The University of Manitoba

The Extraction of Iridium and Platinum from Organic Solvents by the Use of Polyurethane Foam

by

Ruth Albertine Moore

A Thesis
Submitted to the Faculty of Graduate Studies
in Partial Fulfillment of the Requirements for the Degree
of Master of Science

Department of Chemistry
Winnipeg, Manitoba

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ABSTRACT

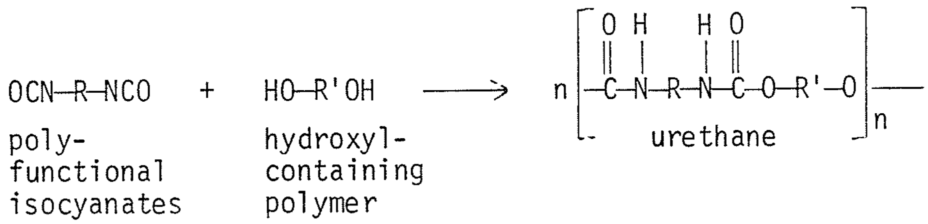
The feasibility of extracting iridium and platinum from organic solvents onto polyurethane foam was studied. Iridium in the form of sodium hexachloroiridate IV was found to be highly extractable from ethyl acetate; this complex was also extractable from acetone. Platinum in the form of sodium hexachloroplatinate IV was extractable from ethyl acetate. Distribution coefficients of the order of 11,000 were obtained for the extraction of iridium from ethyl acetate; 300 for the extraction of iridium from acetone and 4800 for the extraction of platinum from ethyl acetate. Foam capacities of $\simeq$ 16% were obtained for iridium when extraction was carried out in ethyl acetate and $\simeq$ 2.4% when extraction was carried out in acetone.

INTRODUCTION

The Analytical Uses of Polyurethane Foam

Porous polyurethane foams have been widely used for the extraction of metals from solution. These foams belong to the family of cellular plastics and are most commonly prepared by the reaction of di- or poly-functional hydroxy compounds such as hydroxyl-terminated polyethers or polyesters with di- or polyfunctional isocyanates.[1]

The reactions producing polyurethane represent step-growth polymerization of the polyisocyanates and polyols; the mode of propagation involves the addition of a hydroxy group to an isocyanate to yield a substituted amide ester of carbonic acid —— polyurethane.



$$OCN{-}R{-}NCO \quad + \quad HO{-}R'OH \longrightarrow n\left[-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-R-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-O-R'-O \right]_n -$$

Linear or only slightly branched polymers are used to provide flexible foams, whereas more highly branched polymers produce rigid foams.

Foaming is usually accomplished by including water in the system, the reaction between isocyanates and water providing carbon dioxide as the in-situ blowing agent for the foaming process. For rigid foams a low-boiling liquid such as trichlorofluoromethane has been used as a blowing agent. Appropriate catalysts and stabilizers control the foam formation and the curing. The most frequently used catalysts for flexible foam systems are combinations of tertiary and organometallic compounds.

The physical as well as the chemical properties of polyurethane foams are a function of the preparation process.[2] The chemical resistance of some batches of commercial polyurethane foams has been examined.[3] The foam batches tested degraded when heated between 180°C and 220°C, and slowly turned brown in ultraviolet light. They were dissolved by concentrated sulphuric acid and destroyed by concentrated nitric acid; they reduced alkaline potassium permanganate. They are mostly unaltered, apart from reversible swelling by water, hydrochloric acid up to 6M, sulphuric acid up to 2M, glacial acetic acid, 2M ammonia and 2M sodium hydroxide solutions, as well as by solvents such as light petroleum, benzene, carbon tetrachloride, chloroform, diethyl ether, diisopropyl ether, acetone, isobutyl methyl ketone, ethyl acetate, isopropyl acetate and alcohols.

Bowen[1] was the first to use solid flexible polyurethane foams as extractants of a number of substances from aqueous solutions. Bowen noted then that most of the substances absorbed were those which could be extracted from aqueous solutions by the use of diethyl ether; e.g. I_2, C_6H_6, $CHCl_3$ and phenol from water; mercury II and gold III from 0.2M HCl; iron III, antimony V, Mo VI and Rh III from 6M HCl; and uranium VI from saturated aluminum nitrate solutions. He demonstrated that the uptake of different compounds from aqueous solutions by the foams was due to absorption rather than adsorption phenomena, through a correlation of the surface area of foam with the number of molecules taken up on to the foam.

Since the appearance of this work, several investigators have used polyurethane foams, both treated and untreated, for the absorption and recovery of inorganic and organic compounds from aqueous solutions.

Gesser et al[4] successfully used unloaded polyurethane foams for the extraction of polychlorinated biphenyls from aqueous solutions at the part per billion level. Acetone and hexane were employed for elution of the absorbed biphenyls. Polyurethane foam was also used to monitor other trace organic contaminants in water.[5] A detailed study of the different factors affecting the extraction and recovery of various organochloride pesticides with polyurethane foam has been carried out by Musty and Nickless.[6] They found that factors such as flow rate and pH of the medium were important in determining the efficiency of extraction. Both treated and untreated foams were used in this study.

Polyurethane foam has also been used to monitor levels of pesticide vapours in the atmosphere.[7-10] Other organic substances for which extraction by foam from aqueous solution has been successfully applied are phthalate esters at $\mu g\ l^{-1}$ concentrations[11] and alkyl sulphonates.[12] The collection of phthalate esters from air by polyurethane foam has also been reported.[13]

Bowen,[14] in 1971, showed that polyurethane foam could be used for the recovery of gold as gold III chloride from mineral waste waters. Schiller and Cook[15] also applied polyurethane foam to the separation of gold III chloride from natural waters and showed this system to be more efficient for collection of gold III chloride than co-precipitation with iron III hydroxide or separation with Dowex 1-X8 resin.

Braun and Farag[16] investigated the recovery of gold-thiourea complex from acidic perchlorate solution onto open-pore polyurethane foam of both the polyester and polyether type. They reported that the absorption capacities of the polyether type foams for the gold complex were generally greater than those of the polyester type foam.

Further work on the recovery of gold by polyurethane foam has been carried out by Sukiman[17] who described the application of polyether polyurethane foam for the extraction of gold III chloride from acidic aqueous solution, using the flow-through technique.

The extraction of cobalt II and iron III from acidic thiocyanate solutions has been described.[18] Quantitative recoveries of cobalt or iron, in concentrations ranging between 0.2 and 200 μg, at flow rates of 4 ml cm^{-2} min^{-1} were reported.

Gesser et al[19,20] successfully extracted gallium from acidic chloride solutions onto the foam. It was reported that under optimal experimental conditions it was possible to absorb gallium in the foam to the extent of 10% by weight. This relatively high capacity was thought to be due mainly to dissolution of the gallium chloride in the foam material, rather than to adsorption on the foam surfaces. That is, the foam material was thought to act as a polymeric solid extractant for gallium.

Extraction of tin II and antimony III and V by polyurethane foam has been carried out by Lo[21]. Maximum distribution coefficients of 6,150 for antimony III and 35,200 for antimony V were achieved. Distribution coefficients up to 5,600 were obtained for the extraction of tin II. A quantitative recovery of the antimony from this foam was obtained using acetone.

Polyurethane foam with various physically immobilized reagents have been successfully used for several analytical applications.

Palladium II, bismuth III and nickel II in a thiourea-perchloric acid system have been quantitatively separated on TBP-loaded foam by Braun and Farag.[22]

A method for the chemical enrichment of a gold-thiourea complex from acidic solution onto polyurethane foam loaded with tri-n-butyl phosphate has also been described by these authors.[23] The quantitative separation of trace amounts of gold from high concentrations of Zn^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}, Sb^{3+}, Cu^{2+}, Bi^{3+} and Pd^{2+} was achieved on passing the solution through a short foam column at a flow rate of 10-12 ml cm^{-2} min^{-1}. Recovery of the gold was achieved by dissolving the foam in hot concentrated nitric acid.

The separation of cobalt and nickel in hydrochloric acid media by polyurethane foam columns loaded with tri-n-octylamine (TNOA) hydrochloride has been studied.[24] This is an example of a homogeneous ion-exchange foam; TNOA acts as a liquid ion-exchanger. Good results were obtained with 11.4% and 17.7% loadings of the amine. The separation of iron III from cobalt II, copper II and nickel II by reversed-phase foam chromatography in a TBP-HCl system has also been investigated.[25]

Sukiman[26] reported the rapid collection of gold at trace concentrations (0.06 - 25 ppm) from aqueous solutions by polyurethane foams immobilizing methyl isobutyl ketone, diethyl ether, isopropyl ether or ethyl acetate. Gold was eluted from the foam columns with acetone.

Polyurethane foam columns immobilizing finely divided tetrachlorohydroquinone were shown to be suitable for the reduction of some metals in their higher valency state. Reduction of cerium IV, vanadium V and iron III on foam-redox columns by two different methods has been described.[27,28]

Polyurethane foams, treated in various ways, have also been tested for the extraction of several organic compounds from aqueous solution. Gesser and co-workers[29] started the work in this direction by the application of grease-loaded foam for the extraction and recovery of some organochlorine pesticides. Musty and Nickless[9] investigated the extraction of organochlorine insecticides and polychlorinated biphenyls from water using silicone oil DC-200-coated polyurethane foams, and also compared the extraction efficiency of these grease-coated foams with that of uncoated foams. Generally, uncoated foams required lower flow rates than grease-coated foams for high efficiency of extraction.

In some preliminary experiments,[11] polyurethane foam loaded with DOW-200 silicone oil was found to extract different phthalate esters to various extents.

Polyurethane foams immobilizing finely divided inorganic precipitates have also been used in analytical work. Static and dynamic isotope and redox exchange separations of radiosilver on foam immobilizing silver sulphide[30] and copper[31] respectively have been investigated. Columns packed with silver-sulphide foam were suitable for the collection of various levels of radiosilver (0.1 - 100 μg of Ag^+) from nitric acid solution at relatively high flow rates (20 ml cm^{-2} min^{-1}).[30] Quantitative collection of radiosilver at various concentrations in 2M nitric acid by redox exchange reactions on columns packed with copper foam has been reported.[31] Flow rates of 10 - 12 ml cm^{-2} min^{-1} were used in these studies.

Plasticized reagent foams have been prepared and successfully applied to the extraction of various metals from aqueous media. These foams are prepared by dissolving hydrophobic organic reagents in a plasticizer solution and then immobilizing the solution on an open-cell type polyurethane foam by swelling. The plasticizer has a dual purpose;[32] it acts as an efficient non-volatile solvent for the organic reagent, as well as a plasticizer for the foam plastic itself.

Collection of trace amounts of silver and mercury on plasticized zinc dithizonate treated foam has been carried out by Braun.[32,33] The extraction efficiency of plasticized zinc dithizonate foams was found to be better than that of unplasticized zinc dithizonate foams. Quantitative recoveries of silver and mercury from the plasticized zinc dithizonate foams were obtained by elution with sodium thiosulphate solution.

Chow and Buksak[34] used dithizonate treated polyurethane for collection of mercury II and methyl mercury II chloride. Quantitative collection of both mercury compounds was achieved at low flow rates (ca.0.3 ml cm^{-2} min^{-1}). Recoveries of both mercury compounds in concentrations ranging from 0.002

ppb to 100 ppm were reported to be complete.

The preparation of TBP-plasticized iodine and silver dithizonate foams, suitable for isotope exchange separations of the radioactive isotopes radioiodide and radiosilver respectively, has been described.[35] Quantitative collection of radiosilver (0.01 - 1 μg) from 0.1M nitric acid has been realized on columns packed with silver dithizonate foams, at a flow rate of 3 ml cm^{-2} min^{-1}.

The separation of radioiodide with toluene plasticized iodine foam has been performed by Palágyi and Bilá.[36] The efficiency of extraction was found to be improved by the presence of TNOA in the toluene.

Polyurethane foam columns immobilizing a solution of iodine in Alamine 336 in toluene have been used for the separation of radioiodide from milk samples.[37] The method has been reported to be suitable for the rapid determination of ^{131}I in fresh milk, as well as in formaldehyde-preserved milk.

Isotope exchange separation of radiobromide on plasticized polyurethane foam immobilizing bromine has been tested and the results are reported to be quite promising.[38]

Plasticized dithizone and diethyldithiocarbamate foams have been used by Braun and Farag[39] for the extraction of traces of mercury from aqueous solution. It was reported that rapid and quantitative collection of mercury II onto these forms was achieved. These authors also demonstrated that plasticized dithizone foam could be used for the detection and semi-quantitative determination of zinc II or lead II, while copper II and cobalt II could be determined with rubeanic acid foams and Amberlite LA-1 homogeneous ion exchange foams respectively.[40]

Foams pretreated with benzoylacetone were shown by Lypka et al[41,42] to be suitable for extraction and separation of copper and cadmium.

Recovery of cadmium and copper from the treated foam was achieved by elution with 1.5M HCl.

Plasticized 1-nitroso-2-naphthol and diethyl dithiocarbamate foams have been used for collection of traces of cobalt from aqueous solutions.[43] Quantitative collection of cobalt (1 μg - 1000 μg) by columns packed with these foams has been achieved at reasonable flow rates (5 - 6 ml cm^{-2} min^{-1}).

Lee and Halmann[44] suggested the use of polyurethane foam immobilizing dimethyl glyoxime for the quantitative and selective separation of nickel from aqueous solution. Separation of low concentrations of nickel II (less than 5 ppm) is reported to be very efficient by both the static and the dynamic methods.

Recently, plasticized and unplasticized 1-(2-pyridylazo)-2-naphthol (PAN) foams have been tested for the extraction of cobalt, iron and manganese.[45,46] Collection of cobalt and iron was reported to be essentially complete from aqueous solutions of pH 4 to 9, while manganese was completely extracted only above pH 9.

Polyurethane foams loaded with a 1% solution of 1,2-ethanedithiol in benzene have been used by Valente and Bowen[47] for the concentration of antimony from natural waters. The absorption of antimony was found to be independent of the oxidation state of antimony. Highest efficiency of extraction was obtained at pH 1 - 2.5.

Separation of antimony III and antimony V in solution has been achieved[48] using polyurethane foams loaded with sodium diethyl dithiocarbamate by adjusting the pH of the aqueous solution to 9.5. At this pH value, the antimony III complex is quantitatively retained while the antimony V complex is not retained at all.

Heterogeneous ion exchange foams have been prepared by incorporating finely ground commercial ion exchange resins into a polyurethane foam of the open-cell polyether type.[49] The mechanical properties of these ion exchange foams are the same as those containing no ion exchange resin.

The use of polyurethane-Varian KS heterogeneous cation exchange foam for rapid separations in aqueous and alcoholic solutions has been investigated. It was reported that, with these cation exchange foams, microgram and milligram amounts of copper can be retained and eluted quantitatively with hydroxylamine ammonium chloride solution.[50]

In addition to foams prepared by direct physical immobilization of the required reagent on the foams, the preparation of foamed plastics to which specific functional groups are chemically bonded has also been achieved.[49,51,52]

Mazurski et al[51,52] prepared a SH-polyurethane foam by treatment of polyether-type polyurethane with hydrogen sulphide in a discharge tube. These foams have been used for the adsorption of mercury II chloride and methylmercury II chloride from extremely dilute aqueous solutions. Mercury at concentrations of 0.4 to 0.0004 ppm could be quantitatively collected on SH-foam columns from 100 ml of aqueous solution passed at a flow rate of about 13 ml cm^{-2} min^{-1}. Removal of mercury from the column was effected by extraction with 2M hydrochloric acid in a Soxhlet extractor.

Braun and co-workers[49] prepared phenol-formaldehyde resin foam to which sulphonic acid groups were bonded by direct sulphonation of a commercially available phenol-formaldehyde foam. The ion-exchange capacity of these foams was reported to be reasonable, of the order of 1.85 meq/g.

Indirect introduction of ionogenic groups onto polyurethane foam has also been achieved[49] by a method based on a polymer analogue reaction after joining the foam to an easily transformable polymer. Styrene-polyurethane co-polymer foam has been prepared in this way and the anion exchange groups introduced by chloromethylation and amination. Another method of introducing ionogenic groups indirectly onto the foam is based on radiation grafting of open-cell polyurethane foams with methacrylic acid.[49] Foams prepared by this method are weak carboxylic ion-exchange foams and are reported to have good ion exchange capacities (ca. 4 meq g^{-1}).

Polyurethane foams have also found use in biological fields. Reticulated polyester polyurethane foams have been found to be a suitable matrix for immunoadsorption of cells.[53] Untreated foams have a high affinity for guinea pig erythrocytes but the adsorption was not-specific. It was discovered that the non-specific affinity could be greatly reduced by pretreating the foam with various polyanions, e.g. carboxymethyl cellulose polyacrylic acid, gammaglobulin and gum arabic.

Bauman and co-workers[54,55] reported that open-cell polyurethane foam can be used as a support for starch gel containing enzymes. They described a method for the preparation of an immobilized enzyme pad which is used to monitor water and air continuously for atmospheric pollutants which are enzymic inhibitors of cholinesterase. This system consists of immobilized horse-serum cholinesterase products in which the enzyme in the starch gel is physically entrapped on the surface of open-cell polyurethane foam pads.

Goodson et al[56] described an improved method for the preparation of these enzyme pads by co-precipitation of horse-serum cholinesterase with aluminum hydroxide gel, followed by entrapment in starch gel on the surface of open-pore polyurethane foam.

To date, virtually all applications of polyurethane foam for the extraction of various metals have been carried out in aqueous media. The extraction of platinum metal complexes from aqueous media, however, poses several problems; they are especially prone to hydrolysis. By carrying out the foam extraction of these metals in suitable organic solvents, the problem of hydrolysis can be circumvented; in this study such extractions were investigated.

The major part of the present research has been devoted to the extraction of iridium, in the form of the sodium hexachloroiridate IV, from various organic solvents. Extraction of iridium from aqueous solution using polyurethane foam is very difficult, a major problem being the fact that, in the presence of the foam, iridium IV in aqueous solution undergoes reduction to iridium III, which does not appear to be extractable by polyurethane foam to any significant extent. The equation for the process in the case of the hexachloroiridate complex is:

$$IrCl_6^{=}(aq) + e^{-} \xrightleftharpoons{\text{foam}} IrCl_6^{\equiv}(aq)$$

tetravalent iridium complex	tervalent iridium complex

A less detailed study into the feasibility of extracting platinum IV as the sodium hexachloroplatinate complex was also carried out.

EXPERIMENTAL

Apparatus and Reagents

Baird Atomic Model 708 Iso/matic System consisting of a 2" NaI well-type Gamma Detector; Model 530 Spectrophotometer and Model 620 Printer.

Unicam SP 500 Series 2 UV-VIS Absorption Spectrophotometer.

Thermomix (R) - 1441 System supplied by B. Braun - Melsungen.

Soxhlet Extractor.

Sodium hexachloroiridate IV supplied by J. Mattley Chemicals Limited, London.

Sodium hexachloroplatinate IV supplied by J. Mattley Chemicals Limited, London.

^{192}Ir was obtained from Amersham-Searle Limited, Don Mills, Ontario.

Polyurethane foam was obtained locally from a commercial foam wholesale outlet.

Single automatic squeezer (Figure 4).

Multiple automatic squeezer (Figure 5).

Pyrex cells of 250 ml and 100 ml capacities fitted with covers and plungers (Figures 1,2).

Double walled pyrex cell fitted with cover and plunger (Figure 3).

Pyrex column with teflon stopcock (Figure 6).

All chemicals used were of reagent grade unless otherwise specified.

Figure 1. Cell used in manual squeezing.

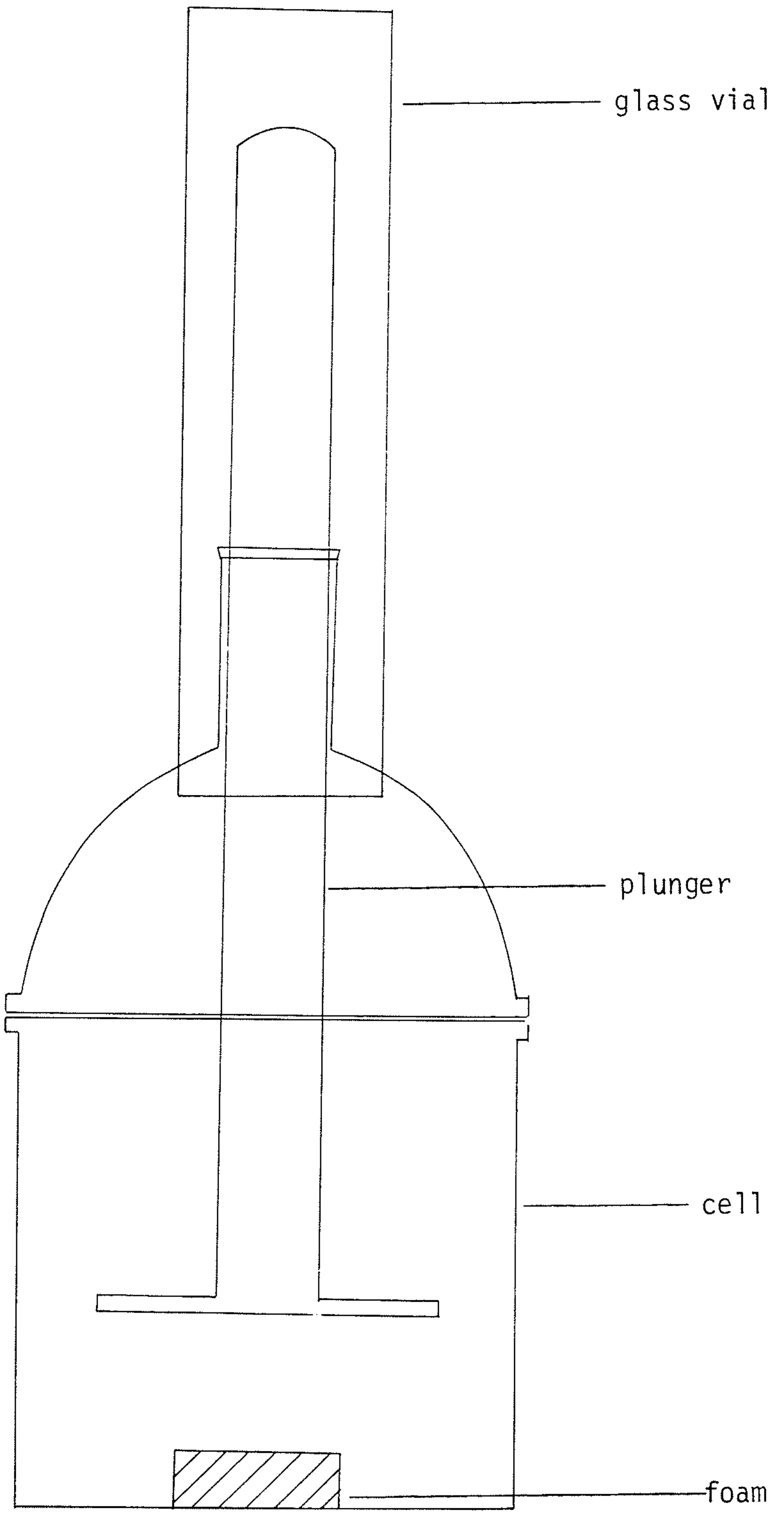

glass vial
plunger
cell
foam

Figure 2. Cell used in automatic squeezing.

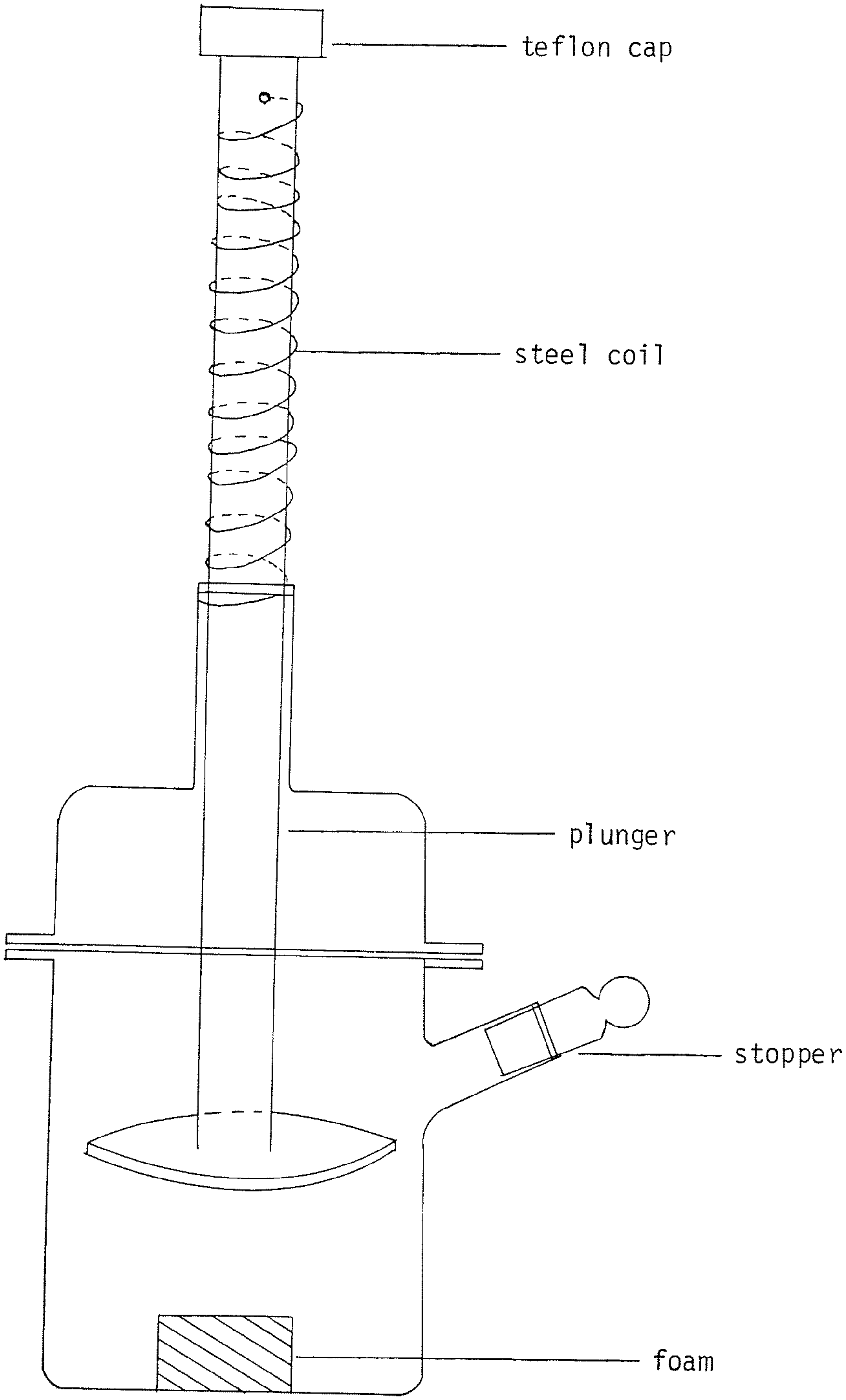

teflon cap
steel coil
plunger
stopper
foam

Figure 3. Double walled cell.

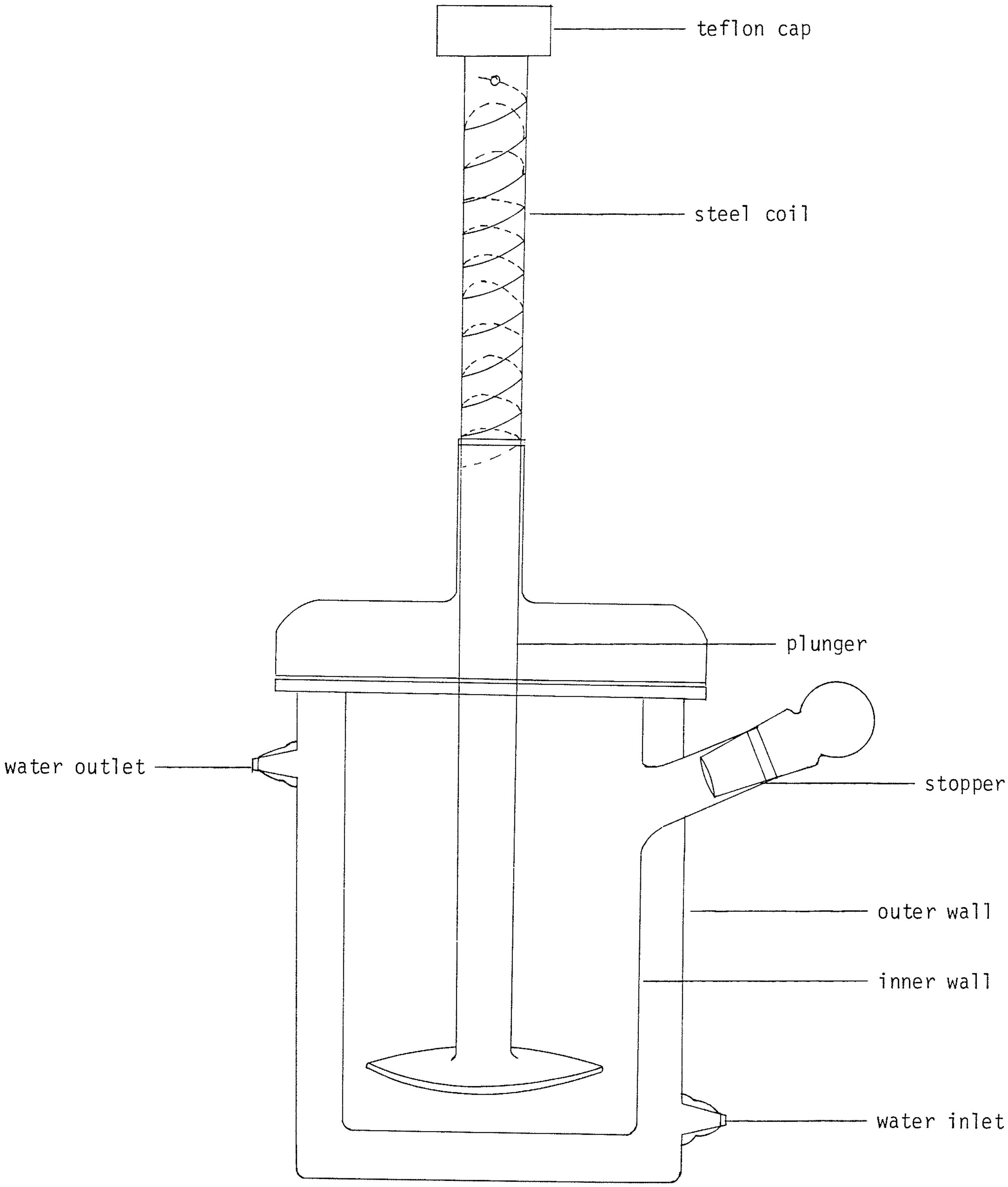

teflon cap
steel coil
plunger
water outlet
stopper
outer wall
inner wall
water inlet

Figure 4. Single automatic squeezer.

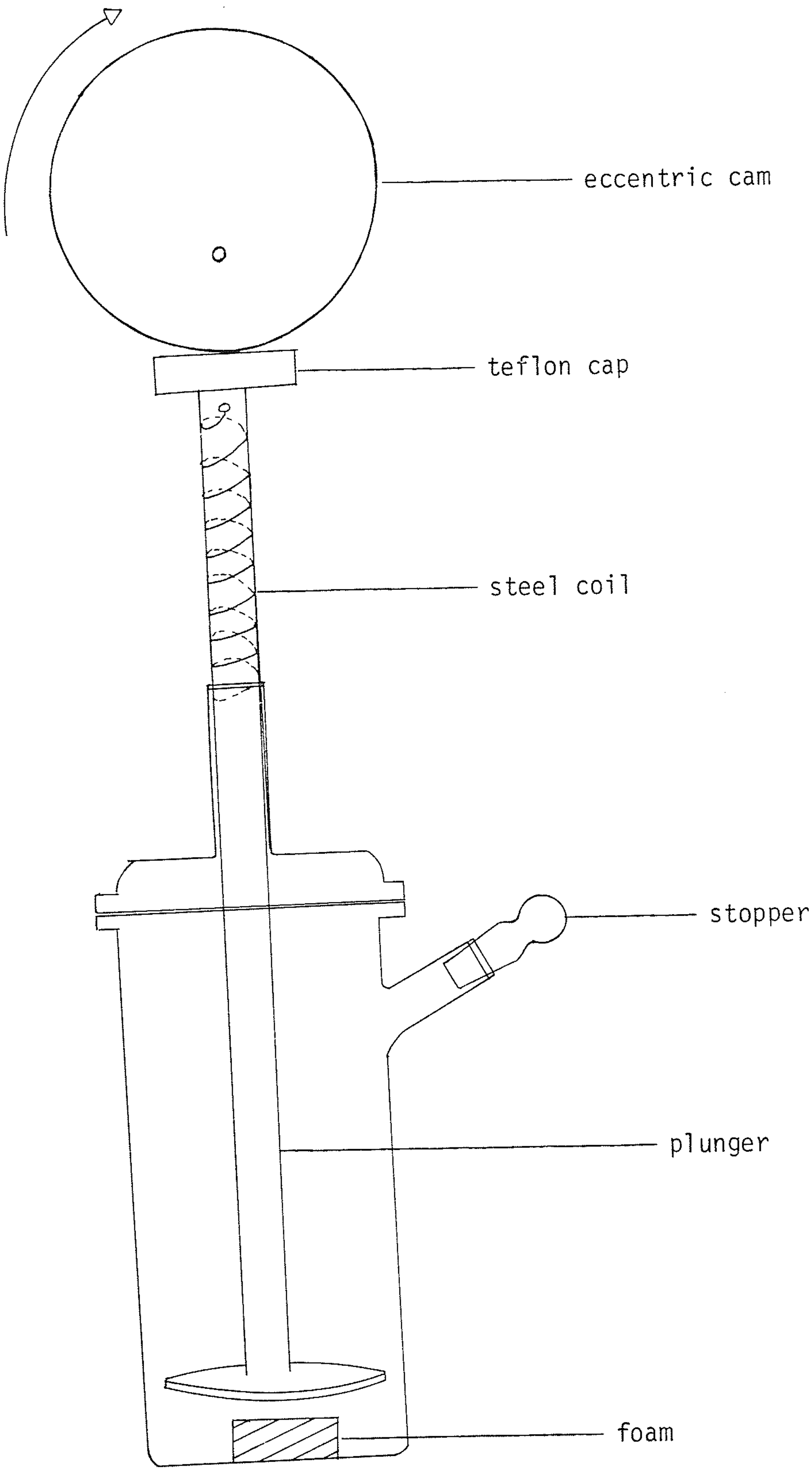

eccentric cam
teflon cap
steel coil
stopper
plunger
foam

Figure 5. Multiple automatic squeezer.

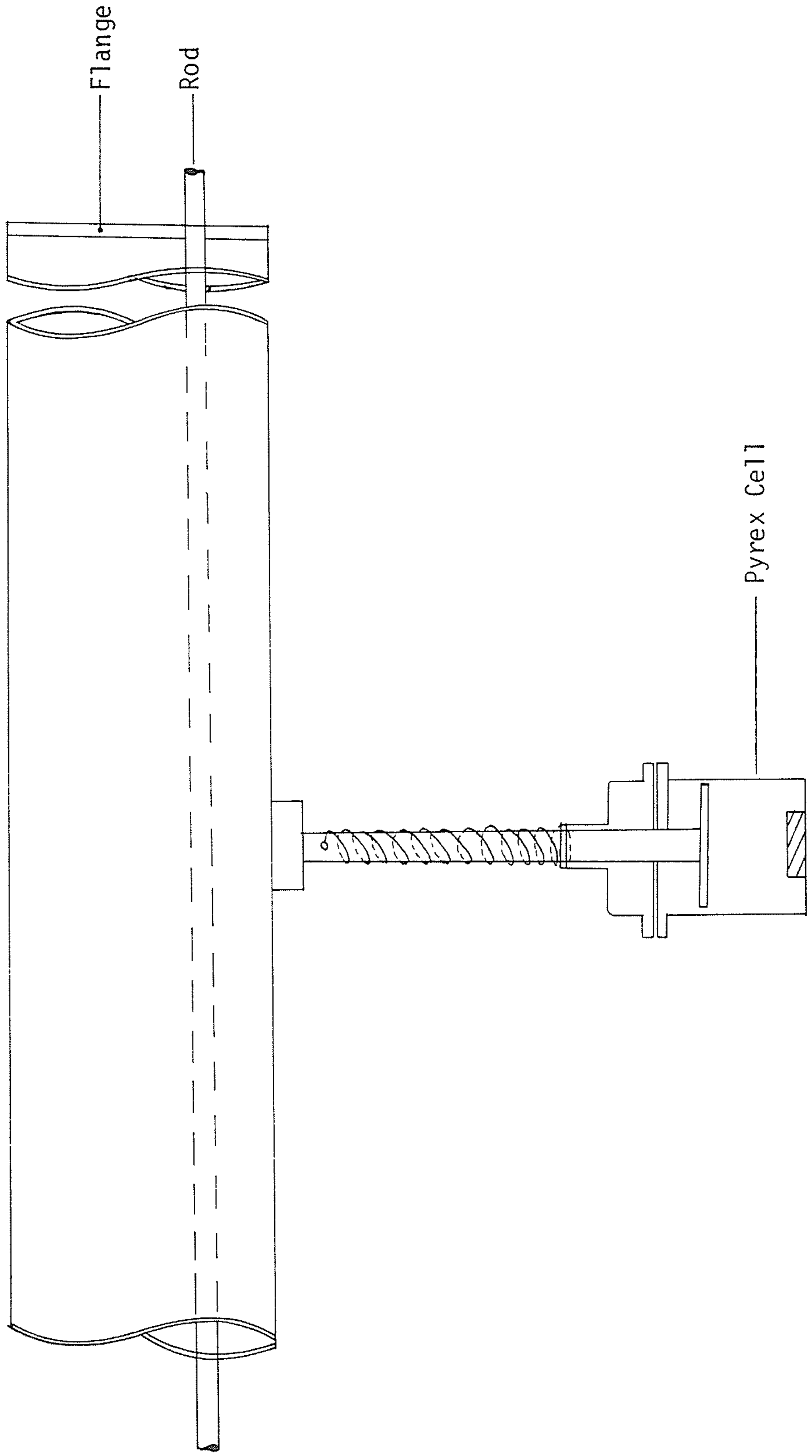
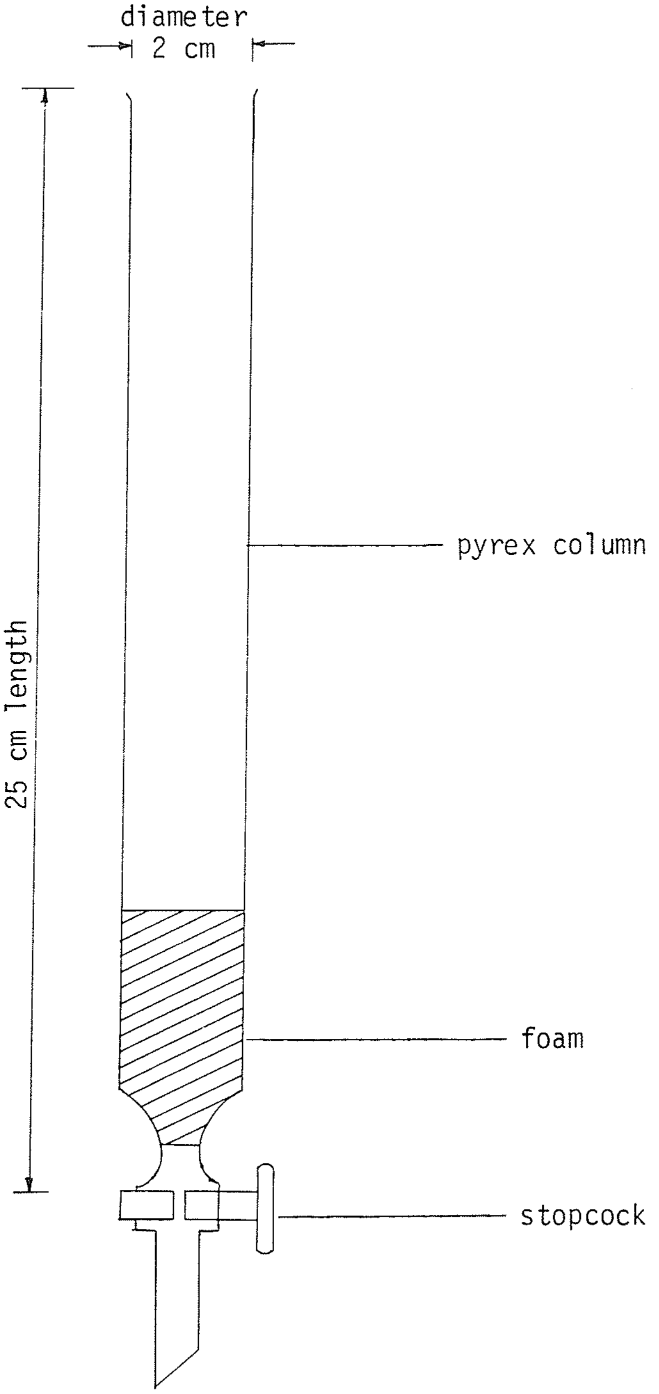

Flange
Rod
Pyrex Cell

Figure 6. Pyrex column with teflon stopcock.


diameter
2 cm
25 cm length
pyrex column
foam
stopcock

General Procedure

Foam Preparation

The foams were soaked in 1M hydrochloric acid for 24 hours with occasional squeezing. They were then washed several times (≃ 10 times) with distilled water and extracted with acetone in a Soxhlet extractor for 12 hr. The foams were air-dried, placed in a vacuum desiccator for a few hours and then stored in a plastic-covered glass beaker in the dark.

Standard Solutions

An iridium IV stock solution containing 500 $\mu g\ ml^{-1}$ Ir was freshly prepared for each experiment by dissolving 0.1538 g sodium hexachloroiridate IV in 100 ml of solution using the appropriate solvent.

A fresh platinum IV stock solution was prepared for each experiment by dissolving 0.132 g sodium hexachloroplatinate in 100 ml of solution of the required solvent; this would yield a solution with a concentration of 500 $\mu g\ ml^{-1}$ Pt.

The Extraction of Metal from Solution with Foam

Sample solutions were prepared by the appropriate dilution of the stock solution. The sample solution and foam were placed in one of the pyrex beakers shown in Figures 1, 2 or 3. By means of the plunger the foam was periodically squeezed in order to flush out solution previously in contact with the foam and allow fresh solution to equilibrate with the foam. This process was continued until equilibrium was reached with respect to the overall extraction. Where manual squeezing was performed, the squeezing was done at fifteen minute intervals (10 plunges each time). Two types of automatic squeezers were used - a single automatic squeezer (Figure 4) and a multiple automatic squeezer capable of handling up to ten samples. The latter was designed by Mr. R. F. Hamon.[57] Automatic squeezing using the multiple automatic squeezer was performed at a rate of twenty-five plunges per minute. The single automatic squeezer could carry out squeezing at an adjustable rate.

The glass vial of Figure 1 served to minimize evaporation of the relatively volatile organic solvents.

Measurement of Extraction Efficiency

Two techniques were employed for measurement of the percentage extraction of metals from solution: UV-visible absorption spectrophotometry and a radioactive tracer technique. UV-visible absorption spectrophotometry was used for platinum extraction and, in some cases, for measurement of extraction of iridium, while the tracer technique was applied to iridium extraction only.

Radioactive Tracer Technique

Sample Preparation: ^{192}Ir in the form of ammonium hexachloroiridate IV in 3M HCl was used. All of the iridium tracer was brought to the quadrivalent oxidation state by the following method: a few drops of the solution containing the radioactive tracer were placed in a beaker and evaporated to dryness on a hot plate. A few millilitres of aqua regia were added to the dry residue and the solution was evaporated to dryness after the action of the aqua regia had ceased. This treatment with aqua regia was repeated four times and followed by several similar treatments with hydrochloric acid to remove any oxides of nitrogen. The final dry residue was then dissolved in two millilitres of the solvent which was to be used in the extraction process.

The sample solutions containing the required amount of iridium were spiked with sufficient radiotracer ^{192}Ir to yield a count rate of at least 150 counts per second for 15 ml of sample contained in a test tube of 15 mm inner diameter. The tracer was well mixed with the sample solution by vigorous shaking.

Counting Technique: A 15 ml aliquot of the sample solution contained in a test tube of 15 mm internal diameter was placed in the well of the NaI detector. The activity of each sample was determined from the average of five successive counts of 100 seconds duration. The average sample activity was then corrected for background counts which was obtained from the average of fifteen measurements.

Determination of Percentage Extraction by Tracer Technique

The percentage extraction was determined by counting the radioactivity of a 15 ml aliquot of the sample solution before and after extraction by the foam.

$$\begin{array}{l}\%\\ \text{Extrac-}\\ \text{tion by}\\ \text{foam}\end{array} = \frac{\text{Activity}_{\text{before extraction}} - \text{Corrected Activity}_{\text{after extraction}}}{\text{Activity}_{\text{before extraction}}} \times 100$$

Both the activity before and after extraction were corrected for background activity but it was necessary to make an additional correction to the activity after extraction for errors due to evaporation of the solvent.

Two different methods were used to correct for the loss of the solvent through evaporation: One method involved the setting up of another "control" cell containing the same volume of solution as the sample and sufficient ^{192}Ir to give an activity similar to that of the sample, but having no foam. This cell was treated in the same way as the sample cell and its activity was monitored over the period of time that extraction was being carried out from the sample solution. By comparison of the activity of the "control" solution at a given time with its initial activity, a correction factor "f" could be obtained. For example,

If average initial activity of control = 20,000 cts/100 sec
and average activity of control after 4 hr = 21,000 cts/100 sec
Difference = 1,000 cts/100 sec
Fractional difference (f) = 0.05

This would mean that the measured activity of the sample at the corresponding time was 5% higher than it would have been if no evaporation had taken place. Therefore, the corrected activity of the sample would be 5% less than the measured value:

$$\text{Corrected Activity} = \text{Activity}_{\text{measured}} - (f \times \text{Activity}_{\text{measured}})$$

The second method of estimating the error due to evaporation was a "volumetric" method which involved comparing the volume of the "control" solution at the beginning and at the end of the extraction period. The percentage difference in the volume would correspond to the percentage by which the measured activity exceeds the activity which would have resulted if there had been no evaporation. Assuming that evaporation occurred at a uniform rate over the period of extraction, the percentage evaporation per unit time can be determined and hence a correction to all activity measurements taken at different times can be applied.

The assumption that evaporation occurs at a uniform rate is reasonable since the surface area of the cell does not change and the temperature of the solution was kept constant over the duration of the extraction. It is also fair to assume that the rate of evaporation of solvent would be the same from both "sample" cells and the "control" cell since the "sample" and "control" cells were of the same dimensions and were treated in the same way during the entire period of extraction.

The two methods of estimating the correction of the measured activity for evaporation compared to within 3% of each other. It is necessary, however, in the case of the method which involves the monitoring of the activity of the "control", to add a sufficiently large amount of carrier to the control solution ($\approx$10-20 μg ml^{-1} Ir). If the "control" solution is very dilute with respect to iridium (<5 μg ml^{-1} Ir) inaccurate results are obtained owing to significant loss of tracer to the walls of the vessel.

Measurement of Extraction by UV-Visible Absorption Spectrophotometry

A series of standard solutions was prepared by appropriate dilution of the iridium stock solution and these solutions were used to prepare a calibration curve of absorbance vs concentration of the metal at a suitable wavelength. The concentration of the metal left in solution after extraction was determined by interpolation from the calibration curve, the absorbance of the solution being measured at the same wavelength and in the same cell which was used for the preparation of the calibration curve. The solvent from which the extraction was being carried out was used as the blank solution in all UV-visible spectrophotometric determinations. The percentage extraction is given by the equation:

$$\%\ \text{Extraction} = 100 \times \frac{\text{Conc. of metal}_{\text{before extraction}} - \text{Conc. of metal}_{\text{after extraction}}}{\text{Conc. of metal}_{\text{before extraction}}}$$

In order to correct measurements of metal concentration after extraction for errors due to evaporation of the solvent, a "control" solution of the metal in the same solvent as the sample was set up in a cell of similar dimensions as that in which the sample was contained. This "control" solution was treated in the same way as the sample, and its concentration was measured at the same time after extractions were carried out. By comparison of the concentration of the "control" solution at any given time with its initial concentration the percentage of the solvent lost due to evaporation could be determined. Since the "control" had the same surface area for evaporation and was kept at the same temperature as the "sample", the loss of solvent by evaporation could be assumed to be the same for both "sample" and "control". Hence the measured concentration of the sample solution after extraction could be corrected by a factor equal to the percentage loss of solution by evaporation.

Determination of Distribution Coefficient

The distribution coefficient for the process is given by the ratio of the concentration of the metal in the foam to the concentration of the metal left in solution at equilibrium. In all experiments this was taken as equivalent to the equation:

$$\begin{array}{l}\text{Distribution}\\ \text{Coefficient}\end{array} = \frac{\text{\% metal on foam}}{\text{wt. of foam (g)}} \times \frac{\text{wt. of solution (g)}}{\text{\% metal left in solution}}$$

The methods of correcting activities and concentration after extraction, and hence correcting overall percentage extraction for evaporation do not take into account the fact that the changes in volume of the solution as the extraction proceeds will affect the amount of metal extracted onto the foam. From the above equation it can be seen that if the distribution coefficient is assumed to be constant for the extraction process at a given temperature, then, with a decrease in volume of the solution, the ratio of the percentage of the metal on the foam to that left in solution will increase. However, the change in percentage of metal extracted onto the foam for a given percentage change in the volume of solution is always very small compared to the percentage change in volume of the solution. For example, a 10% change in solution volume will correspond to a change of about 1% in the percentage of metal extracted onto the foam.

Recovery Studies

Determination of Percentage Recovery using Radiotracer

The foam was loaded with Ir IV at 25°C, the amount of Ir IV extracted onto the foam being measured by the radiotracer technique previously described (pp. 22). The foam was then squeezed by compressing it with a plunger to expel as much liquid as possible, then rinsed quickly in the solvent from which extraction was carried out. This would serve to rinse off radioactive liquid from the foam without leaching out the metal. The foam was then placed between two clean dry paper towels and compressed until no more liquid was observed to come out onto the towels. The "dry" foam was then placed in the bottom of a test tube and its activity was counted. The foam was then transferred to a clean glass cell containing the solution for recovery and the squeezing procedure was repeated as in the extraction process. After squeezing for a desired length of time the foam was taken out of the cell, rinsed quickly with some of the recovery solution, squeezed dry between paper towels and its activity was redetermined in the same test tube that was used in the intial count. The percentage recovery was determined by means of the following equation:

$$\% \text{ Recovery} = \frac{\text{Activity}_{\text{before recovery}} - \text{Activity}_{\text{after recovery}}}{\text{Activity}_{\text{before recovery}}} \times 100$$

The small foam sizes used (0.10 g) ensured that all of the foam occupied the active volume of the counter when pushed to the bottom of a test tube of 15 mm internal diameter. Because of this, foam geometry was not an important consideration in these experiments as the activity of all of the foam was counted, regardless of the geometry of the foam.

In both extraction and recovery studies, all experiments were carried out in triplicate unless otherwise specified. The standard deviation (S) in any measurement was defined as:

$$S = \left[\sum_{j=1}^{N} \frac{(x_j - \bar{x})^2}{N-1} \right]^{\frac{1}{2}}$$

where x_j is the measured value

$\bar{x}$ is the arithmetical mean

N is the number of measurements carried out.

RESULTS AND DISCUSSION

Preliminary Studies

Some preliminary studies were carried out to determine in what organic solvents sodium hexachloroiridate IV was stable and from which solvent extraction by the foam was feasible. All of the preliminary studies with respect to extraction of the metal onto the foam were done using the flow-through system as follows: a polyurethane foam plug, about 5 cm long and 2 cm in diameter, was squeezed with 2 ml of the solvent which was to be used in the extraction. The wet foam plug was introduced into the pyrex column shown in Figure 6, with the aid of a glass rod. An aliquot of 20 ml of the test solution was carefully introduced onto the foam plug using a long-stemmed glass funnel and the solution was then passed through the foam at a flow rate of 0.5 ml per minute. After all of the test solution had passed through the foam, fresh solvent was passed quickly through the foam and added to the collected effluent. The effluent (25 ml total volume) was analyzed by UV-visible absorption spectrophotometry and the percentage of the metal extracted by the foam was determined.

Sodium hexachloroiridate IV appeared to be stable in acetone and ethyl acetate solutions. The results of these preliminary studies also showed that the extraction of the complex from these solvents was feasible, the efficiency of extraction being especially high for extraction from ethyl acetate. For example, by using foam plugs of total weight ≈0.4 g, extractions of 98 to 99% Ir IV could be obtained from 20 ml ethyl acetate solutions containing 4 to 10 mg total weight of Ir. For extractions from acetone, extraction of 80% to 90% were obtained from 20 ml of solution containing 1 to 4 Mg Ir. The extraction of Ir IV from both solvents is improved with lower flow rates.

The extraction of Ir IV could also be carried out from ethanol solutions, but solutions of sodium hexachloroiridate IV in ethanol are not stable. Sodium hexachloroiridate IV undergoes reduction to the corresponding tervalent complex in ethanolic solutions and the reduction process is accelerated in the presence of polyurethane foam.

The extent of reduction of Ir IV in solution at any time was determined spectrophotometrically by the measurement of the absorbance of the solution at 490 nm as a function of time. Figures 7 and 8 show the absorption spectra of aqueous solutions of $IrCl_6^{2-}$ and $IrCl_6^{3-}$ respectively. The molar extinction coefficient of $IrCl_6^{2-}$ at 490 nm is about three hundred times that of $IrCl_6^{3-}$. Therefore reduction of $IrCl_6^{2-}$ to $IrCl_6^{3-}$ leads to a decrease in the absorbance at 490 nm.

The extent of reduction of $IrCl_6^{2-}$ in the presence of foam was determined in the following manner: the foam was squeezed in a solution of the Ir IV complex for a certain period of time. The resultant solution was then divided into two portions, one of which was subjected to oxidation by chlorine water, while the other was not oxidized, but to it was added an equivalent amount of distilled water. The absorbance of the two solutions at 490 nm was measured. The difference in the absorbances of the two solutions was a measure of the extent of reduction in the presence of the foam over the specified period of time.

Extraction of the Ir IV complex from propan-2-ol is also possible. However, the Ir IV complex undergoes reduction to the Ir III complex in propan-2-ol solutions as well, although the rate of reduction is slower than in ethanolic solution. The percentage of extraction of sodium hexachloroiridate IV by foam decreases in the order:

propan-2-ol > absolute ethanol > 95% ethanol

Figure 7. UV-Visible Absorption Spectrum of $IrCl_6^{2-}$

Reference 58

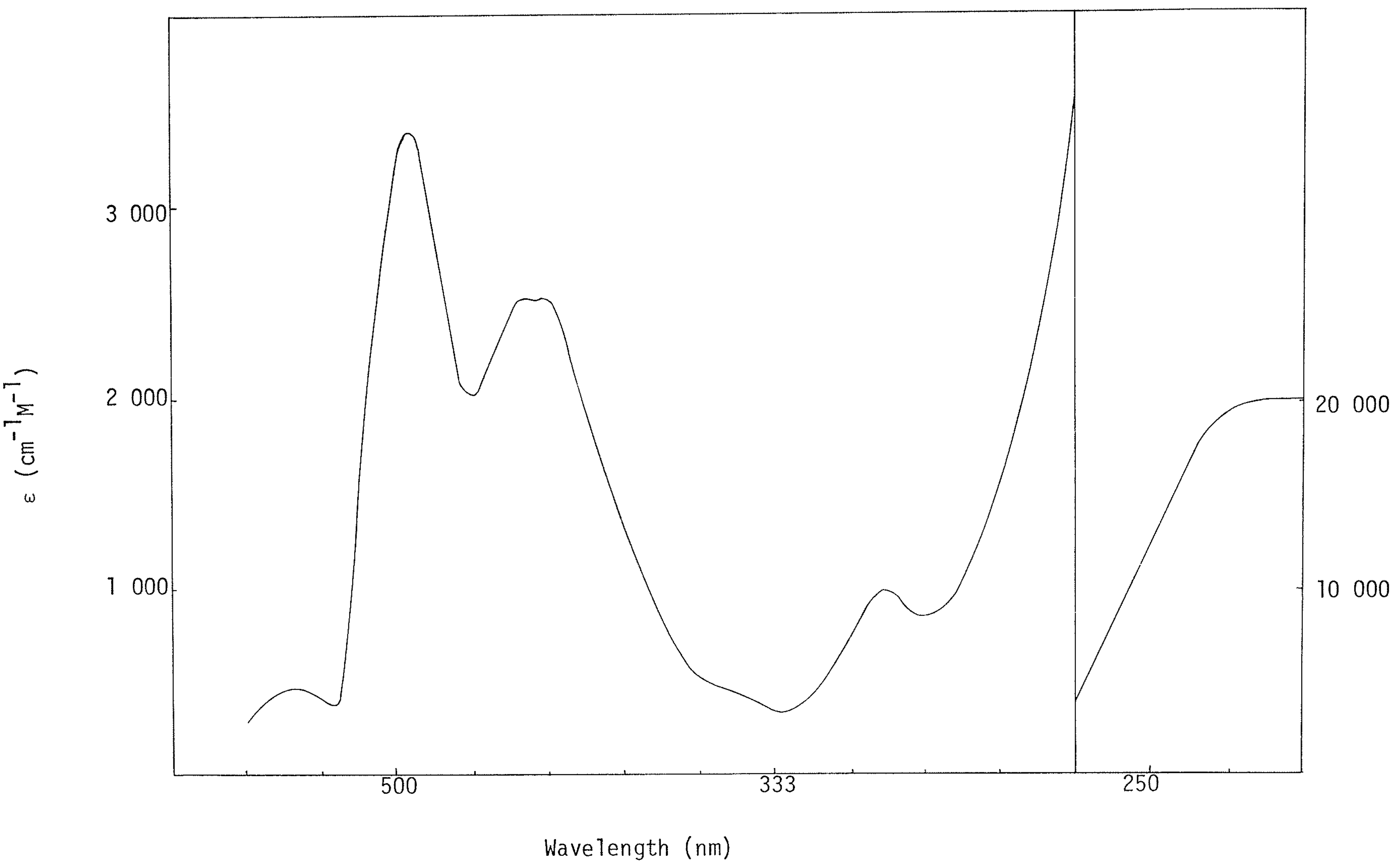
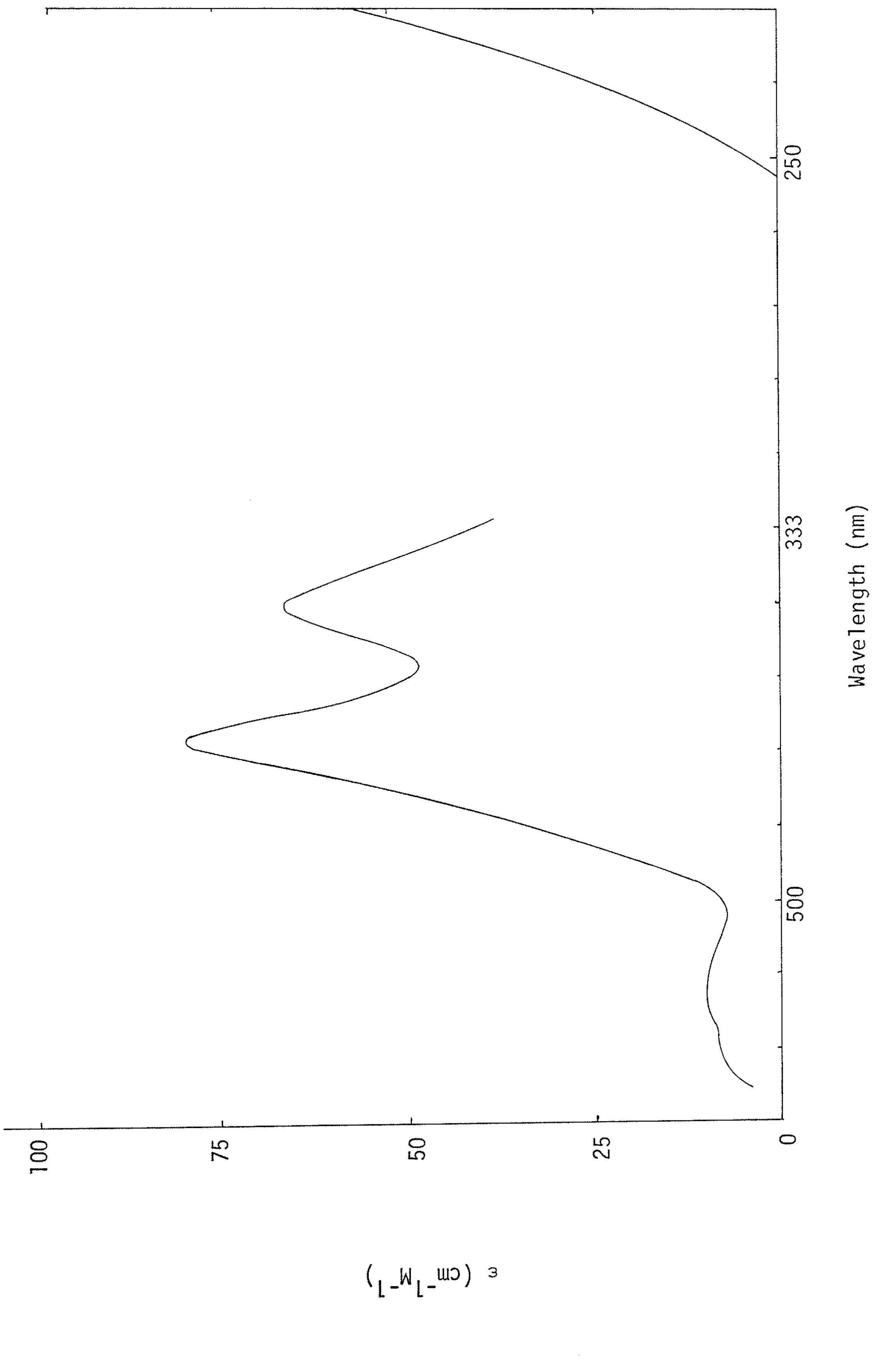

ε (cm^{-1}M^{-1})
3 000
2 000
1 000
20 000
10 000
500
333
250
Wavelength (nm)

Figure 8. UV-Visible Absorption Spectrum of $IrCl_6^{3-}$ in Aqueous Solution

Reference 59


ε (cm^{-1}M^{-1})
100
75
50
25
0
500
333
250
Wavelength (nm)

Extraction of Sodium Hexachloroiridate IV from Acetone

Extraction of Sodium Hexachloroiridate IV as a Function of Time

In order to determine the time required to reach equilibrium with respect to the extraction of sodium hexachloroiridate IV, measurements of the extraction as a function of time were carried out. Fifty millilitres of solution with a concentration of 10 $\mu g\ ml^{-1}$ Ir IV was prepared by dilution of the stock solution. A foam weighing 0.05 g was placed in the solution and the foam was squeezed manually at fifteen minute intervals. The percentage of Ir IV extracted by the foam was measured at time intervals of a few hours by the tracer technique.

The results of this study are shown graphically in Figure 9. The percentage extraction increases rapidly up to a certain time after which extraction slows down and remains essentially unchanged with further squeezing. At this point it is considered that equilibrium with respect to the extraction has been reached. Equilibrium with respect to the extraction of sodium hexachloroiridate IV from acetone is attained in approximately 20 hr at 25°C.

Variation of Distribution Ratio with Concentration of Ir IV for Extraction from Acetone

The variation of the distribution ratio with concentration was investigated by measuring the percentage extraction of Ir IV at equilibrium from solutions of different Ir IV concentrations. The volume of solution, weight of foam and temperature were kept constant in these experiments. Determinations of percentage extraction were carried out using the tracer technique.

Figure 10 shows a plot of the logarithm of the distribution ratio versus initial concentration of Ir IV. The distribution ratio remained essentially

Figure 9. Extraction of Sodium Hexachloroiridate IV from Acetone as a Function of Time.

Wt. of foam = 0.05 g

Conc. of solution = 10 μg ml^{-1} Ir IV

Volume of solution = 50 ml

Temperature = 25.0 ± 0.05°C

Measurements by radiotracer ^{192}Ir

Mode of squeezing: manual

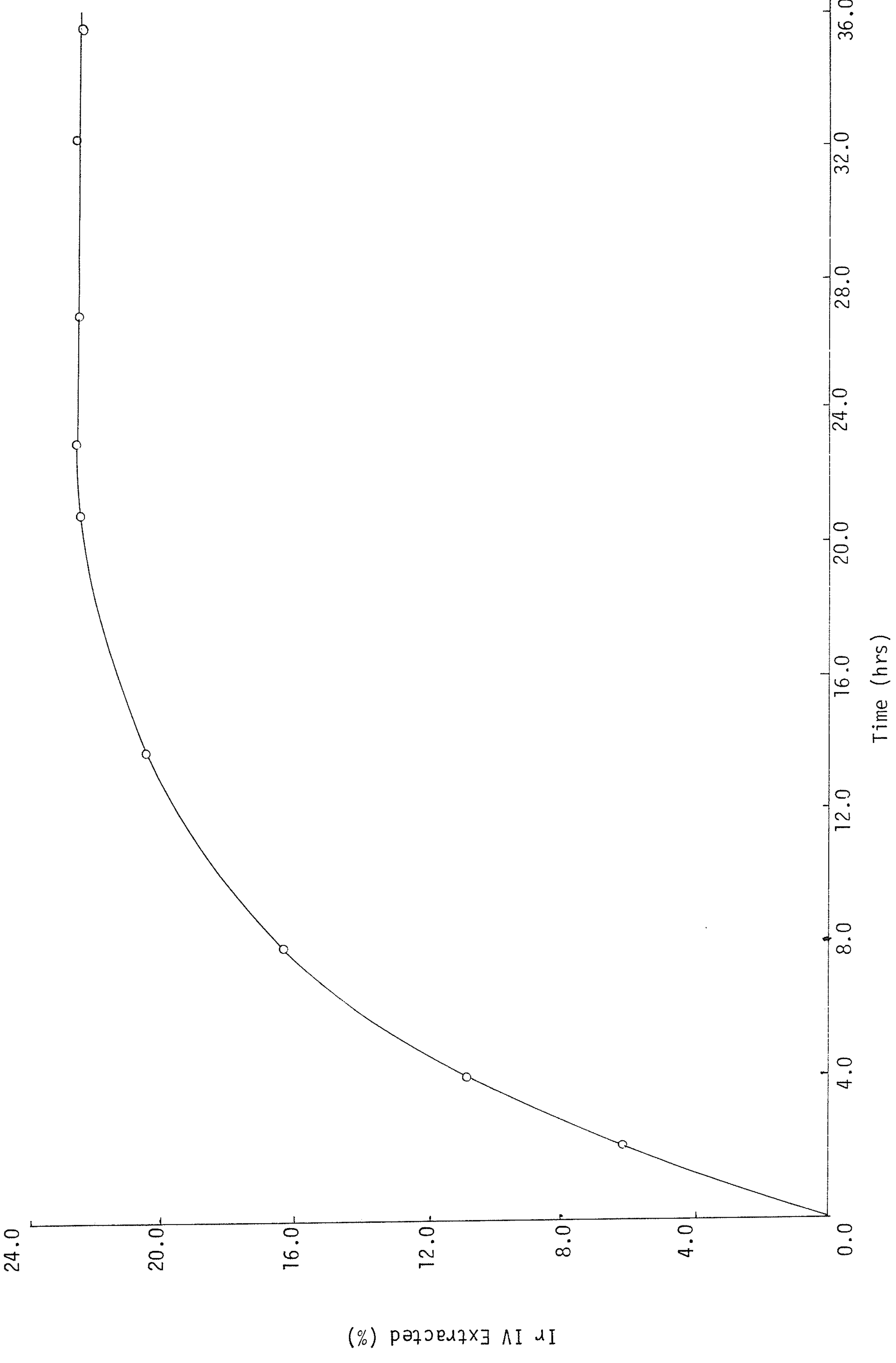

Ir IV Extracted (%)
0.0
4.0
8.0
12.0
16.0
20.0
24.0
Time (hrs)
0.0
4.0
8.0
12.0
16.0
20.0
24.0
28.0
32.0
36.0

Figure 10. Variation of Distribution Ratio with Initial Conc. of Ir IV for Extraction from Acetone Solution.

Vol. of solution = 50 ml

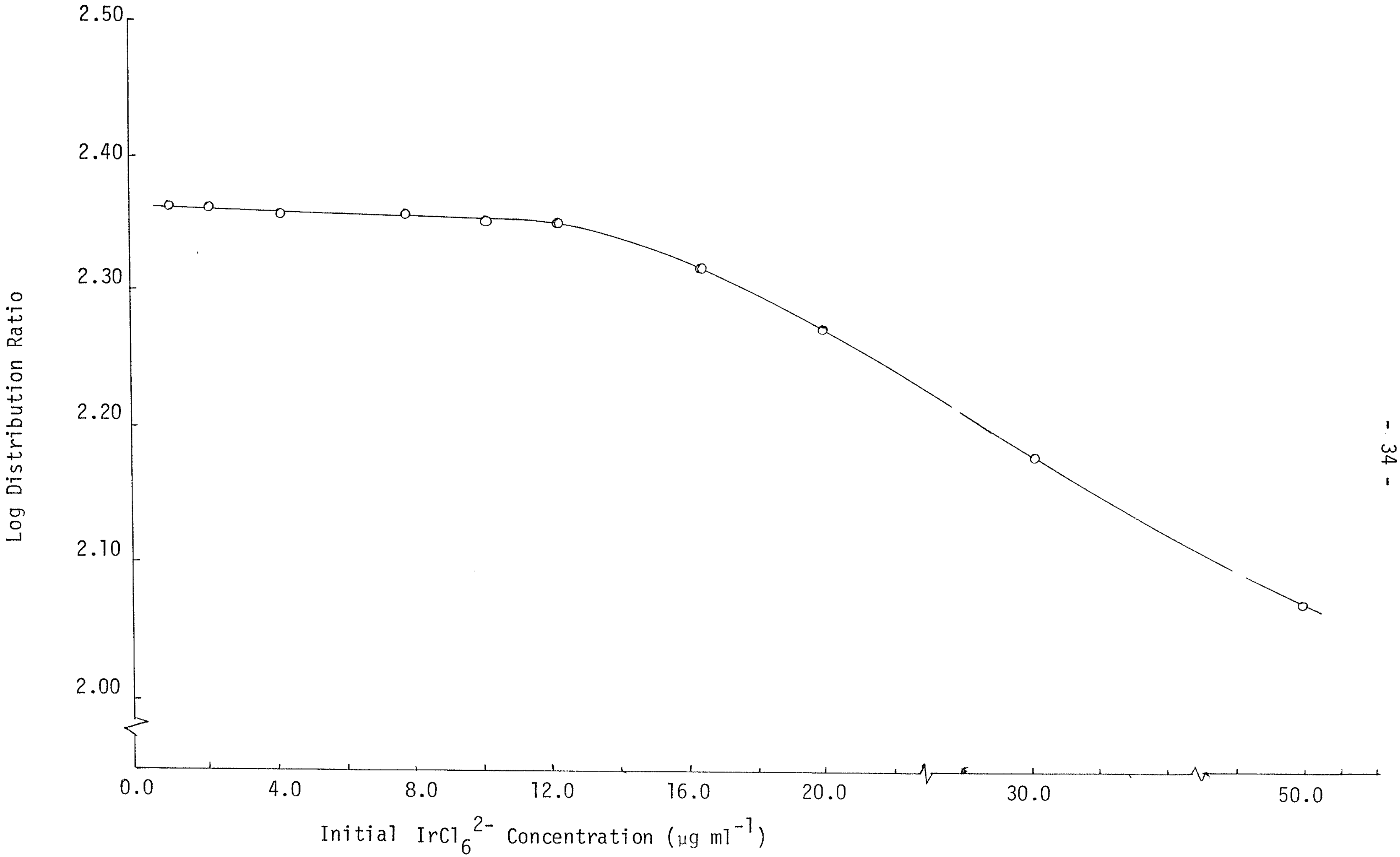
Wt. of foam = 0.05 g

Temperature = 25.0 ± 0.05°C

Determinations by radiotracer ^{192}Ir

Measurements carried out after 24 hr

Mode of squeezing: manual


Log Distribution Ratio
2.50
2.40
2.30
2.20
2.10
2.00
0.0
4.0
8.0
12.0
16.0
20.0
30.0
50.0
Initial $IrCl_6^{2-}$ Concentration (μg ml^{-1})

independent of concentration over a certain concentration range then eventually fell off. In this case, where 0.05 g foam and 50 ml of solution were being employed at 25°C, the distribution ratio remained approximately independent of concentration up to concentrations of 12 $\mu g\ ml^{-1}$ Ir IV, and then started falling off. The fall-off of the distribution ratio above a concentration of 12 $\mu g\ ml^{-1}$ is not due to the fact that the capacity of the foam was being approached. Its implications are discussed in Appendix 1b.

Effect of H_2O on the Extraction of Sodium Hexachloroiridate IV from Acetone

In attempting to establish the optimum conditions for extraction of sodium hexachloroiridate IV from acetone, the effect of various proportions of H_2O on the extraction efficiency was investigated. Solutions were prepared by adding the appropriate amount of water to acetone which had been previously dried with anhydrous magnesium sulphate and then distilled. All solutions were made up to 50 ml total volume and contained 10 $\mu g\ ml^{-1}$ Ir IV.

The UV-visible absorption spectra of solutions containing H_2O but having no foam were followed with time. Figure 11 shows the spectra of these solutions after 20 hr. The intensities of the absorption peaks of $IrCl_6^{2-}$ at 584, 490 and 440 nm were significantly decreased at H_2O concentrations of 2% and higher. This decrease in the peak intensities indicates that the $IrCl_6^{2-}$ species was being converted to some other complex in these solutions. There are two possible explanations: the aquation of $IrCl_6^{2-}$ to species such as $Ir(OH_2)Cl_5^-$ and $Ir(OH_2)_2Cl_4$; or the reduction of $IrCl_6^{2-}$ from the quadrivalent state to the tervalent complex $IrCl_6^{-3}$.

Figure 11. UV-Visible Spectra of $IrCl_6^{2-}$ in Acetone Solutions Containing Various Proportions of H_2O.

Conc. of Ir IV = 10 μg ml^{-1}

Cell path length = 1 cm

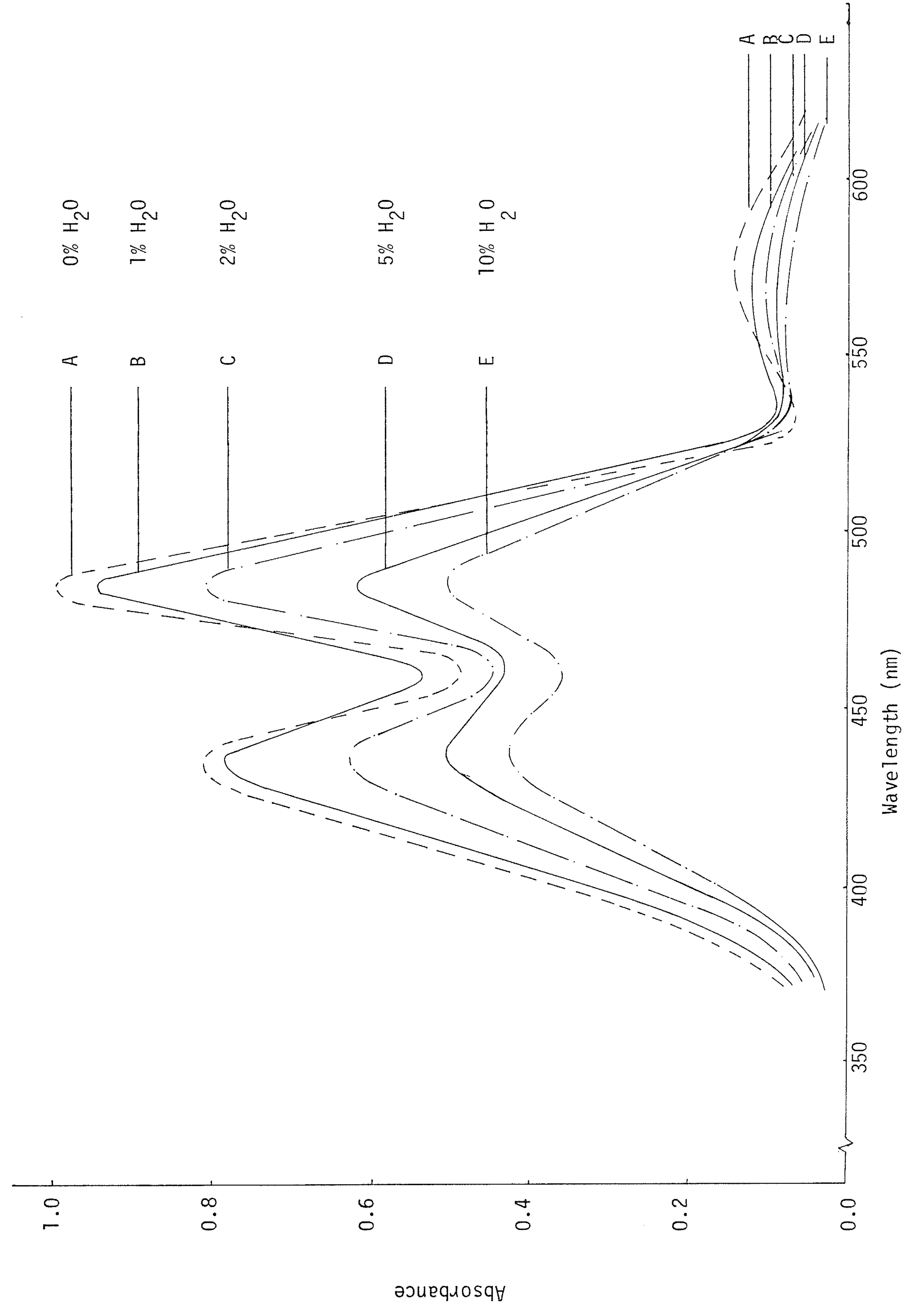

Absorbance
0.0
0.2
0.4
0.6
0.8
1.0
Wavelength (nm)
350
400
450
500
550
600
A 0% H_2O
B 1% H_2O
C 2% H_2O
D 5% H_2O
E 10% H_2O
A
B
C
D
E

Figure 12 shows the spectra of the hexachloro iridium IV complex and the various aquo complexes viz. $Ir(OH_2)Cl_5^-$, $Ir(OH_2)_2Cl_4$ and $Ir(OH_2)_3Cl_3^+$. If $IrCl_6^{2-}$ was being mainly converted to either of the aquocomplexes $Ir(OH_2)Cl_5^-$ or $Ir(OH_2)Cl_4$ there would be a decrease in absorbance at 490 and 440 nm, but this would be accompanied by a significant increase in the absorbance in the wavelength region 445 to 450 nm and 525 to 590 nm. Production of the aquocomplex $Ir(OH_2)_3Cl_3^+$ would result in a marked increase in absorbance at 425 nm and 373 nm. However, no significant increases in absorbance at these wavelengths were observed. Hence the results cannot be explained on the basis of aquation of the $IrCl_6^{2-}$ species in solutions containing H_2O.

The changes in the spectrum of $IrCl_6^{2-}$ due to the presence of water are most likely attributable mainly to the reduction of the Ir IV complex to the Ir III complex. The molar absorptivity of $IrCl_6^{3-}$ in the wavelength region 350 - 625 nm is much less than that of $IrCl_6^{2-}$ so reduction of $IrCl_6^{2-}$ to $IrCl_6^{3-}$ would lead to a marked decrease in intensity of absorption in this wavelength region.

Figure 13 shows the extent of reduction of Ir IV to Ir III with time due to the various proportions of water. The rate of reduction increased with increasing proportion of H_2O. Also, for any given proportion of water, the rate of reduction of Ir IV to Ir III decreased with time; presumably eventually beyond a certain time there will be no further reduction of Ir IV to Ir III representing a state of equilibrium for the reaction

$$IrCl_6^{2-} + e^- \rightleftharpoons IrCl_6^{3-}$$

In these experiments the concentration of Ir IV in solution at any time was assumed to be proportional to the absorbance at 490 nm. This assumption is reasonable since any $IrCl_6^{3-}$ formed would not contribute significantly to the absorbance at 490 nm since its molar absorptivity at 490 nm is some three hundred times less than that of $IrCl_6^{2-}$.

Figure 12. Visible Absorption Spectra of the Hexachloro complex of Ir IV and Various Aquated Species in Cl_2-Saturated 2.5 F $HClO_4$ - 1.2 F $NaClO_4$ at 25°C.

A, $IrCl_6^{2-}$; B, $Ir(OH_2)Cl_5^-$; C, $Ir(OH_2)_2Cl_4$;
D, $Ir(OH_2)_3Cl_3^+$.

Reference 60

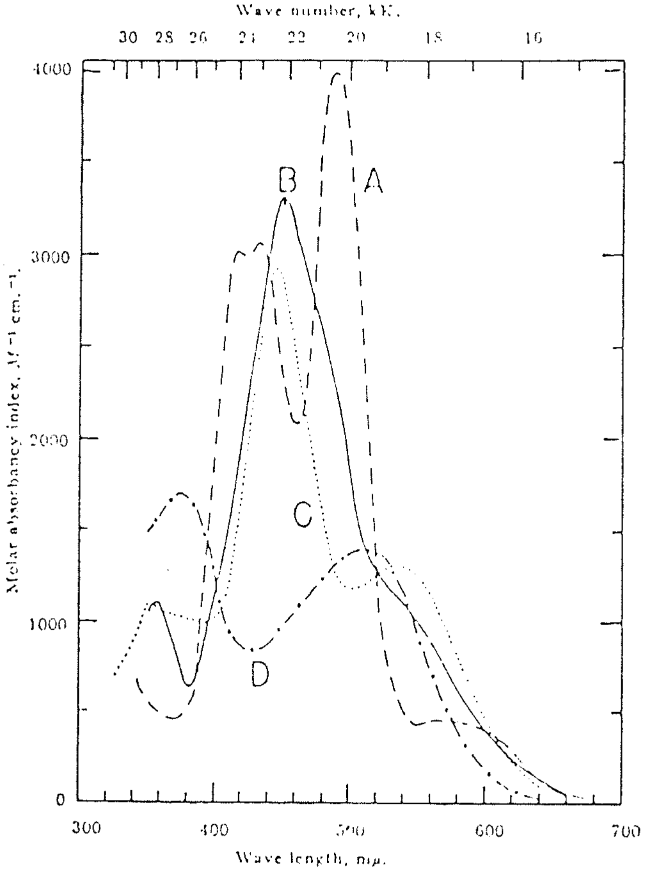

Wave number, kK.
30
28
26
24
22
20
18
16
4000
3000
2000
1000
0
Molar absorbancy index, M^{-1} cm.$^{-1}$.
A
B
C
D
300
400
500
600
700
Wave length, mμ.

Figure 13. Extent of Reduction of $IrCl_6^{2-}$ to $IrCl_6^{3-}$ with Time in Acetone Solutions Containing Various Proportions of H_2O.

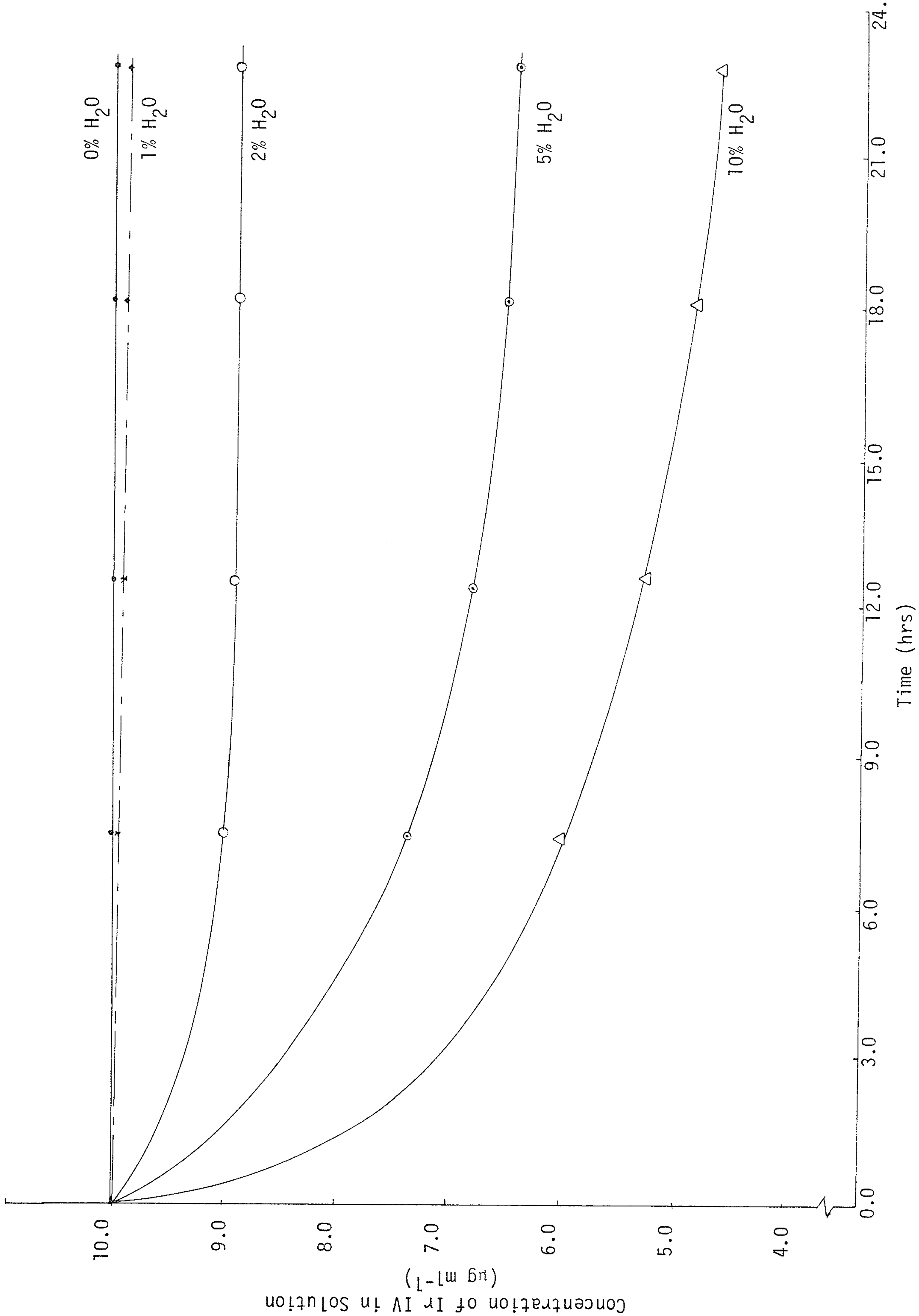
Vol. of solution = 50 ml

Conc. of Ir IV = 10 μg ml^{-1}

Wt. of foam = 0.05 g

Temperature = 25.0 ± 0.05°C

Determinations by Absorption Spectrophotometry at 490 nm.


Concentration of Ir IV in Solution
(μg ml-1)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
0.0
3.0
6.0
9.0
12.0
15.0
18.0
21.0
24.0
Time (hrs)
0% H_2O
1% H_2O
2% H_2O
5% H_2O
10% H_2O

Tervalent iridium does not appear to be extractable by the foam, therefore one might expect that the extraction efficiency might decrease in solutions in which reduction of Ir IV to Ir III was taking place.

Figure 14 shows the extraction of $IrCl_6^{2-}$ from solutions containing various proportions of H_2O. The efficiency of extraction decreased with increasing proportions of H_2O. The major reason for these results might be the fact that the rate of reduction of Ir IV to Ir III increases with increasing proportions of H_2O. The maximum percentage extraction of Ir IV under the conditions used in these experiments dropped from ≈22% in the absence of water to 15% in solutions containing 10% water.

An attempt was made to use UV-visible absorption spectrophotometry to carry out these determinations. This involved a comparison of the absorbances of solutions from which the extraction was being carried out with the absorbances of solutions of similar composition but having no foam, the amount of Ir IV extracted at any time being taken as the difference between the Ir IV concentration of the two solutions. The Ir IV concentration in any solution was taken as being proportional to the absorbance at 490 nm. Inherent in such an approach is the assumption that the rate of reduction of Ir IV to Ir III is the same in solutions of similar composition, whether or not foam was present. However, the reduction process seems to be accelerated in the presence of foam, so UV-visible absorption spectrophotometric determination yields misleading results.

The unfavourable effect of water in bringing about reduction of $IrCl_6^{2-}$ to the unextractable $IrCl_6^{3-}$ species makes it desirable to dry and distil the acetone to obtain better extraction efficiencies for extraction of $IrCl_6^{2-}$ from acetone. Another reason for carrying out a study of the effect of H_2O on extraction of Ir IV was to find out if a certain amount

Figure 14. Effect of Various Proportions of H_2O on the Extraction of Na_2IrCl_6 from Acetone Solution.

Vol. of solution = 50 ml

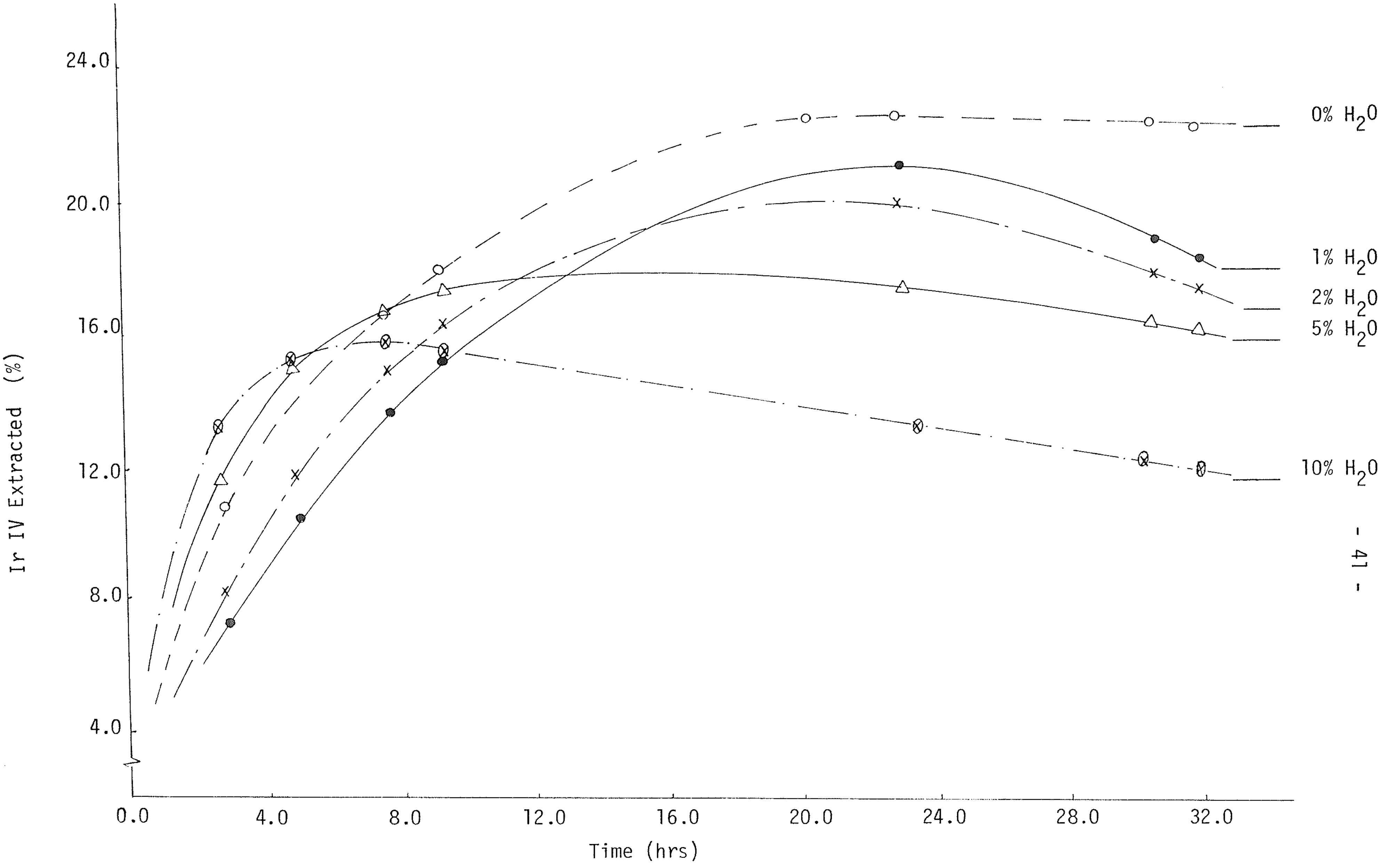
Wt. of foam = 0.05 g

Conc. of Ir IV = 10 μg ml^{-1}

Temperature = 25.0 ± 0.05°C

Determinations by radiotracer ^{192}Ir

Mode of squeezing: manual


24.0
20.0
16.0
12.0
8.0
4.0
Ir IV Extracted (%)
0.0
4.0
8.0
12.0
16.0
20.0
24.0
28.0
32.0
Time (hrs)
0% H_2O
1% H_2O
2% H_2O
5% H_2O
10% H_2O

of H_2O could be tolerated with no significant effect on the efficiency of extraction. If so, this would allow one to take an aqueous solution of the Ir IV complex, add the appropriate amount of dried acetone and then carry out the extraction without the need to evaporate all of the water from the original sample. However, the results show that such an approach would not be feasible if maximal extraction efficiency is desired.

Effect of Organic Acids on the Extraction of Sodium Hexachloroiridate IV from Acetone Solution

The effect of organic acids on the extraction of Ir IV from acetone was investigated in the hope of improving the efficiency of extraction. Figure 15 shows the effect of trichloroacetic acid on the spectrum of $IrCl_6^{2-}$ in acetone. In acetone, the $IrCl_6^{2-}$ complex shows absorbance maxima at 440, 584 and 490 nm. In the presence of trichloroacetic acid, absorbance maxima appear at 460 nm and 550 nm and the intensities of the absorption peaks at 440, 490 and 584 nm decrease. This shows that at least one additional species is produced in the presence of trichloroacetic acid. Acetic acid produces a similar effect on the spectrum of $IrCl_6^{2-}$ in acetone. It is possible that the additional species formed in the presence of acetic acid or trichloroacetic acid is due to the replacement of chloride ligands of $IrCl_6^{2-}$ by acetate or trichloroacetate ligands according to the equations:

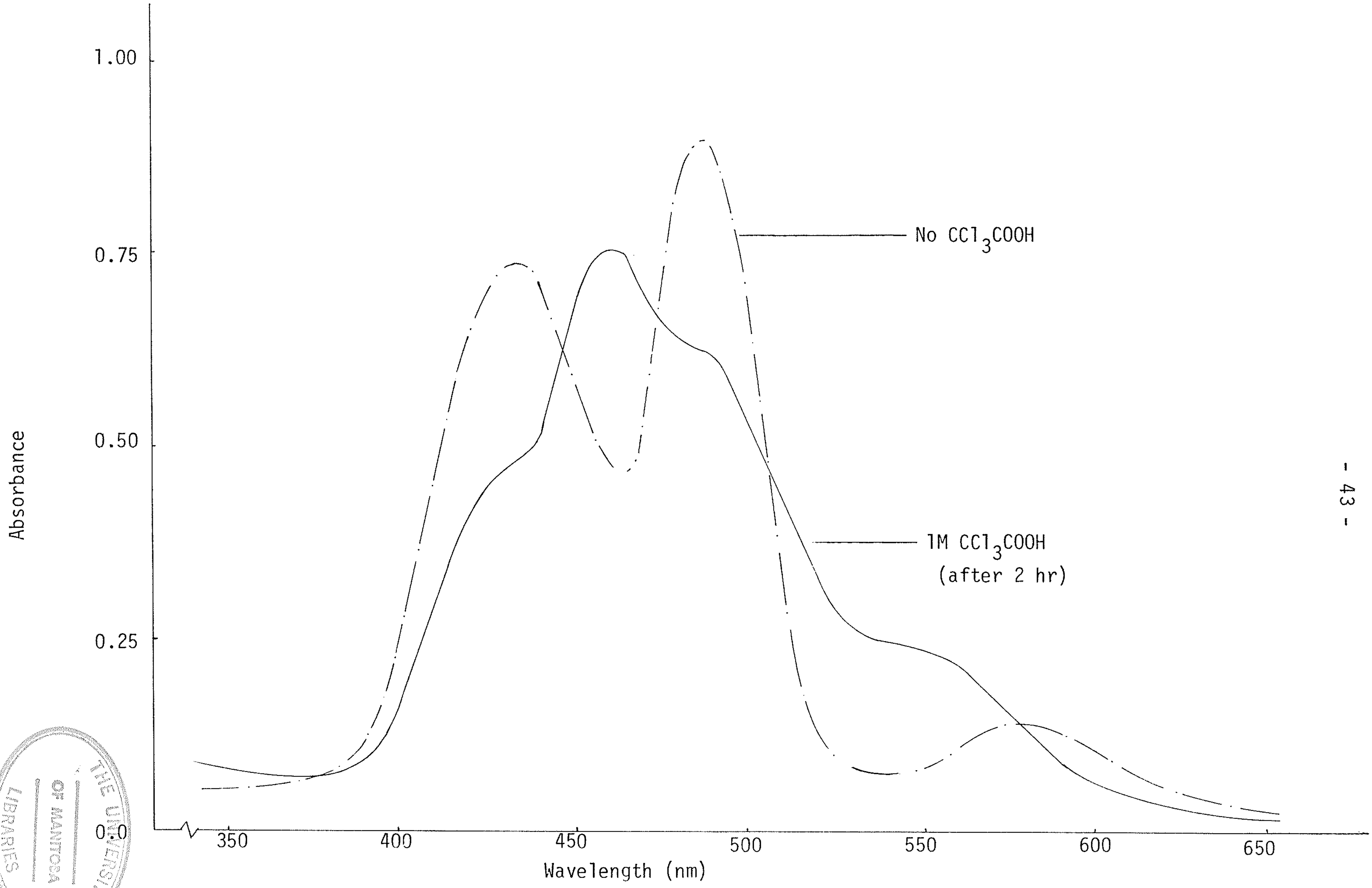
$$CCl_3COOH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CCl_3COO^- + H^+ \qquad (1)$$

$$IrCl_6^{2-} + CCl_3COO^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Ir(CCl_3COO)Cl_5^{=} + Cl^- \qquad (2)$$

Figure 15. Effect of Trichloroacetic Acid on the Spectrum of $IrCl_6^{2-}$ in Acetone.

Conc. of Ir IV = 10 μg ml^{-1}

Cell path length = 1 cm



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and possibly

$$Ir(CCl_3COO)Cl_5^{=} + CCl_3COO^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Ir(CCl_3COO)_2Cl_4^{=} + Cl^- \quad (3)$$

If the trichloroacetate ligand acts as a bidentate ligand with iridium IV ion then the substitution reactions will be as follows:

$$IrCl_6^{2-} + CCl_3COO^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Ir(CCl_3COO)Cl_4^- + 2Cl^- \quad (2')$$

and

$$Ir(CCl_3COO)Cl_4^- + CCl_3COO^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Ir(CCl_3COO)_2Cl_2 + 2Cl^- \quad (3')$$

If the peaks at 460 nm and 550 nm are due to such substitutions of chloride ligands by trichloroacetate or acetate ligands, then one might expect that the absorbance at these wavelengths at any given time would increase with concentration of the acid. This was in fact found to be the case, as the results of Table 1 show. A ten-fold increase in the trichloroacetic acid concentration does produce a significant increase in the absorbance at 460 and 550 nm at any given time and there is a corresponding decrease in absorbance at 490 nm and 440 nm, the wavelength regions which are characteristic of the absorption by the $IrCl_6^{=}$ species.

From Table 1, it is also apparent that at a high concentration of trichloroacetic acid (1M) there is a significant decrease in the absorbance at 460 nm and 550 nm after about 31 hours, while such a decrease in absorbance at these wavelengths is not observed for lower concentrations of the acid. The results suggest that some other reaction becomes important at high concentrations of the acid. There can possibly be further substitutions of chloride ligands of $IrCl_6^{=}$ by trichloroacetate ligands. Another

Table 1. Effect of Various Concentrations of Trichloroacetic Acid on the Spectrum of Solutions of Na_2IrCl_6 in Acetone.

Conc. of Ir IV = 10 μg ml^{-1}

Cell path length = 1 cm

ABSORBANCE AS A FUNCTION OF TIME

	ACID CONC. (Molarity)	3 1/2 hr	11 1/2 hr	25 1/2 hr	31 1/2 hr	35 3/4 hr	47 hr	57 hr	70 3/4 hr
490 nm	0.05	0.715	0.705	0.690	0.690	0.692	0.693	0.699	0.700
	0.10	0.710	0.708	0.690	0.688	0.690	0.688	0.700	0.700
	0.50	0.660	0.650	0.630	0.628	0.630	0.620	0.630	0.640
	1.00	0.620	0.620	0.590	0.580	0.590	0.580	0.583	0.560
440 nm	0.05	0.488	0.480	0.444	0.450	0.450	0.447	0.454	0.460
	0.10	0.488	0.480	0.454	0.450	0.460	0.447	0.454	0.452
	0.50	0.408	0.400	0.373	0.372	0.380	0.365	0.378	0.388
	1.00	0.395	0.373	0.347	0.340	0.355	0.347	0.360	0.340
460 nm	0.05	0.720	0.750	0.740	0.750	0.758	0.756	0.772	0.780
	0.10	0.710	0.730	0.728	0.738	0.748	0.747	0.772	0.780
	0.50	0.770	0.790	0.780	0.782	0.790	0.780	0.800	0.810
	1.00	0.770	0.790	0.788	0.760	0.752	0.745	0.735	0.740
550 nm	0.05	0.221	0.228	0.220	0.225	0.230	0.227	0.240	0.240
	0.10	0.220	0.225	0.218	0.220	0.230	0.227	0.240	0.240
	0.50	0.270	0.272	0.260	0.265	0.270	0.260	0.274	0.280
	1.00	0.265	0.280	0.250	0.250	0.260	0.250	0.240	0.250

possibility is that the results can be due to some reduction of Ir IV to Ir III since small amounts of water would be introduced with the trichloroacetic acid and the higher the concentration of the acid, the greater the amount of water which would be present in the solution.

The extraction of Ir IV as a function of time in the presence of trichloroacetic and acetic acids respectively is shown in Figure 16. In both cases, the percentage extraction increases rapidly up to a certain time after which the rate of extraction slows down and eventually the percentage of Ir IV extracted remains unchanged with further squeezing of the foam. In the case of solutions containing acetic acid, equilibrium was reached after about 24 hours while in the case of those containing trichloroacetic acid approximately 31 hours were required to reach equilibrium for the extraction.

The fact that equilibrium is achieved at different times for the two systems might be due to differing pH conditions in the two systems, or it might suggest that the Ir IV complex being extracted from the two systems is not the same. The latter would support the theory that substitution of chloride ligands by acetate and trichloroacetate ligands occurs in solutions containing acetic acid and trichloroacetic acid respectively.

The effect of various concentrations of acetic and trichloroacetic acid on the extraction of Ir IV from acetone solution is shown in Figure 17. Both acids improved the efficiency of extraction of Ir IV by the foam at all acid concentrations. Extraction increased with increasing acid concentration. With trichloroacetic acid, better than two-fold increase in extraction efficiency was obtained at a concentration of 0.7M of the acid. At concentrations of trichloroacetic acid above 0.7M, no further increase in the extraction was obtained. Acetic acid was not as effective in improving the extraction efficiency. An improvement in extraction efficiency of the percentage which could be brought about by 0.3M CCl_3COOH required a concentration of 5M acetic acid.

Figure 16. Extraction of Ir IV as a Function of Time from Acetone Solutions Containing Acetic Acid and Trichloroacetic Acid (respectively).

Conc. of Ir IV = 10 μg ml^{-1}

Vol. of solution = 50 ml

Wt. of foam = 0.05 g

Conc. of CH_3COOH = 3.0M

Conc. of CCl_3COOH = 0.1M

Temperature = 25.0 ± 0.05°C

Measurements by tracer ^{192}Ir

Mode of squeezing: manual

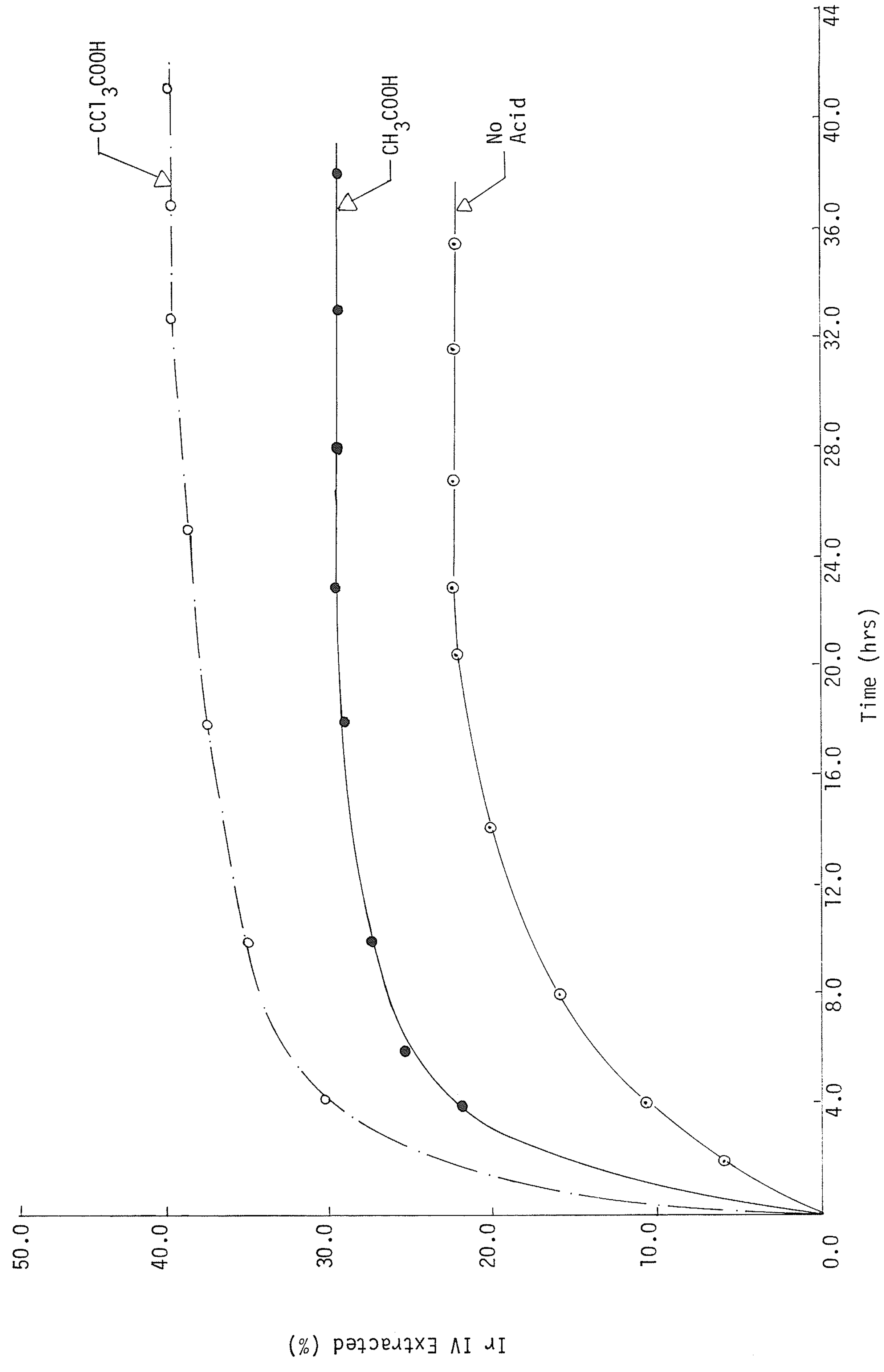
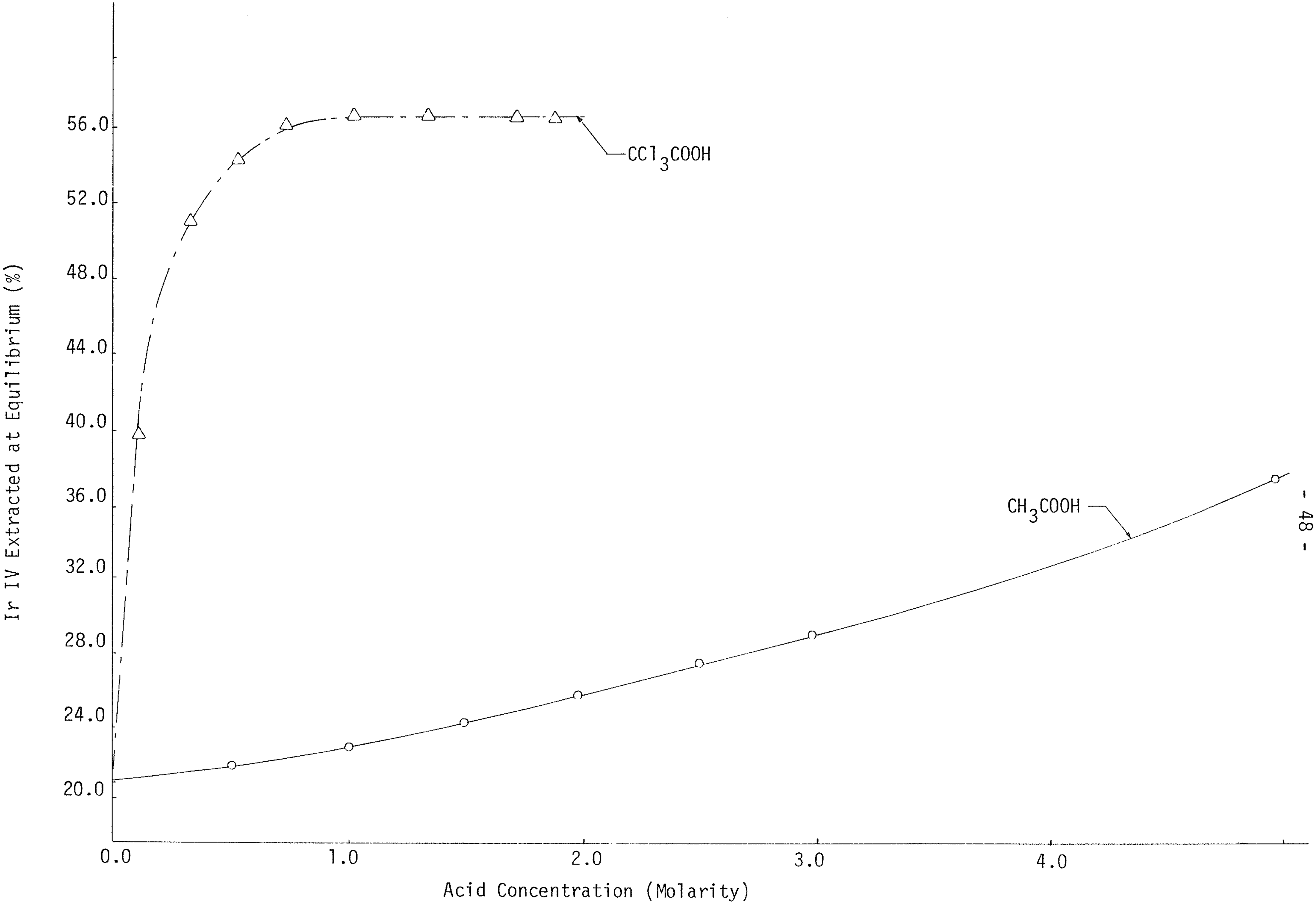

CCl$_3$COOH
CH$_3$COOH
No Acid
Ir IV Extracted (%)
0.0
10.0
20.0
30.0
40.0
50.0
Time (hrs)
4.0
8.0
12.0
16.0
20.0
24.0
28.0
32.0
36.0
40.0
44.0

Figure 17. Effect of Various Concentrations of Acetic and Trichloroacetic Acids on Efficiency of Extraction of Ir IV from Acetone Solution.

Conc. of Ir IV = 10 μg ml^{-1}
Vol. of solution = 50 ml
Wt. of foam = 0.05 g
Temperature = 25.0 ± 0.05°C
Measurements by tracer ^{192}Ir
Mode of squeezing: manual


Ir IV Extracted at Equilibrium (%)
56.0
52.0
48.0
44.0
40.0
36.0
32.0
28.0
24.0
20.0
0.0
1.0
2.0
3.0
4.0
Acid Concentration (Molarity)
CCl_3COOH
CH_3COOH

The increase in the extraction brought about by the presence of acetic acid or trichloroacetic acid might be attributable to one of, or both of, two possibilities:

(1) The new species which is formed, most likely by the substitution of acetate or trichloroacetate ligands for chloride ligands of $IrCl_6^{=}$, are more extractable than the $IrCl_6^{2-}$ species for both the case of substitution by acetate and trichloroacetate ligands. By increasing the acid concentration more of the new species will be produced, leading to an increase in extraction with increasing concentration of acid;

(2) The new species is not necessarily more extractable than $IrCl_6^{2-}$; the improvement in extraction is due to a pH effect, i.e. the greater acidity of the medium causes all or some of the Ir IV complexes existing in the solution to be extracted to a higher degree than in the case where no acid is present.

If the first possibility is the main factor responsible for the improvement in extraction, then the fact that a given concentration of CCl_3COOH produces a significantly greater improvement in the efficiency of extraction of Ir IV by the foam would suggest the following:

(a) the complex formed through the substitution of chloride ligands of $IrCl_6^{2-}$ by CCl_3COO^- ligands is more extractable than that formed through substitution by acetate ligands;

(b) there might not be any significant difference in extractability of the two complexes but the complex with trichloroacetate ligands is formed in significantly larger quantity than those with acetate ligands, for a given concentration of acid.

The dissociation constant for the reaction equilibrium

$$CCl_3COOH(aq) \rightleftharpoons CCl_3COO^-(aq) + H^+(aq)$$

is about 10,000 times higher than that for the corresponding dissociation of acetic acid. It is reasonable to assume that trichloroacetic acid will dissociate to a much larger extent than acetic acid in acetone solutions also. Therefore, for a given concentration of acid, there will be more trichloroacetate ligands than acetate ligands available for substitution of chloride ligands.

The acetate ligand can be expected to be a stronger ligand than the trichloroacetate ligand with respect to coordination to Ir^{4+}. The extent to which the substitution reactions represented by equations 2, 2', 3 and 3' will occur in a given solution will be determined by both the number of ligands available for substitution of chloride ligands of $IrCl_6^{2-}$ and by the strength of the ligands with respect to coordination with Ir^{4+}.

If a pH effect is the main factor responsible for the improvement in the efficiency of the extractions, then one would expect that for a given concentration of acid, trichloroacetic acid will improve the extraction efficiency to a greater extent since it is a stronger acid than acetic acid.

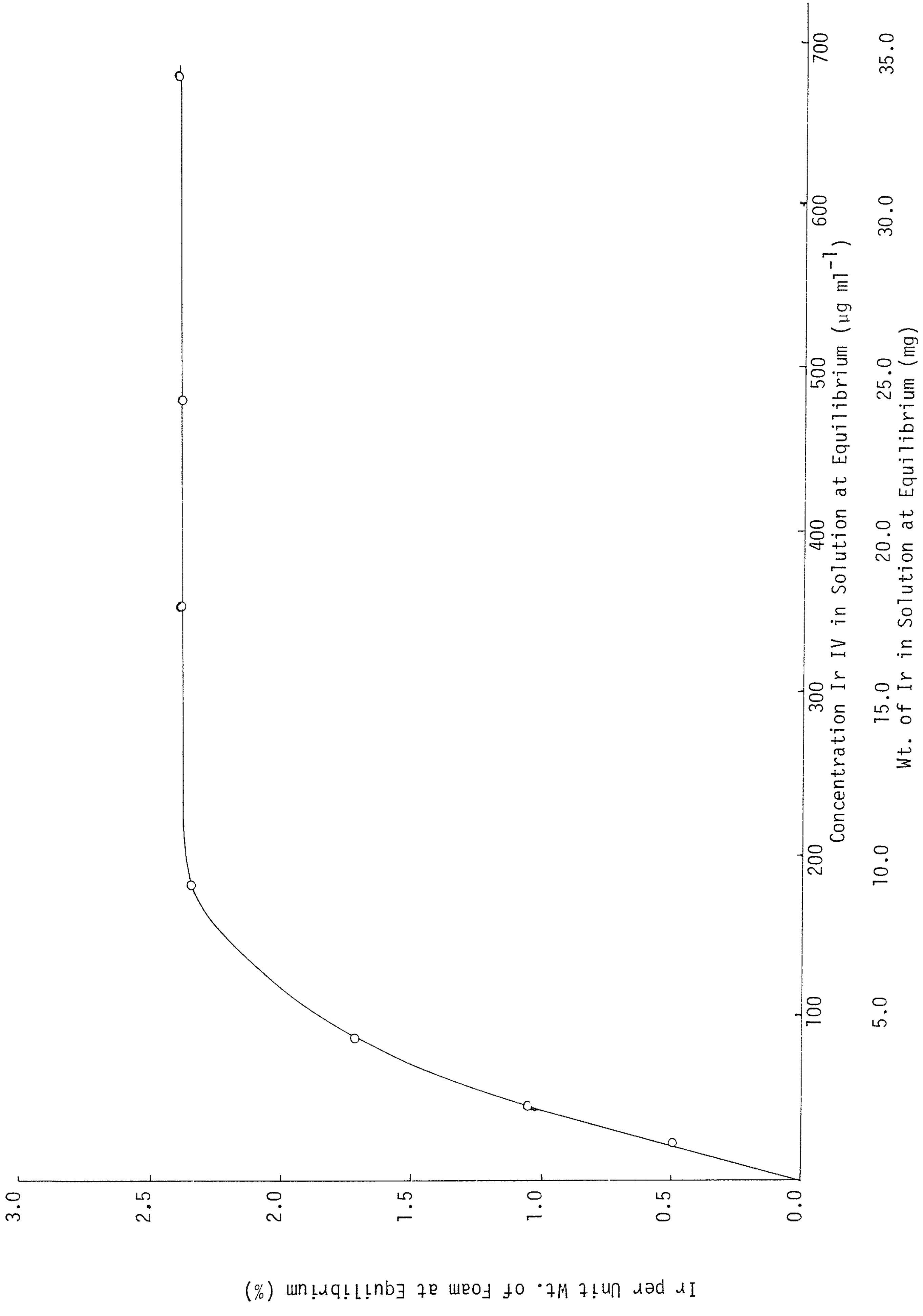
Foam Capacity for Ir IV for Extraction from Acetone

Figure 18 shows the capacity of the foam for Ir IV for extractions from acetone under the conditions outlined. "Capacity" is used to indicate the maximum amount of iridium which the foam will absorb under the specified conditions. These results were obtained by determining the absolute weight of iridium extracted from solutions of concentrations ranging from 50 to 600 $\mu g\ ml^{-1}$ Ir, and expressing these weights as a percentage of the weight of foam used for the extractions.

The capacity of the foam for iridium under the experimental conditions used for this study was found to be ≃ 2.4%.

Figure 18. Capacity of the Foam for Iridium for Extractions Carried Out in Acetone Solution

Vol. of solution = 50 ml
Wt. of foam = 0.04 g
Temperature = 25.0 ± 0.05°C
Measurements carried out after 24 hr
Determinations by UV-visible spectrophotometry
Mode of squeezing: manual


Ir per Unit Wt. of Foam at Equilibrium (%)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
Concentration Ir IV in Solution at Equilibrium (μg ml^{-1})
100
200
300
400
500
600
700
Wt. of Ir in Solution at Equilibrium (mg)
5.0
10.0
15.0
20.0
25.0
30.0
35.0

Extraction of Sodium Hexachloroiridate IV from Ethyl Acetate

Extraction of Sodium Hexachloroiridate IV as a Function of Time

This study was carried out in order to determine the time required to obtain equilibrium with respect to the extraction of the Ir IV complex from ethyl acetate. The results are shown in Figure 19. Approximate equilibrium with respect to the extraction was reached after about 20 hr for concentrations up to 30 $\mu g\ ml^{-1}$ Ir under these conditions. Solutions of higher Ir concentration required a longer time for equilibrium to be reached. The percentage extraction started falling off slowly after about 30 hr. This was especially noticeable with more dilute solutions of the Ir IV complex. This fall-off might have been due to some reduction of Ir IV to Ir III in the presence of the foam, but the reduction process appears to take place very slowly and it would therefore become important only after a long period of time. There may be specific sites on the foam capable of reducing Ir IV; if this is the reason then there should be a limit to the amount of Ir IV which can be reduced by a given weight of foam. Therefore the reduction will affect the Ir IV extraction in terms of actual percentage of Ir IV extracted in dilute solutions to a greater extent than in the case of the more concentrated solutions. If this is the case, the amount of Ir IV held by the foam represents a balance between the extraction and reduction processes and this can explain why approximate equilibrium and the eventual fall-off of log D occurred sooner for the more dilute solutions.

Variation of Distribution Ratio with Concentration of Ir IV for Extraction from Ethyl Acetate

This study was carried out in the same manner as described previously for the extraction of Ir IV from acetone.

Figure 19. Extraction of Ir IV from Ethyl Acetate as a Function of Time.

Concentration of Ir IV = 10 $\mu g\ ml^{-1}$

Volume of solution = 150 ml

Wt. of foam = 0.1 g

Temperature = 25.0 ± 0.05°C

Measurements by radiotracer ^{192}Ir

Mode of squeezing: automatic using multiple automatic squeezer

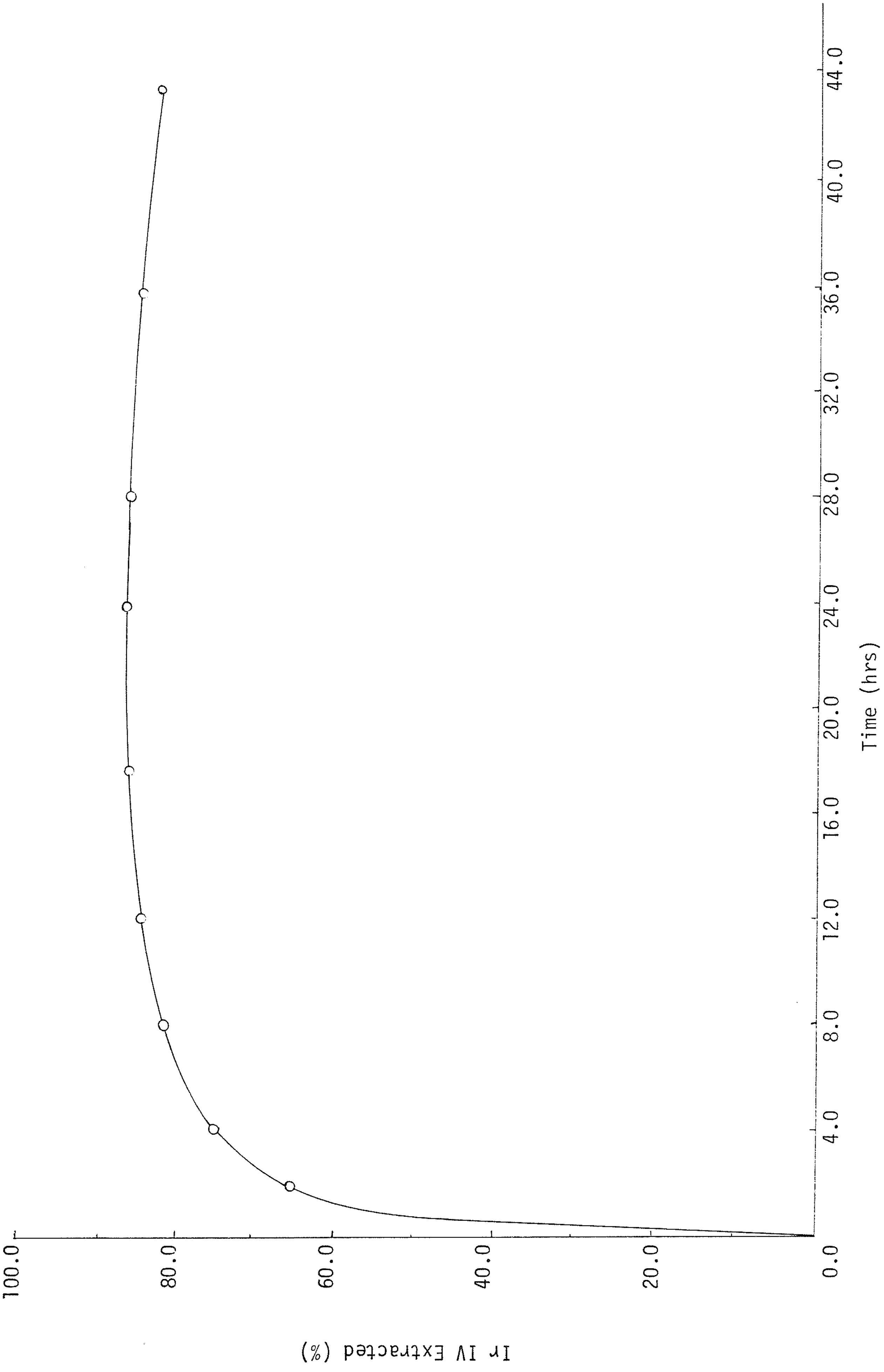

Ir IV Extracted (%)
100.0
80.0
60.0
40.0
20.0
0.0
Time (hrs)
4.0
8.0
12.0
16.0
20.0
24.0
28.0
32.0
36.0
40.0
44.0

Figure 20 shows a plot of the logarithm of the distribution ratio versus the initial concentration of Ir IV in solution. There was a continuous fall-off of the distribution ratio with concentration above solution concentrations of 5 $\mu g\ ml^{-1}$ Ir IV. At the range of solution concentrations used in this study the capacity of the foam would not be approached even if there were quantitative extractions of Ir IV . The results suggest that the phenomenon involved in the uptake of Ir IV from ethyl acetate is not simply solvent extraction. The results which would be expected if a solvent extraction mechanism is assumed for the extraction are discussed in Appendix 1b.

A possible explanation for the results is that there may be various sites for Ir IV "absorption" onto the foam and these sites have varying degrees of accessibility. The most easily accessible sites are occupied first, after which it becomes increasingly difficult for Ir IV to be "absorbed" by the foam. However, because this "absorption sites" theory cannot by itself explain the high capacity of the foam for Ir IV, other factors must be involved in the absorption process.

Capacity of the Foam for Ir IV for Extraction from Ethyl Acetate

The capacity of the foam for Ir IV for extraction from ethyl acetate solution was determined in the same manner as previously described for extraction from acetone solution. The results of this study are shown in Figure 21. The capacity of the foam for Ir IV was considerably higher for extractions from ethyl acetate than for extractions from acetone. Under the conditions outlined in Figure 21 a capacity of about 16% was obtained which is more than six times higher than that obtained for extraction from acetone.

The fact that such different foam capacities for Ir IV were obtained in different solvents supports the suggestion that the process responsible

Figure 20. Variation of Distribution Ratio with Initial Concentration of Ir IV for Extraction from Ethyl Acetate

Volume of solution = 150 ml

Weight of foam = 0.1 g

Temperature = 25.0 ± 0.05°C

Measurements by tracer ^{192}Ir

Mode of squeezing: automatic using multiple automatic squeezer

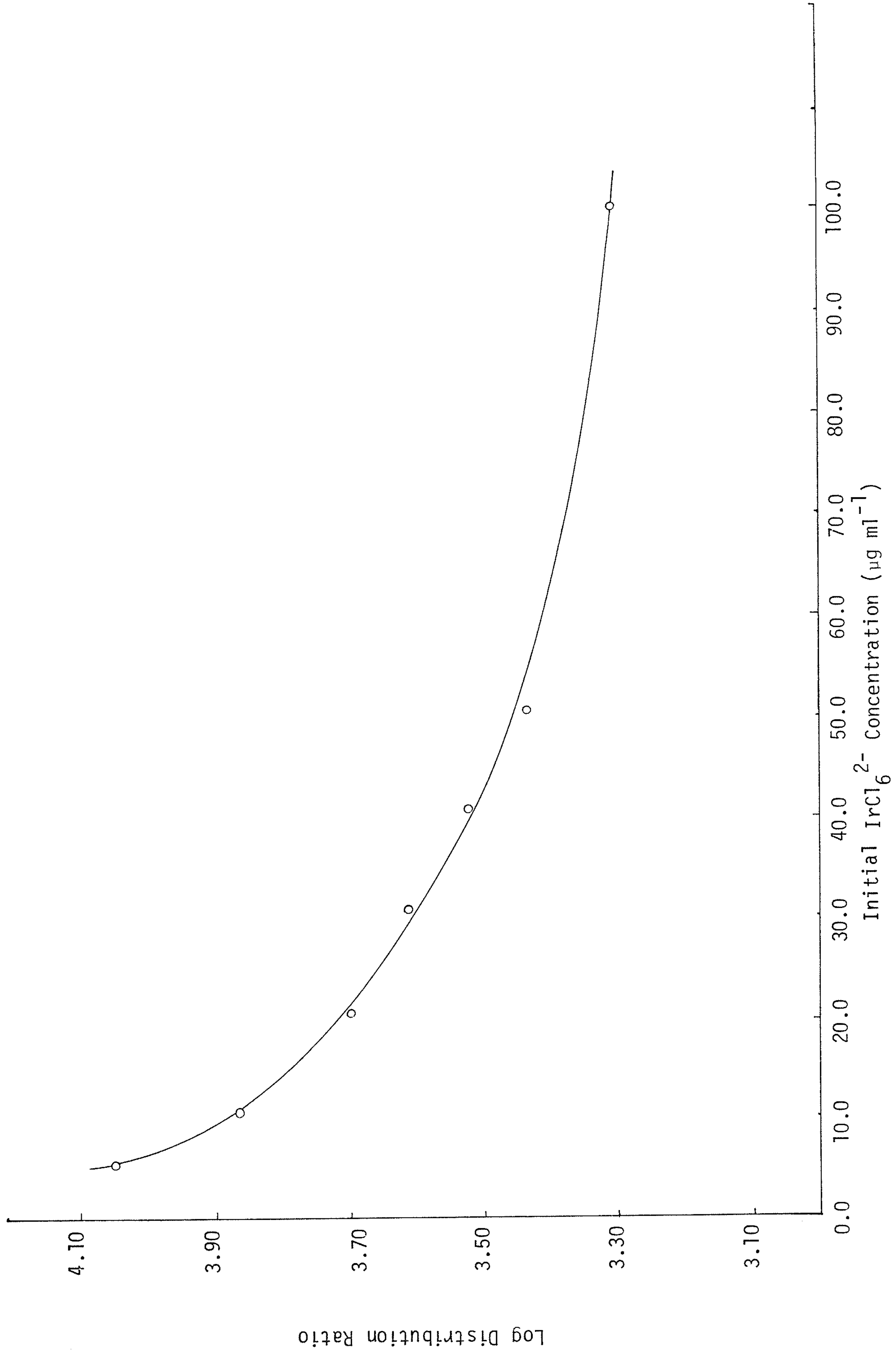
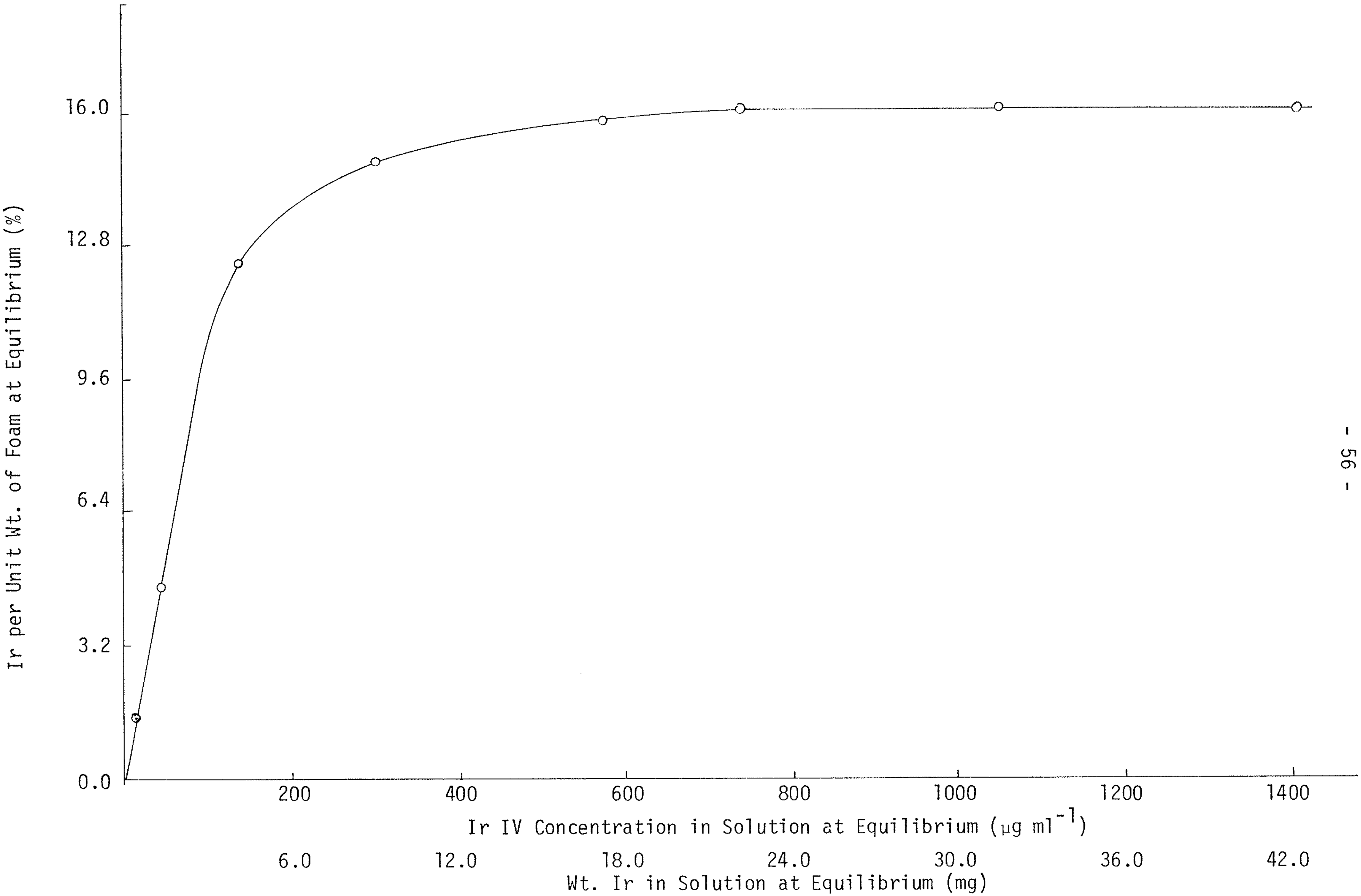

Log Distribution Ratio
4.10
3.90
3.70
3.50
3.30
3.10
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
Initial $IrCl_6^{2-}$ Concentration ($\mu g\ ml^{-1}$)

Figure 21. Capacity of the Foam for Ir IV for Extraction from Ethyl Acetate Solution.

Volume of solution = 30 ml

Temperature = 25 ± 0.05°C

Determination by UV-visible absorption spectrophotometry


Ir per Unit Wt. of Foam at Equilibrium (%)
16.0
12.8
9.6
6.4
3.2
0.0
200
400
600
800
1000
1200
1400
Ir IV Concentration in Solution at Equilibrium (μg ml⁻¹)
6.0
12.0
18.0
24.0
30.0
36.0
42.0
Wt. Ir in Solution at Equilibrium (mg)

for the uptake of Ir IV onto the foam is not a simple solvent extraction process. It is obvious that the solvent plays an important role in determining the maximum amount of Ir IV which can be held by the foam under a given set of experimental conditions. It is possible that the species being taken up by the foam must be considered to be the solvated $IrCl_6^{2-}$ complex. If this is the case then, in effect, the species being "absorbed" by the foam is different for extractions from different solvents and it is reasonable to expect that the foam would have different capacities for different species. Another possible explanation for the different foam capacities in acetone and ethyl acetate is that a different phenomenon may be involved in the extraction of Ir IV from the two solvents.

Effect of Temperature on the Extraction of Sodium Hexachloroiridate IV from Ethyl Acetate

The double-walled cell of Figure 3 was used in these experiments. Water at the desired temperature was circulated around the cell containing the sample solution. Squeezing of the foam was carried out automatically using the single automatic squeezer.

The results of this study are shown in Figure 22. Under the conditions used in these experiments, viz. squeezing rate of 40 strokes/min, changes in temperature did not seem to have a significant effect on the percentage of iridium extracted at equilibrium in the temperature range 0°C to 15°C. At 0°C, 92.71 ± 0.31% iridium was extracted at equilibrium and at 15°C 92.63 ± 0.34% was extracted. The percent extraction at equilibrium decreased to some extent, but not dramatically, with increasing temperature above 15°C. For example, on raising the temperature from 15°C to 25°C the percentage extraction at equilibrium decreased from 92.63 ± 0.34% to 89.83 ± 0.49%.

Figure 22. The Effect of Temperature on the Extraction of Sodium Hexachloroiridate IV from Ethyl Acetate.

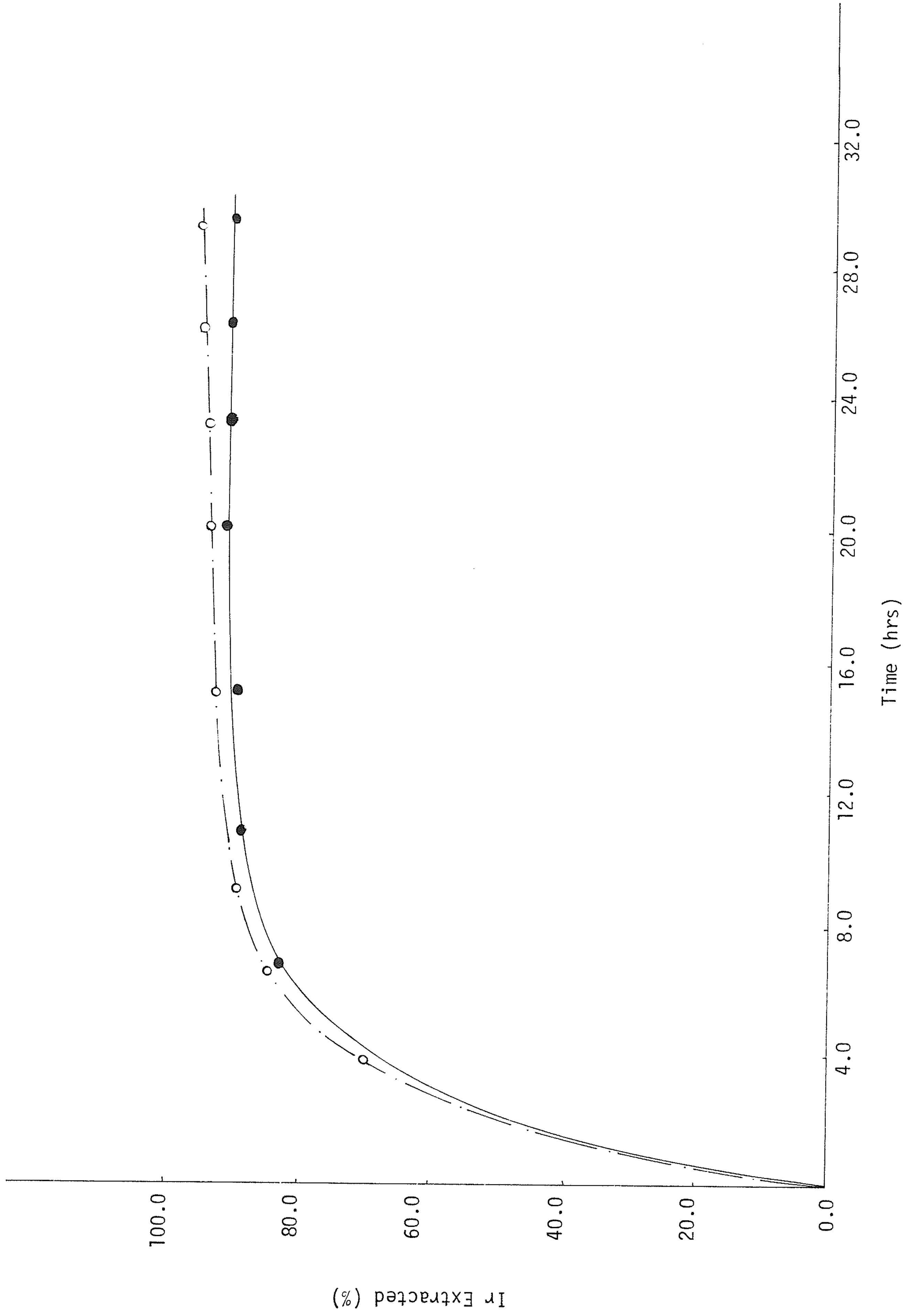
Weight of foam = 0.1 g

Volume of solution = 150 ml

Concentration of Ir IV in solution = 10 μg ml^{-1}

● ● ● 25°C

○ ○ ○ 0°C


Ir Extracted (%)
0.0
20.0
40.0
60.0
80.0
100.0
Time (hrs)
4.0
8.0
12.0
16.0
20.0
24.0
28.0
32.0

Recovery of Iridium from the Foam

Attempts were made to recover iridium from the foam by using HCl solutions of various concentrations (0.1M to 5M) as the recovery solutions. The percentage recovery of iridium at any time increased with increasing HCl concentration. Squeezing of 0.1 g of foam loaded with ≃ 3.4 mg Ir in 100 ml of 5M HCl for 7 hr at 25°C resulted in an 85.4% recovery of iridium from the foam. Replacement of this recovery solution with 100 ml of fresh recovery solution and further squeezing for about 15 hr increased the overall recovery of Ir to 87.4%. The foams were then swollen in acetone, then squeezed in 100 ml of fresh recovery solution for 5 hr. This treatment increased the overall recovery of Ir to 88.5%.

Since Ir III is not extracted by the foam it was thought that by using solutions capable of reducing Ir IV to Ir III for recovery, it should be possible to remove the iridium from the foam as an Ir III species. Reducing agents used in these studies were: NaSCN, $Na_2C_2O_4$, NaI, hydroxylamine hydrochloride and hydrazine hydrochloride in various concentrations of HCl solutions ranging from 0.1 to 5M. All of these solutions gave better than 80% recoveries of Ir after squeezing 0.1 g foam loaded with ≃ 3.4 mg Ir for about 7 hr at 25°C. Hydrazine hydrochloride in 5M HCl solution was the most effective in removing iridium from the foam. Therefore, more detailed recovery studies were carried out using this reducing agent only.

Recovery of Iridium from the Foam by Hydrazine Hydrochloride

The recovery of Ir as a function of time was investigated for various concentrations of hydrazine hydrochloride in 5M HCl. Hydrazine hydrochloride for use in these studies was prepared by reacting the appropriate amount of hydrazine hydrate with concentrated HCl. The results of this study are shown in Figure 23. Most of the Ir is removed from the foam within the first hour after which the percentage Ir recovered increases only very slowly with further squeezing. A 1% solution of hydrazine hydrate in 5M HCl was a more effective recovery solution than a 0.33% solution of hydrazine but concentrations of hydrazine hydrochloride above 1% did not give any significant increase in recovery of Ir at any given time. Using a 0.33% solution of hydrazine, 86% of the Ir was recovered after 40 min; solutions containing 1% hydrazine hydrochloride and higher gave approximately 93% recovery of Ir after 40 min.

In another series of experiments, the recovery of Ir as a function of time was again investigated, but in these experiments the recovery solution was replaced with a fresh 100 ml aliquot after each measurement. This approach did not, however, improve the percentage of Ir recovered at any given time. The incomplete recoveries, even after as much as 30 hr, might suggest that possibly a small amount of the iridium is not readily available for recovery. It is possible that some iridium is reduced to the metal in the foam either before or during recovery.

Figure 23. Recovery of Iridium as a Function of Time

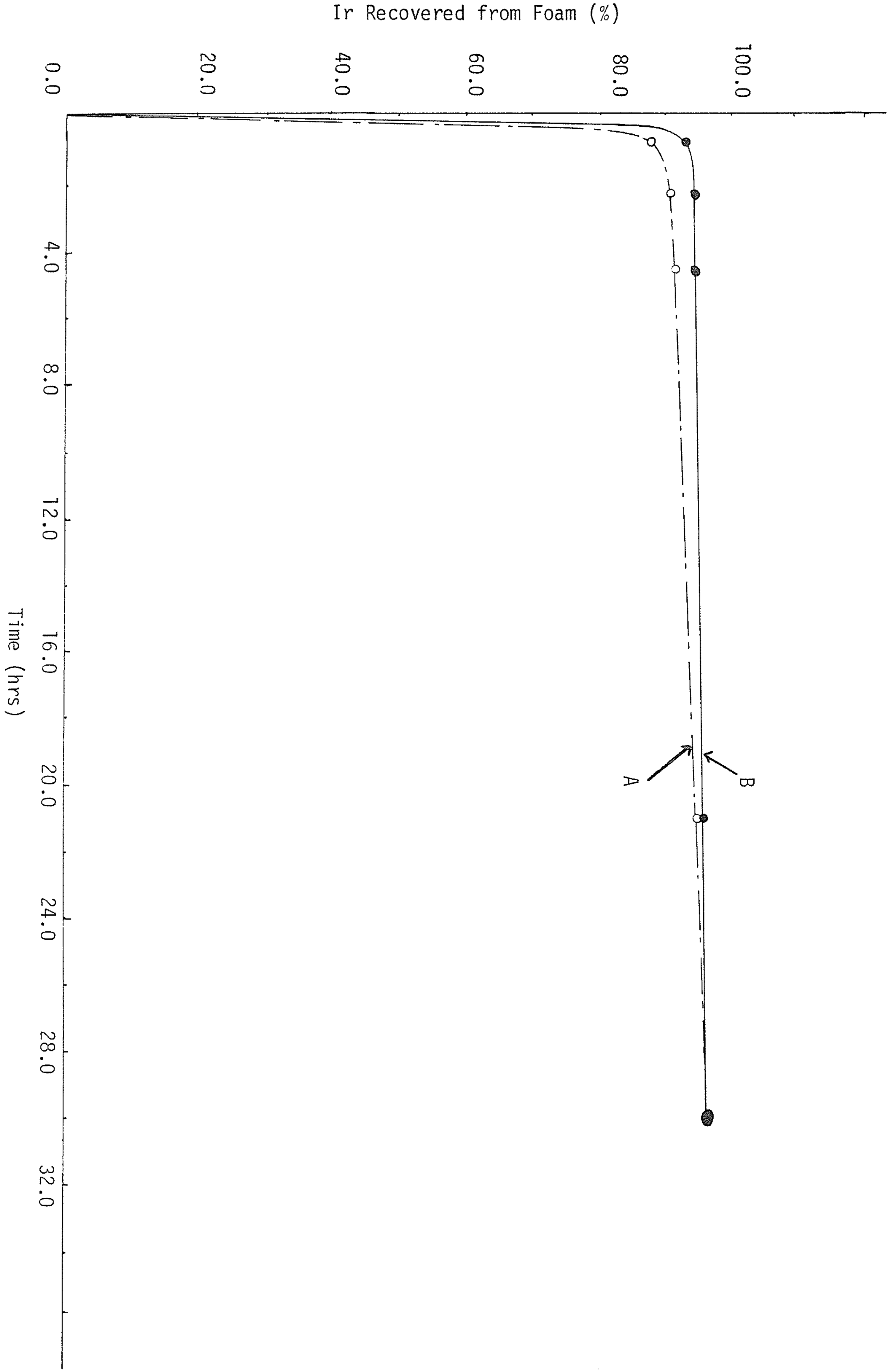
Weight of Foam = 0.1 g

Volume of recovery solution = 100 ml

Weight of iridium on foam = 3.4 mg

Temperature = 25 ± 0.05°C

A	0.33% Hydrazine Hydrochloride
B	1.0% Hydrazine Hydrochloride


Ir Recovered from Foam (%)
0.0
20.0
40.0
60.0
80.0
100.0
Time (hrs)
4.0
8.0
12.0
16.0
20.0
24.0
28.0
32.0
A
B

Extraction of Sodium Hexachloroplatinate from Organic Solvents

Preliminary work using the flow-through method for extraction indicated that platinum could be extracted from the same organic solvents which were suitable for iridium extraction viz. acetone, absolute alcohol, propan-2-ol and ethyl acetate. The efficiency of the extraction from these solvents decreased in the order:

ethyl acetate > propan-2-ol > absolute alcohol > acetone

The extraction of sodium hexachloroplatinate from ethyl acetate was investigated in a little greater detail. Investigations on platinum extraction were carried out in duplicate.

The Extraction of Sodium Hexachloroplatinate IV from Ethyl Acetate

Extraction of Sodium Hexachloroplatinate IV as a Function of Time

Studies of the extraction of $PtCl_6^{2-}$ as a function of time indicated that about twenty-four hours were required in order to reach approximate equilibrium for the extraction. All determinations of percentage extraction of $PtCl_6^{2-}$ were carried out by UV-visible absorption spectrophotometry. Measurements were made at a wavelength of 263 nm.[61]

Variation of Distribution Ratio with Pt IV Concentration for Extraction from Ethyl Acetate

A plot of the logarithm of the distribution ratio versus Pt IV concentration is shown in Figure 24. The distribution ratio remained essentially independent of Pt IV concentration for solutions of concentrations ranging from 10 to 20 $\mu g\ ml^{-1}$ Pt IV. Within this concentration range the distribution coefficient for the extraction was $\simeq$ 4800. Beyond a concentration of 20 $\mu g\ ml^{-1}$ Pt IV the distribution ratio decreased with increasing Pt IV concentration.

The determinations of the percentage extraction of Pt in these experiments presented certain problems. The percentage extraction of Pt IV in these experiments was taken to be the percentage difference in the $PtCl_6^{2-}$ concentrations between two solutions of similar composition, one of which was subjected to platinum extraction by foam while no extraction was carried out from the other. This method assumes either that there is no reduction of $PtCl_6^{2-}$ to $PtCl_4^{2-}$ in both solutions or, if there is some reduction, then the extent of reduction at any time is the same in both solutions. If the latter assumption is not valid, then the percentage extraction as calculated by this method will be incorrect unless both $PtCl_6^{2-}$ and $PtCl_4^{2-}$ are extracted and retained to the same extent by the foam.

Figure 24. Variation of Distribution Ratio with Pt IV Concentration for Extraction from Ethyl Acetate.

Volume of solution = 150 ml
Wt. of foam = 0.1 g
Temperature = 25 ± 0.05°C
Mode of squeezing: automatic using multiple automatic squeezer
Determinations by UV-visible absorption spectrophotometry

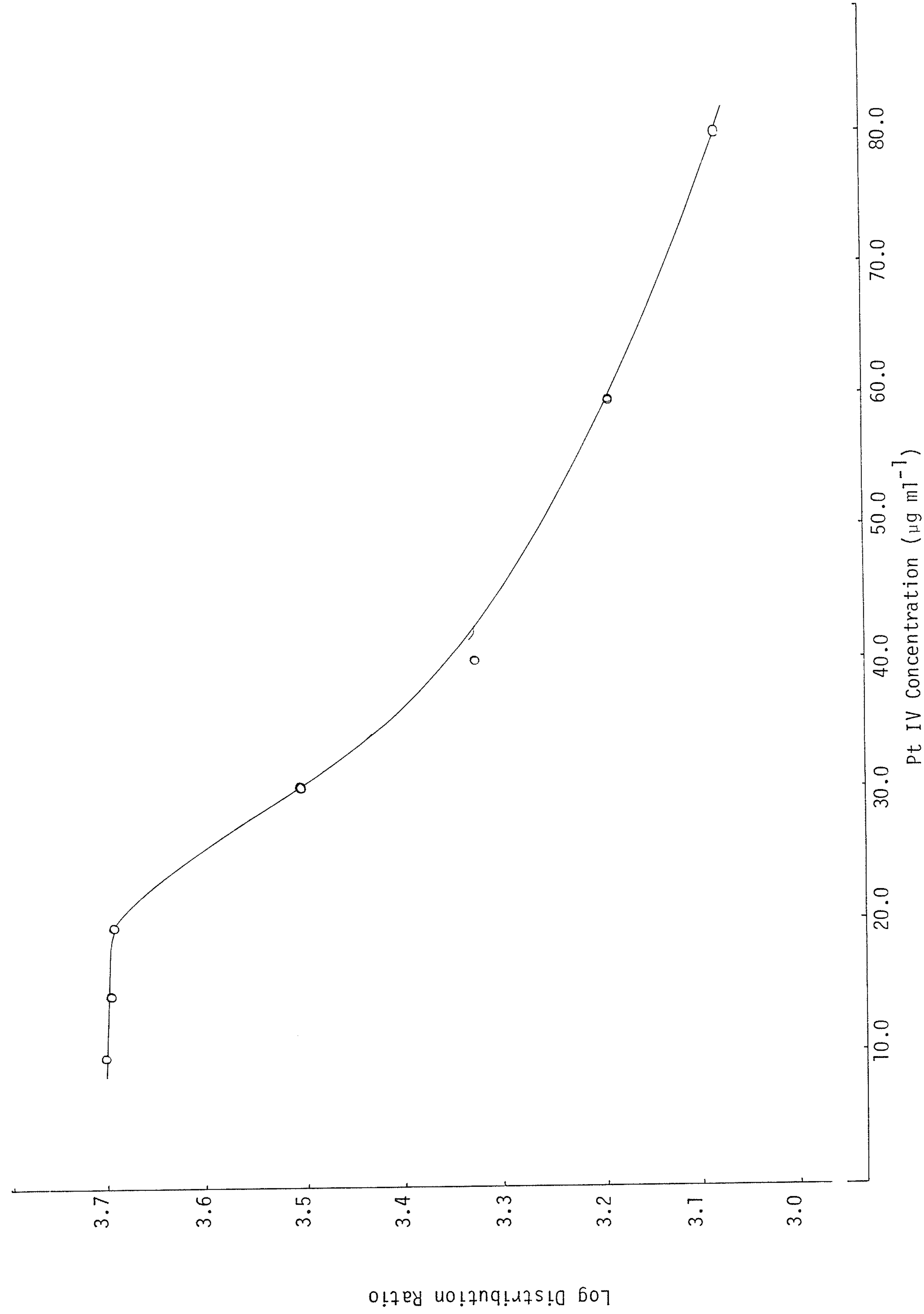

Log Distribution Ratio
3.7
3.6
3.5
3.4
3.3
3.2
3.1
3.0
Pt IV Concentration (μg ml^{-1})
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0

Figure 25 shows the UV-visible absorption spectra of $PtCl_6^{2-}$ and $PtCl_4^{2-}$ respectively. $PtCl_6^{2-}$ can be determined fairly accurately in the presence of $PtCl_4^{2-}$ by carrying out measurements in the wavelength region of 263 nm owing to the very large molar absorptivity of $PtCl_6^{2-}$ at this wavelength as compared with that of $PtCl_4^{2-}$. From the absorbance measurements of the standard solutions of $PtCl_6^{2-}$ at this wavelength, it was apparent that these solutions remained fairly stable over a 24 hr period (beyond this time some decrease in absorbance was observed especially in the case of the more dilute standards). There is, however, the possibility that the presence of the foam can bring about reduction in the sample solutions. If this happens, then the values obtained for the percentage extraction by these experiments will be higher than the actual values.

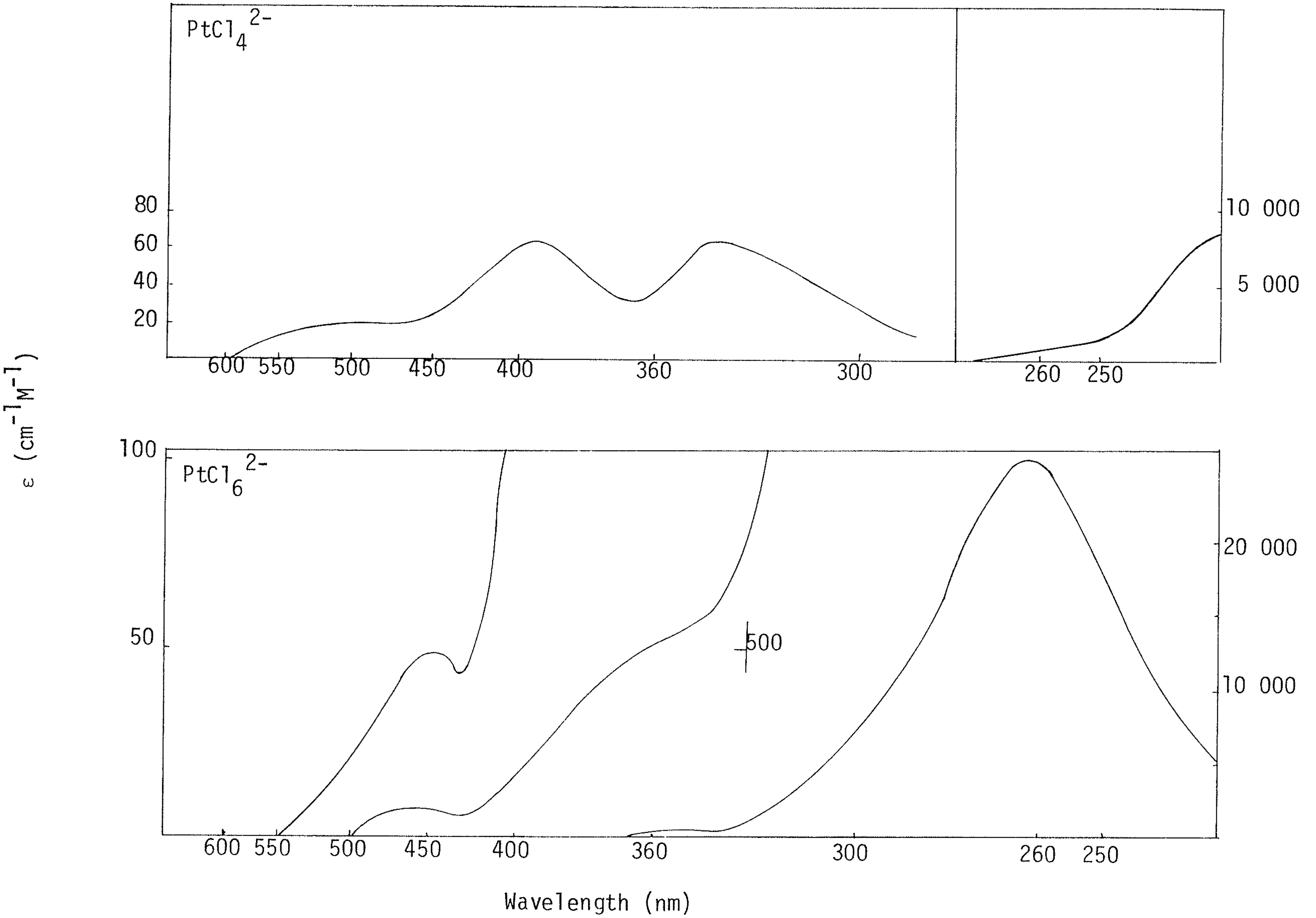
It was not possible to determine the amount of $PtCl_4^{2-}$ in the presence of $PtCl_6^{2-}$ by UV-visible absorption spectrophotometry in the solvent used for these experiments, ethyl acetate. This solvent absorbs strongly in the UV region that is characteristic of $PtCl_4^{2-}$ in the presence of $PtCl_6^{2-}$.

An attempt to investigate the extraction of $PtCl_4^{2-}$ from ethyl acetate was not successful owing to the fact that the complex Na_2PtCl_4 proved to be almost totally insoluble in ethyl acetate.

An analytical method which would measure the total amount of Pt directly, regardless of the valency state of the metal, would have served to alleviate the problems presented by the measurements of the percentage extraction. Atomic absorption was attempted but this method was not suitable owing to the relatively low sensitivity to Pt. The optimum working range for Pt is at concentrations of 10 to 100 $\mu g\ ml^{-1}$ Pt. The concentrations of Pt in many of the solutions after extraction of Pt by the foam were well below 10 $\mu g\ ml^{-1}$ Pt.

Figure 25. UV-Visible Absorption Spectra of $PtCl_6^{2-}$ and $PtCl_4^{2-}$.

Reference 61


$PtCl_4^{2-}$
80
60
40
20
600 550 500 450 400 360 300
260 250
10 000
5 000
ε (cm^{-1}M^{-1})
$PtCl_6^{2-}$
100
50
500
20 000
10 000
600 550 500 450 400 360 300 260 250
Wavelength (nm)

A white precipitate formed in the stock solution of Pt after several hours. Analysis of the precipitate showed, however, that it did not contain Pt and its formation therefore would not have affected the Pt concentration of the solution. The precipitate appeared to be NaCl. Although precipitation was not visible in the more dilute sample and standard solutions, these solutions were centrifuged for 5 minutes before each absorbance measurement.

In spite of the problems which accurate measurement of the extraction of Pt presented, these experiments demonstrated that the extraction of Pt from ethyl acetate by the foam is feasible and the efficiency of extraction is fairly high.

No attempt was made to recover platinum from the foam.

CONCLUSION

This work demonstrates that it is feasible to extract iridium and platinum from organic solvents, such as ethyl acetate and acetone, onto polyurethane foam. By carrying out the foam extraction of these metals in organic solvents the problems of hydrolysis which are encountered in the extraction of platinum metals from aqueous systems are circumvented.

The distribution ratios for the foam extraction of iridium and platinum from ethyl acetate are fairly high, of the order of 11,000 and 4,800 respectively, and the extracted iridium can be readily removed from the foam by reducing agents such as hydrazine hydrochloride and hydroxylamine hydrochloride in acidic solutions. The capacity of the foam for iridium is very high, $\simeq$ 16% by weight, when extraction of the sodium hexachloroiridate IV complex is carried out in ethyl acetate.

Several of the results of this work seem to indicate that the foam extraction of iridium from ethyl acetate is not a simple solvent extraction process. Some results seem to indicate that there might be specific sites on the foam capable of "absorbing" the iridium complex. However, such a theory cannot by itself explain other features of the foam extraction of iridium such as the very high capacity of the foam for iridium.

Studies of foam extraction in non-aqueous systems will provide results which can supplement the results of similar studies in aqueous systems in providing explanations of the mechanisms of the foam extraction process. One can, therefore, expect to see more investigations in the area of foam extraction in non-aqueous systems in the near future.

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APPENDIX Ia

Variation of the Distribution Ratio with Concentration of the Metal Complex in Solution at Equilibrium

The data pertaining to Figures 10 and 20 are presented here in the form of plots of the logarithm of the distribution ratio as a function of the molar concentration of the hexachloroiridium (IV) complex in solution at equilibrium.

FIGURE i

Logarithm of Distribution Ratio vs Molar Concentration of Na_2IrCl_6 in Solution at Equilibrium for Extraction from Acetone

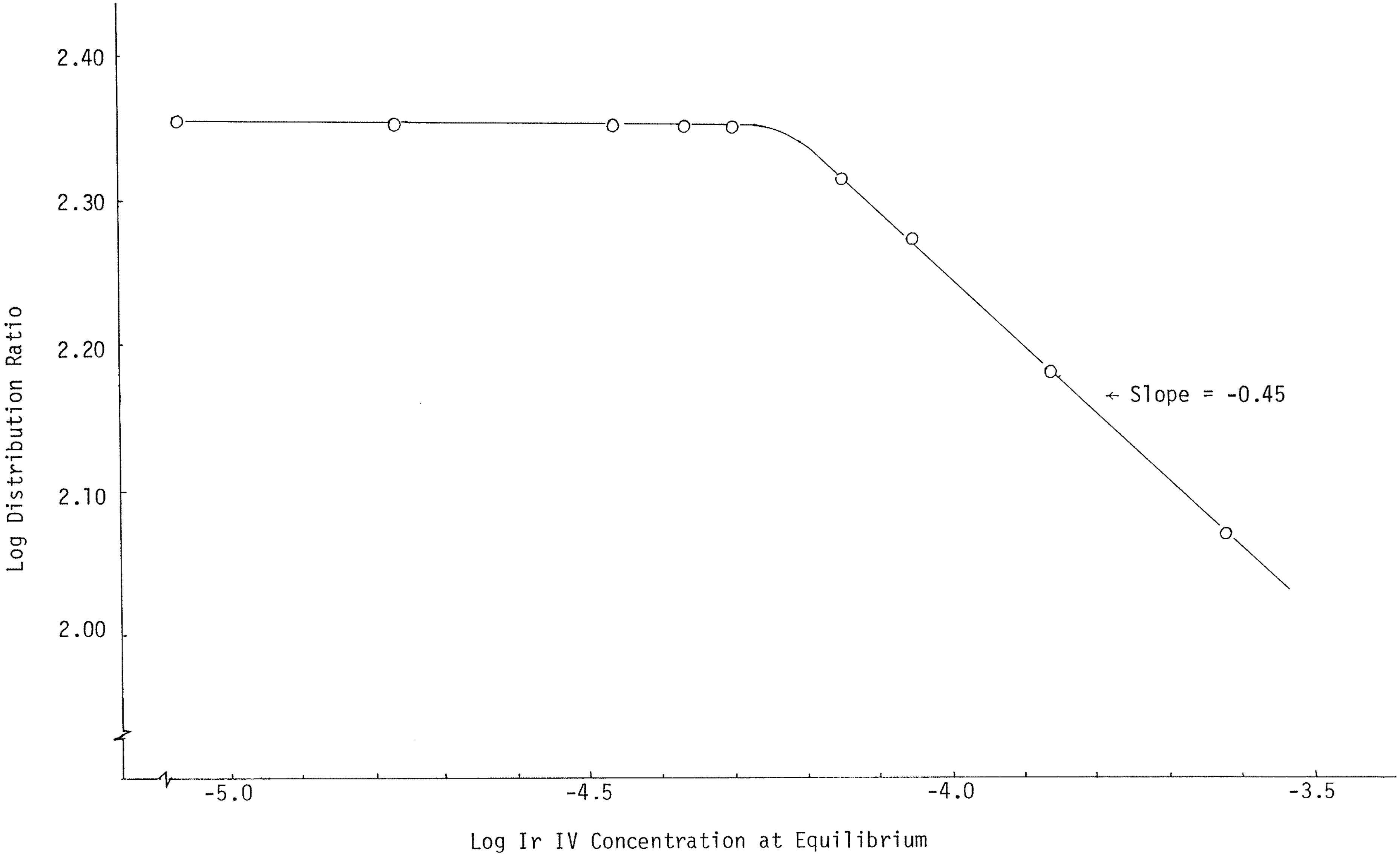
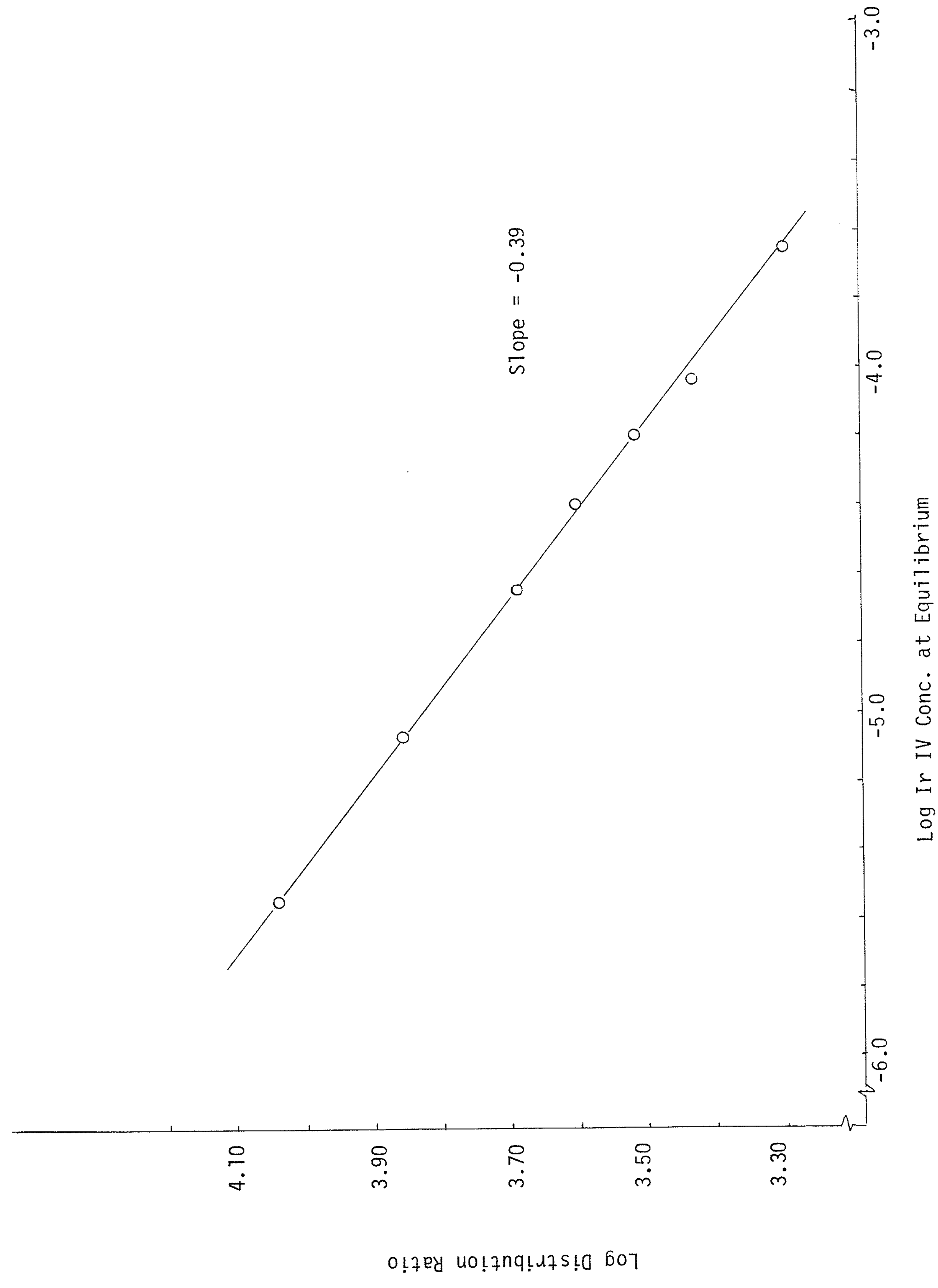

2.40
2.30
2.20
2.10
2.00
Log Distribution Ratio
-5.0
-4.5
-4.0
-3.5
Log Ir IV Concentration at Equilibrium
← Slope = -0.45

FIGURE ii

Logarithm of Distribution Ratio vs Molar Concentration of Na_2IrCl_6 in Solution at Equilibrium for Extraction from Ethyl Acetate


Slope = -0.39
Log Ir IV Conc. at Equilibrium
-6.0
-5.0
-4.0
-3.0
Log Distribution Ratio
4.10
3.90
3.70
3.50
3.30

APPENDIX Ib

The Results Which Can Be Expected for the Variation of Distribution Ratio with Ir IV Concentration in Solution at Equilibrium if a Solvent Extraction Mechanism is Assumed for the Extraction of the Complex onto the Foam

The chemical equilibrium involved in the solvent extraction process can be represented by the following scheme:

$$\begin{tikzcd}
HMX_o \arrow[r, "k_{ex}", shift left] \arrow[d, shift left] & HMX_f \arrow[l, shift left] \arrow[d, shift left] \\
H^+_o + MX^-_o \arrow[u, "k_o"', shift left] & H^+_f + MX^-_f \arrow[u, "k_f"', shift left]
\end{tikzcd}$$

HMX represents the undissociated complex in "ion pair" which can be either H_2IrCl_6 or Na_2IrCl_6.

H^+ and MX_4^- are the products of dissociation of the complex. The complex H_2IrCl_6 can dissociate to $HIrCl_6^-$ which can lose another proton to give $IrCl_6^{2-}$. Similarly, if the complex being extracted onto the foam is Na_2IrCl_6, dissociation of the complex can produce either $NaIrCl_6^-$ or $IrCl_6^{2-}$.

Subscripts "o" and "f" refer to the solution and to the foam respectively.

k_{ex} is the extraction coefficient of the undissociated complex.

In the following equations the square brackets refer to the equilibrium molar concentration of the various species.

$$k_{ex} = \frac{[HMX]_f}{[HMX]_o} \qquad \qquad \text{..........(1)}$$

$$\therefore \quad [HMX]_f = k_{ex}[HMX]_o \qquad \text{..........(2)}$$

$$k_o = \frac{[H^+]_o[MX^-]_o}{[HMX]_o} \qquad \text{..........(3)}$$

$$k_f = \frac{[H^+]_f[MX^-]_f}{[HMX]_f} \qquad \text{..........(4)}$$

The distribution ratio of iridium IV is given by:

$$\text{Distribution Ratio} \quad D = \frac{[M]_{f_{total}}}{[M]_{o_{total}}} = \frac{[HMX]_f + [MX^-]_f}{[HMX]_o + [MX^-]_o} \qquad \text{..........(5)}$$

By substituting Equations (2), (3) and (4) into (5) and rearranging, we can write:

$$D = \frac{k_{ex} + k_{ex}k_f[H^+]_f^{-1}}{1 + k_o[H^+]_o^{-1}} \qquad \text{..........(6)}$$

For electroneutrality in solution and in the foam, the following equations can be written:

$$[H^+]_o = [MX^-]_o \qquad \text{..........(7)}$$

and

$$[H^+]_f = [MX^-]_f \qquad \text{..........(8)}$$

From Equation 3

$$[H^+]_o = (k_o[HMX]_o)^{\frac{1}{2}} \qquad \text{..........(9)}$$

and from Equation 4

$$[H^+]_f = (k_f[HMX]_f)^{\frac{1}{2}} \qquad \text{..........(10)}$$

Substituting Equations (9) and (10) into (6), we can write:

$$D = \frac{k_{ex} + k_{ex}(k_f[HMX]_f^{-1})^{\frac{1}{2}}}{1 + (k_o[HMX]_o^{-1})^{\frac{1}{2}}} \qquad \text{..........(11)}$$

By substituting Equation (2) into (11) and rearranging, we can write:

$$D = \frac{k_{ex}(k_{ex}\ [HMX]_o)^{\frac{1}{2}} + k_{ex}k_f^{\frac{1}{2}}}{(k_{ex}[HMX]_o)^{\frac{1}{2}} + k_{ex}^{\frac{1}{2}}k_o^{\frac{1}{2}}} \qquad \text{..........(12)}$$

If k_a and k_f both → o, then D = constant = k_{ex}.

If only $k_f \rightarrow o$, then

$$D = \frac{k_{ex}(k_{ex}[HMX]_o)^{\frac{1}{2}}}{k_o^{\frac{1}{2}}k_{ex}^{\frac{1}{2}} + (k_{ex}[HMX]_o)^{\frac{1}{2}}} \qquad \text{..........(13)}$$

and D will increase with increasing $[HMX]_o$ to a value which approaches k_{ex} at high values of $[HMX]_o$.

If only $k_o \rightarrow o$, then

$$D = k_{ex} + \frac{k_f^{\frac{1}{2}}k_{ex}}{(k_{ex}[HMX]_o)^{\frac{1}{2}}} \qquad \text{i.e. } D \propto [HMX]_o^{-\frac{1}{2}}$$

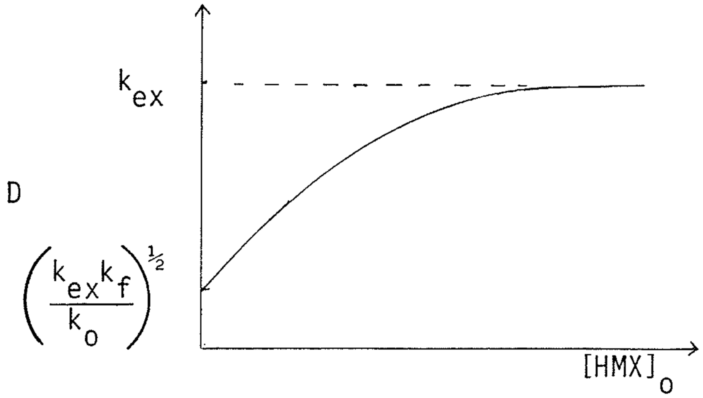
D decreases with increasing $[HMX]_o$.

If neither k_f nor $k_o \rightarrow o$, then at very low values of $[HMX]_o$

$$D \rightarrow \frac{k_{ex}k_f^{\frac{1}{2}}}{k_o^{\frac{1}{2}}k_{ex}^{\frac{1}{2}}}$$

and at high values of $[HMX]_o$, $D \rightarrow k_{ex}$.

If k_f and k_0 are similar in magnitude, a plot of D vs $[HMX]_0$ takes a form similar to that shown in the following sketch:



Only if $k_f >> k_0$ will a fall-off of D with increasing $[HMX]_0$ occur.

The dielectric constant of acetone (20.7 at 25°C; $\varepsilon_{vac}=1$) can be expected to be considerably greater than that of the foam and therefore it is very unlikely that k_f will be greater than k_0 in the case where the complex is being extracted from acetone. The dielectric constant of ethyl acetate ($\simeq$ 6.02 at 25°C) is much lower than that of acetone and presumably k_f might approach k_0 in the case where the complex is being extracted from ethyl acetate. A fall-off of D with increasing $[HMX]_0$, however, requires that k_f exceed k_0 by a factor greater than k_{ex}; k_{ex} for extraction from ethyl acetate can be expected to be of the order 10^3.

This analysis shows that a solvent extraction mechanism cannot, by itself, explain the results obtained for the variation of the distribution ratio with concentration of the complex in solution (Figures 10 and 20 and Appendix 1a). Other processes must be involved in the uptake of iridium from acetone and ethyl acetate onto the foam. There may be specific sites on the foam which are capable of absorbing iridium; presumably an ion exchange mechanism might play a role in the extraction. It is also possible that different phenomena predominate in the extraction of the iridium complex from the two different solvents.