plastics Division, Welwyn Garden City, for this information.

Table 5.9 Reproducibility study on PP type 2 using 1 mg dm<sup>-3</sup> silver solution and 7 days contact

| Vial No | Fraction adsorbed | Ag adsorbed /mg cm <sup>-2</sup> x 10 <sup>6</sup> |
|---------|-------------------|--|
| 1       | 0.0125            | 3.4  |
| 2       | 0.1518            | 41.7   |
| 3       | 0.0101            | 2.7  |
| 4       | 0.1012            | 27.8   |
| 5       | 0.0142            | 3.9  |

It was obvious from the results in table 5.9 that the reproducibility was poor. Further inspection of the vials showed the presence of striations in the vial walls, to varying degrees, in fact the remaining vials within this batch also contained striations. The writer contacted the manufacturer who reported that the marks had originated from the injection moulds, and promised a replacement batch after the moulds had been re-polished. When the new vials arrived the majority were found to be striation-free to the naked eye. The above experiment was then repeated using six more PP type 2 vials, and the results are shown in table 5.10.

Table 5.10 Reproducibility study on further sample of PP type 2 vials using 1 mg dm<sup>-3</sup> silver solution and 7 days contact

| Vial No | Corrected c.p.m. IN | Corrected c.p.m. OUT | Fraction adsorbed | Ag adsorbed /mg cm <sup>-2</sup> x 10 <sup>6</sup> |
|---------|---------------------|----------------------|-------------------|--|
| 6       | 57167               | 76                   | 0.0013            | 0.3  |
| 7       | 57565               | 87                   | 0.0015            | 0.4  |
| 8       | 57694               | 83                   | 0.0014            | 0.3  |
| 9       | 57359               | 97                   | 0.0017            | 0.4  |
| 10      | 57935               | 108                  | 0.0019            | 0.5  |
| 11      | 57565               | 91                   | 0.0016            | 0.4  |

The count rates have been included because the OUT counts were small compared to a background of 133 c.p.m., although the total counts for each vial were taken over 20 minutes giving a total count of 4000 to 5000. It would seem from a comparison of PP types 1 and 2, and the second sample of type 2, that the quality of the surface finish, i.e. micro-surface area has probably resulted in the difference in adsorption values observed per geometric area.

Since no other vial supply was available, further experiments were carried out using this second sample of PP type 2 vials.

#### 5.2.5 Contact time study for PP type 2 vials using $1 \text{ mg dm}^{-3}$ silver solution

Fourteen vials were prepared in the manner described in section 3.3.2. A  $3 \text{ cm}^3$  aliquot of  $1 \text{ mg dm}^{-3}$  labelled silver solution was then added to each vial. The vials were sealed, wrapped in foil and placed in a thermostat-bath at 298 K. After various contact times, duplicate vials were removed for extraction and counting as described in sections 3.3.4 and 3.3.5. The results are given in table 5.11.

It can be shown from figure 5.2 that the results are both erratic and lower than those for PP type 1 shown in figure 5.1. A straight line has been drawn that passes through each duplicate pair of results, however, due to the poor reproducibility we cannot be sure that the relationship is linear.

A further experiment was carried out using PP type 2 vials to try to determine whether pH affects the adsorption of silver on this substrate. It was thought that we may not observe the same effect as seen for glass in Chapter IV, because in experiment 5.2.3 washing with acid or alkali solution had no effect on adsorbed silver.

#### 5.2.6 The effect of pH on the adsorption of silver on PP type 2 vials from a $0.5 \text{ mg dm}^{-3}$ silver solution after 7 days contact

Twelve vials were prepared in the standard manner as described in section 3.3.2. A  $0.1 \text{ cm}^3$  aliquot of nitric acid solution was then added to each vial, followed by a  $3 \text{ cm}^3$  aliquot of  $0.5 \text{ mg dm}^{-3}$  labelled silver solution.

Table 5.11 Contact time study for PP type 2 vials using  $1 \text{ mg dm}^{-3}$  silver solution at 298 K

| Vial No | Contact Time/days | Fraction adsorbed | Ag adsorbed / $\text{mg cm}^{-2} \times 10^6$ |
|---------|-------------------|-------------------|---|
| 1       | 7                 | 0.0013            | 0.3   |
| 2       | 7                 | 0.0015            | 0.4   |
| 3       | 15                | 0.0051            | 1.4   |
| 4       | 15                | 0.0065            | 1.8   |
| 5       | 22                | 0.0133            | 3.7   |
| 6       | 22                | 0.0071            | 1.9   |
| 7       | 29                | 0.0048            | 1.3   |
| 8       | 29                | 0.0145            | 4.1   |
| 9       | 57                | 0.0167            | 4.7   |
| 10      | 57                | 0.0106            | 3.0   |
| 11      | 78                | 0.0067            | 1.8   |
| 12      | 78                | 0.0419            | 11.7  |
| 13      | 92                | 0.0192            | 5.3   |
| 14      | 92                | 0.0666            | 18.6  |

The above results have been plotted in figure 5.2

The concentration of the acid was varied to produce solutions with a pH range of 0.3 to 4.4. The highest pH obtainable was 4.4 due to the amount of isotope solution required to label the silver solution in order to increase the count rates observed. The vials were then sealed, wrapped in foil and placed in a thermostat-bath at 298 K for 7 days. After this time the vials were removed for extraction and counting as described in sections 3.3.4 and 3.3.5.

The results are shown in table 5.12.

FIG. 5.2 Graph of silver adsorption from a  $1.0 \text{ mg dm}^{-3}$  silver solution on polypropylene type 2 against contact time at 298K

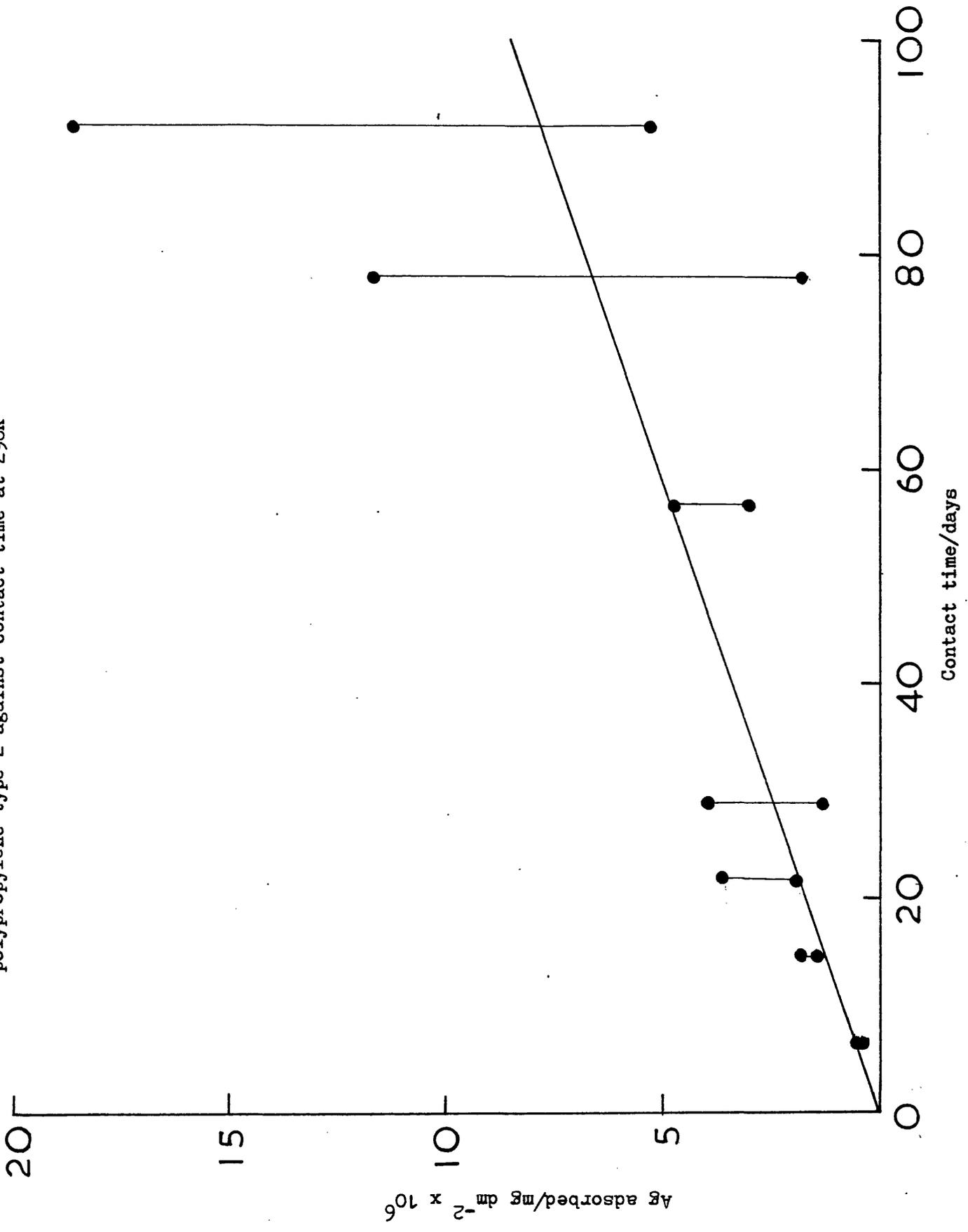


Table 5.12 The adsorption of silver from  $0.5 \text{ mg dm}^{-3}$  silver solution  
on PP type 2 vials over a range of pH values

| Vial No | pH  | Fraction adsorbed | Ag adsorbed<br>$/\text{mg cm}^{-2} \times 10^6$ |
|---------|-----|-------------------|---|
| 1       | 4.4 | 0.0035            | 0.5   |
| 2       | 4.4 | 0.0045            | 0.6   |
| 3       | 3.4 | 0.0032            | 0.4   |
| 4       | 3.4 | 0.0042            | 0.6   |
| 5       | 2.5 | 0.0037            | 0.5   |
| 6       | 2.5 | 0.0034            | 0.5   |
| 7       | 1.5 | 0.0030            | 0.4   |
| 8       | 1.5 | 0.0041            | 0.6   |
| 9       | 0.5 | 0.0025            | 0.3   |
| 10      | 0.5 | 0.0019            | 0.3   |
| 11      | 0.3 | 0.0040            | 0.5   |
| 12      | 0.3 | 0.0033            | 0.5   |

It can be shown from table 5.12 that the effect of pH on the adsorption of silver was negligible over the range indicated.

Time did not permit an investigation into a wider variety of substrates, however, further work of this nature could prove interesting, in particular at pH's greater than 4.4.

CHAPTER VIDISCUSSION6.1 Silver adsorption and analytical procedure

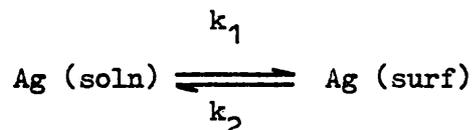
Analytical technique regarding the quantitative detection of silver at trace levels can be significantly improved by applying the observations made in sections 4.1, 4.2, 4.3, 4.4, 4.5, 5.1 and 5.2, which may be summarised as follows :-

- (a) Sampling should be carried out as much as possible using glassware rather than polyethylene or polypropylene. Although the results in chapter V suggest that the latter two substrates adsorb much less than glass under the same conditions of temperature, concentration and pH, this cannot be guaranteed due to the erratic results obtained with polyethylene and polypropylene. It is, therefore, suggested that it is preferable to use vessels of a more predictable nature, i.e. glass. Having said this the following statements refer to glassware..
- (b) All silver solutions should be at a pH value of less than three, however, if a particular analysis necessitates alkaline conditions then the pH should be greater than 13.5.
- (c) Storage of silver solutions at low temperatures reduces adsorption losses.
- (d) Silver solutions or water samples for silver analysis should be taken into glassware already containing acid solution. Acidification at a later stage involves a considerable induction period before desorption reaches a limiting value.
- (e) The history of the glassware is important, prolonged acid soaking is advised to remove adsorbed silver. Also selected glassware should preferably be reserved for each particular cation, to minimise the possibility of cross-contamination.

## 6.2 Representation of Experimental Data

### 6.2.1 A kinetic treatment of silver adsorption and desorption

Wharmby (1) used a simple kinetic treatment, based on the process :



to represent his experimental data at 298 K, where  $k_1$  and  $k_2$  are first order specific rates. The application was, however, restricted to adsorption from an initial solution concentration of  $0.5 \text{ mg dm}^{-3}$  silver, which Wharmby argued, was insufficient to allow occupation of more than a relatively small fraction of the available glass surface. The net rate of adsorption at time  $t$  is represented as :

$$\frac{dx}{dt} = k_1(a-x) - k_2x \quad (1)$$

where "a" is the initial solution concentration and "x" the concentration adsorbed. Integration yields :

$$x = \theta a (1 - e^{-(k_1 + k_2)t}) \quad (2)$$

where  $\theta = \frac{k_1}{(k_1 + k_2)}$ ,

Equation (2) reduces to :

$$x_{eq} = \theta a$$

when  $t$  is sufficiently large for the exponential term to become negligible, and Wharmby assigned a value to  $(k_1 + k_2)$  by estimating the time,  $\tau$ , taken for  $x$  to reach a value of  $x_{eq}/2$ , when  $(k_1 + k_2)$  is equal to  $\ln 2/\tau$ , and where  $x_{eq}$  is the equilibrium concentration adsorbed. Individual values could, then, be assigned to  $k_1$  and  $k_2$ . The relevant experiment appears, so far as can be ascertained, to have been carried out at a pH of about 5.3.

A similar analysis of data reported in this thesis (see figure 4.19) for pH values of 5.0 and 4.6 yields the following values in tables 6.1 and 6.2. (Wharmby's values are included in table 6.2 for comparison).

Table 6.1 Values of  $x$  and  $t$  at pH's 5.0 and 4.6, at 298 K

| pH 5.0, $x_{eq} \sim 30 \times 10^{-6} \text{ mg cm}^{-2}$ |                                      | pH 4.6, $x_{eq} \sim 22 \times 10^{-6} \text{ mg cm}^{-2}$ |                                      |
|--|--------------------------------------|--|--------------------------------------|
| t/days   | $x/\text{mg Ag cm}^{-2} \times 10^6$ | t/days   | $x/\text{mg Ag cm}^{-2} \times 10^6$ |
| 2  | 7.6                                  | 2  | 6.7                                  |
| 5  | 15.0                                 | 5  | 13.2                                 |
| 10   | 22.5                                 | 10   | 18.4                                 |
| 20   | 28.1                                 | 20   | 21.4                                 |
| 30   | 29.5                                 | 30   | 21.9                                 |
| 40   | 29.9                                 | 40   | 22.0                                 |
| 60   | 30.0                                 | 60   | 22.0                                 |

The results in table 6.1 have been plotted in figure 6.1 and compared to the experimentally derived curves from figure 4.19. The curves are a reasonable fit to each other, apart from the initial rapid adsorption observed experimentally.

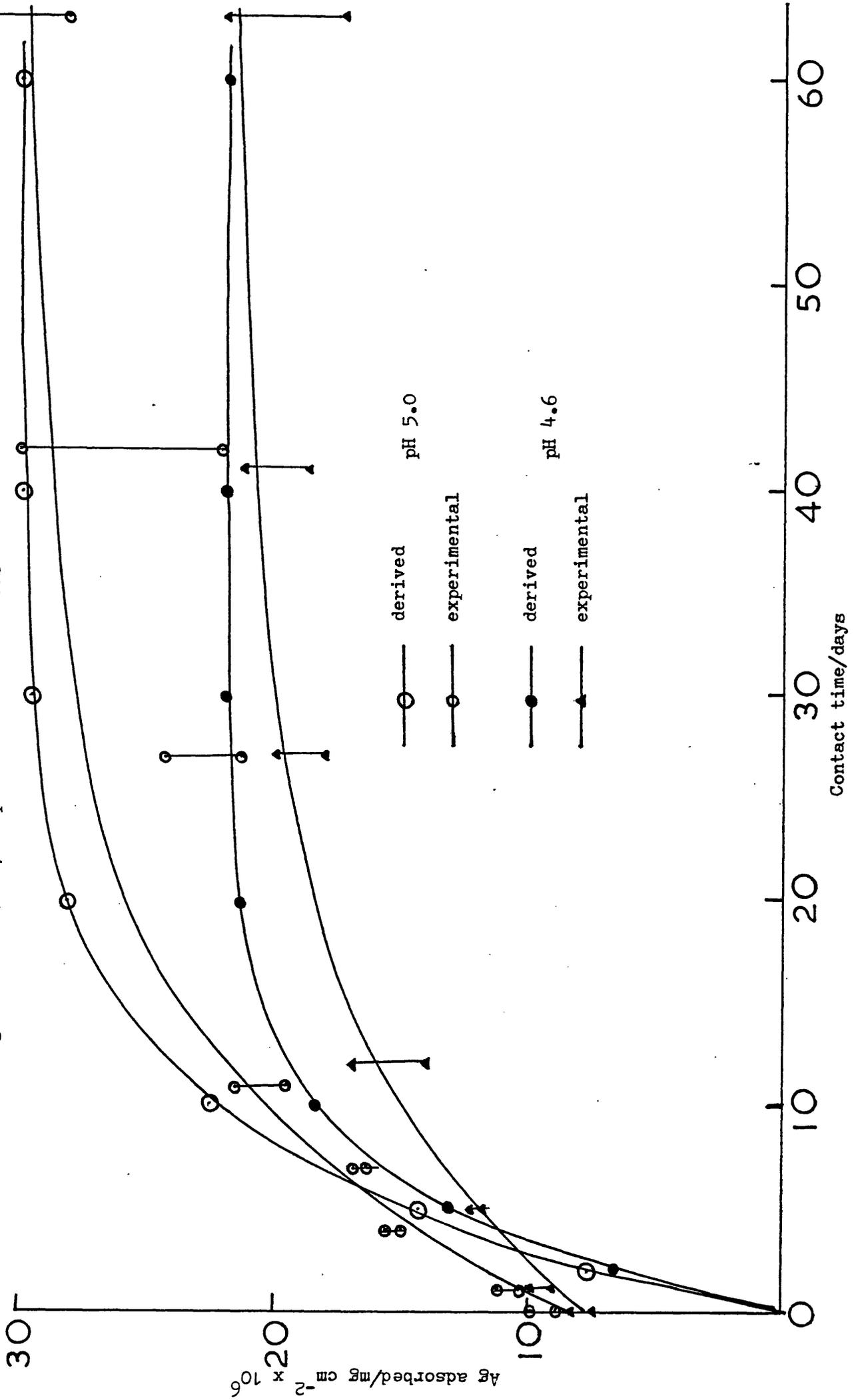
Table 6.2 Comparison of specific rates at pH's 5.3, 5.0 and 4.6

| pH                     | 5.3 (Wharmby)        | 5.0                   | 4.6                   |
|------------------------|----------------------|-----------------------|-----------------------|
| $k_1/\text{days}^{-1}$ | $2.3 \times 10^{-2}$ | $2.5 \times 10^{-2}$  | $2.4 \times 10^{-2}$  |
| $k_2/\text{days}^{-1}$ | $7.6 \times 10^{-2}$ | $1.14 \times 10^{-1}$ | $1.58 \times 10^{-1}$ |
| $k_2/k_1$              | 3.3                  | 4.6                   | 6.6                   |

While the reproducibility of the experimental data is not such as to enable precise conclusions to be drawn, the influence of pH on the ratio  $k_2/k_1$  is apparent.

Wharmby established that the adsorption occurring over periods of days or weeks is preceded by a more rapid process which appears to reach its equilibrium over the first ten minutes or so. The data reported in table 4.19

FIG. 6.1 Graphs of silver adsorption against contact time at pH's 4.6 and 5.0 at a concentration of  $0.5 \text{ mg dm}^{-3}$  and  $298 \text{ K}$ , compared to derived curves



of this thesis not only confirm the presence of this more rapid process but also tend to indicate that its extent appears to vary but little, if at all, with pH over the range 5.3 to 4.6. Equation (2) may, then, better represent experimental data if a constant "c" is added to take account of the initial rapid adsorption :

$$x = c + x_{eq}^1 (1 - e^{-(k_1 + k_2)t}) \quad (3)$$

x is the observed concentration of silver on the glass surface at time t (t must be sufficiently long to enable the initial rapid adsorption to have achieved its constant extent represented by c),  $x_{eq}^1$  is given by  $(x_{eq} - c)$ , where  $x_{eq}$  is the observed concentration of silver on the glass when t is sufficiently long for equilibrium to have been attained. An inspection of the results in table 4.20 leads to an approximate value of  $9 \times 10^{-6} \text{ mg cm}^{-2}$  for "c", by averaging the ten readings up to  $4.17 \times 10^{-2}$  days. The results in table 6.3 were then derived using equation (3), and values of  $x_{eq}$  from the curves in figure 4.19. Appropriate values of  $(k_1 + k_2)$  were determined by trial and error.

Table 6.3 Values of x and t at pH's 5.3, 5.0 and 4.6

| t<br>/days | x/mg Ag cm <sup>-2</sup> x 10 <sup>6</sup> |        |        |
|------------|--|--------|--------|
|            | pH 5.3                                     | pH 5.0 | pH 4.6 |
| 2.5        | 13.5                                       | 12.3   | 10.8   |
| 5          | 17.4                                       | 15.2   | 12.2   |
| 10         | 23.5                                       | 19.5   | 14.5   |
| 20         | 31.2                                       | 24.8   | 17.3   |
| 30         | 35.3                                       | 27.4   | 18.6   |
| 40         | 37.5                                       | 28.7   | 19.3   |
| 50         | 38.7                                       | 29.3   | 19.7   |
| 60         | 39.3                                       | 29.7   | 19.8   |
| 70         | 39.6                                       | 29.8   | 19.9   |
| 80         | 39.8                                       | 29.9   | 20.0   |
| 90         | 39.9                                       | 30.0   | -      |
| 100        | 39.9                                       | -      | -      |

FIG. 6.2 Graph showing a comparison of experimental points and the derived curve, for silver adsorption against contact time at pH 5.3 and 298 K from a  $0.5 \text{ mg dm}^{-3}$  silver solution.

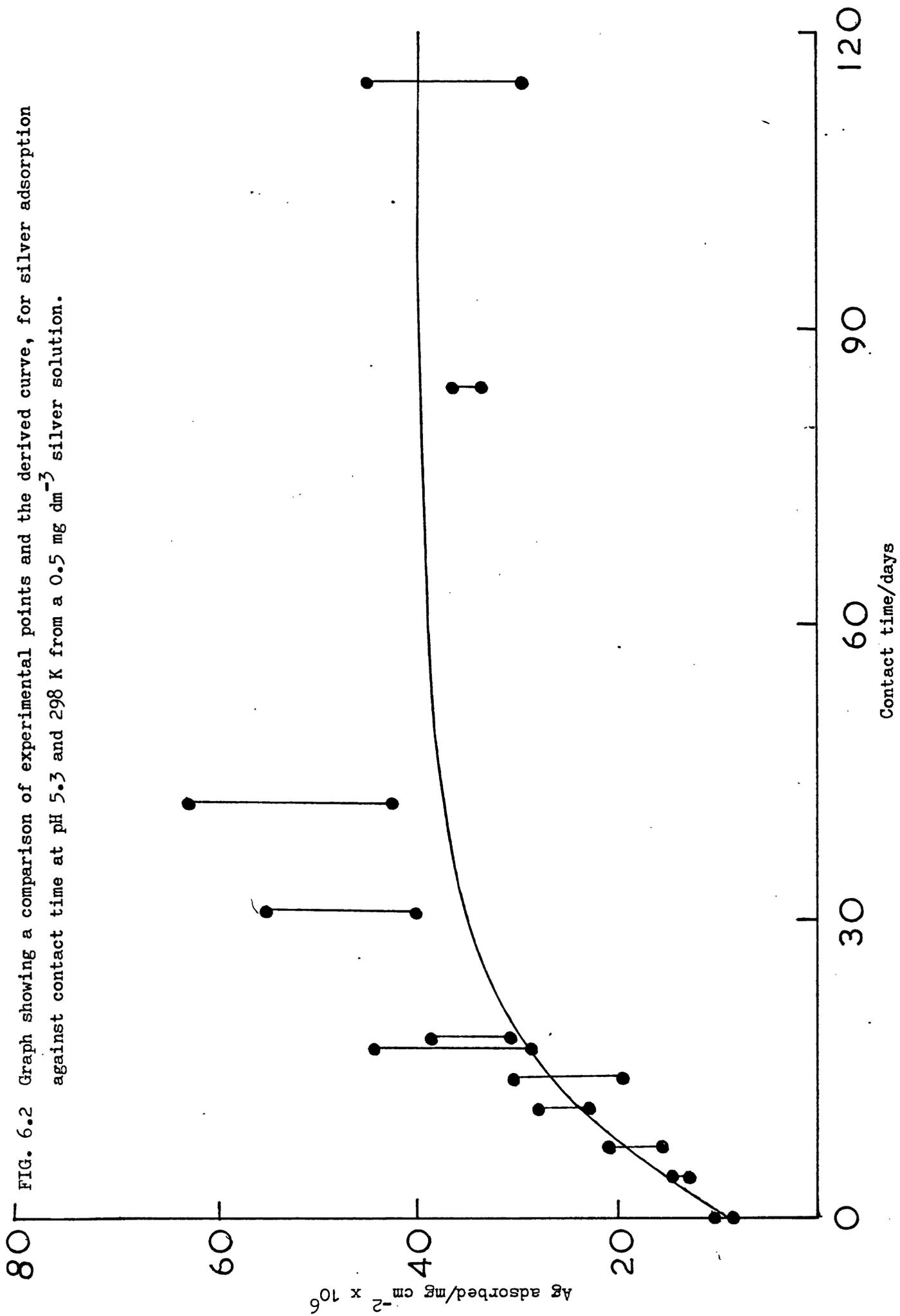


FIG. 6.3 Graph showing a comparison of experimental points and the derived curve, for silver adsorption against contact time, at pH 5.0 and 298 K, from a  $0.5 \text{ mg dm}^{-3}$  silver solution.

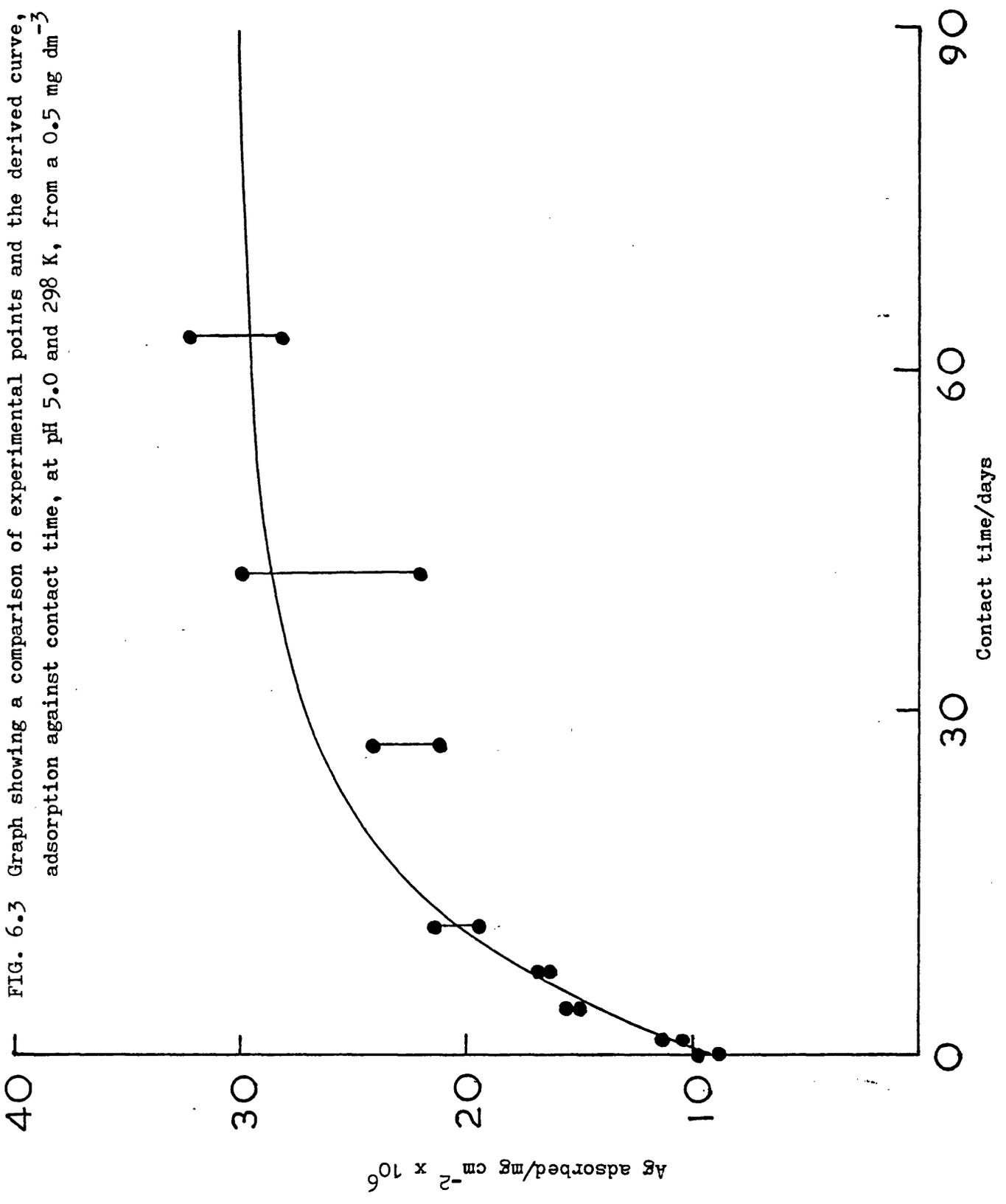
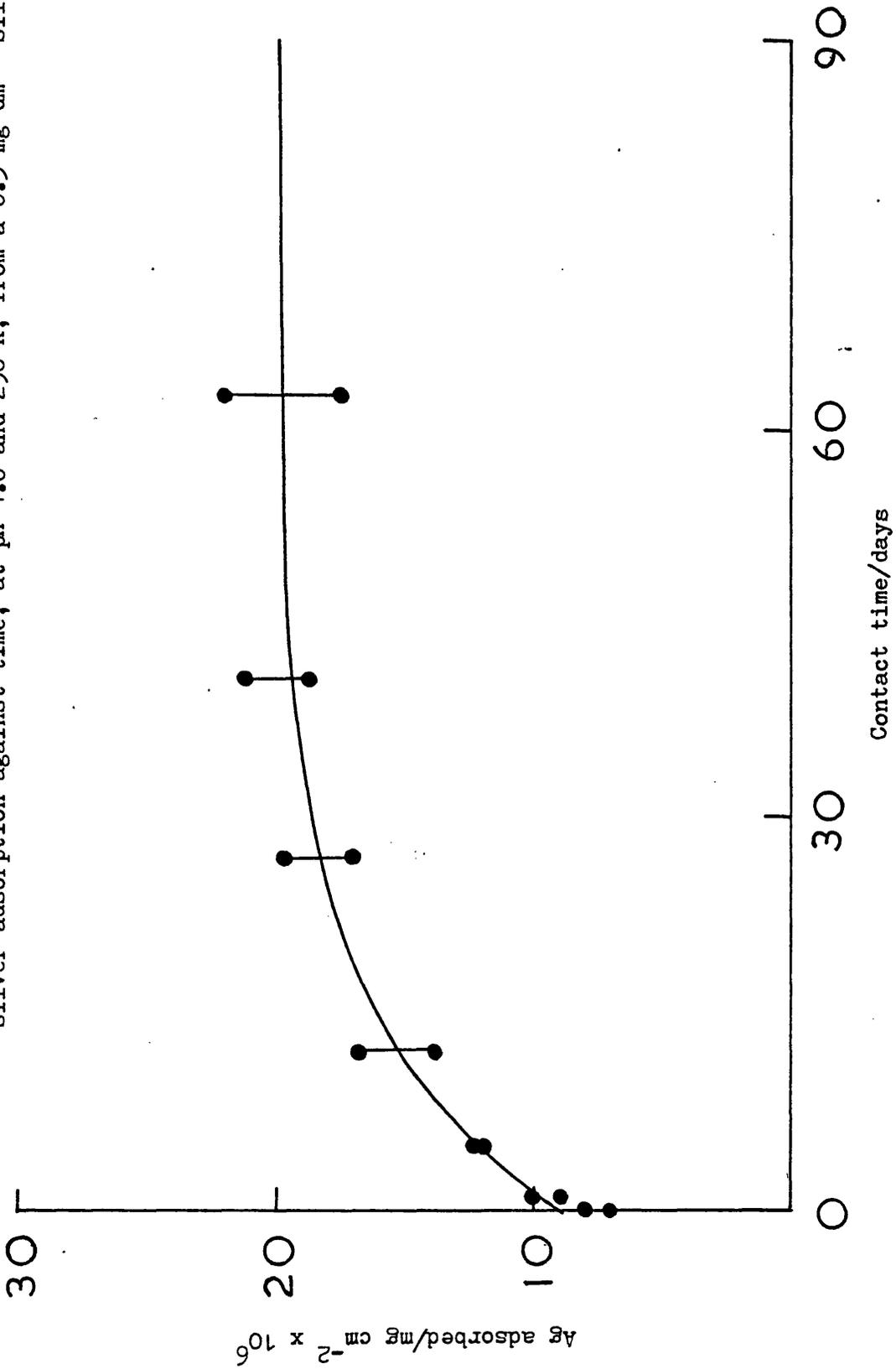


FIG. 6.4 Graph showing a comparison of experimental points and the derived curve, for silver adsorption against time, at pH 4.6 and 298 K, from a  $0.5 \text{ mg dm}^{-3}$  silver solution



The results in table 6.3 are depicted in figures 6.2, 6.3 and 6.4, which show curves drawn through the points from table 6.3 superimposed on the experimental points from table 4.20. It can be seen from these figures that this treatment has produced better curve fits to experimental data by introducing the constant "c".

Table 6.4 summarises experimental data and collects constants derived therefrom via equation (3).

Table 6.4

| pH                                       | 5.3                   | 5.0                   | 4.6                   |
|--|-----------------------|-----------------------|-----------------------|
| $x_{eq}/\text{mg cm}^{-2} \times 10^6$   | 40                    | 30                    | 20                    |
| $x^1_{eq}/\text{mg cm}^{-2} \times 10^6$ | 31                    | 21                    | 11                    |
| $\frac{k_1}{k_1+k_2} = \frac{x_{eq}}{a}$ | $1.86 \times 10^{-1}$ | $1.26 \times 10^{-1}$ | $6.60 \times 10^{-2}$ |
| $(k_1+k_2)/\text{days}^{-1}$             | $6.3 \times 10^{-2}$  | $6.93 \times 10^{-2}$ | $6.93 \times 10^{-2}$ |
| $k_1/\text{days}^{-1}$                   | $1.17 \times 10^{-2}$ | $8.73 \times 10^{-3}$ | $4.57 \times 10^{-3}$ |
| $k_2/\text{days}^{-1}$                   | $5.13 \times 10^{-2}$ | $6.06 \times 10^{-2}$ | $6.47 \times 10^{-2}$ |
| $k_2/k_1$                                | 4.38                  | 6.94                  | 14.2                  |

Although the magnitude is slightly different, the influence of pH on the ratio  $k_2/k_1$  follows the same trend as reported in table 6.2.

This type of representation of experimental data is based on the assumption of equilibria involving a first order (in silver) adsorption opposed by a first order desorption. It takes no account of the possibility that the glass surface may have a limited capacity for silver and that, when the extent of adsorption is an appreciable fraction of this capacity, the forward rate may be influenced by changes in the effective surface area still available. It is, then, perhaps appropriate to modify equation (1) by

including a term  $(x_m - x)$ , where  $x_m$  represents the maximum concentration of silver which can be adsorbed at the prevailing temperature :

$$\frac{dx}{dt} = k_1^1 (a - x)(x_m - x) - k_2 x \quad (4)$$

$k_1^1$  is, of course, a second order specific rate.

Equation (4) may be integrated to yield  $x$  as a function of  $t$ , but in view of the difficulties in assigning a reliable value to  $x_m$ , and in measuring  $x$  sufficiently precisely, it is doubtful whether the advantage gained would be worthwhile.

The largest adsorption at 298 K recorded in this thesis is  $942.4 \times 10^{-6} \text{ mg cm}^{-2}$  (table 4.15) after 112 days contact with silver solution at an initial concentration of  $100 \text{ mg dm}^{-3}$ . In this case the solution concentration has decreased only to about  $97 \text{ mg dm}^{-3}$  during the long contact period, and the term  $(a - x)$  has remained effectively constant throughout. Under these circumstances equation (4) reduces to :

$$\frac{dx}{dt} = k_1^{11} (x_m - x) - k_2 x$$

where  $k_1^{11} = k_1^1 (a - x)$ , and the kinetics are controlled by the still-available surface area rather than the solution concentration of silver.

It is reasonable to suppose that  $x_m$  is not smaller than the largest adsorption recorded. If this is indeed so, in cases where  $x_{eq}$  does not exceed, say  $40 \times 10^{-6} \text{ mg cm}^{-2}$ , the term  $(x_m - x)$  varies but little during adsorption, and equation (4) reduces to equation (1), where  $k_1 = k_1^1 (x_m - x)$ , and the adsorption kinetics are controlled by the solution concentration of silver.

It seems, then, that equation (3) is probably adequate to represent the experimental data reported in this thesis, in the pH range of about 4.6 to 5.3, in cases where only a small fraction of the glass surface capacity to adsorb silver has been taken up; the values obtained for  $k_1$  and  $k_2$ ,

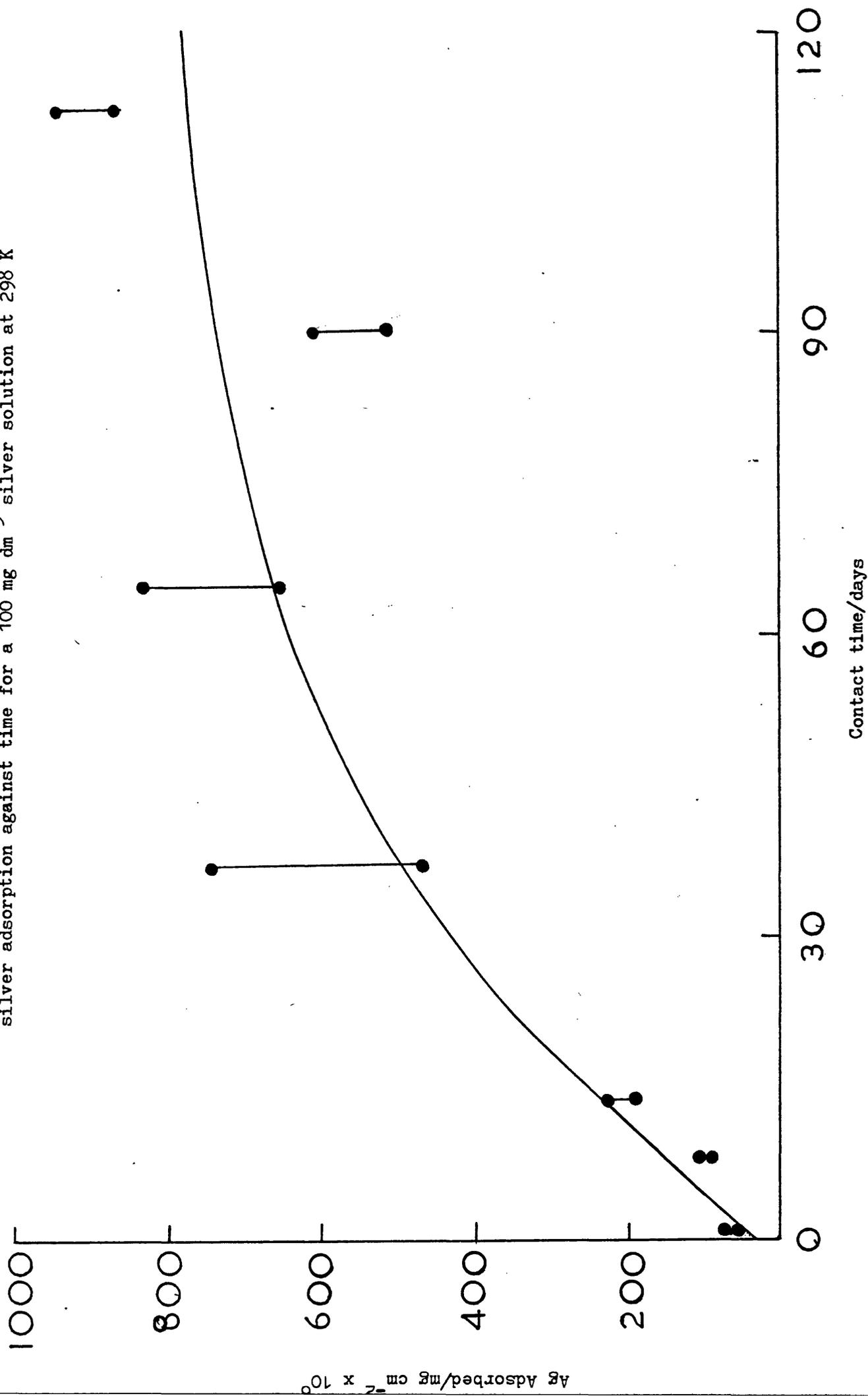
while lacking somewhat in precision, provide a useful guide to the rate and extent of adsorption that may be expected to occur on glass from silver solutions at concentrations below about  $1 \text{ mg dm}^{-3}$ . Experience shows, too, that with more concentrated solutions the pattern of adsorption can still be represented reasonably well by equation (3), although the values of  $k_1$  and  $k_2$  are now appreciably lower and markedly concentration dependent. In all cases, however,  $k_1$  and  $k_2$  should be regarded as empirical constants and certainly not, at the present state of knowledge, as established specific rates of individual processes which constitute a supposed mechanism of the adsorption.

Representation of experimental data in table 4.15, using estimated values of  $900 \times 10^{-6} \text{ mg cm}^{-2}$  for  $x_{eq}$  and  $46 \times 10^{-6} \text{ mg cm}^{-2}$  for "c", illustrate how calculated values of  $x$ , from equation (3) fit the adsorption of silver from an initial silver concentration of  $100 \text{ mg dm}^{-3}$  at 298 K. The values of  $x$  are given in table 6.5.

Table 6.5 Calculated values of  $x$  for  $a = 100 \text{ mg Ag dm}^{-3}$

| t/days | $x/\text{mg cm}^{-2} \times 10^6$ |
|--------|-----------------------------------|
| 1      | 61.6                              |
| 2      | 76.8                              |
| 4      | 106.5                             |
| 8      | 162.8                             |
| 16     | 263.6                             |
| 24     | 350.6                             |
| 32     | 425.7                             |
| 48     | 546.6                             |
| 64     | 636.6                             |
| 128    | 818.8                             |

FIG. 6.5 Graph showing a comparison of experimental points and the derived curve, for silver adsorption against time for a  $100 \text{ mg dm}^{-3}$  silver solution at 298 K



The results in table 6.5 are depicted in figure 6.5, showing the calculated curve superimposed on the experimental data from table 4.15. The curve fits the experimental results quite well. The constants derived from equation (3) were as follows :-

$$\begin{aligned}(k_1 + k_2) &= 1.84 \times 10^{-2} \text{ days}^{-1} \\ k_1 &= 4.71 \times 10^{-4} \text{ days}^{-1} \\ k_2 &= 1.79 \times 10^{-2} \text{ days}^{-1} \\ k_2/k_1 &= 38\end{aligned}$$

As previously stated, the marked concentration dependence of  $k_1$  and  $k_2$  is now apparent.

Wharmby's type of simplified kinetic treatment may also be applied, though with caution, to the desorption of silver in the presence of nitric acid (see section 4.3.2).

If a glass surface with an initial concentration "p" of adsorbed silver is maintained in contact with acid solution over time "t", the rate of desorption may be expressed as :-

$$\frac{dx}{dt} = k_2(p - x) - k_1x \quad \text{-----} \quad (1)$$

where "x" is the concentration of silver, desorbed into solution

$$\text{i.e. } \frac{dx}{dt} = (k_2 + k_1)(\gamma p - x)$$

$$\text{and } \frac{dx}{(\gamma p - x)} = (k_2 + k_1)dt$$

$$\text{where } \gamma = \frac{k_2}{k_1 + k_2}$$

Integration yields :

$$x = \gamma p(1 - e^{-(k_2 + k_1)t})$$

$$\text{therefore } (p - x) = p - \gamma p(1 - e^{-(k_2 + k_1)t})$$

$$\text{and } \frac{(p - x)}{p} = 1 - \gamma(1 - e^{-(k_2 + k_1)t}) \quad \text{-----} \quad (2)$$

at equilibrium, i.e. when  $t$  is large equation (2) reduces to :-

$$\frac{p - x_{eq}}{p} = 1 - \gamma \quad (3)$$

By inspection of table 4.11,  $p$  was taken as  $24.5 \times 10^{-6}$  mg Ag cm<sup>-2</sup>, by averaging the initial amount of silver adsorbed for the twelve vials used, and from figure 4.11,  $x_{eq}$  was taken as  $22.5 \times 10^{-6}$  mg Ag cm<sup>-2</sup>. Using equation (3) the following data were calculated :-

$$\frac{k_2}{k_2 + k_1} = 0.918$$

$$\text{and } k_2/k_1 = 11.2$$

A further evaluation to predict individual values for  $k_1$  and  $k_2$  was not carried out, because the slope from figure 4.11 is steep initially, and consequently small changes in  $t$  give rise to large variations in  $x$ , therefore there would be a high degree of uncertainty attached to the values calculated for  $k_1$  and  $k_2$ . However, in molar nitric acid we can say with some certainty that desorption requires days, and perhaps the relatively small ratio of  $k_2/k_1$  is surprising in view of the fact that molar nitric acid was present. The total amount of silver adsorbed was only that from an initial silver solution of concentration  $1 \text{ mg dm}^{-3}$ , and it may be that, if say, a  $100 \text{ mg dm}^{-3}$  silver solution had been used, the adsorbed silver would reach the  $x_{eq}$  value of the  $1 \text{ mg dm}^{-3}$  solution in the same time " $t$ ", or, after a much longer time. It is, therefore, suggested that future work, should include desorption experiments to enable more reliable specific rates to be allocated to these processes.

#### 6.2.2 Application of the Langmuir equation and the Van't Hoff isochore to adsorption data at several temperatures

In previous adsorption studies of cations other than silver, the Langmuir model has been used extensively to describe the adsorption process

of ions in solution on to glass and other substrates (4,5,20,30,31).

In particular Benes and Majer (31) found that a concentration dependence of trace adsorption often conforms to one of two basic types of adsorption isotherm, that of Langmuir or Freundlich.

The Langmuir isotherm was derived on the basis of three assumptions:

(a) only a monolayer of adsorbate is formed on the adsorbent, (b) the adsorbate particles do not interact during adsorption on the surface, and (c) all the adsorption sites taking part in the adsorption process are equivalent.

The Langmuir treatment may be adapted for the present situation as follows:-

It is postulated that the glass surface has a maximum capacity  $x_m$ . However, it is unnecessary to postulate a monolayer; it is indeed likely that the silver ions can penetrate the glass surface.

Then, the rate of adsorption =  $k_1 C_E (x_m - x)$

and the rate of desorption =  $k_2 x$ , where

$C_E$  is the equilibrium concentration of the solution and  $x$  is the concentration of silver on the surface. At equilibrium, we have :-

$$k_1 C_E (x_m - x) = k_2 x \quad \text{_____} \quad (1)$$

and the equilibrium constant  $K$ , for the process is given by

$$K = \frac{k_1}{k_2} = \frac{x}{C_E (x_m - x)} \quad \text{_____} \quad (2)$$

rearrangement of equation (2) gives :

$$C_{E/x} = \frac{C_E}{x_m} + \frac{1}{Kx_m} \quad \text{_____} \quad (3)$$

Hence a plot of  $C_{E/x}$  against  $C_E$  should produce a straight line with a gradient of  $\frac{1}{x_m}$  if the above conditions are satisfied. Now using the 40-day isotherm results in table 4.21, the values of  $C_E$  and  $C_{E/x}$  have been tabulated in 6.6.

Table 6.6 Values of  $C_E$  and  $C_E/x$  at 281, 293, 298 and 303 K

| Equilibrium Concentration ( $C_E$ )/mg dm <sup>-3</sup> |       |       |       | $C_E/x / \text{cm}^{-1} \times 10^5$ |       |       |       |
|---|-------|-------|-------|--------------------------------------|-------|-------|-------|
| 281 K   | 293 K | 298 K | 303 K | 281 K                                | 293 K | 298 K | 303 K |
| 0.919   | 0.932 | 0.897 | 0.879 | 3.40                                 | 4.12  | 2.62  | 2.18  |
| 0.925   | 0.923 | 0.888 | 0.879 | 3.70                                 | 3.59  | 2.37  | 2.18  |
| 1.892   | 1.854 | 1.816 | 1.789 | 5.26                                 | 3.80  | 2.97  | 2.54  |
| 1.874   | 1.852 | 1.825 | 1.771 | 4.46                                 | 3.75  | 3.13  | 2.32  |
| 3.829   | 3.783 | 3.644 | -     | 6.72                                 | 5.22  | 3.07  | -     |
| 3.790   | 3.736 | 3.712 | 3.769 | 5.41                                 | 4.25  | 3.86  | 3.44  |
| 7.733   | 7.724 | 7.535 | 7.393 | 8.69                                 | 8.40  | 4.86  | 3.66  |
| 7.739   | 7.628 | 7.518 | 7.408 | 8.9                                  | 6.15  | 4.68  | 3.75  |
| 9.652   | 9.556 | 9.341 | 9.340 | 8.32                                 | 6.45  | 4.25  | 4.25  |
| 9.757   | 9.486 | 9.457 |       | 12.05                                | 5.53  | 5.22  | -     |

The Langmuir type isotherms have been plotted in figures 6.6, 6.7, 6.8 and 6.9. Straight lines were then drawn through the points, thus enabling the maximum capacity to be calculated. A least squares fit was carried out using a linear least squares program on a Commodore Pet Computer, and the following information was obtained :-

$$\begin{aligned} \text{At 281 K the gradient} &= (7.3 \pm 0.9) \times 10^{-3} \\ \text{and } x_m &= (137 \pm 24) \times 10^{-6} \text{ mg Ag cm}^{-2} \end{aligned}$$


---

$$\begin{aligned} \text{At 293 K the gradient} &= (3.5 \pm 0.9) \times 10^{-3} \\ \text{and } x_m &= (282 \pm 103) \times 10^{-6} \text{ mg Ag cm}^{-2} \end{aligned}$$


---

$$\begin{aligned} \text{At 298 K the gradient} &= (2.7 \pm 0.4) \times 10^{-3} \\ \text{and } x_m &= (369 \pm 66) \times 10^{-6} \text{ mg Ag cm}^{-2} \end{aligned}$$


---

$$\begin{aligned} \text{At 303 K the gradient} &= (2.3 \pm 0.2) \times 10^{-3} \\ \text{and } x_m &= (426 \pm 50) \times 10^{-6} \text{ mg Ag cm}^{-2} \end{aligned}$$


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FIG. 6.6 Graph of  $C_E/x$  against  $C_E$  at 281 K

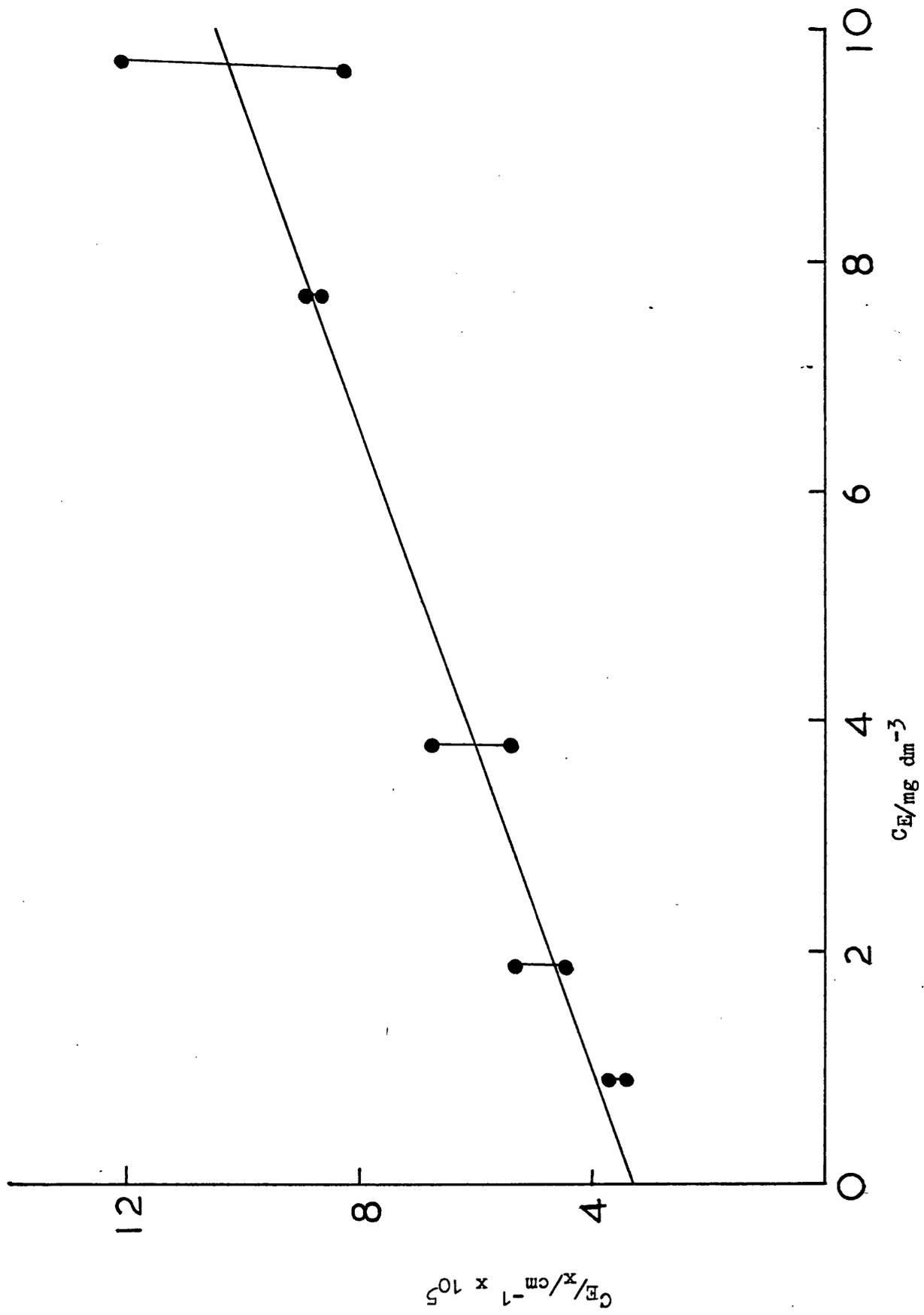


FIG. 6.7 Graph of  $CE/x$  against  $CE$  at 293 K

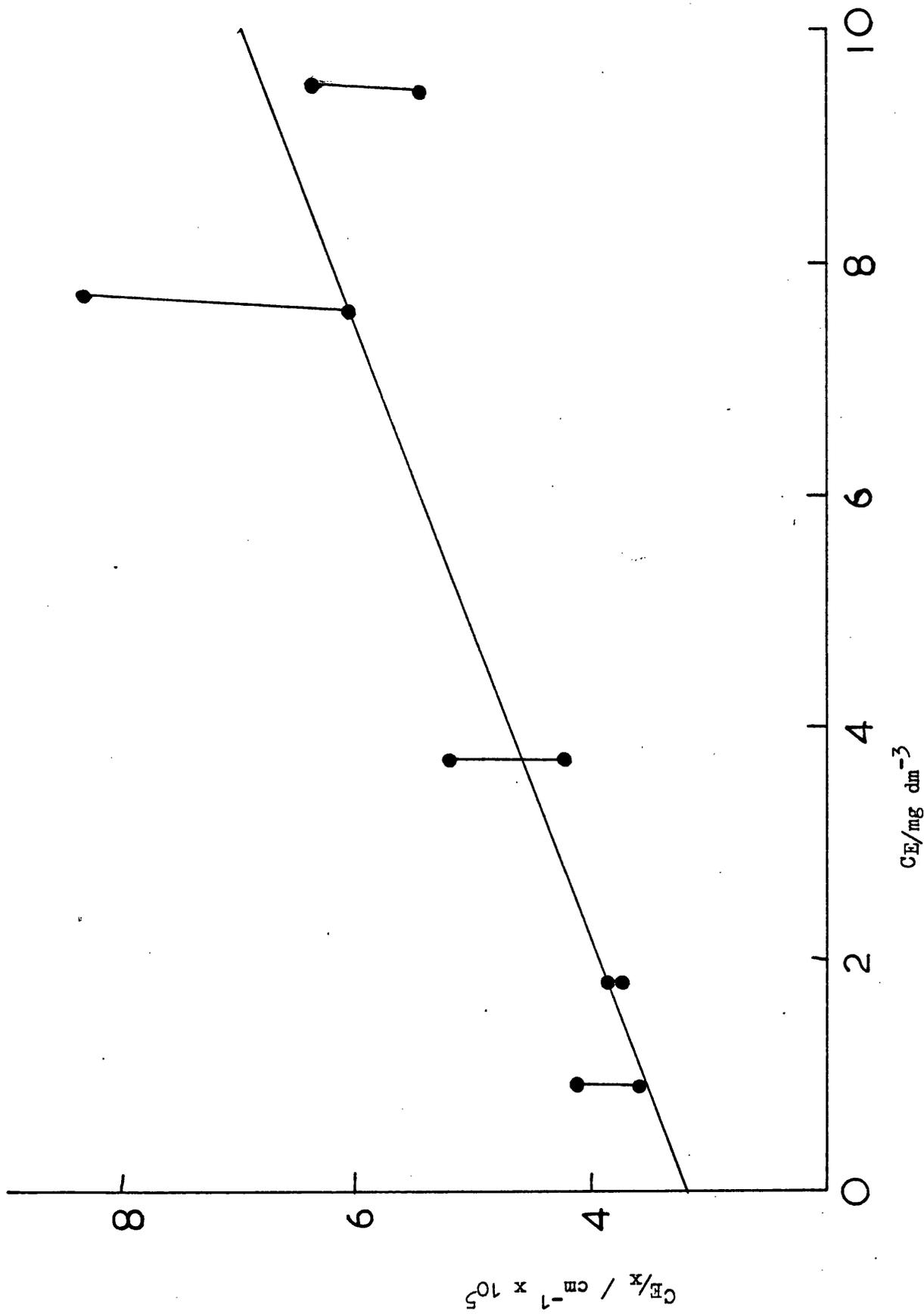


FIG. 6.8 Graph of  $C_E/x$  against  $C_E$  at 298 K

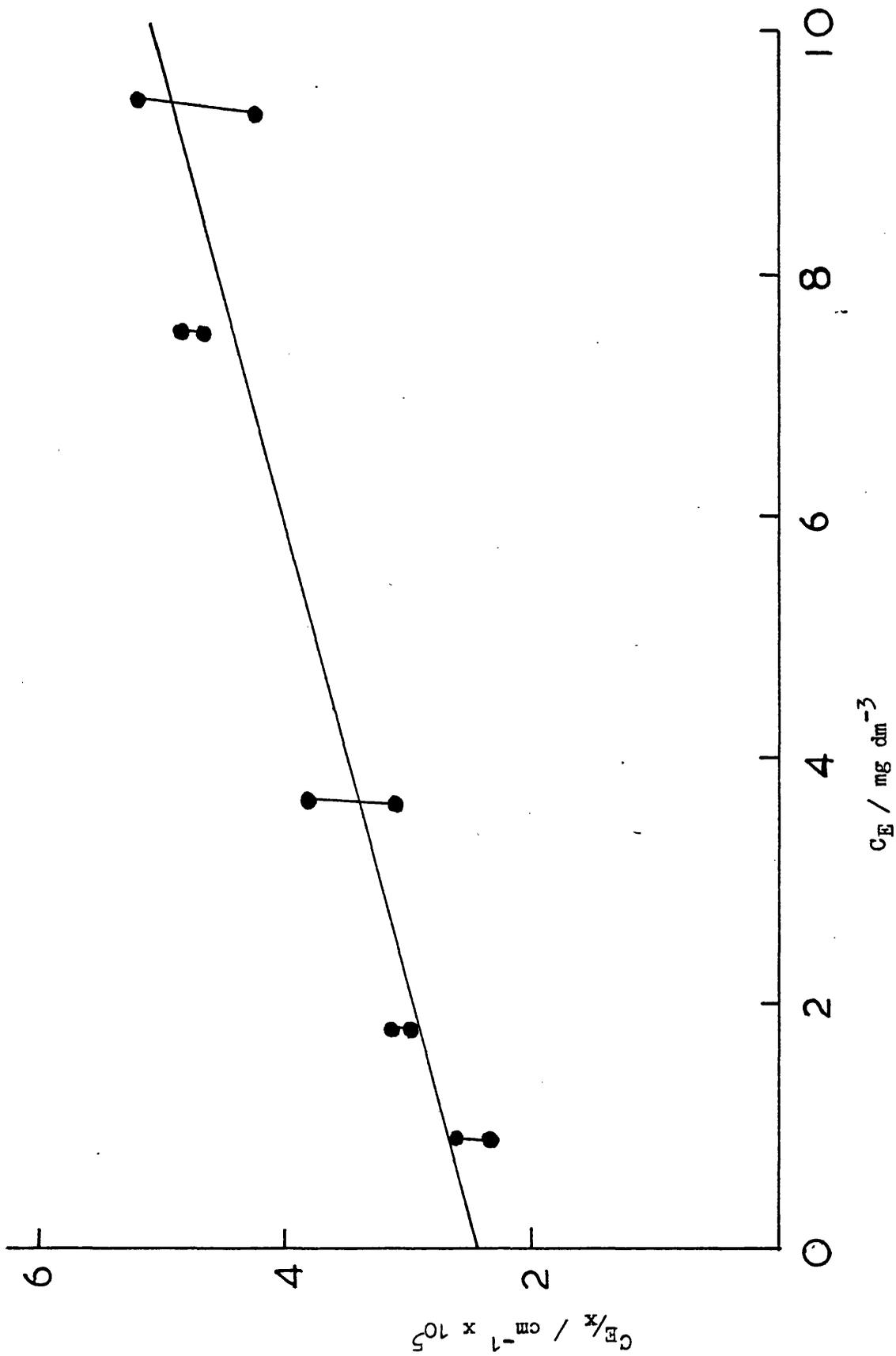
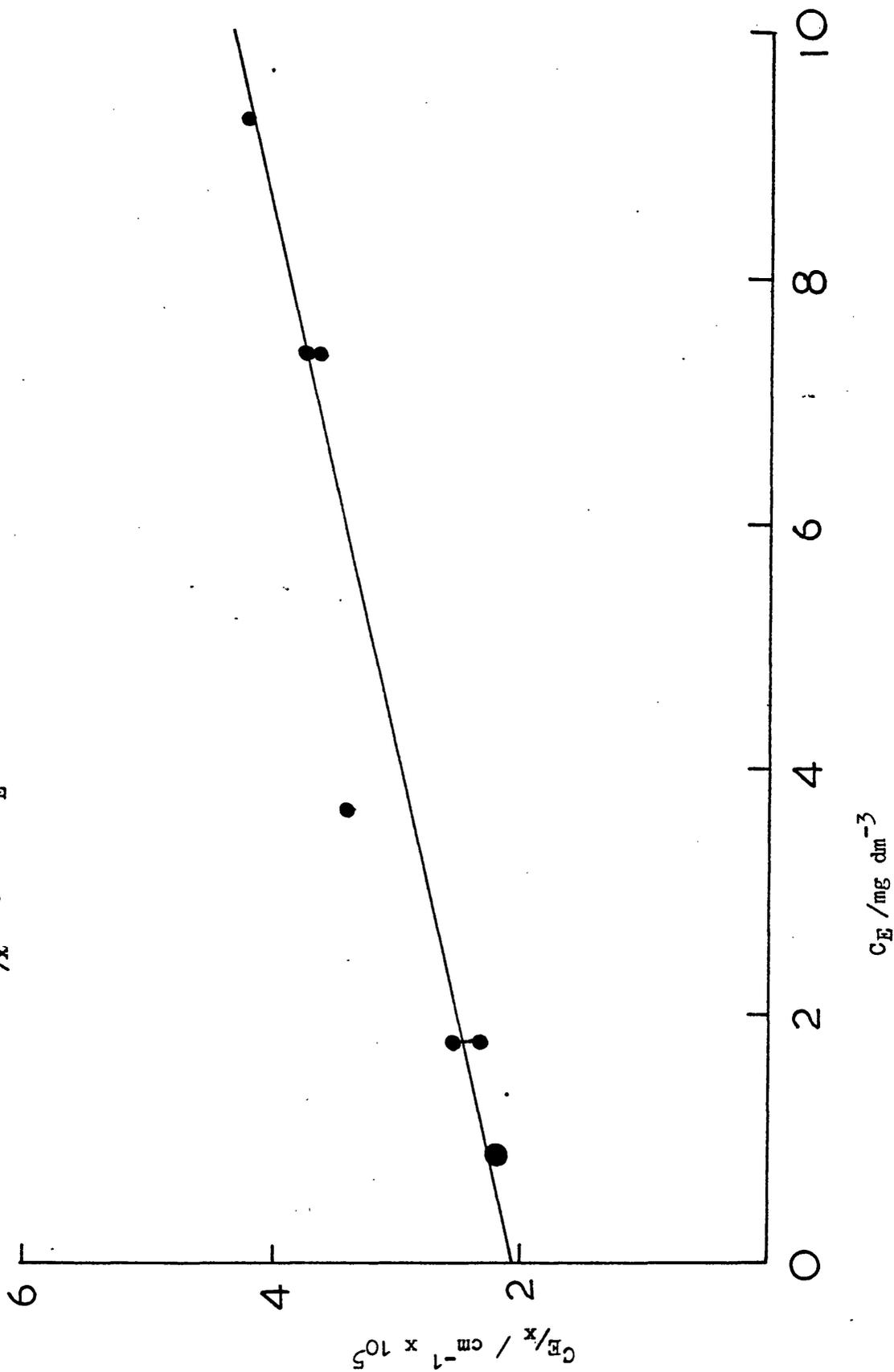


FIG. 6.9 Graph of  $C_E/x$  against  $C_E$  at 303 K



The values of  $x_m$  can be seen to vary significantly with temperature, and it has also been shown for a  $100 \text{ mg dm}^{-3}$  silver solution at 298 K (see figure 4.14), that the equilibrium value for adsorption is about  $800 \times 10^{-6} \text{ mg cm}^{-2}$ . It therefore appears that maximum capacity  $x_m$  also varies with concentration. Furthermore, close inspection of the plots in figures 6.6, 7, 8 and 9 suggest that there is some curvature which again support the idea that  $x_m$  is larger at higher solution concentrations.

In principle it should be possible to calculate the value of K at each of the four temperatures, from the value of the slope/intercept, and the results of this calculation are shown in table 6.7.

Table 6.7 Calculation of equilibrium constant K

| Temp/K | $K/(\text{mg dm}^{-3})^{-1}$ |
|--------|------------------------------|
| 281    | $0.228 \pm 0.05$             |
| 293    | $0.103 \pm 0.04$             |
| 298    | $0.111 \pm 0.03$             |
| 303    | $0.114 \pm 0.02$             |

However, in practice, the uncertainties are so large that the values are not very meaningful. Furthermore, it seems possible that in the case of the results obtained at 281 K, a longer period than 40 days may be needed before equilibrium is established. It is noteworthy that the value of  $x_m$  obtained at 281 K is particularly small. If this is indeed the case, then the value of K at 281 K is subject to further error.

It was hoped that it might be possible to calculate the value of the enthalpy of adsorption,  $\Delta H^\ominus$ , from the temperature dependence of the values of K, using the Van't Hoff isochore :-

$$\log_e K = - \frac{\Delta H^\ominus}{RT} + c$$

However, the uncertainty in the values of K is too large to estimate a value of  $\Delta H^\ominus$  with any degree of confidence.

A further approach was used to calculate the isosteric heat of adsorption, i.e. the enthalpy change for a constant value of the amount adsorbed,  $x$ . This approach assumes that the equilibrium constant  $K$  is proportional to  $x/C_E$ , and if  $x$  is held constant, a plot of  $\ln C_E$  against  $1/T$  should give a straight line with a slope of  $\frac{\Delta H^\ominus}{R}$  (isosteric).

Using the isotherms in figure 4.20, values of  $C_E$  were taken for a given amount of adsorption at four temperatures. The values of  $\log_e C_E$  and  $1/T$  are given in table 6.8.

Table 6.8 Values of  $\log_e C_E$  and  $1/T$  for three values of  $x$

| $x/\text{mg cm}^{-2} \times 10^6$ | $T/\text{K}$ | $1/T/\text{K}^{-1} \times 10^3$ | $C_E/\text{mg dm}^{-3}$ | $\log_e C_E$ |
|-----------------------------------|--------------|---------------------------------|-------------------------|--------------|
| 60                                | 303          | 3.3003                          | 1.38                    | 0.3221       |
| "                                 | 298          | 3.3557                          | 1.74                    | 0.5539       |
| "                                 | 293          | 3.4129                          | 2.44                    | 0.8920       |
| "                                 | 281          | 3.5587                          | 3.92                    | 1.3661       |
| 80                                | 303          | 3.3003                          | 1.93                    | 0.6678       |
| "                                 | 298          | 3.3557                          | 2.55                    | 0.9361       |
| "                                 | 293          | 3.4129                          | 3.70                    | 1.3083       |
| "                                 | 281          | 3.5587                          | 6.74                    | 1.9081       |
| 100                               | 303          | 3.3003                          | 2.68                    | 0.9858       |
| "                                 | 298          | 3.3557                          | 3.51                    | 1.2556       |
| "                                 | 293          | 3.4129                          | 5.25                    | 1.6582       |
| "                                 | 281          | 3.5587                          | 11.20                   | 2.4159       |

Graphs of  $\ln C_E$  against  $1/T$  are shown in figure 6.10.

The resulting three plots give reasonable straight lines, and a linear least squares fit to the results in table 6.8 gave the following values for  $\Delta H^\ominus$  (isosteric) :-

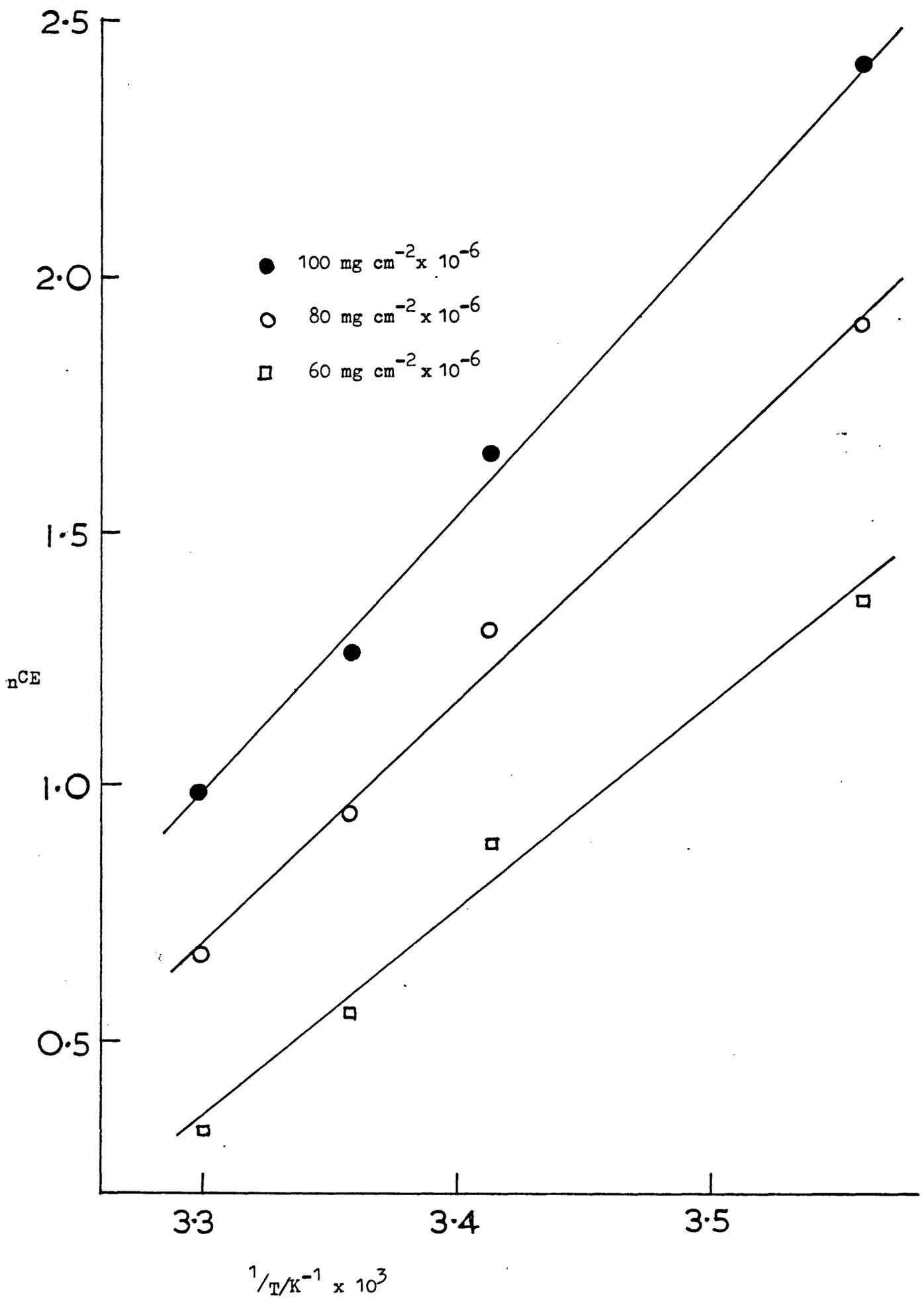


FIG. 6.10 Graphs of  $\ln CE$  against  $1/T$  for three values of  $x$

| $x/\text{mg Ag cm}^{-2} \times 10^6$ | $\Delta H^{\ominus}$ (isosteric)/kJ mol <sup>-1</sup> |
|--------------------------------------|---|
| 60                                   | 33.7 $\pm$ 3.0  |
| 80                                   | 40.0 $\pm$ 2.6  |
| 100                                  | 46.5 $\pm$ 1.8  |

However, from equation (2), it is clear that the original assumption that  $K$  is proportional to  $x/C_E$  will only be true if the maximum capacity  $x_m$  is constant. In the present work this appears not to be the case, and in consequence the author feels that the values of  $\Delta H^{\ominus}$  (isosteric), obtained using this approach are probably not reliable.

Future work aimed at improving the precision of the experimental data embodied in the isotherms would, perhaps, enable a more reliable value of  $\Delta H^{\ominus}$  to be calculated, especially if the range of concentrations studied were sufficiently restricted for  $x_m$  to become effectively constant.

### 6.2.3 Silver adsorption on to glass and the relevance of pH

An important consequence of this research has been the realisation of the marked dependence of silver adsorption on pH.

In contrast to the experience of Dyck (2), the results reported by the present author in section 4.1 (figures 4.1.1, 2 and 3) indicate a significant reduction of silver adsorbed with lowering of pH. This effect was observed at three silver concentrations, i.e. 0.5, 10.0 and 100.0 mg dm<sup>-3</sup>. Dyck found that lowering the pH reduced the amount of silver adsorbed, but the effect was only significant at concentrations less than 0.01 mg dm<sup>-3</sup>.

In the critical review presented by Wharmby (1) the effect of pH on silver adsorption was not considered, although mention was made of an apparent dependence on the specific activity of the tracer used. This may well have resulted from pH variation accompanying tracer solutions at different specific activities.

The lack of emphasis previously placed on the pH dependence of silver adsorption is surprising, because adsorption studies with other cations

have considered the effect of pH in some depth (7,8). Benes and Garba (7) observed an almost identical pH dependence for manganese adsorption, to that reported for silver by the present author (see figures 4.8 and 2.1).

Furthermore, Benes and Majer discuss the importance of pH in greater detail in their recent book (9), and comment that at high pH values, trace colloidal hydroxides usually adsorb irreversibly. The present author suspects that during the silver adsorption process there may be a concentration effect at the glass surface, at which the solubility product for silver oxide is exceeded, and colloidal species formed. On further increasing the pH dissolution occurs to produce anionic hydroxo-complexes which are adsorbed less readily than the parent cation. Silver oxide is more soluble in concentrated alkali solution than in water, and it has been shown that the ion  $[\text{Ag}(\text{OH})_2]^-$  is formed (6).

The pH value at which the colloid surface is uncharged is, of course, the iso-electric point, or the point of zero-charge. Some iso-electric points have been determined for "MO" type hydrated oxides. While very few data are available for "M<sub>2</sub>O" type hydrated oxides, a pH value of approximately 11.5 has been suggested (9).

The present author believes that this provides a reasonable explanation for the adsorption profile observed in figure 4.8, with the iso-electric point for silver at pH of approximately 11.5, in accord with the figure quoted for M<sub>2</sub>O type hydrated oxides.

It should also be mentioned that in section 4.2.5 it has been demonstrated that other cations also undergo competitive adsorption with silver ions, but none of the cations investigated by the author proved as effective as hydrogen ions in reducing silver adsorption.

It was also shown that substituting the anion ( $\text{NO}_3^-$ ) for acetate ions had very little effect on the adsorption process (see experiment 4.4.6).

Adsorption from saturated silver chloride solution also seems to be similar to that from silver nitrate solution at similar concentrations.\*

#### 6.2.4 Isotopic Equilibrium

The experiments described in section 4.6.3, where the adsorbed silver is not at isotopic equilibrium with the silver in solution, merit some discussion here. The specific activity of the tracer changes during the course of an experiment, and the concentrations of silver adsorbed deduced from the original relationships between count-rate and weight of silver are apparent rather than real. The experiments may be regarded as effectively involving 14-days of contact time at 298 K, between 3 ml of silver solution and a glass vial, some silver is lost during washing at 7-days, and some is gained as the new silver solution is brought into contact with/

\* The author is grateful to Mr. D. P. Green of the City of Birmingham Polytechnic for this information.

adsorbed silver rather than clean glass. Count rate data are as follows :-

| Vial No.       | Net c.p.m. 'IN' | Net c.p.m. 'OUT' |
|----------------|-----------------|------------------|
| 1              | 32139           | 2012             |
| 2              | 31723           | 2025             |
| 3              | 31974 ) Mean =  | 1426 ) Mean =    |
| 4              | 32091 ) 32032.5 | 1661 ) 1543.5    |
| 5 <sup>1</sup> | 33089           | 1914             |
| 6 <sup>1</sup> | 33174           | 1798             |
| 5 <sup>2</sup> | 1784 ) Mean =   | 497 ) Mean =     |
| 6 <sup>2</sup> | 1684 ) 1734     | 449 ) 473        |

Vials 1, 2, 5<sup>1</sup> and 6<sup>1</sup> were brought into contact with labelled silver solution for the first seven day period; the specific activity of the tracer remained constant throughout, and enables an estimate to be made of the mass of silver adsorbed on the glass at this stage.

Mean of 'IN' c.p.m. for vials 1, 2, 5<sup>1</sup> and 6<sup>1</sup> = 32531  $\approx 3 \times 10^{-3}$  mg Ag

∴ Adsorbed silver at 7 days =  $\frac{1937.25}{32531} \times 3 \times 10^{-3}$  mg =  $1.79 \times 10^{-4}$  mg  
( $\approx 20 \times 10^{-6}$  mg cm<sup>-2</sup>)

where 1937.25 is the mean 'OUT' c.p.m. for the four vials

Thus, the total weight of silver present during the second 7-day contact period is  $3 \times 10^{-3} + 1.79 \times 10^{-4}$  mg =  $3.18 \times 10^{-3}$  mg.

The weight of adsorbed silver at the end of the second 7-day contact period may, perhaps, be estimated by "adjusting" the 7-day value by factors

of  $3.18/3$  (to allow for the slight increase in silver present) or 1.15  
( $= x_{14}/x_7$  as evaluated from the equation :  $x = C + x_{eq}^1 (1 - e^{-(k_1 + k_2)t})$ ),

by inserting average values, from the data in various sections of the thesis, for  $x_7$ , C and  $x_{eq}^1$ ). On this basis, the final weight of adsorbed silver is approximately  $2.18 \times 10^{-4}$  mg.

Thus, the situation at the end of the second 7-day contact period may be taken approximately as :-

|                                |   |                          |
|--------------------------------|---|--------------------------|
| Total weight of silver present | : | $3.18 \times 10^{-3}$ mg |
| Weight of silver on glass      | : | $2.18 \times 10^{-4}$ mg |
| Weight of silver in solution   | : | $2.96 \times 10^{-3}$ mg |

With vials 3 and 4,  $1.79 \times 10^{-4}$  mg of unlabelled adsorbed silver, at 7-days, is brought into contact with  $3 \times 10^{-3}$  mg of labelled silver in solution. If isotopic equilibrium had been reached by the end of the second 7-day period, we could write :-

$$\text{c.p.m. adsorbed silver} = \frac{2.18 \times 10^{-4}}{3.18 \times 10^{-3}} \times 32032.5 = 2195.9$$

However, observed c.p.m. of adsorbed silver = 1543.5

Thus, during the second 7-day contact period, the adsorbed silver has progressed through  $1543.5/2195.9$ , i.e. approximately 70%, of the passage to isotopic equilibrium.

With vials 5 and 6,  $1.79 \times 10^{-4}$  mg of labelled adsorbed silver, at 7-days, is brought into contact with  $3 \times 10^{-3}$  mg of unlabelled silver in solution. If isotopic equilibrium had been reached by the end of the second 7-day period, we could write :-

$$\text{c.p.m. silver in solution} = \frac{2.96 \times 10^{-3}}{3.18 \times 10^{-3}} \times 1734 = 1614$$

However, observed c.p.m. of silver in solution =  $1734 - 473 = 1261$

Thus, during the second 7-day period, the silver in solution has progressed through  $1261/1614$ , i.e. approximately 73%, of the passage to isotopic equilibrium.

Isotopic exchange between the adsorbed silver and silver in solution is, then, a relatively slow process which takes place at a rate not very different from the rate of adsorption. It may be that the passage to isotopic equilibrium occurs simply via the dynamic adsorption/desorption process; however a closer study is necessary if firm conclusions are to be drawn.

6.3 A model for silver adsorption on glass, and the effect of pH, temperature and concentration on the model proposed.

The distinction between so called primary and secondary adsorption is based on the different location of the trace element on the surface of the solid phase. According to this classification, primary adsorption assumes desolvation and incorporation of the adsorbed species into the surface crystal lattice of the solid phase, whereas in secondary adsorption the solvated trace species remains in the layer of solution closely adjacent to the surface (11). On the basis of these definitions this thesis deals with primary adsorption. Secondary adsorbed species have been shown to be removed by the standard washing procedure described in section 3.3.4.

It has been demonstrated by Wharmby (1), that the adsorption of silver takes place in two stages, a rapid initial adsorption during the first 30-minutes of contact, followed by a much slower process. This slower process can take up to 40-days or more to reach a limiting value, depending on the silver concentration and temperature.

At 298 K the "half period" of the adsorption appears to increase as initial the concentration "a" increases, as follows, e.g.

| $t_{1/2}$ /days | a/mg Ag dm <sup>-3</sup>        |
|-----------------|---------------------------------|
| below 7         | 0.5, 1.0 (figures 4.20 and 5.1) |
| ~ 30            | 100 (figure 4.14)               |

It can also be shown that  $t_{1/2}$  decreases as temperature increases, at a given initial solution concentration, e.g.

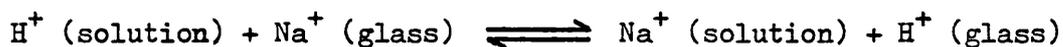
| $t_{1/2}$ /days | a/mg Ag dm <sup>-3</sup>  |
|-----------------|---------------------------|
| ~ 30            | 100, (298 K, figure 4.14) |
| ~ 3             | 100, (318 K, figure 4.13) |

The physico-chemical nature of adsorption phenomena determines both the distribution of the adsorbate and the strength of its bond to the adsorbent. The question of the nature of the adsorption is concerned mainly with the mechanism of the process, particularly the nature of the forces acting between the adsorbed species and the adsorbent. Three basic kinds of adsorption can be distinguished: physical adsorption, chemisorption and electrostatic adsorption (12). Physical adsorption requires no activation energy; bonding forces are weak and unlikely to withstand the washing procedures described in section 3.3.4. It is also unlikely that physical adsorption would show a positive temperature coefficient. For these reasons physical adsorption can be reasonably eliminated as a possibility. On the other hand, forces associated with chemisorption are usually large and may approach those involved in chemical bond formation. Also chemisorption may require a lengthy contact time to reach a limiting value, and the processes are much more temperature dependent.

Electrostatic adsorption is probably the most frequently encountered type of adsorption from electrolyte solutions, owing to the attractive coulombic forces between the electrically charged surface of the adsorbent and the oppositely charged particles of adsorbate. This type of adsorption is sometimes called ion exchange. However, ion exchange can also apply to chemisorption. Exchange chemisorption forces extend only over very short distances and show characteristic saturability which limits their action to monolayer adsorption (13).

As yet, we know little about the mechanism of silver adsorption; the following model proposed can, then, only be speculative, but it does conveniently summarise most of the phenomena so far observed.

It is well known that a solid gel forms at glass surfaces in contact with aqueous solution. For example with a glass electrode soaking in water or an aqueous buffer, the following ion exchange reaction occurs (14).



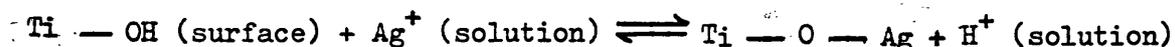
The equilibrium is driven far to the right by prolonged soaking, and results in the formation of a hydrated gel layer at the glass surface. The gel layer is reported to be approximately  $10^{-5}$  cm. thick, which is large in comparison with the likely radius of  $\text{Ag}^+$  ions in solution (10).

If silver ions can adsorb both on to the surface, and within this hydrated gel, then further speculations can be made. The rapid initial adsorption observed by Wharmby (1) could be represented by adsorption at the immediate surface of the gel, and the slower adsorption process that follows, by penetration into the gel. The latter process is likely to be affected by the tendency of silver to bond to oxygen atoms. It is also possible that the observed temperature dependence of  $x_m$  could be due to expansion of the "gel", in thickness, as temperature increases.

It may be that congestion of silver ions at the immediate surface of the gel, at higher solution concentrations may explain the increased  $t_{\frac{1}{2}}$  values.

A two dimensional representation of the atomic arrangement in bulk glass is given by Adams (15), and is illustrated in figure 6.11.

Using the basing structure of figure 6.11, the adsorption of silver on to glass might be represented as in figure 6.12, where the speculations have been extended to include the suggestion that  $\text{Ag}^+$  can adsorb via two routes, the replacement of a proton on a hydroxyl group, and by direct exchange with  $\text{Na}^+$ . This would give another possible explanation for fast and slow adsorption. The implication is that silver becomes bonded to oxygen, a type of bonding postulated by Misra (4), for silver adsorption on titanium dioxide :



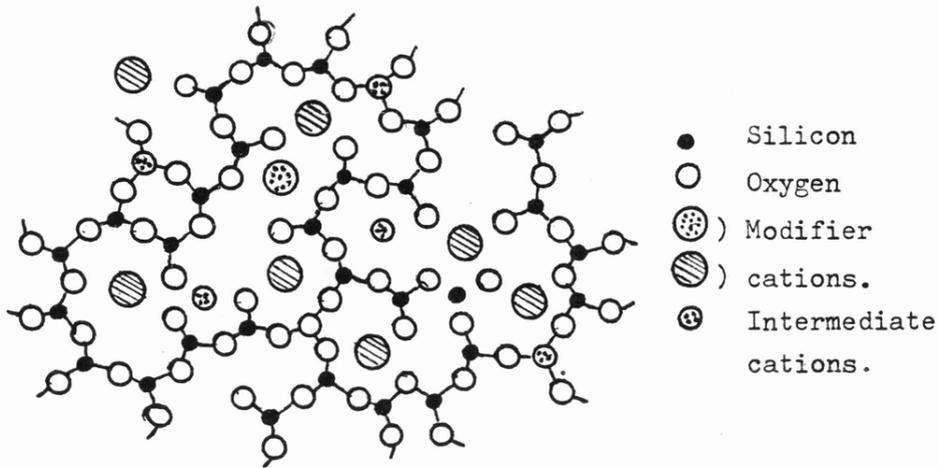


FIG. 6.11 Two-dimensional representation of the atomic arrangement in bulk glass

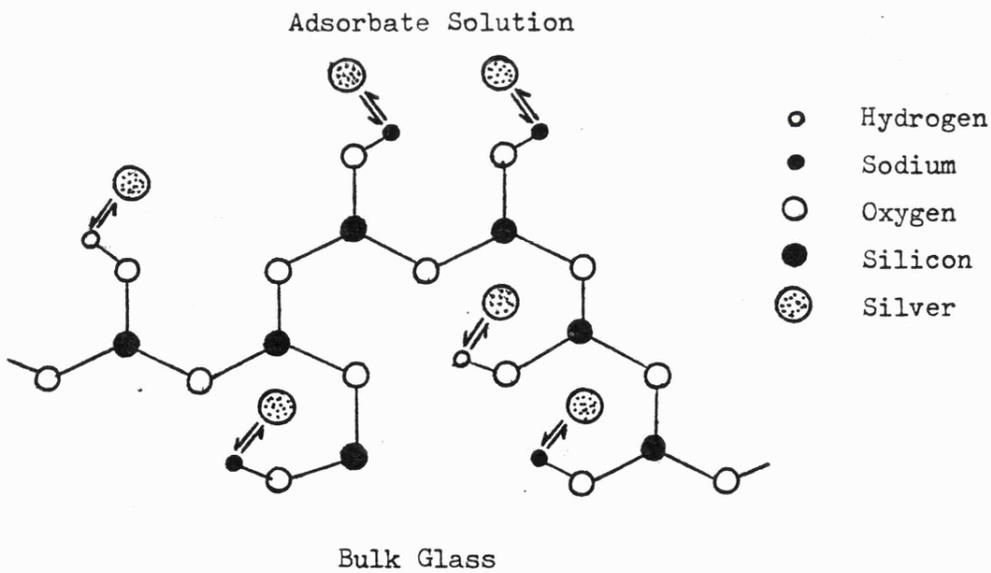


FIG. 6.12 A possible atomic model for silver adsorption

Similarly, Ahmed and Cleave (16), have suggested Si-O-M<sup>+</sup> type bonding where M was calcium.

The "hydrated gel" model readily explains why other cations, in particular hydrogen ions, are able to affect the extent of silver adsorption.

Ionic mobility, too (see section 4.2.5), may have some effect on the process.

Preliminary adsorption studies using sodium-22, labelled sodium chloride solutions, carried out by Green,\* do not appear to show the slow adsorption process observed with silver. After contact periods of up to six weeks, at 298 K, the adsorbed sodium appears unable to withstand the standard washing procedure and is almost completely removed. This is interesting and suggests that the replacement of hydroxyl hydrogen by silver may be associated with the slow adsorption process. The sodium cation in solution may be expected to exchange readily with another sodium cation within the gel, but is very unlikely to be able to replace a hydroxyl hydrogen.

#### 6.4 A comparison of soda glass, polyethylene and polypropylene as adsorbents

The first observation to be made when comparing the adsorption of silver on glass, polyethylene and polypropylene, is that the reproducibility of experimental data is poorer with the latter two substrates, and that PE exhibits the most erratic behaviour. Therefore, trends can be predicted with less certainty for PE and PP. However, there are general observations which can usefully be made on the data reported in Chapter V.

The surface area of the adsorbent influences the extent of adsorption, and, so long as other factors remain constant, an increase in the contact area usually results in enhanced adsorption (23). It is probable, then, that at least part of the erratic behaviour observed with PE and PP is related to

\* The author is indebted to Mr. D. P. Green of the City of Birmingham Polytechnic for this information.

surface defects, i.e. variations in the micro surface area, imparted during manufacture of the vials, such as the striations on the surface, which were observed only after close inspection of the vials.

At around 7-days contact, at the same temperature, concentration, and solution pH, PE and PP adsorb approximately 10% as much silver as soda-glass per unit area (see tables 5.1 and 5.7). Also the rate of adsorption of silver on PP seems to increase linearly, in contrast to the rapid initial uptake on glass, followed by a slower process which eventually reaches a limiting value. A linear relationship possibly holds for PE, although the data are somewhat limited to allow confident assertions to be made (see tables 5.1, 5.8 and 5.11).

The generally more erratic behaviour of PE relative to PP may be related to the water vapour permeability of these polymers (24).

PE being  $2100 \frac{\text{cm}^3 (\text{S.T.P.})(\text{m.m.}) \times 10^{-10}}{(\text{sec})(\text{cm}^2)(\text{cmHg})}$  at 20-30°C.

and PP 700 " " "

The apparent linear relationship between adsorption and time implies that these materials may be suitable for short term storage of solutions, but that, as the storage time increases, the advantage over glass becomes less.

Comparison of the results in table 5.3 with those in 5.1 indicate that at 28-days contact with PE or PP the extent of adsorption is about 25% of that observed for glass.

Other workers have also found that elements, such as silver and caesium, at trace concentrations, adsorb less readily on PE and PP than on glass; Durst and Duhart (25) report that PE adsorbed much less than pyrex, and West, West and Iddings (3) state that after 10-days contact, adsorption on pyrex was five times that on PP. Skulskii and Glasmov (26) have shown the adsorption coefficient of glass to be ten times that of PE and PTFE.

The washing cycle curves for PE and PP (see figures 3.7 and 3.8) are quite different from those for glass (see figures 3.5 and 3.6). Repeated washing of glass with D.D.H<sub>2</sub>O removes minute quantities of silver, whereas on PE and PP a limiting value is reached after one or two washes.

Furthermore, washing glass and PP with other reagents produced quite different results. Table 4.13 shows that acid washing can remove as much as 60% of the adsorbed silver from glass, whereas experiment 5.2.3 shows that acid of a similar concentration removed very little silver from PP.

The pattern of silver adsorption is, then, markedly different from that encountered with glass, and it is possible that the process observed with PE and PP is one of absorption rather than adsorption. This view is consistent with the following evidence :-

- (a) The extent of silver uptake on PE and PP appears to increase linearly with time, and there is no indication of a limiting value being reached, suggesting penetration of silver solution into the porous surface.
- (b) Washing with acid or alkali solutions have no more effect than washing with D.D.H<sub>2</sub>O. This again suggests penetration of the polymer pores by the silver solution.
- (c) Pre-washing PE with hot water increases the amount of silver taken up, by a factor of at least ten (see table 5.6); this is consistent with PE swelling and increasing its water-vapour-permeability.
- (d) There appears to be no pH dependence of silver adsorption on PP (see table 5.12) over the pH range used. This is not consistent with the competitive adsorption of silver and hydrogen ions previously demonstrated for glass.

So far as the storage of silver solutions at trace concentrations is concerned, glass is preferred to PE or PP, provided that the pH value

is maintained at below three. The behaviour of PE and PP is more unpredictable and further work is required before recommendations can be confidently made.

#### 6.5 Concluding Remarks

The main aim of this research has been to provide guidance on the practical conditions required to minimise adsorption losses when storing and analysing solutions at trace concentrations of silver. However, useful information has been gained to enable speculation on the adsorption process.

The present author believes this secondary theme could, with advantage, be further developed by future workers. For example, studies aimed at obtaining more precise data over a range of temperatures and at controlled pH values would enable an estimate of the enthalpy of adsorption to be made. A study of the isotopic exchange of silver between an adsorbed film and the equilibrium solution in contact, again at different temperatures, could perhaps yield pointers to the mechanism of the process, as could a comparison of the adsorption behaviour of silver with that of other substances at trace concentrations. It could also prove interesting to extend the work on polymeric adsorbents, using a wider range of pH values, at a series of temperatures and trace concentrations. The present author has found the work to be both interesting and rewarding; he hopes that future workers may benefit from his experience over the past four years.

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An abstract from a thesis presented for the  
degree of Doctor of Philosophy in the  
Faculty of Science of Leicester University,  
William Allen.

AN INVESTIGATION OF THE ADSORPTION OF SILVER FROM AQUEOUS SOLUTION

The work presented in this thesis is concerned with the adsorption of silver from aqueous solution, on soda-glass, polyethylene and polypropylene. The silver concentrations used, ranged from 0.5 to 100 mg dm<sup>-3</sup>, and were investigated at a series of temperatures.

The silver was present as AnalaR silver nitrate in doubly deionised water, and the adsorbed silver was detected as silver -110m using a NaI(Tl) well-type crystal to count the gamma activity.

The study indicates that silver adsorption on glass is extremely pH sensitive, increasing with increasing pH, and reaching a maximum value at pH 11.5. At pH values greater than 11.5 silver adsorption is significantly reduced. The pH dependence was shown to be important at silver concentrations ranging from 0.5 to 100 mg dm<sup>-3</sup>.

The presence of added cations, other than the hydrogen ion, also inhibit the adsorption of silver.

The pH work was extended to include desorption under acid conditions, and the results have been used to formulate a set of guidelines, in an attempt to improve existing analytical technique when handling trace concentrations of silver.

A contact-time study was carried out at various temperatures and concentrations of silver, to establish a tentative equilibrium time for the adsorption process. A kinetic analysis has been applied, from which specific rates for the forward and reverse processes have been assigned. The effect of pH and concentration on these rates has also been considered.

The temperature dependence of silver adsorption was investigated, and a series of isotherms were produced at 281, 293, 298 and 303 K. The isotherms indicate a positive temperature coefficient for the adsorption of silver on glass. A thermodynamic treatment was applied, and a heat of adsorption calculated.

A possible mechanism for the adsorption of silver on soda-glass has been proposed.

The work was extended to investigate the adsorption of silver on substrates apart from glass, namely polyethylene and polypropylene. The results have been compared with those obtained for glass.