

THE UNIVERSITY OF MANITOBA

THE EXTRACTION OF TIN AND ANTIMONY BY  
THE USE OF POLYURETHANE FOAM

BY

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A dissertation submitted to the Faculty of Graduate Studies of  
the University of Manitoba in partial fulfillment of the requirements  
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## Psalm 33

Sing for joy in the Lord, O you righteous ones;  
Praise is becoming to the upright.  
Give thanks to the Lord with the lyre;  
Sing praises to Him with a harp of ten strings.  
Sing to Him a new song;  
Play skillfully with a shout of joy.  
For the word of the Lord is upright;  
And all His work is done in faithfulness.  
He loves righteousness and justice;  
The earth is full of the lovingkindness of the Lord.

By the word of the Lord the heavens were made,  
And by the breath of His mouth all their host.  
He gathers the waters of the sea together as a heap;  
He lays up the deeps in storehouses.  
Let all the earth fear the Lord;  
Let all the inhabitants of the world stand in awe of Him.  
For He spoke, and it was done;  
He commanded, and it stood fast.  
The Lord nullifies the counsel of the nations;  
He frustrates the plans of the peoples.  
The counsel of the Lord stands forever,  
The plans of His heart from generation to generation.  
Blessed is the nation whose God is the Lord,  
The people whom He has chosen for His own inheritance.

The Lord looks from heaven;  
He sees all the sons of men;  
From His dwelling-place He looks out  
On all the inhabitants of the earth,

He who fashions the hearts of them all,  
He who understands all their works.  
The king is not saved by a mighty army;  
A warrior is not delivered by great strength.  
A horse is a false hope for victory;  
Nor does it deliver anyone by its great strength.

Behold, the eye of the Lord is on those who fear Him,  
On those who hope for His lovingkindness;  
To deliver their soul from death,  
And to keep them alive in famine.  
Our soul waits for the Lord;  
He is our help and our shield.  
For our heart rejoices in Him,  
Because we trust in His holy name.  
Let Thy lovingkindness, O Lord, be upon us,  
According as we have hoped in Thee.

(P.788-9, New American Standard Bible, Gospel Light Publications,  
Glendale, California, U.S.A., 1971)

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### Abstract

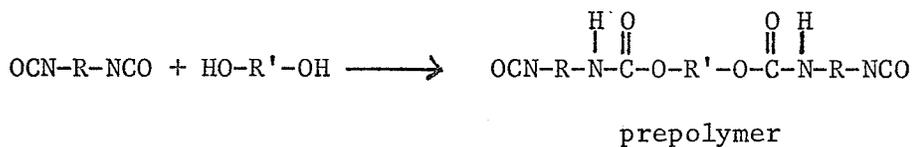
Three types of polyurethane foams were studied for the extraction of tin and antimony. Static and flow-through systems were used for tin. The amount of metal extracted varied with the type of foam, acid strength, chloride concentration, concentration of metal ion and volume of metal ion solution. Quantitative extraction and recovery of tin and antimony were achieved. Open cell polyurethane foam is thought to act as a "solvent extractor" for tin and antimony from aqueous solution. The capacity of the foam (up to 8% tin by weight) was much higher than that due to surface adsorption.



the composition of the foam is normally obtained by varying the structure of the polyhydroxy resin component. The equivalent weights for rigid foams vary from 100 to 150 and for flexible foams vary from 1,000 to 10,000. The equivalent weight is defined as the ratio of molecular weight to the number of hydroxyl groups of the hydroxy resin. The rigid foams have a higher cross-link density and a higher degree of branching than the flexible foams.

Producing polyurethane foam on a commercial scale is usually done by:

- (1) One-shot process - all the ingredients for producing the foam are mixed together and then discharged from the mixer onto a suitable surface.
- (2) Prepolymer process - the polyhydroxyl component is reacted with enough polyisocyanate to result in formation of a prepolymer with isocyanate groups plus excess isocyanate.



The prepolymer mixture is then reacted with water to simultaneously release carbon dioxide for expansion and to link to chains together in a cross-linked matrix. Foams made in this way could be open-celled or closed-celled. These cells may be interconnected in a manner such that gas may pass from one to another, in which case the material is termed open-celled. If the cells are discrete and the gas phase of each is independent of that of the other cells, the material is termed closed-celled.

The physical phenomena and chemical principles in the production of polyurethane foams have been studied. Bailey<sup>4</sup> studied the principles of hydrogen bonding, steric hindrance, simultaneous and consecutive reactions, equilibrium and polymerization as applied to polyurethanes. A method of measuring the surface area of polyurethane foams using stearic acid-1-<sup>14</sup>C in n-heptane was described by Bowen<sup>5</sup>.

The chemical properties of polyurethane foam were also investigated<sup>6,7</sup>. The foams remained unchanged except for swelling reversibly, in water, hydrochloric acid up to 10 M, hydrobromic acid up to 8 M, hydriodic acid up to 4 M, sulfuric acid up to 4 M, nitric acid up to 2 M, glacial acetic acid, 2 M ammonia, 2 M sodium hydroxide, and in the following solvents, light petroleum, benzene, carbon tetrachloride, chloroform, diethyl ether, di-isopropyl ether, acetone, isobutyl methyl ketone, ethyl acetate, isopentyl acetate and alcohols.

Since 1970, there has been an increasing interest in the study of polyurethane foam for the extraction and separation of inorganic and organic species from aqueous solution. In these studies, both flexible and rigid polyurethane foams have been used. The flexible foams could be used untreated or treated either physically by the coating with reagents or chemically by the introduction of a functional group into the foam backbone structure. The rigid foams were merely used as a solid inert support in chromatography.

### Untreated Flexible Polyurethane Foams

In 1970, Bowen<sup>7</sup> began the use of flexible polyurethane foams as an absorbent for a number of substances from dilute aqueous solutions. The extraction of mercury (II) and gold (III) from 0.3 M hydrochloric acid, iron (III), antimony (V), thallium (III), molybdenum (VI) and rhenium (III) from 6 M hydrochloric acid; and uranium (VI) from saturated aluminium nitrate solution was found to be successful. The foams also removed iodine, benzene, chloroform, and phenol from water. Desorption of most of these species was obtained without difficulty.

In 1971, Gesser, Chow, Davis, Uthe and Reinke<sup>8</sup> examined the removal of polychlorinated biphenyls (PCB) and other pesticides from water by a column filled with open-pore polyurethane foam; PCB at the ppb level was extracted into the foam from aqueous solution and 93 to 100% of PCB could be recovered from the foam by sequential elution with acetone and hexane. Polyurethane foams were also used to monitor organics in river and drinking water<sup>9</sup>. Water was passed through the foam column at  $2-4 \text{ ml cm}^{-2} \text{ min}^{-1}$  flow-rate. The extracted organic compounds were removed from the foam with hexane in a soxhlet extractor and then analyzed by gas chromatography. It was reported that organic contaminants were found and their concentration was estimated to be 0.005 to 0.010 ppb in drinking and river water. Musty and Nickless<sup>10</sup> also used six different types of polyurethane foams for the extraction and recovery of PCB from water. The extracted species were quantitatively recovered.

Polyurethane foams were used by Bindleman and Olney<sup>11</sup> to monitor PCB, DDT and chlordane levels in the atmosphere above the Sargasso Sea. Several million cubic meters of air was drawn in at a rate of 0.4 to 0.8 m<sup>3</sup>/min through the foam plug measuring 15 cm long and 10 cm diameter. PCB, DDT and chlordane concentrations were measured in the 0.005 to 100 ng/m<sup>3</sup> range. Subsequently, Bindleman and Olney<sup>12</sup> used PCB coated on glass beads as a known source contaminant and put them in front of the collection system. Samples of 550 to 987 m<sup>3</sup> of air were drawn through foams of 8.9 cm in diameter at a flow-rate of 0.57 to 1.13 m<sup>3</sup>/min, 0.22 to 0.65 ng/m<sup>3</sup> of PCB was collected. Porous polyurethane foam with a polyester backbone was tested by Turner and Glotfelty<sup>13</sup> as adsorbers for pesticide vapour in air. It was reported that a single cylindrical foam plug measuring 4.5 cm in diameter and 5 cm in length could trap 98% or more of the total pesticide vapour added at a flow-rate of 5 m<sup>3</sup>/hour. The pesticides tested were easily removed by soxhlet extraction with acetone and hexane. The highest amount of pesticide tested was 300 µg and was retained by the foam even when pesticide-free air was drawn through the exposed foam for an additional 18 hours. If this is true, then, it would appear that absorption would be more likely than adsorption.

Schiller and Cook<sup>14</sup> suggested the use of flexible polyurethane foam for the preconcentration of gold (III) (ppb range) from tap water acidified with hydrochloric acid. An extraction of 99.4% of the gold

from solution was achieved. Bowen<sup>15</sup> also reported the extraction of gold (III) with polyurethane foam from liquid mine waste. A 0.02 mg of gold was taken up by 10 g of foam from 1 kg of liquid waste. Sukiman<sup>16</sup> also reported the extraction of gold chloride. The gold-198 tracer at a concentration of 0.02 ppm and unlabelled gold chloride solution at a concentration of 20 ppm in 1 M hydrochloric acid were passed through a foam column of 20 mm internal diameter at 30-40 ml/min. Gold chloride was recovered quantitatively from the same column with 20-50 ml of acetone at 3 ml/min. Braun and Earag<sup>66</sup> investigated the retention of gold thiourea complexes with untreated and treated foams. Various samples of foam material of different cell size, chemical composition and manufacture were used. Results showed that the uptake of gold-thiourea complex decreased as the cell size decreased for the unloaded foam. Furthermore, the absorption capacities of gold-thiourea complex on the polyether type foams were found to be generally better than on the polyester type. Palladium (II) thiourea complex was also found to be completely retained by untreated foam. However, it could not be completely eluted even by 300 ml of distilled water.

Lypka<sup>17</sup> described the extraction of copper (II) and cadmium acetylacetonates from dilute aqueous solution by untreated open pore polyurethane foam. Copper was quantitatively extracted at pH 10.2 and recovered with 1.5 M hydrochloric acid at a flow-rate of 2 ml/min through a column of 4.0 cm outside diameter. The

extraction and recovery of copper acetylacetonate were found to be very different at various pHs and acidities.

Gesser and co-workers described the use of polyurethane foam with the polyether backbone in the extraction and recovery of gallium from hydrochloric acid<sup>18</sup>. Gallium was absorbed into the foam by three passes of 100 ml solution of 7.5 N hydrochloric acid containing 50 ppm gallium. It was then removed by passing 50 ml of water or weakly basic solution at a flow rate of 64 ml/min through a column of 32 mm internal diameter. Quantitative extraction and recovery was possible. Iron (III) was also absorbed in the foam at 7.5 N hydrochloric acid.

The Canadian Plant and Process Engineering Ltd.<sup>19</sup> demonstrated that polyurethane foam could be used as an oil filter to clean up oil spills in both fresh and salt water. It was reported that flexible polyurethane foam was effective in the removal of 99% for "Bunker C" oil, 70% for marine diesel oil, 60% for crude oil and less than 5% for phenol at flow rate of 407 l/min/m<sup>2</sup>.

Gough et al.<sup>20</sup> reported the removal of phthalate esters from water by polyurethane foam. Five types of foam and phthalates with side-chains varying in length from one to ten carbons were investigated. A 100 ml of water spiked with 0.1 µg of phthalate was run on a column of 5 foam plugs at 10 ml/min through a column of 15 mm internal diameter. The absorption of the phthalates was found to be dependent on the size of the phthalate and its structure. In her thesis<sup>21</sup>, Gough reported that open pore polyurethane foam

was used to remove phthalates from air at the ppb level. Five foam plugs were put into a column and air was drawn through. Phthalates were then recovered with hexane and analyzed by gas chromatography.

#### Treated Flexible Polyurethane Foams

Polyurethane foams can be treated either physically with immobilized reagents and extractants by coating or soaking the foam or chemically by the introduction of functional groups into the foam structure before or after foaming.

#### Physically Treated Polyurethane Foams

In 1972, Braun and Farag<sup>22</sup> reported that foam polymer was loaded with tributyl phosphate (TBP) as a stationary phase and compressed into a chromatographic column which would give flow-rates of 1-4 ml/min through a column of 1.5 cm internal diameter. A solution containing both palladium (II) and nickel (II) each at a concentration of 1 mg/ml was first passed into the column. Then nickel was eluted first with 0.1 M perchloric acid containing 0.39 M thiourea and 0.08 M sodium perchlorate in water saturated with TBP. Palladium was then eluted with water saturated with TBP. Open cell polyurethane foam was reported to have the advantage of taking up TBP better than other inert supports in granular form, thus giving a higher capacity for the foam. Braun et al.<sup>23</sup> continued their investigation of TBP-treated foam as a column filling on

reverse-phase foam chromatography. Separation of nickel (II), bismuth (II) and palladium (II) was achieved. The metals were prepared in 0.2 M perchloric acid containing 0.78 M thiourea and 0.16 M sodium perchlorate. Nickel was then eluted with 0.1 M perchloric acid, 0.39 M thiourea and 0.08 M sodium perchlorate. Bismuth was eluted with 0.5 M perchloric acid and palladium eluted with water.

Braun et al.<sup>24</sup> separated gold (III) quantitatively from Zn (II), Co (II), Ni (II), Fe (III), Sb (III), Cu (II), Bi (III), and Pd (II) using polyurethane foam loaded with TBP. The extraction of gold-thiourea complex was later examined with different polyether and polyester types of polyurethane foams loaded with TBP. Polyurethane foams of the polyether type were found to retain TBP much more efficiently than the polyester foam and hence gave a better extraction. It was confirmed that the foam material behaved as an inert support in the loaded state. Braun and co-workers<sup>25</sup> continued to use TBP-loaded polyurethane foam and separated iron (III) from copper (II), cobalt (II) and nickel (II). The distribution of iron, copper, cobalt ions between the TBP-hydrochloric acid system on the foam was measured and found to be dependent on the concentration of the hydrochloric acid in the system. Separation was achieved because the different metals formed readily-extractable chloride complexes in aqueous solutions at different hydrochloric acid concentrations. Iron was eluted by 0.1 M hydrochloric acid, copper and nickel by 4 M

hydrochloric acid and cobalt by 5 M hydrochloric acid after all the metals had been loaded onto the foam.

Uthe et al.<sup>26</sup> used polyurethane foam coated with chromatographic grade greases for the extraction of organochlorine pesticides from water. Polyurethane coated with Dow Corning 200 oil was found to give better than 90% recovery of all ten pesticides tested. Musty and Nickless<sup>10</sup> also used silicone oil DC 200 coated porous polyurethane foams in the extraction and recovery of chlorinated insecticides and PCB from water. One litre of tap water was doped with the insecticide of interest at the ppb level and passed through the column. The extracted species were found to be quantitatively recovered. Uthe and co-workers<sup>27</sup> again used a 5% solution of DC 200 silicone oil in ethyl acetate to coat polyurethane foam plugs. Coated foam plugs were attached to the bottom of a wooden float and were kept under the surface of water near industrial and agricultural areas. Periodically, foam plugs were removed from the water and organic material in the foam was extracted with hexane. Recoveries of chlorinated pesticides and biphenyls were found to be successful. Gough and Gesser<sup>20</sup> studied the removal of phthalate esters from water with uncoated and DC 200 silicone oil-coated polyurethane foam. The results differed little from those with

uncoated foam which were described earlier. Di-n-octyl phthalate which was not extracted by untreated foam showed a 9% extraction with treated foam.

Braun et al.<sup>28</sup> used flexible polyurethane foam as an inert, solid support for chloranil. The reduction of Ce (IV), V (V) and Fe (III) on foam-filled column was carried out quantitatively and rapidly. Subsequently, Braun et al.<sup>29</sup> placed chloranil-loaded polyurethane foam in a syringe column. The reduction of micro and semimicro amounts of cerium (V), vanadium (V), and iron (III) to their lower valency states was successful.

The use of tri-n-octylamine in hydrochloric acid to load open-cell polyether type polyurethane foam column was described<sup>30</sup>. Trace amounts of cobalt (II) and nickel (II) were separated using 11.4 and 17.7% tri-n-octylamine-hydrochloric acid-polyurethane loadings. For the 11.4% tri-n-octylamine columns, nickel passed through the column without any retention and cobalt was later eluted with 1 M hydrochloric acid. Both metals could be adsorbed on the 17.7% tri-n-octylamine columns from which nickel could be eluted with 8 M hydrochloric acid and cobalt with 1 M hydrochloric acid.

Sukiman<sup>16</sup> prepared polyurethane foams treated with methyl isobutyl ketone, diethyl ether, isopropyl ether and ethyl acetate. These loaded foams were compared with untreated foams in the taking up of gold (III) from acid aqueous solution. They were shown to behave similarly. Gold chloride at a concentration of

20 ppm or 25 ppm in 1 M hydrochloric acid containing  $^{198}\text{AuCl}_3$  as a tracer was passed through the column of 20 mm internal diameter at 30-40 ml min<sup>-1</sup>.

Braun et al.<sup>31</sup> prepared plasticized foams by dissolving hydrophobic organic reagents such as dithizone, zinc dithizonate and 1-nitroso-2-naphthol in a plasticizer solution such as TBP,  $\alpha$ -di-n-nonylphthalate, di-n-octylphthalate or dibutyladipate and then immobilizing the solution on open cell polyurethane foam. Polyurethane foam loaded with  $3.9 \times 10^{-4}$  M zinc dithizonate in TBP solution retained 99% of 0.01  $\mu\text{g}$ . Separation of silver from lead and copper was also done. Dithizonate foams were prepared for the preconcentration of traces of mercury (II)<sup>32</sup>. The capacity for mercury (II) of a TBP-plasticizer zinc dithizonate foam at pH 6 was  $23.4 \mu\text{eq g}^{-1}$ . Chromogenic organic reagents dissolved in  $\alpha$ -di-n-nonylphthalate was mixed with polyurethane foams<sup>33</sup>. The "chromofoams" thus formed were used in the quantitative determination of zinc (II) and lead (II) with dithizonate foams, copper (II) with rubeanic acid foams and cobalt with Amberlite LA-1 foams at ppb level. Braun<sup>34</sup> prepared TBP plasticized 1-nitroso-2-naphthol and diethylammonium diethyldithiocarbamate foams for the preconcentration of metal ions from aqueous solutions. Cobalt (II) was quantitatively recovered for concentrations ranging between 1 and 1,000  $\mu\text{g}$  at pH values ranging between 6.6 and 9.9 at a flow rate of 5-6 ml cm<sup>-2</sup> min<sup>-1</sup>. TBP plasticized polyurethane

foam containing iodine or silver dithizone was also prepared<sup>35</sup>. Radioactive isotopes  $^{131}\text{I}$  and  $^{111}\text{Ag}$  were used with or without non-radioactive carrier. The isotopes of iodine and silver were found to be quantitatively exchanged with the isotope loaded on the I or Ag-treated foam.

Lypka et al.<sup>36</sup> described the extraction and separation of a copper-cadmium system by benzoylacetone-treated polyurethane foam and untreated foam. The benzoylacetone-treated foam gave a quantitative recovery of copper and cadmium from aqueous solution. Separation of copper from cadmium was found to be more effective by absorbing copper selectively from the solution at pH 4.86 rather than by first loading both metals on the treated foam and then sequentially eluting them.

Chow and Buksak<sup>37</sup> reported the use of dithizone-treated polyurethane foams in the extraction of mercury (II) and methylmercury (II) chloride from aqueous solution over a wide pH range and at various flow rates. Mercury (II) and methylmercury (II) chloride were quantitatively extracted up to 10 ppm. The mercury was then totally recovered from the foam by elution with acetone.

Lee et al.<sup>38</sup> used flexible open-pore urethane foam impregnated with dimethylglyoxime for the extraction of nickel (II) from aqueous solution. About 2 mg of nickel was extracted per gram of treated foam from aqueous solution in the pH range of 8-10. Quantitative extraction was obtained for nickel (II) at

concentrations from 0.5 to 5 ppm at pH 9. Nickel could be recovered by elution with a 1 to 1 mixture of 1 M hydrochloric acid and ethanol.

#### Chemically Treated Polyurethane Foams:

In 1973, Mazurski, Chow and Gesser<sup>39</sup> reported a study of the adsorption of mercury (II) chloride and methylmercury (II) chloride by polyurethane foams which had been treated with hydrogen sulphide. SH-polyurethane foam was prepared by subjecting clean and dry foams to an electric discharge in an H<sub>2</sub>S atmosphere. The extraction of mercury in concentrations of 4.0-0.0004 ppm in dilute aqueous solution and the recovery of the adsorbed mercury from the foam by soxhlet extraction with 2 M HCl was found to be quantitative.

Braun and co-workers<sup>40</sup> prepared ion-exchange foams by introducing ion-exchange groups on commercially available phenol-formaldehyde polyurethane and polyethylene foams. The maximum ion-exchange capacity of the produced sulfonated phenol-formaldehyde cation exchange foams was 1.85 meq g<sup>-1</sup>. The styrene-polyurethane interpolymer anion exchange foams was 2.2 meq g<sup>-1</sup>. Weak carboxylic ion-exchange foams were also prepared by radiation grafting of polyurethane and polyethylene foams. Heterogeneous ion-exchange foams were prepared by foaming a fine powder of an cation-exchange with the precursor of foam. The capacity studies were carried out using Sr(NO<sub>3</sub>)<sub>2</sub> solution labelled with <sup>85</sup>Sr.

Open cell polyurethane foam immobilizing a very fine silver sulfide precipitate was prepared by mixing heterogeneous cation-exchange foam with silver nitrate and washing with sodium sulfide<sup>41</sup>. Complete retention of radiosilver in 0.1 M nitric acid was achieved.

Polyurethane heterogeneous cation-exchange foam was prepared using Vario KS<sup>42</sup>. Distribution coefficients of Cd (II), Zn (II), Fe (III) and Ca (II) were determined for foam material and compared with conventional bead exchanger. The overall capacity of the ion-exchange foams was about 40% of the original capacity of the beads and both have about the same selectivity.

Braun et al.<sup>43</sup> extended their studies by changing the heterogeneous cation-exchange foam to the copper form. Quantitative collections of various concentrations of radiosilver by redox exchange reaction on columns packed with Cu-foam at flow rate of 10-12 ml cm<sup>-2</sup> min<sup>-1</sup> were reported.

#### Treated Polyurethane Foams for Biological Applications

In 1965, Bauman and Goodson<sup>44</sup> introduced the use of polyurethane foam as an inert support for the enzyme horse serum cholinesterase. The enzyme immobilized by the use of a starch matrix was placed on a urethane pad. Enzyme inhibitors of cholinesterase in air and water which affected the activity of the enzyme on the foam pad were monitored electrochemically.

Bauman et al.<sup>45</sup> subsequently reported the addition of enzyme additives to preserve the activity of starch gel immobilized

cholinesterase on a pad of open cell urethane foam up to 56 days at 60° C.

Evans et al.<sup>46</sup> reported that reticulated polyurethane foam is particularly suitable as an insoluble support for the immunoadsorption of cells. He also found that open cell polyurethane foam with a polyester backbone to which a specific antibody had been coupled, served as a matrix for the immunologic binding of erythrocytes.

Goodson and collaborators<sup>47</sup> demonstrated that cholinesterase could be better immobilized on the surface of open pore urethane foam if it were first adsorbed before preparation of the starch gel. It was used to monitor the presence of organophosphate and carbamate insecticides in water and air.

#### Rigid Polyurethane Foams

Rigid open-pore polyurethane foam as a novel chromatography support was first reported by Ross and Jefferson<sup>48</sup> in 1970. They described an in situ synthesis method and the physical properties of the open pore polyurethanes as supports for gas-solid, gas-liquid and liquid-liquid chromatography. A solvent containing the monomer precursor was quickly drawn into the chromatographic column until the column was completely filled. The filled column was then clamped shut at both ends. It was then fastened to a turntable in a vertical position and revolved at a slow speed during this

polymerization or gelation period. The solvent was then removed from the rigid porous polymer. Liquids which served as a stationary phase on the inert foam support could be added by incorporation in the precursor agent prior to foaming or by coating the column after polymerization. Electron photomicrographs revealed that the polymer consists of highly uniform spherules with diameter 1 to 10  $\mu\text{m}$ . Normal aliphatic hydrocarbons, aromatic compounds, gasoline and metal complexes such as Cu (III), Co (II), Co (III) heptafluorodimethyl octanedionates were found to give a good separation in the columns studied. For uncoated polyurethane, gas-solid behavior was exhibited; upon the addition of a suitable liquid phase the properties were markedly altered and typical gas-liquid behavior resulted.

Hileman et al.<sup>49</sup> examined the preparation of an open pore polyurethane chromatographic column of varying permeability; the permeability could be varied by changing the monomer concentrations and reaction conditions. An uncoated polyurethane foam column was found to give good gas chromatographic separation of metal chelates such as  $\text{Cr}(\text{tfa})_3$ ,  $\text{Be}(\text{tfa})_3$ ,  $\text{Al}(\text{tfa})_3$  and  $\text{Rh}(\text{tfa})_3$  (tfa = the anion 1,1,1, trifluoro-2,4,-pentanedione), and also for alcohols and aromatic hydrocarbons.

Lynn and co-workers<sup>50</sup> prepared polyurethane foam chromatographic column with different isocyanate-polyol ratio. Various solutions were made where the NCO/OH ratio was varied to give useful gels. Dichloroanilines, o-aminophenol and acetone

were successful separated by liquid chromatography with rigid open pore polyurethane prepared in situ.

Hansen et al.<sup>51</sup> synthesized by in situ polymerization polyurethane chromatographic columns. They investigated the use of polyurethane in liquid chromatography system with respect to particle size and size distribution, gross packing structure, column permeability and the effects of particle swelling by polar solvents, the type of solute-packing interaction of various open pore polyurethane formulations, and the capacity of different open pore polyurethane formulations. Separation of phenol from its derivatives; benzyl alcohol from cinnamyl alcohol, benzene from nitrobenzene was done using open pore polyurethane.

#### Silicone Rubber Foam

In 1975, Gregoire and Chow<sup>52</sup> prepared open-pore silicone rubber foam and then treated the foam with dimethylglyoxime for the separation of palladium and platinum. Separation was achieved in  $10^{-4}$  M hydrochloric acid at a flow rate of  $35 \text{ ml min}^{-1}$  through a column of 2.4 cm diameter. The palladium was retained by the treated foam column while the platinum passed through. The palladium could be eluted by 8 M nitric acid at a flow rate of  $10 \text{ ml min}^{-1}$  through the same column.

Baghai and Bowen<sup>53</sup> prepared silicone rubber foam and then loaded it with tri-n-octylamine. The separation of rhodium from iridium was by extracting the iridium on the treated foam

while rhodium remained in the aqueous solution and was not retained by the foam. Foam loaded with 1 g of tri-n-octylamine extracted 98.5% of 10  $\mu$ g of iridium from 6 M hydrochloric acid. Iridium could be recovered quantitatively by elution with a small amount of ethanol.

In the studies described above, untreated or treated polyurethane foams have been claimed to act as absorbent or adsorbent for organic or inorganic species. It is considered here that polyurethane foams would act as a solid "solvent extractor". Bowen<sup>5</sup> measured the surface areas of polyurethane foam and concluded that the process of separation of metal ions in aqueous solution by the use of polyurethane foam was absorption rather than adsorption. The amount of material that was extracted was higher than that which could be explained only by a surface effect. Earlier work in this laboratory showed that the mechanism of separating Ga and Fe from aluminium in acid chloride solution by open cell polyurethane foam was solvent extraction<sup>18</sup>. Moreover, the extraction and recovery of phthalate esters from water using porous polyurethane foam was by absorption<sup>20</sup>. Work to be published by this laboratory indicates that the flexible polyurethane foam acts as a solid organic solvent extractor in the extraction of cobalt from aqueous thiocyanate solution<sup>54</sup>.

In order to confirm these findings, tin and antimony were studied. Tin has been greatly used in plating, alloys, canning, foil, plastics, rubber, fungicides, insecticides, drugs and

toothpaste. Antimony sulfide, in the form of kohl, has been used as a cosmetic by women for perhaps 6,000 years. Antimony is found in ceramic enamels, pewter, and britannia metal, in clothing impregnated with antimony trioxide for flame-proofing, and also in rubber, dyes, paint and medicines. Tin has a low order of toxicity but antimony is very toxic. They do not constitute important health hazards at the present time, although they could if industrial uses increased markedly. Polyurethane foam could be used for the preconcentration of tin and antimony from aqueous solution.

Several workers<sup>55,56,57,58,59,60,61</sup> have contributed to the investigation of the solvent extraction system of tin and antimony from acids of HX, where X is F, Cl, Br, or I, using diethyl ether. The extraction of tin and antimony increases in the order of chloride, bromide and iodide. Tin was extracted completely from HF while antimony was barely extracted. Other ether systems have also been studied; isopropyl ether<sup>62,63</sup>, diamyl ether<sup>64</sup>, isoamyl ether<sup>65</sup>, n-hexyl ether<sup>65</sup>, and  $\beta,\beta'$ -dichlorodiethyl ether<sup>67</sup>. These systems all gave quantitative solvent extraction.

The separation of tin or antimony from other metals has been effected by precipitation, liquid-liquid extraction, distillation, liquid-liquid chromatography, ion-exchange chromatography and gas chromatography<sup>75,76</sup>. Separation techniques which seem related to the polyurethane foam system are liquid-liquid extraction and chromatography. Ross and White<sup>68</sup> described the extraction of tin from acidic chloride sulfate solutions with a cyclohexane solution

of tris(2-ethyl hexyl) phosphine oxide and color development in ethyl alcohol dilutions of the organic phase with Pyrocatechol Violet. Klement and Kuhn<sup>69</sup> reported the absorption of the thiocyanate complexes of tin, arsenic and antimony onto an anion exchange "Dowex"2(OH). Tin was eluted with 0.5 M potassium hydroxide. Arsenic was eluted with 1.2-2.5 M potassium hydroxide and antimony with 3.5 M potassium hydroxide. Paper chromatography<sup>70</sup> has been widely used in the separation of tin and antimony from other metallic species. Good separations of antimony (V) and tin (IV) mixtures can be made with a butyl alcohol-hydrochloric acid solution. Keller and Freiser<sup>71</sup> demonstrated that tin chloride was separated from titanium, niobium and tantalum chlorides at a temperature up to 200°C by a gas chromatography column of "Chromosorb" coated with a hydrocarbon of high molecular weight. Pentavalent antimony was extracted into ethyl acetate from a solution of 1-2 M in hydrochloric acid, to which oxalic and citric acids have been added to prevent extraction of various other elements<sup>72</sup>. According to Lure and Fillippora<sup>73</sup>, antimony was separable from arsenic and tin by passage of a dilute hydrochloric acid solution through the sulfonic acid cation exchanger Wofatit-P in the hydrogen form. Separation of arsenic (III), and antimony (III) and tin (IV) has been obtained in a butanol-hydrochloric acid media by paper chromatography<sup>74</sup>.

In this thesis, the extraction of tin and antimony from aqueous halogen acid solution and metal halide solution by the open cell polyurethane foam was studied.

## Experimental

### Apparatus and Reagents

Perkin Elmer Model 306 Atomic Absorption Spectrophotometer

Varian Techtron Hollow Cathode Lamps

Baird Atomic Model 530 Gamma Spectrometer And Model 810 C well-type NaI(Tl) Detector (Baird Atomic, Bedford, Massachusetts)

Pyrex Column With Teflon Stopcock (Figure 1)

Pyrex Cell (Figure 2)

Single Automatic Squeezer (Figure 3)

Multiple Automatic Squeezer (Figure 4)

Tin-119m, Catalog No. NEZ 099B, Specific Activity: 350 mci/mg, half-life: 250 days (New England Nuclear Canada Ltd., Montreal, P.Q.)

Antimony-124, Catalog No. NEZ 004, Specific Activity: 0.185 mci/mg, Half-life: 60 days (New England Nuclear Canada Ltd., Montreal, P.Q.)

All Chemicals used were of reagent grade unless otherwise indicated.

The water was doubly distilled and passed through an ion-exchanger: Research Model I, (Illinois Water Treatment Co.)

#### Polyurethane Foams:

- DiSPo Plugs (Canlab, Winnipeg), Size: 2.2 cm diameter x 3.8 cm length
- Acid Resistant Foam  
Union Carbide Type "A", (Dr. C.G. Seefried, Union Carbide Corp., Chemicals and Plastics, P.O.Box 8361, South Charleston, W. Virginia, U.S.A. 25303), size: 46 cm x 46 cm x 6.4 cm  
Plugs cut from these sheets, size: 2.1 cm diameter x 4.1 cm length
- Regular Polyurethane Foam  
B.F. Goodrich Co. Canada. Code No. 1338, foams cut to size 4.0 cm diameter x 1.5 cm length

Figure 1 : Pyrex Column with Teflon Stopcock

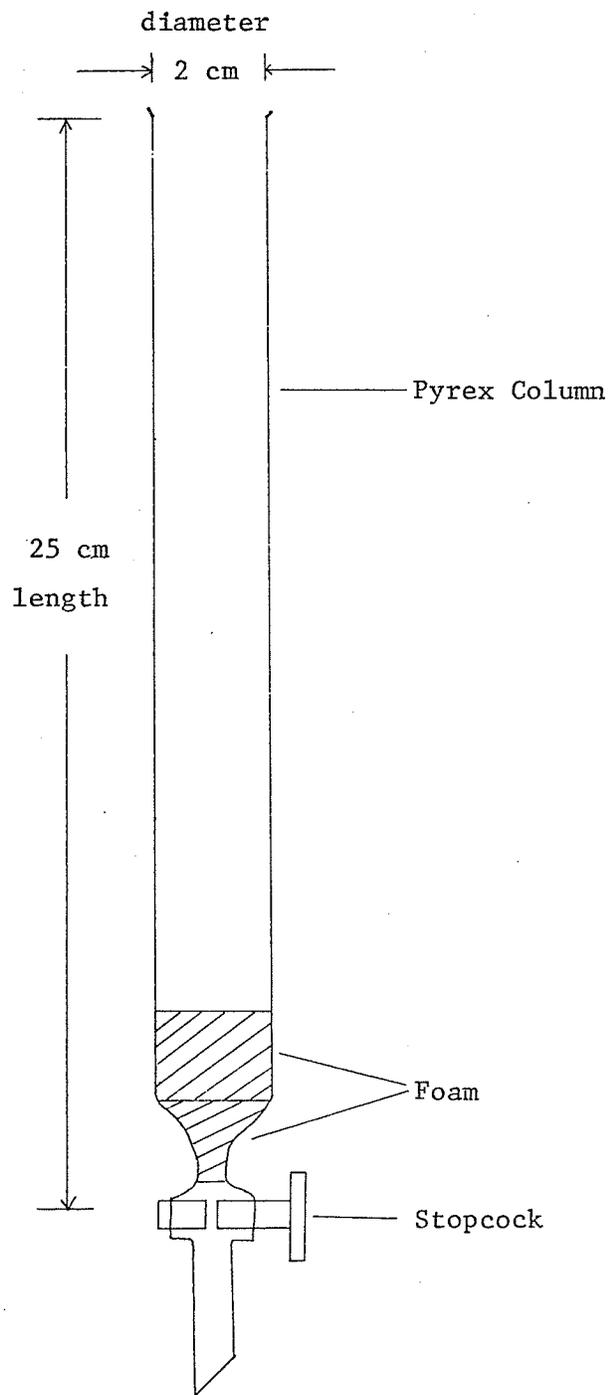


Figure 2 : Pyrex Cell for Multiple Automatic Squeezer

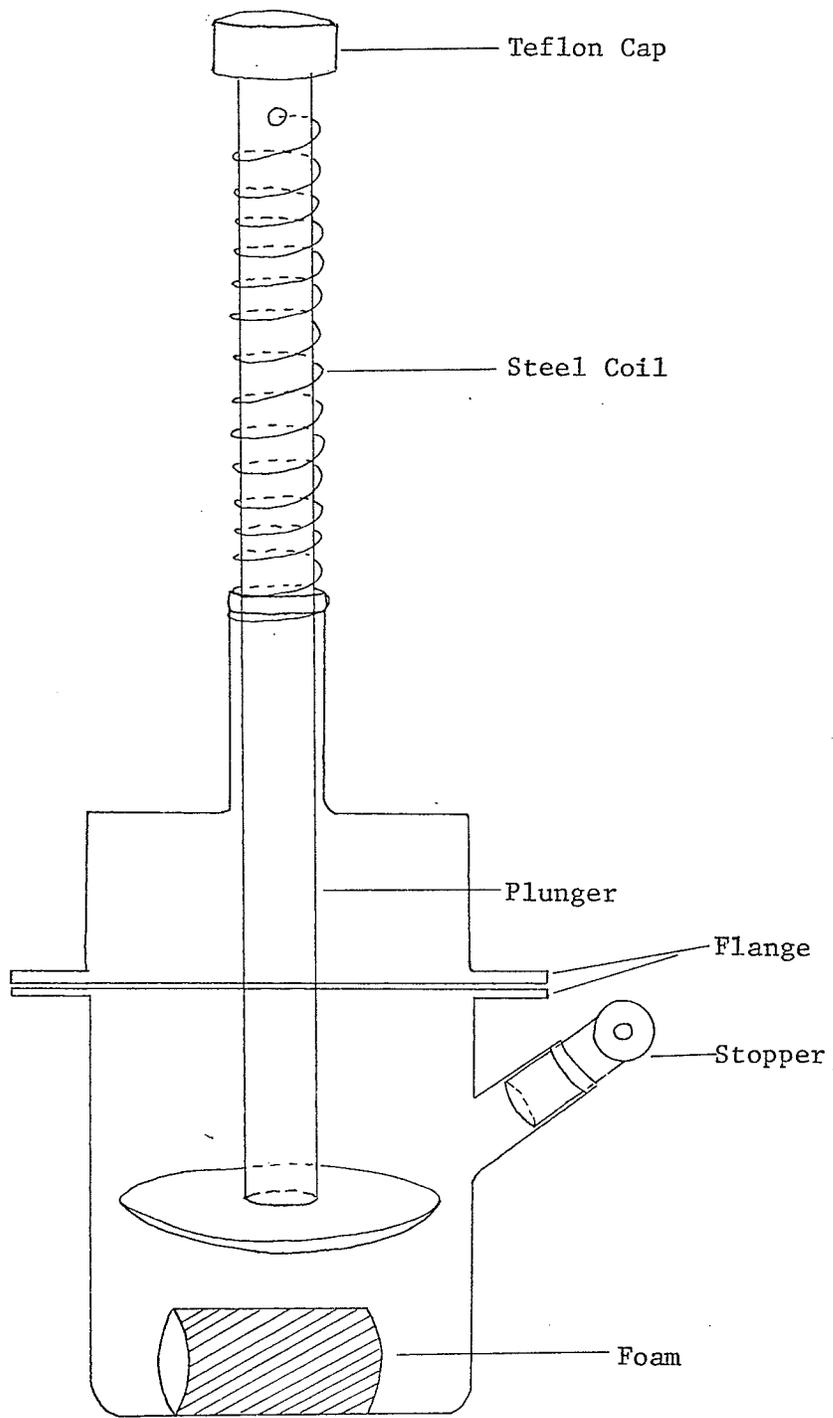


Figure 3 : Single Automatic Squeezer

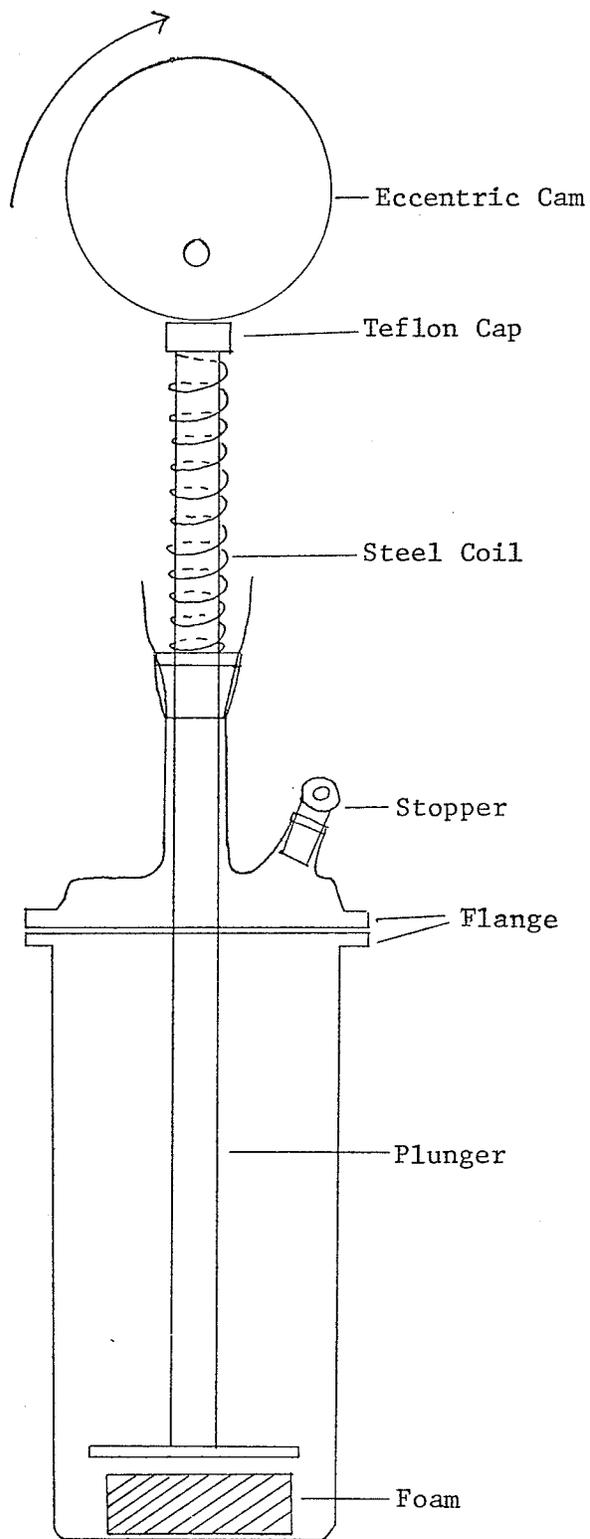
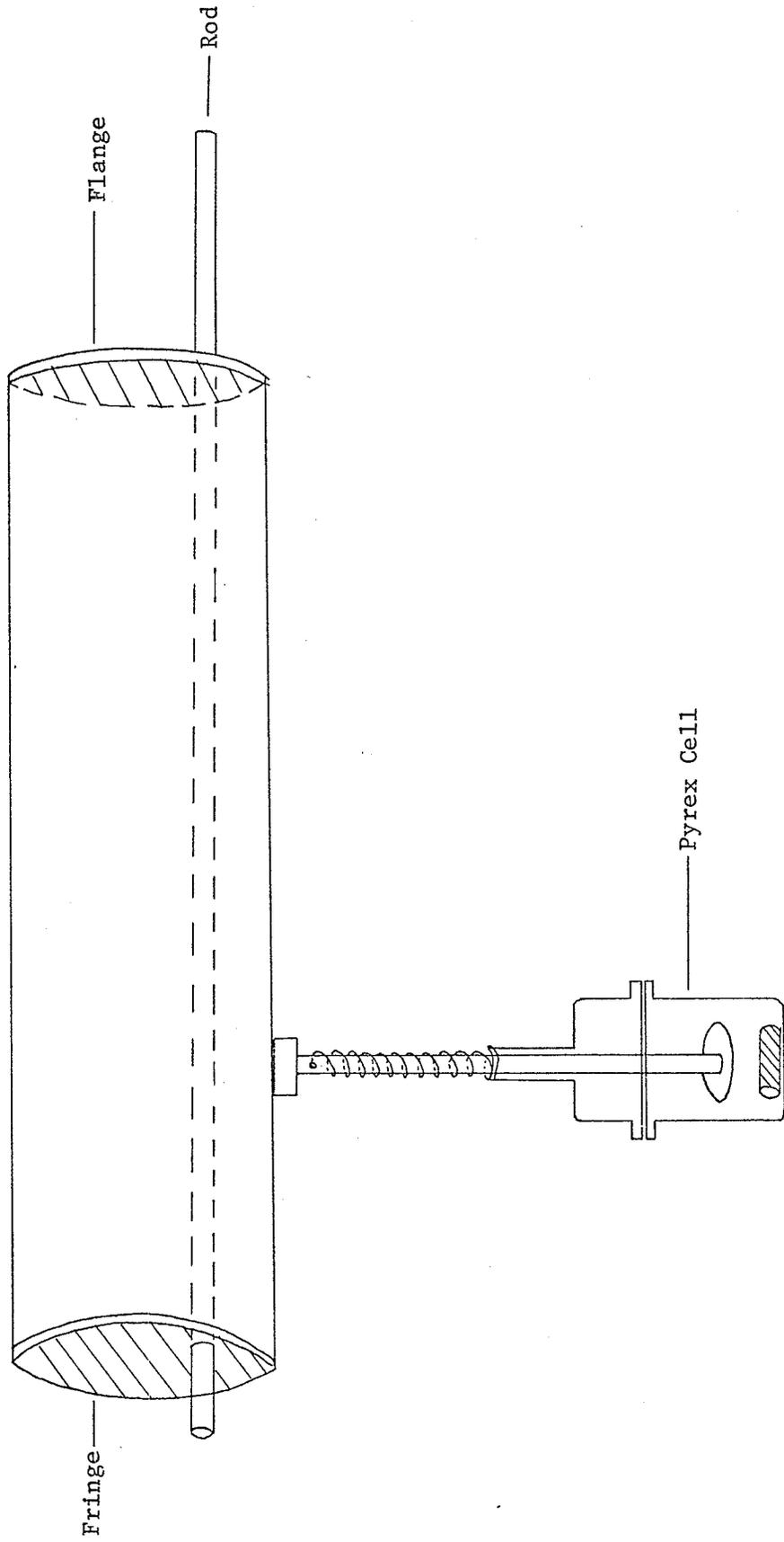


Figure 4 : Multiple Automatic Squeezer



### Standard Solutions

Tin (IV) : A stock solution containing 1,000 ppm of tin was prepared by accurately weighing out 1.000 gram of tin metal, dissolving it in 100 ml of 12 M HCl and making the solution up to a liter in 1.2 M HCl. The solution was tested with mercuric chloride to determine that tin was in its 4+ valency state.

Antimony : A stock solution containing 1,000 ppm of antimony (III) (III) was prepared by dissolving 0.937 gram of antimony trichloride in 12 M HCl and making the solution up to 500 ml in 7 M HCl.

Antimony : A stock solution containing 1060 ppm of antimony (V) (V) was prepared by dissolving 1.303 gram of antimony pentachloride in 12 M HCl and making the solution up to 500 ml in 7 M HCl.

### Foam Preparation

The diSPo plugs and regular polyurethane foam were used as they were.

The acid resistant foam was washed with 1 M HCl for 24 hours by squeezing occasionally with the base of a graduated cylinder and then Soxhleted in acetone for 6 hours. It was then air-dried and stored in glass bottle, in the dark.

### General Procedure

The tracer technique was used except for those experiments specified to be performed by atomic absorption spectrometry.

#### Tracer and Counting Technique

Tin- 119m and antimony-124 tracers were used in this research and they were diluted prior to use. The tin tracer was brought to its 4+ oxidation state by bubbling chlorine into the diluted tracer solution for 2 hours. This should change all the tin in solution to its higher valency. The antimony-124 tracer was in its 3+ oxidation state. Antimony (V) was prepared by taking a third of the diluted antimony (III) tracer and bubbling chlorine into it for 2 hours. This should convert the antimony<sup>124</sup> trichloride into antimony<sup>124</sup> pentachloride. Sufficient tracer was added to the sample to yield a counting rate at least ten times background. The tracer was mixed well with the sample solution by shaking the volumetric flask vigorously. A 15 ml aliquot was taken from each sample and counted in 20 mm O.D. test tubes which fit exactly into the well of the sodium iodide scintillation counter. The activity of all samples was determined by counting five successive times, each for a period of 100 seconds and the average activity determined. The average sample activity was then corrected for background which was determined by taking the average of 15 counting intervals before and after each series of measurements. All counting was done with the lid of the well-counter closed.

### Extraction of Tin(II) and Tin(IV) by DiSpo Plugs Using Static System

A 1,000 ppm of tin(II) solution in 3 M HCl was freshly prepared from stannous chloride on the day of use. A 1,000 ppm of tin(IV) solution was made by dissolving stannic chloride in 3 M HCl. Dilute tin solutions were prepared to the required HCl concentration from stock. A diSpo plug was placed in a beaker and soaked in the test solution. It was squeezed gently with the base of a graduated cylinder to remove any air from the foam. After a period of time, with the base of the cylinder compressing the foam, the solution in the beaker was poured into another container. The concentration of tin remaining in the solution was determined by atomic absorption spectrometry.

### Extraction of Tin(II) and Tin(IV) by DiSpo Plugs Using Flow-Through System

Two diSpo plugs were used in this system and packed using the vacuum technique. Foams were first introduced to the column and soaked in the same concentration of acid which was to be tested. Vacuum was gently applied to suck out trapped air from the foam. The stopcock was then allowed to drain the solution out and air was applied to blow out excess water on the foam. This would allow the plugs to pack snugly and avoid dilution effect. The test solution was introduced and vacuum was applied to remove any trapped air. The solution was then passed through the foam at a flow rate of 0.07 to 0.11 ml min<sup>-1</sup> cm<sup>-2</sup>. The effluent was collected and analyzed by atomic absorption spectrometry.

### Extraction of Tin and Antimony by Polyurethane Foams Using Static System

Tin (IV) and antimony (III) and (V) were made up by dilution from the stock. The volume required was measured out by volumetric flask and mixed with 0.005 g of foam in the cell. It was then squeezed by automatic squeezer. Two types of automatic squeezer were used. The first type which could operate on a single cell and is shown in figure 3. This squeezer has an eccentric cam driven by a motor so that it pushed a glass plunger up and down (2.5 cm stroke, 30 times a min). Foams were placed underneath the plunger and squeezed by the up and down motion of the plunger. The other type of squeezer (designed by Mr. R.F. Hamon<sup>54</sup>), was called the multiple automatic squeezer and is shown in figure 4. This squeezer has an eccentric cam, measuring 91 cm long and 14 cm diameter, turned by a heavy duty motor, depressed and released up to ten glass plungers (5 cm stroke, 24 times a min) in a thermostatically controlled air bath at 22±0.5°C. The sample could be analyzed by either atomic absorption spectrometry or tracer technique.

### Determination of Percentage Extraction and Distribution Coefficient

The percentage extraction for the atomic absorption studies was determined by measuring the absorbance of the sample before and after extraction by the foam. It was then compared to the calibration curve and concentration values were obtained. For atomic absorption spectrometry standards, the matrix was matched with the sample.

$$\% \text{ Extraction by the foam} = \frac{\text{Concentration}_{\text{before}} - \text{Concentration}_{\text{after}}}{\text{Concentration}_{\text{before}}} \times 100$$

The percentage extraction for the tracer technique was determined by counting the radioactivity of the sample before and after the extraction by the foam.

$$\% \text{ Extraction by the foam} = \frac{\text{Activity}_{\text{before}} - \text{Activity}_{\text{after}}}{\text{Activity}_{\text{before}}} \times 100$$

$$\text{Distribution Coefficient} = \frac{\text{Concentration of metal in foam}}{\text{Concentration of metal in solution}}$$

#### Determination of Percentage Recovery by Tracer Technique

The foam was first loaded with tin or antimony under optimum conditions. The foam was then squeezed dry by compressing the foam with a plunger. It was then placed between two clean paper towels and compressed until no liquid was observed to come out of the foam. The foam was then transferred to a clean and dry cell. The procedure was repeated as in the extraction process except that the foam was now placed in a solution which would leach out the metal. At the end of the recovery, the resulting solution was counted. Since the radioactivity was counted in different media, the counts had to be corrected before calculation. The matrix effect (i.e. different counts for tracer in different media) was investigated by first diluting "enough tracer" (final tracer's activity was at least five times background) in a suitable volume with water. A 5 ml aliquot of the diluted tracer was then pipetted into a 50 ml volumetric flask and made up with acid and/or salt as the original

sample was in (e.g. 3 M HCl, 10 M LiCl). Another 5 ml of the dilute tracer was pipetted into a 50 ml volumetric flask and prepared in the same concentration of the stripping solution (e.g. 0.1 M HCl). These solutions were mixed well and counted in the same test tube. The correction factor,  $f$ , would be the ratio of the activity of the solution with concentration as the stripping solution to the activity of the solution with concentration as what the original sample was in. Before finding the percentage recovery, the percentage stripping was first obtained.

$$\% \text{ Stripping} = \frac{\text{Activity of stripping solution}}{\text{Activity of original sample solution} \times f} \times 100$$

$$\% \text{ Recovery} = \frac{\% \text{ Stripping}}{\% \text{ Extraction}} \times 100$$

Another method of determining the percentage of recovery was by counting the radioactivity on the foam. The foam was first loaded with tin or antimony under optimum conditions. The foam was then rinsed with same concentration of salt solution which the tin or antimony was originally in except without the metal. This would rinse off some radioactive liquid which had adhered to the foam and yet would not leach out the absorbed metal. The wash solution was counted and found to be less than 1% higher than background. The foam was then squeezed dry by first compressing the foam with a plunger, then placing it between two clean paper towels and pressing until no liquid was observed to come out of the foam. The foam was then introduced into the end of a 20 mm test-tube

with the help of a glass rod. The radioactivity on the foam was counted. The foam was transferred into a clean and dry cell containing the liquid for recovery. The recovery procedure was identical to the extraction method except that the solution was different. It was then taken out of the cell and rinsed quickly with a small amount of recovery liquid. The foam was again squeezed dry between two clean paper towels and then put into a test-tube. The radioactivity on the foam was again counted. The percentage recovery was determined by means of the following equation:

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

Triplicates were done for each experiment unless specified and standard deviations were hence calculated.

Standard deviation (S) was defined as :

$$S = \left[ \frac{\sum_{j=1}^N (X_j - a)^2}{N} \right]^{1/2}$$

where  $X_j$  is the measured value

$a$  is the arithmetical mean

$N$  is the number of measurements

## Part I

### Extraction of Tin by Polyurethane Foams

Open cell polyurethane foam sponge (OCPFS) was examined for the extraction of tin from aqueous solution. In the present study, three types of foams were investigated (A) DiSPo Plugs, (B) Acid Resistant Foam and (C) Regular Polyurethane Foam. Both static and flow-through systems were used.

#### (A) Extraction of Tin by DiSPo Plugs

DiSPo plugs are polyurethane foams with a polyester backbone, originally designed as test-tube stoppers for biological samples. The average weight of the diSPo plugs used was  $0.419 \pm 0.037$  g; the average size was 2.2 cm diameter x 3.8 cm length. The present study investigated the extraction of tin (II) and tin (IV) from solutions of different hydrochloric acid concentrations by using static and flow-through systems.

##### Static System

##### Effect of Acidity on the Extraction of Tin Using DiSPo Plugs

Tin (II) and tin (IV) solutions of 100 ppm were prepared from stock of 1,000 ppm. The 100 ppm solutions were prepared in varying concentrations of HCl by adding a known amount of standardized HCl solution. A foam plug was soaked in 10 ml of solution and squeezed every 10 minutes for 30 minutes. A foam plug would soak up to about 6 ml of solution. The concentrations of tin (II) and tin (IV) before and after extraction was determined by atomic absorption spectrometry.

Figure 5 and figure 6 show the acid dependent curves for the extraction of tin (II) and tin (IV) by diSPo plugs in a static system. The two curves are similar showing a maximum extraction at 6 M HCl. The foam became very soft in 8 M HCl after 30 minutes and fell apart after 45 minutes.

The equilibrium reactions for tin (II) and tin (IV) could be the following:

Figure 5 : The Acid Dependent Curve for the Extraction of Tin (II)  
by DiSPo Plugs in a Static System

Tin (II) Concentration : 100 ppm

Volume of Solution : 10 ml

Squeezing Time : 30 minutes

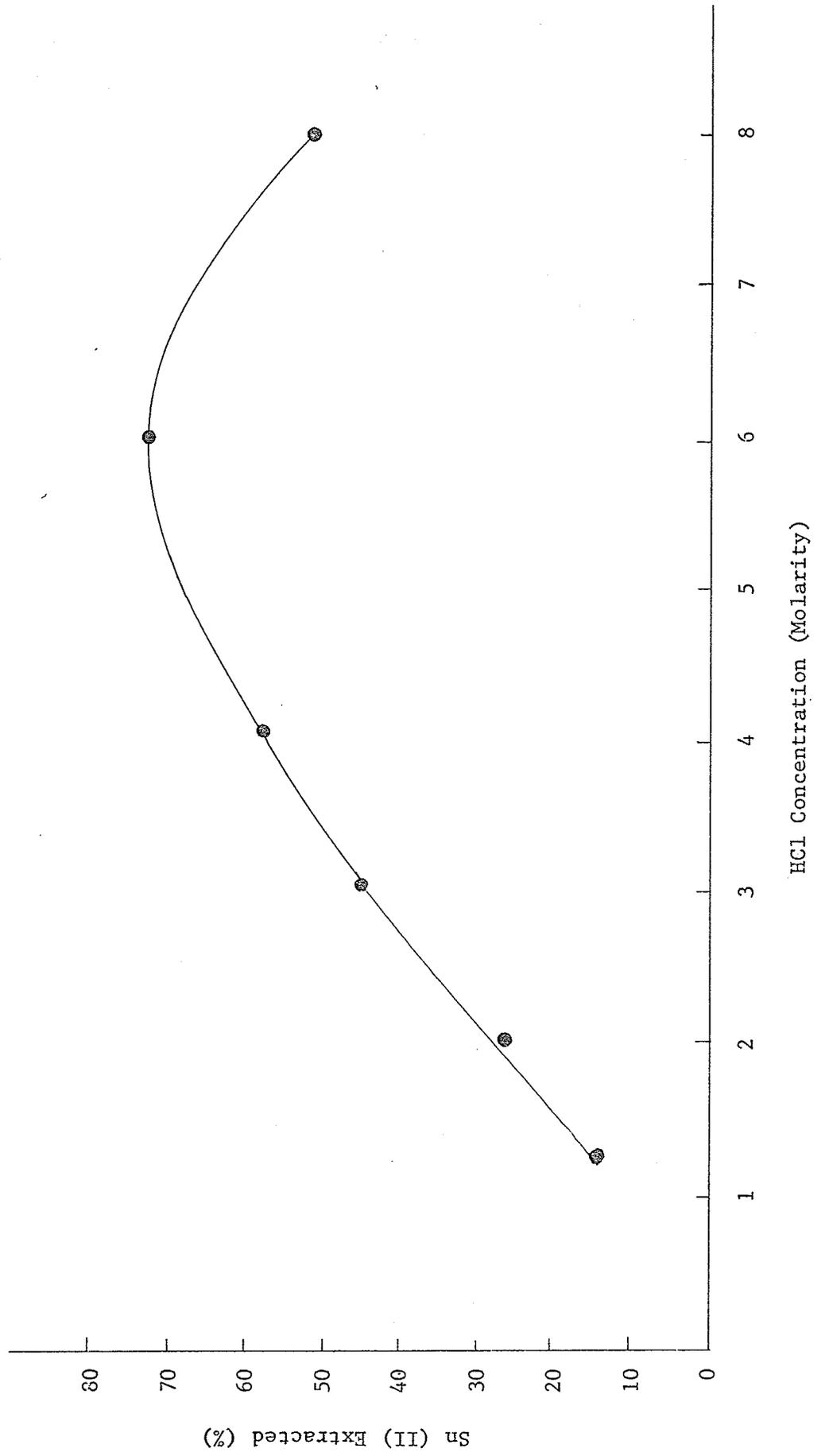
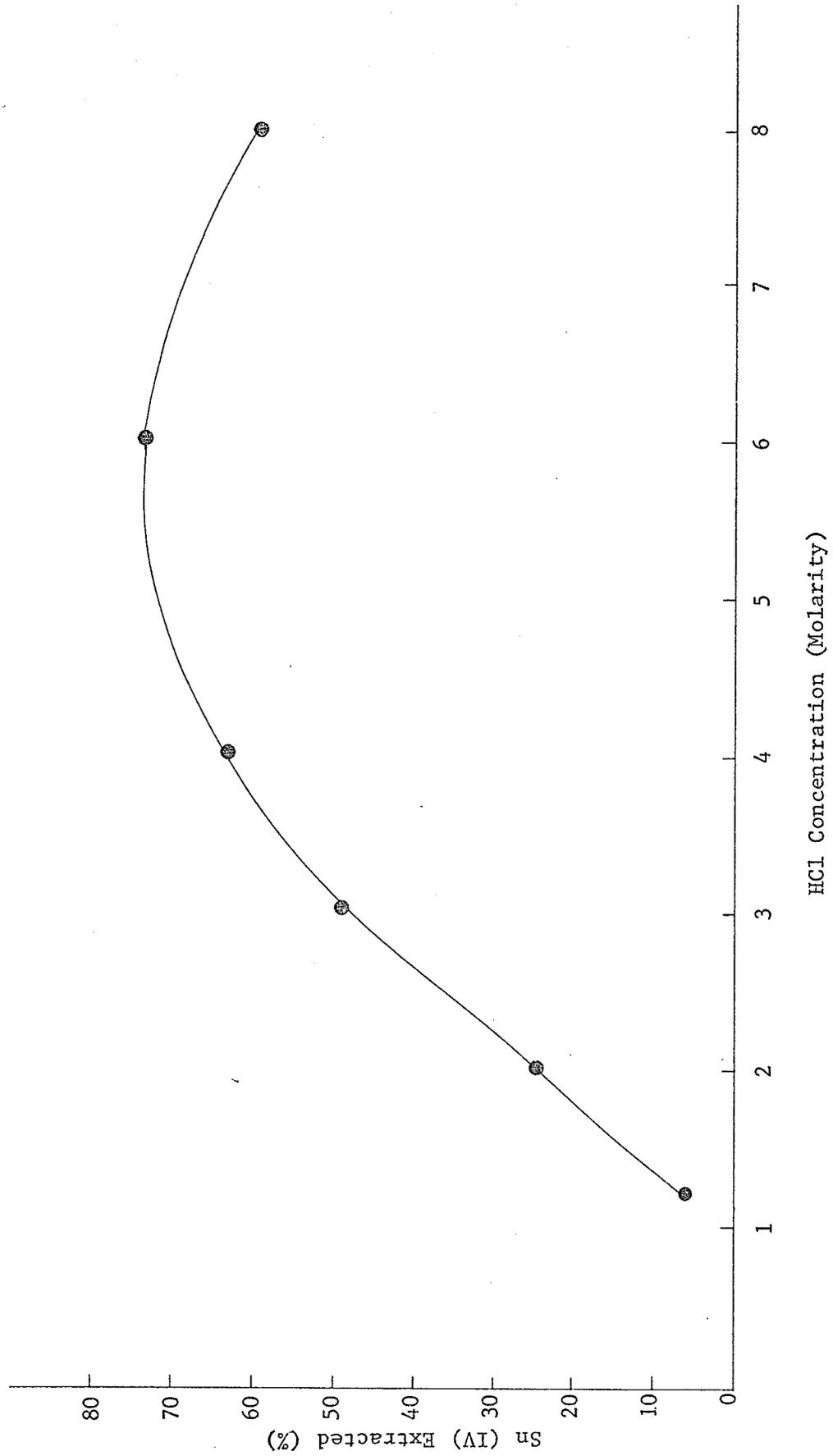


Figure 6 : The Acid Dependent Curve for the Extraction of Tin (IV)  
by DiSPo Plugs in a Static System

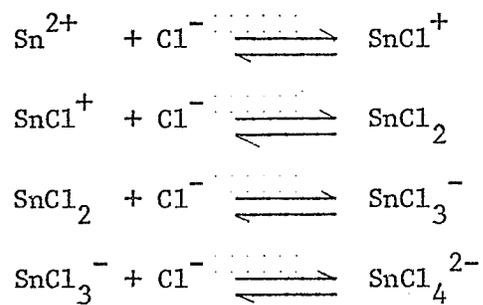
Tin (IV) Concentration : 100 ppm

Volume of Solution : 10 ml

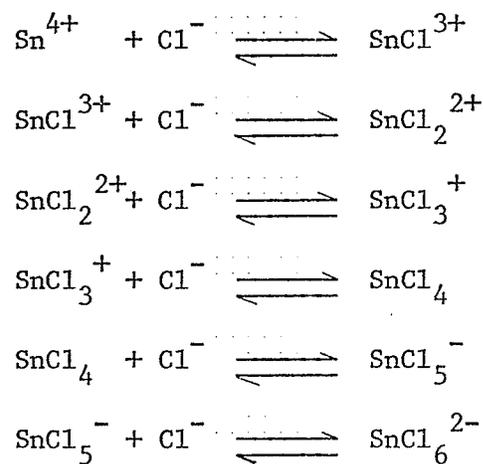
Squeezing Time : 30 minutes



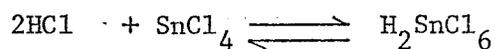
Tin (II)



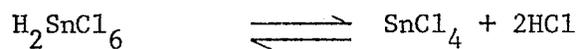
Tin (IV)



Stannic chloride is stable in aqueous solution



where in dilute acid



All of these species are present in solution but only a few of them could be extracted.

As was observed in the extraction curves, the extraction decreased after 6 M HCl. This decrease may be due to the formation of some species which were not extracted by the foam. The formation of the species which favor the extraction depend on the hydrogen and chloride concentrations. It is possible that at 8 M HCl, some species thus formed were not extracted. Moreover, at high HCl concentrations, the activities of all tin species in solution would be decreased. All of these effects result a maximum in the extraction curves.

#### Effect of Volume of Tin Solution on the Extraction

DiSPo plugs were soaked in either 10 ml or 20 ml of tin (II) and tin (IV) solutions prepared at 100 ppm in 6 M HCl. They were allowed to squeeze for 45 minutes and then the remaining solutions were analyzed by atomic absorption spectrometry.

Table 1 shows the percentage extracted and distribution coefficient of tin (II) and tin (IV) in different volumes of solution in the extraction by diSPo plugs.

With an increase of the volume of tin solution, the amount of tin in the solution was also increased. For tin (II), the percentage extraction was decreased by about 20%, while for tin (IV), the difference was not large.

Table 1 : Effect of Volume on the Extraction of Tin (II) and Tin (IV) by DiSPo Plugs in a Static System

Volume (ml)	Percentage Extracted		Distribution Coefficient	
	Tin (II)	Tin (IV)	Tin (II)	Tin (IV)
10	77±3	74±4	72±9	85±16
20	55±2	74±4	56±3	129±20

Tin (II)/Tin (IV) Concentration : 100 ppm

Squeezing Time : 45 minutes

HCl Concentration : 6 M

## Flow-Through System

### Effect of Acidity on the Extraction of Tin by DiSPo Plugs

Two foams were packed into the column by the vacuum technique. A 20 ml of 100 ppm of tin (II) or tin (IV) at various HCl concentrations was introduced and passed through the foams at a flow-rate of 0.07 to 0.11 ml min<sup>-1</sup> cm<sup>-2</sup>. The effluent was collected and analyzed by atomic absorption spectrometry.

Figure 7 and figure 8 show the acid dependence of the extraction of tin (II) and tin (IV) for diSPo plugs in the flow-through system.

Both curves show a maximum extraction at 6 M HCl which agrees with the static system. Tin (II) was 86% extracted while tin (IV) was completely extracted. The flow-through system would be like a continuous extractor as compared to the single batch static system. As the sample flows down the column, it is being continuously brought into contact with "fresh" foam. However, the problem in the column technique is channelling, sample may pass through without being extracted. The diSPo plug was again observed to fall apart at high acid concentration. It would be due to the strong hydrogen ions attacking the foam. The use of lithium chloride which provides the chloride ions for the extraction would prevent the falling apart of diSPo plugs.

Figure 7 : The Acid Dependent Curve for the Extraction of Tin (II)  
by DiSPo Plugs in a Flow-through System

Tin (II) Concentration : 100 ppm

Volume of Solution : 20 ml

Flow-rates : 0.07 - 0.11 ml/min/cm<sup>2</sup>



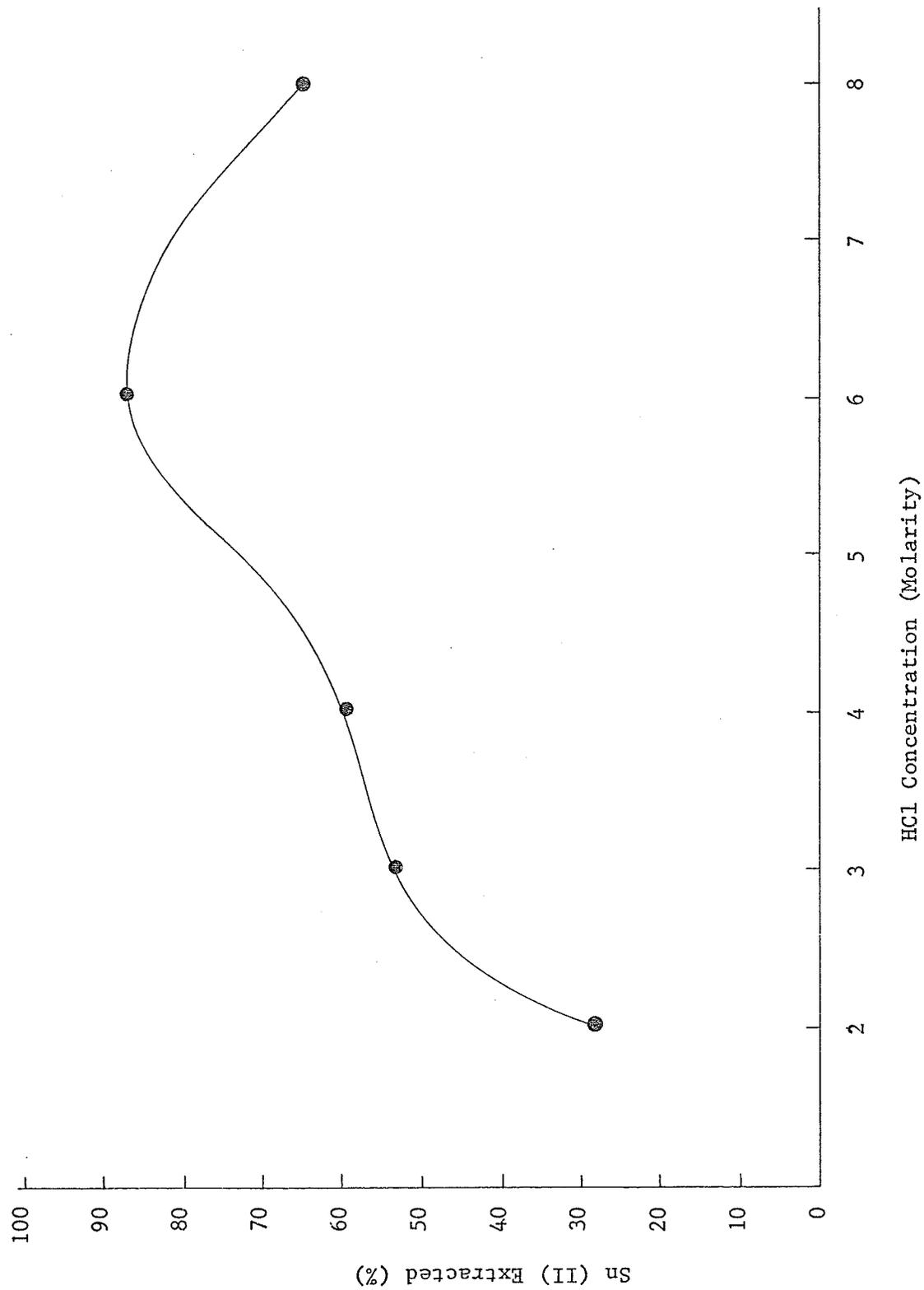
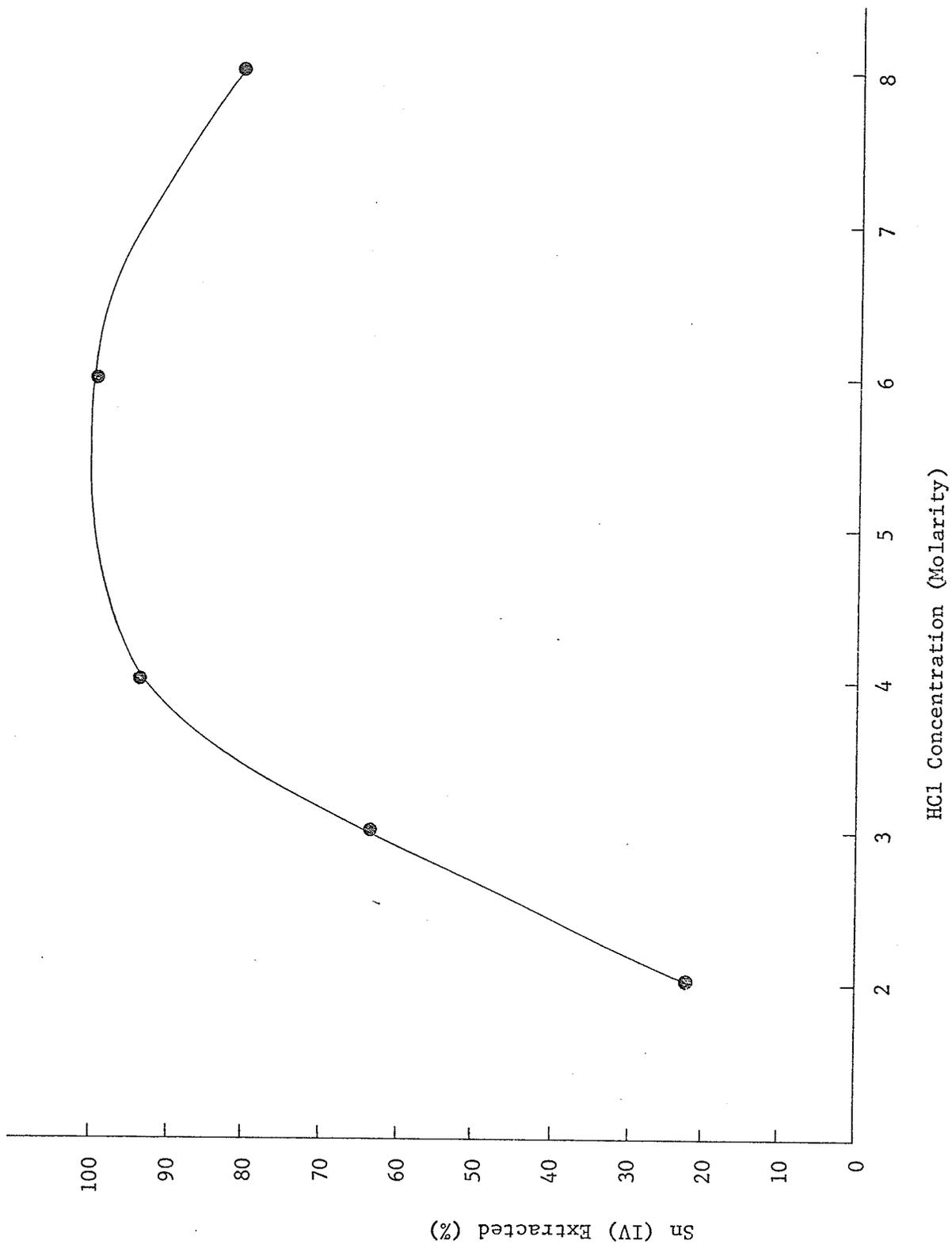


Figure 8 : The Acid Dependent Curve for the Extraction of Tin (IV)  
by DiSPo Plugs in a Flow-through System

Tin (II) Concentration : 100 ppm

Volume of Solution : 20 ml

Flow-rates : 0.07 - 0.11 ml/min/cm<sup>2</sup>



Effect of Lithium Chloride on the Extraction of Tin (IV) by DiSPo Plugs

A 150 ml of tin (IV) solution at 100 ppm in 0.12 M HCl and with various lithium chloride concentrations were prepared. The multiple automatic squeezer was used to squeeze the foam for 24 hours at  $22.0 \pm 0.5^\circ\text{C}$ . The tracer technique was used.

Table 2 shows the percentage of extraction and distribution coefficients of tin (IV) in diSPo plugs.

It could be seen from the results that there was a significant increase of extraction as seen from the distribution coefficient with higher LiCl concentration. Due to the incapability of diSPo plugs to withstand high acid concentration, the use of acid resistant foam was investigated.

Table 2 : Effect of Lithium Chloride on the Extraction of Tin (IV)  
by DiSPo Plugs in a Static System

Lithium Chloride Concentration (Molarity)	10	7	4
Percentage Extracted	63±2	24±2	3±2
Distribution Coefficient	732±46	129±11	12±7
Density (g/ml)	1.21	1.15	1.09

Tin (IV) Concentration : 100 ppm

Volume of Solution : 150 ml

Squeezing Time : 24 hours

HCl Concentration : 0.12 M

## (B) Extraction of Tin(IV) by Acid Resistant Foam

### Introduction

Acid resistant foam was obtained from Union Carbide Co. Ltd. (P.O.Box 8361, South Charleston, W.VA.25303). The ratio of the polyol to polymer-polyol was 60 to 40. The polyol used was NIAX Polyol 11-34, which is an oxypropylene/oxyethylene copolymer of 5000 number average molecular weight. The polymer-polyol was NIAX Polyol 34-28 consisting of 20 percent by weight graft dispersion of a styrene/acrylonitrile copolymer in the 500 number average molecular weight polyol. The foam was found to withstand high acid concentrations for a prolonged time.

### Effect of Hydrochloric Acid Concentrations on the Extraction of Tin(IV) by Acid Resistant Foam

Tin (IV) was made up to 150 ppm in various hydrochloric acid concentrations from stock solution. A 150 ml volume was mixed with 0.500 gram of foam and squeezed by the automatic squeezer for 30 minutes. The samples were then analyzed by atomic absorption spectrometry.

Figure 9a shows the effect of HCl concentrations on the extraction of tin (IV) by the acid resistant foam.

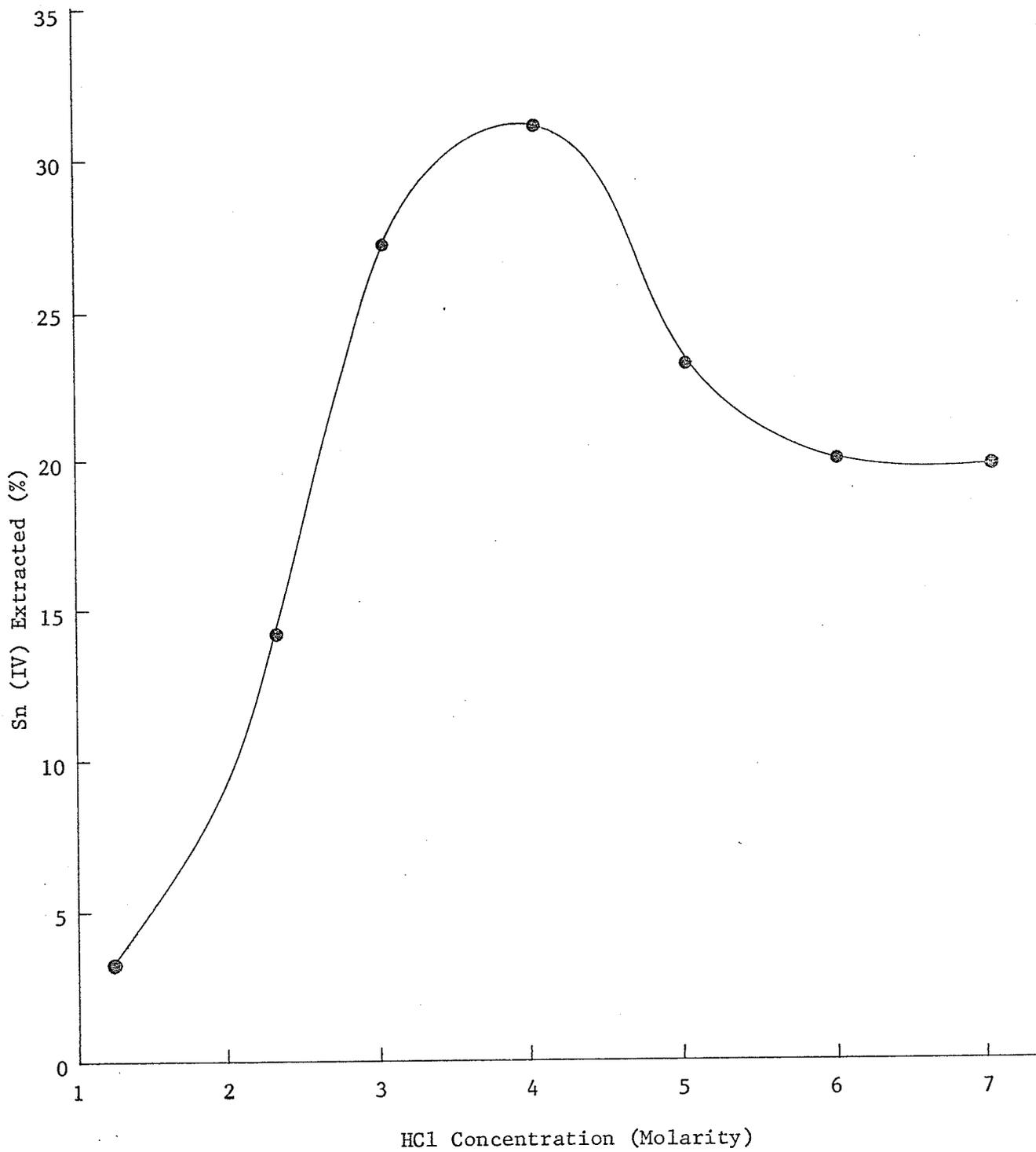
Tin (IV) shows a maximum extraction at 4 M HCl by acid resistant foam. The acid resistant foam was found to have a distribution coefficient of  $120 \pm 9$  at 4 M HCl. As the concentration of HCl increases, i.e. greater than 4 M, the extraction decreases. This could be due to the formation of some species which were not well extracted. It was considered that the mechanism of

Figure 9 a : The Effect of HCl Concentration on the Extraction of Tin (IV)  
by Acid Resistant Foam

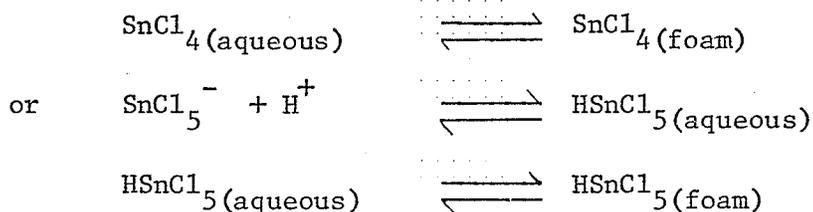
Tin (IV) Concentration : 150 ppm

Volume of Solution : 150 ml

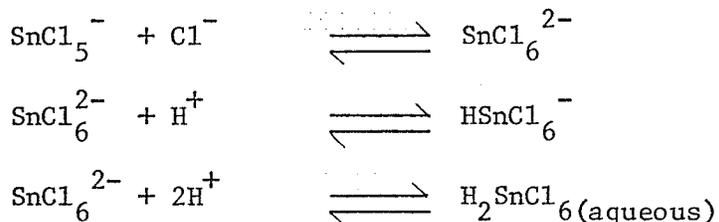
Time of Squeezing : 30 minutes



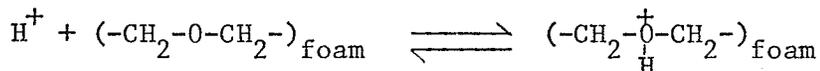
extraction could be:



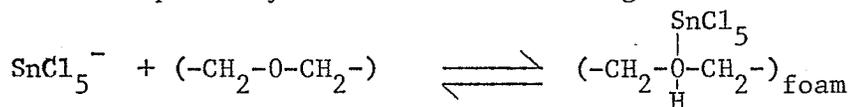
With an increase in the HCl concentration, it could be:



and if this species was not well extracted then the extraction would decrease. Moreover, Gesser et al.<sup>77</sup> have proposed a mechanism involving the protonation of ether sites in the polymer.



It would probably be like the following for the extraction of  $\text{SnCl}_5^-$ .



#### Effect of the Volume of Tin (IV) Solution on the Extraction by Acid Resistant Foam

Tin (IV) was prepared at 100 ppm in 4 M HCl from stock.

Tin tracer was added to different volumes of solution and mixed with foam by squeezing with the multiple automatic squeezer for one hour.

Table 3 shows the effect of the volume of tin (IV) solution on the extraction.

An increase of 10-fold in volume decreases extraction by a factor of 2. A doubling of volume from 25 to 50 ml decreased extraction by 14% from 65 to 56 % while doubling from 50 to 100

Table 3 : Effect of the Volume of Tin (IV) solution on the Extraction by Acid Resistant Foam

Volume (ml)	10	25	50	100	150
Tin (mg)	1	2.5	5.0	10.0	15.0
Percentage Extracted (mg)	76±1 0.8	65±1 1.6	56±2 2.8	37±1 3.7	31±2 4.7
Distribution Coefficient	58±3	87±3	113±7	115±4	120±9
Weight of Foam (g)	0.5495	0.5368	0.5644	0.5098	0.5616

Tin(IV) Concentration : 100 ppm

HCl Concentration : 4 M

Squeezing Time : 1 hour

decrease by 34%. It is therefore considered that this system could not give quantitative extraction. In another experiment, it was found that there was no difference in percentage of extraction by squeezing for 30 minutes or 1 hour. The equilibrium was attained after 30 minutes.

#### Effect of the Concentration of Tin on the Extraction by Acid Resistant Foam

Various concentrations of tin solution in 4 M HCl were made up from stock. A 100 ml of solution was used and squeezed by automatic squeezer for 1 hour.

Table 4 shows the effect of concentration of tin (IV) on the extraction.

From the results, it is shown that the foam has high capacity for the extraction of tin. The percentage of extraction decreases slightly as the concentration of tin increases from tracer to 1,000 ppm. Mylius et al.<sup>56</sup> reported 17% of tin (IV) was extracted in 6 M HCl by diethyl ether. The results here indicated that polyurethane foam could extract tin (IV) from HCl solution more efficiently than could diethyl ether.

Figure 9b shows the plot of log Distribution Coefficient (D) vs log tin (IV) concentration. It has a slope of  $-0.179 \pm 0.014$  which suggests that it is mononuclear tin species and contains one tin atom per molecule.

#### Effect of Hydrobromic Acid Concentration on the Extraction of Tin (IV) by Acid Resistant Foam

Tin (IV) tracer was used to monitor the extraction from hydrobromic acid. Solutions of tin (IV) tracer were prepared in

Table 4 : Effect of the Concentration of Tin (IV) on the Extraction by the Acid Resistant Foam

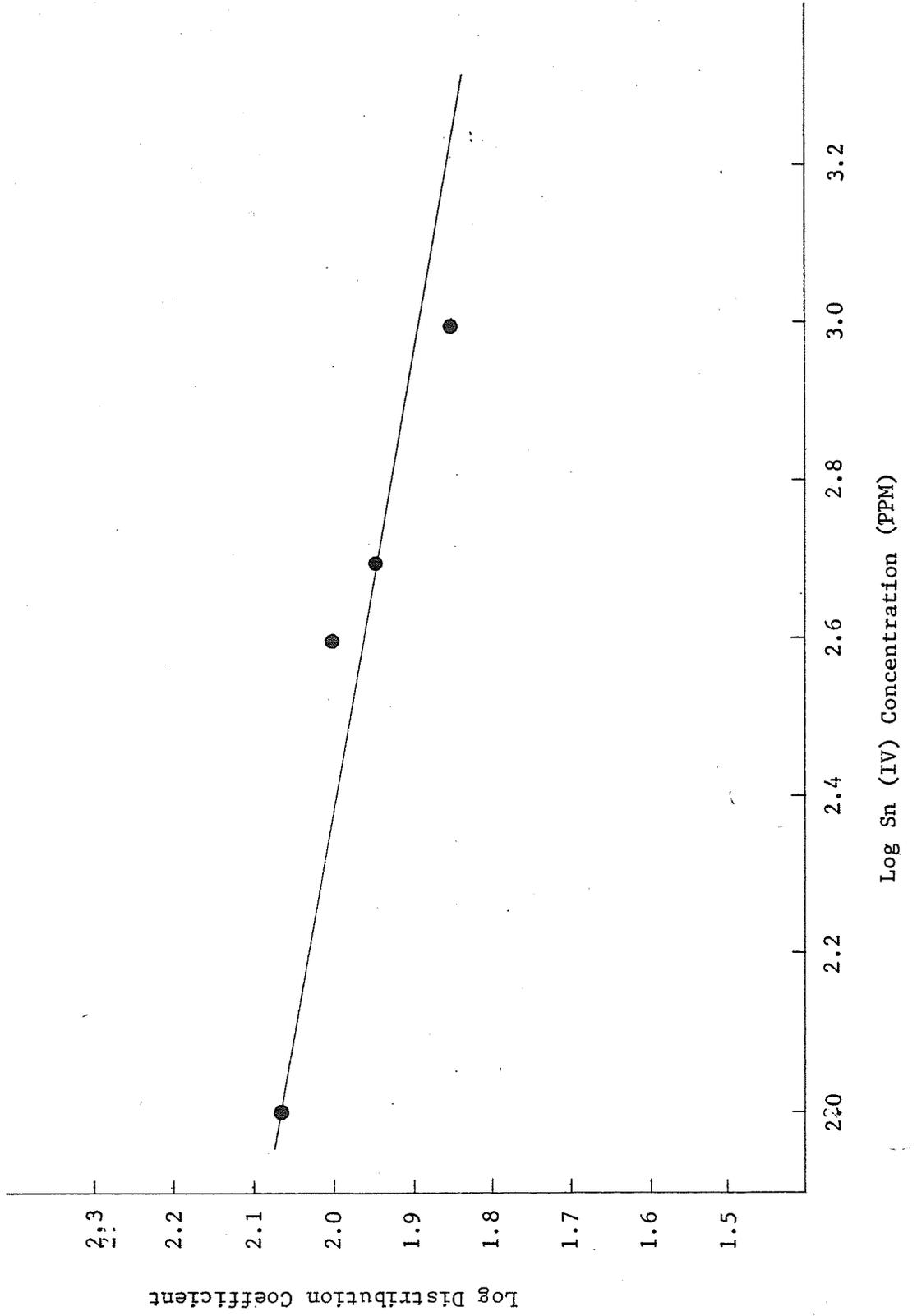
Tin (IV) Concentration (ppm)  ( $1 \times 10^{-4}$ M)	Tracer	100	400	500	1,000
		0.843	3.370	4.213	8.425
Percentage Extracted	37±1	38±1	35±1	33±1	28±1
Distribution Coefficient	115±4	120±4	101±3	90±3	71±3
Weight of Foam (g)	0.5172	0.5496	0.5340	0.5495	0.5456

Squeezing Time : 1 hour

Volume of Solution : 100 ml

HCl Concentration : 4 M

Figure 9b : Variation of log D with log Sn (IV) Concentration at  
4 M HCl



150 ml of hydrobromic acid of varying concentration and squeezed by the multiple squeezer for 2 hours.

Figure 9c shows the effect of HBr concentration on the extraction of tin (IV) by acid resistant foam.

The maximum extraction is shown to be at 7 M HBr. The percentage extraction is higher than the HCl system (60% vs 31%) and the distribution coefficient is  $446 \pm 27$ . This is much higher than that of the diethyl ether system which is reported by Bock and co-workers<sup>59</sup> to be 6.

Although there is an improvement in the percentage of extraction using hydrobromic acid, quantitative extraction is not yet obtained. According to the mechanisms which were previously proposed, the extraction might depend on the hydrogen and/or chloride ion. It is therefore investigated by increasing the chloride concentration using lithium chloride.

Effect of Different Volumes of Tin (IV) solutions in HCl and LiCl on the Extraction by Acid Resistant Foam

Tin (IV) solution was prepared, 100 ppm in 0.12 M HCl and 10 M LiCl (purified). Foam was placed in different volumes of solution and squeezed for 30 minutes.

Table 5 shows that the effect of volume of tin solution on the extraction.

The amount of tin (IV) extracted was better than the maximum amount of tin (IV) extracted in the HCl system. The hydrogen ion concentration was kept fairly low and constant. It is suspected that the increase of extraction would depend on the chloride concentration. The 30 minutes squeezing time may not be long enough for the equilibrium of tin to develop between the foam and solution due to high salt concentration. A time study experiment was therefore carried out.

Figure 9c : The Effect of HBr Concentration on the Extraction of Tin (IV) by Acid Resistant Foam

Tin (IV) Concentration : Tracer

Volume of Solution : 150 ml

Squeezing Time : 2 hours

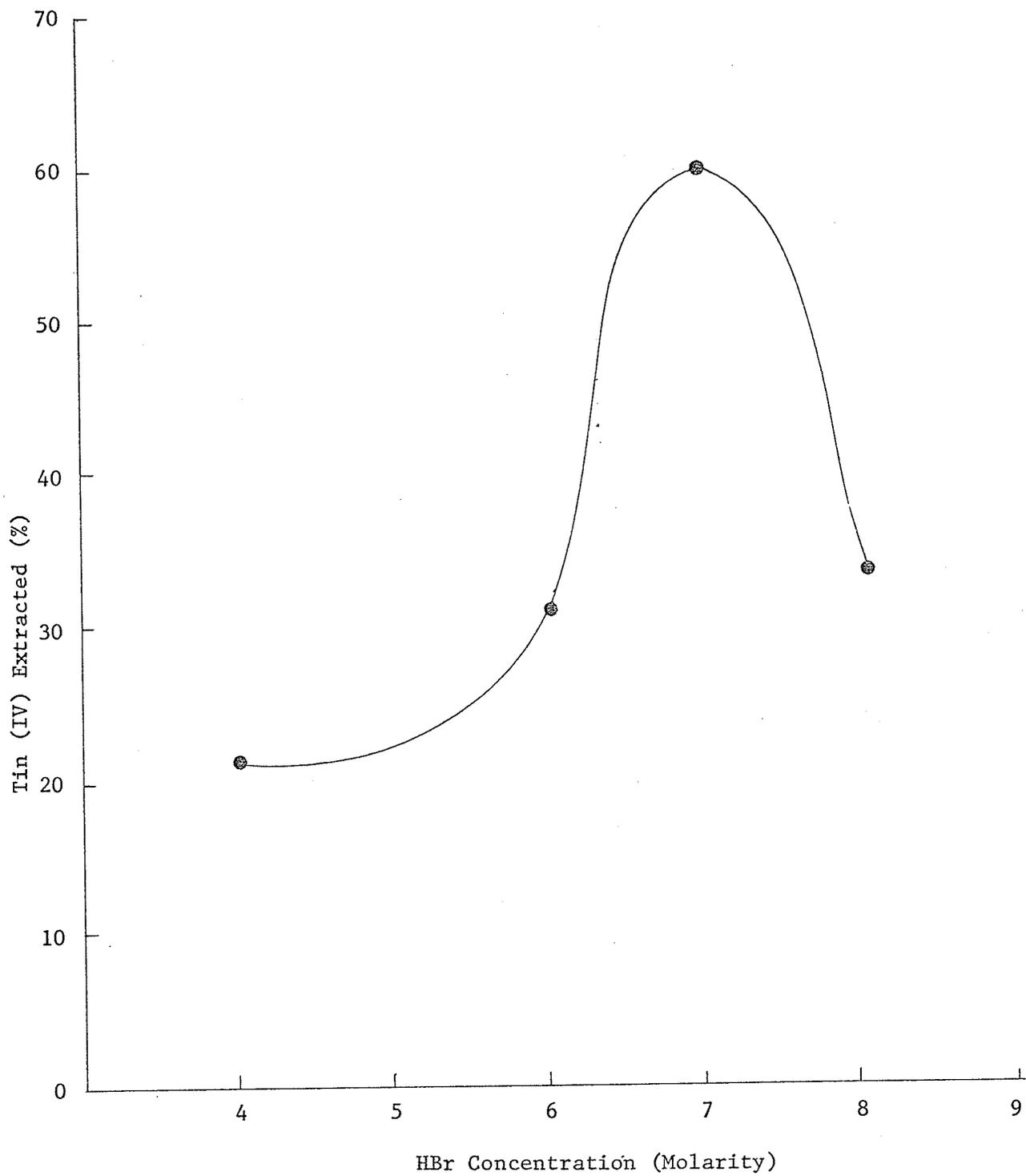


Table 5 : Effect of Volume of Tin (IV) solution on the Extraction by Acid Resistant Foam from Lithium Chloride and HCl

Volume (ml)	10	25	50	100
Tin (mg)	1.0	2.5	5.0	10.0
Percentage Extracted	91±1	81±1	64±1	45±1
Tin in the foam (mg)	0.9	2.0	3.2	4.5
Weight of Foam (g)	0.5465	0.5326	0.5124	0.5448

Tin (IV) Concentration : 100 ppm in 0.12 M HCl and 10 M LiCl

Density of 10 M LiCl : 1.21 g/ml

Squeezing Time : 30 minutes

Effect of Squeezing Time on the Extraction of Tin (IV) from 0.12 M HCl and 10 M LiCl by Acid Resistant Foam

Tin (IV) solution 100 ppm was prepared at 0.12 M HCl and 10 M LiCl. A 50 ml volume was mixed with foam. A 15 ml sample was withdrawn from the cell at proper intervals and its radioactivity determined. The sample was then poured back into the cell until the next determination.

Figure 10 shows the effect of squeezing time on the extraction of tin (IV) from 0.12 M HCl and 10 M LiCl. From the curve, it is observed that the percentage extracted rises rapidly from start to 2 hours and then slows down. The extraction was unchanged after 6 hours. It is considered that the equilibrium has been reached. The experiment was later repeated for five samples and squeezed for 6 hours at  $22.0 \pm 0.5^\circ\text{C}$ . The percentage extraction was  $95 \pm 2\%$  and the distribution coefficient was calculated to be  $2280 \pm 48$ . Quantitative extraction of tin (IV) was thus obtained.

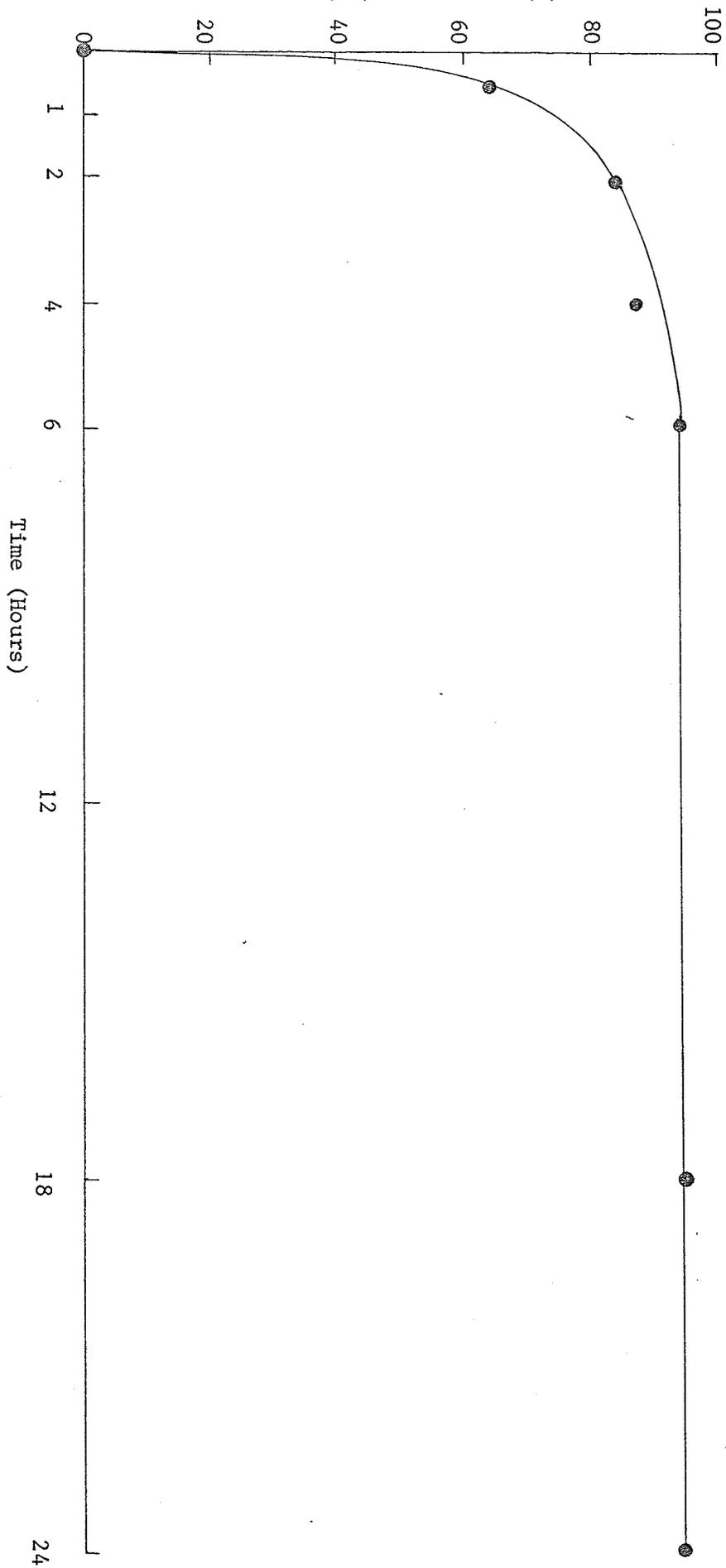
Tin was shown before to be extracted well at 4 M HCl. In order to find out the effect of chloride ion at 4 M HCl in the extraction, an experiment was performed with solutions at 4 M HCl and increasing chloride concentration.

Figure 10 : Effect of Squeezing Time on the Extraction of Tin (IV)  
from 0.12 M HCl and 10 M LiCl by Acid Resistant Foam

Tin (IV) Concentration : 100 ppm

Volume of Solution : 50 ml

Tin (IV) Extracted (%)



Effect of Chloride Concentration at 4 M HCl on the Extraction of Tin (IV) by Acid Resistant Foam

Tin (IV) solutions were prepared at 100 ppm in 4 M HCl and various lithium chloride concentrations. Foams were squeezed with 150 ml of solution by the automatic squeezer for 6 hours at  $22.0 \pm 0.5^\circ\text{C}$ .

Figure 11 shows the effect of increasing chloride concentration on the extraction of tin (IV) from 4 M HCl.

The percentage extraction is constant up to 4.5 M LiCl and then increases slightly to 45% with a distribution coefficient calculated to be  $246 \pm 11$  and a combined chloride concentration of 10.5 M. This distribution coefficient is far less than  $2280 \pm 48$  obtained by 0.12 M HCl and 10 M LiCl. The hydrogen ion is therefore thought to have a negative effect on the extraction of tin (IV) at high acid concentration.

Effect of HCl and LiCl Concentrations on the Extraction of Tin (IV) by Acid Resistant Foam

Tin (IV) solutions at 100 ppm were prepared at a total chloride concentration of 10 M by gradually increasing the HCl concentration while decreasing the LiCl concentration. Solutions of 150 ml were squeezed by the multiple automatic squeezer for 6 hours at  $22.0 \pm 0.5^\circ\text{C}$ .

Figure 12 shows the effect of hydrogen ion on the extraction of tin (IV) by acid resistant foam.

The curve indicates that at high acid concentration the extraction decreases drastically. This agrees with the results of the study before, in which it is proposed the formation of

Figure 11 : Effect of Increasing Chloride Concentration on the Extraction of Tin (IV) by Acid Resistant Foam at 4 M HCl

Tin (IV) Concentration : 100 ppm

Volume of Solution : 150 ml

Squeezing Time : 6 hours

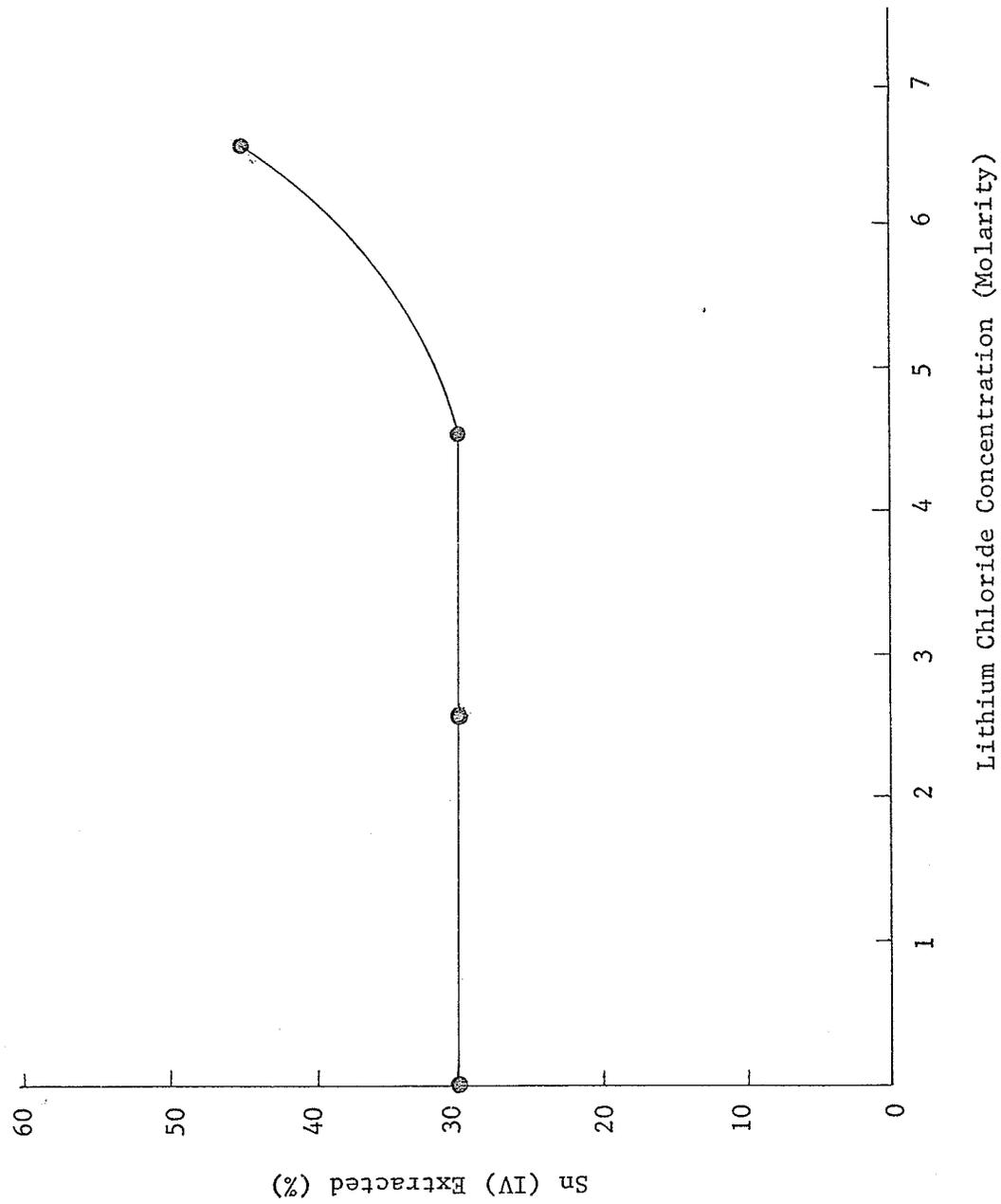
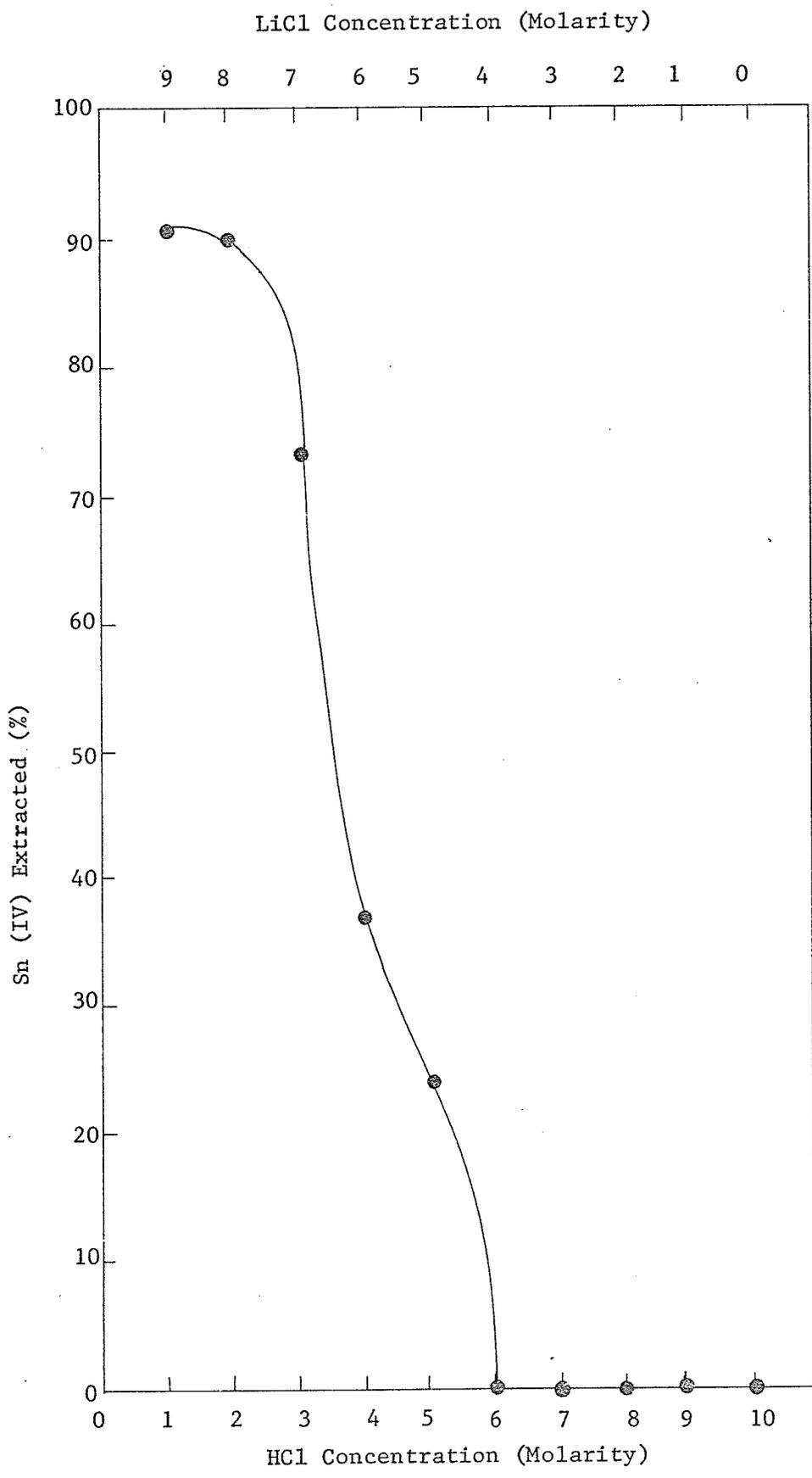


Figure 12 : Effect of HCl and LiCl Concentrations on the Extraction of Tin (IV) by Acid Resistant Foam

Tin (IV) Concentration : 100 ppm

Volume of Solution : 150 ml

Squeezing Time : 6 hours



species which are not well extracted at high HCl concentration. However, it was not known at that time whether the decrease in extraction was due to the hydrogen ion or chloride ion. From the results here, it is the hydrogen ion which contributes to the decrease in extraction. Also, it is observed that the foam swells at high acid concentration. An explanation to this could be the protonation of the foam which causes an expansion of the polymer. The chains of polymer could then be moved apart from each other and bonds between them weakened. As a result, tin complexes could not be effectively bonded to the available sites and consequently the extraction is decreased. Selecting the points from 2, 3, 4 and 5 M hydrogen ion concentration and a plot of  $\log D$  versus  $\log H^+$  ion concentration is shown in figure 12 a.

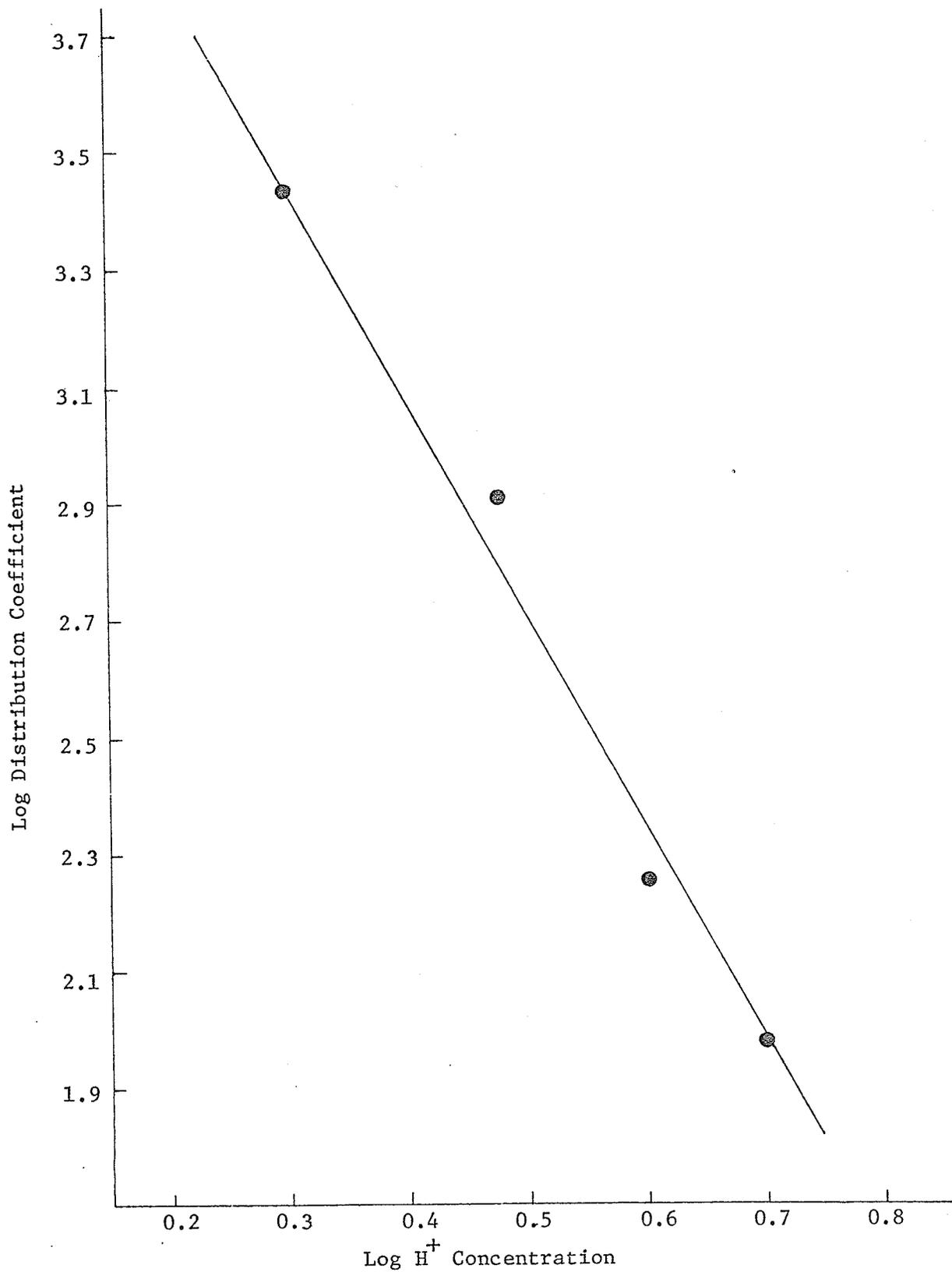
A least square slope of  $-3.8 \pm 0.5$  was obtained. This may indicate the presence of one or a combination of a few non-extractable species bearing a total of three or four hydrogen per species, e.g.  $H_3SnCl_7$ ,  $H_4SnCl_8$  or a combination of  $HSnCl_5$  and  $H_2SnCl_6$ .

#### The Capacity of Tin (IV) on Acid Resistant Foam

The capacity of tin was determined by preparing various amounts of tin (IV) in 0.12 M HCl and 10 M LiCl. A 150 ml solution was mixed with the foam and squeezed for 24 hours at  $22.0 \pm 0.5^\circ C$ . The foams and solutions used were accurately weighed.

Table 6 shows the capacity of tin (IV) on acid resistant foam.

Figure 12a : Variation of Log D with Log  $H^+$  Concentration for Tin (IV)  
by Acid Resistant Foam



The average for the three highest results was calculated to be  $62 \pm 8$  mg/g of foam. Thus, a 6% by weight of tin could be extracted by the acid resistant foam. This is considered to be higher than that due to surface adsorption. The surface area of the foam was shown to be  $0.081 \text{ m}^2/\text{g}$  by the B.E.T. method using Krypton (Mr. P.J. Dawson of Quantochrome Corp., Greenvale, N.Y.).  $\text{SnCl}_4$  was assumed to be the extractable species, one molecule would occupy a surface area of  $7.98 \times 10^{-19} \text{ m}^2$ . The 6% by weight of tin would need an area of  $111 \text{ m}^2/\text{g}$  of foam if the extractable species was just on the surface of the foam.

Table 6 : The Capacity of Tin (IV) on Acid Resistant Foam

Tin (IV) Concentration (ppm)	1,000	800	600	400	200
Tin (IV) (mg)	150	120	90	60	30
Percentage Extracted	23±2	27±2	30±2	40±2	55±2
Weight of Tin (IV) Extracted (mg)	35±3	32±2	27±2	24±1	16±1
Capacity (Weight of Tin (IV) Extracted/ g of foam)	68±6	63±4	54±4	47±2	31±2
Weight of Foam (g)	0.5117	0.5114	0.5123	0.5109	0.5128

Squeezing Time : 24 hours

Volume of Solution : 150 ml

Density of Solution : 1.21 g/ml

### Recovery of Tin (IV) from Acid Resistant Foam

Tin (IV) was first loaded on the foam using the optimum conditions previously stated (50 ml volume, 100 ppm in 0.12 M HCl and 10 M LiCl and squeezed for 6 hours at  $22.0 \pm 0.5^\circ \text{C}$ ). Water, 0.1 M sodium hydroxide, and 0.1 M hydrochloric acid were tested to recover tin (IV) from the foam. An equal amount of solution, i.e. 50 ml was used and squeezed for the same length of time as in extraction. The resulting solution was then counted. Since the radioactivity was counted in different media, the counts had to be corrected before calculation. The correction factor was calculated to be  $1.40 \pm 0.02$

$$f = \frac{12399 \pm 111}{8856 \pm 94} = 1.40 \pm 0.02$$

for tin tracer in 0.1 M HCl to 0.12 M HCl and 10 M LiCl.

Water and sodium hydroxide were shown in preliminary experiments to recover only 40 to 50 % of the tin extracted. using 0.1 M HCl,  $95 \pm 3\%$  of tin was recovered.

$$\% \text{ Stripping} = \frac{24654 \pm 157}{19529 \pm 140 \times 1.40 \pm 0.02} \times 100 = 90 \pm 2$$

$$\% \text{ Recovery} = \frac{90 \pm 2}{95 \pm 2} \times 100 = 95 \pm 3$$

### (C) Extraction of Tin (IV) by Regular Polyurethane Foam

It was shown in the previous section that quantitative extraction and recovery of tin (IV) from aqueous solution is possible using acid resistant foam. The acid resistant foam is not commercially available. To study the extraction of tin (IV) using products readily available (the most feasible method for commercial application), the commercially available regular polyurethane foam was used.

#### Effect of HCl Concentration on the Extraction of Tin (IV) by Regular Polyurethane Foam

Tin-119m tracer was used in various HCl concentrations. The foam was allowed to mix with a 150 ml of solution and squeezed by the multiple squeezer for 2 hours.

Figure 13 shows a maximum at 3 M HCl and a distribution coefficient equal to  $141 \pm 9$ . The decrease in extraction after 3 M HCl could be due to the hydrogen ion which causes the formation of some not well extracted species and protonation of the sites on the foam. In order to obtain quantitative extraction, an increase of chloride concentration in the extraction was investigated.

Figure 13a shows the plot of log D against log HCl concentration.

The graph shows a curve and deviates from what is expected from an assumption which was developed according to the following equilibrium reactions.

Figure 13 : Effect of HCl Concentration on the Extraction of Tin (IV)  
by Regular Polyurethane Foam

Squeezing Time : 2 hours

Volume of Solution : 150 ml

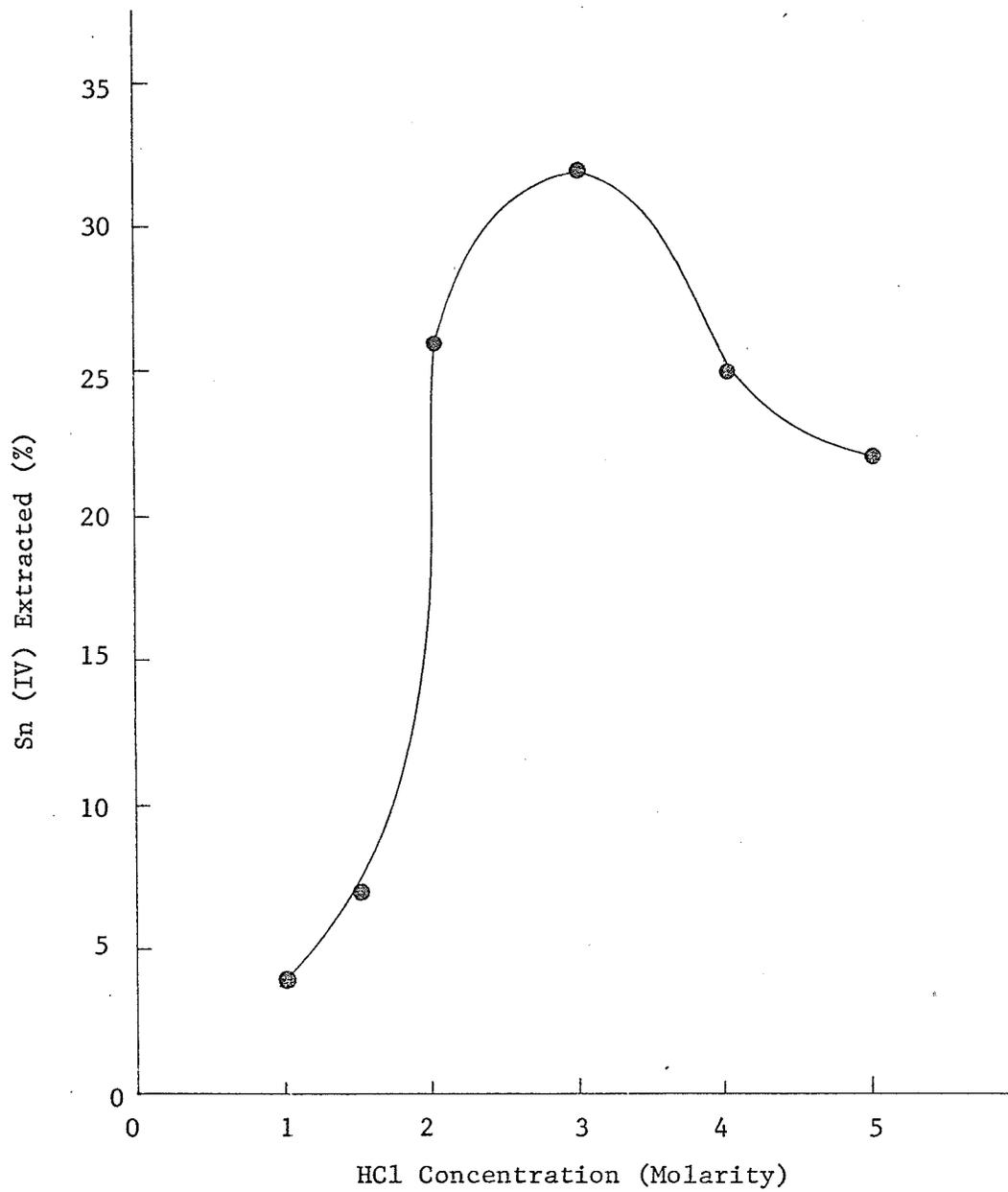
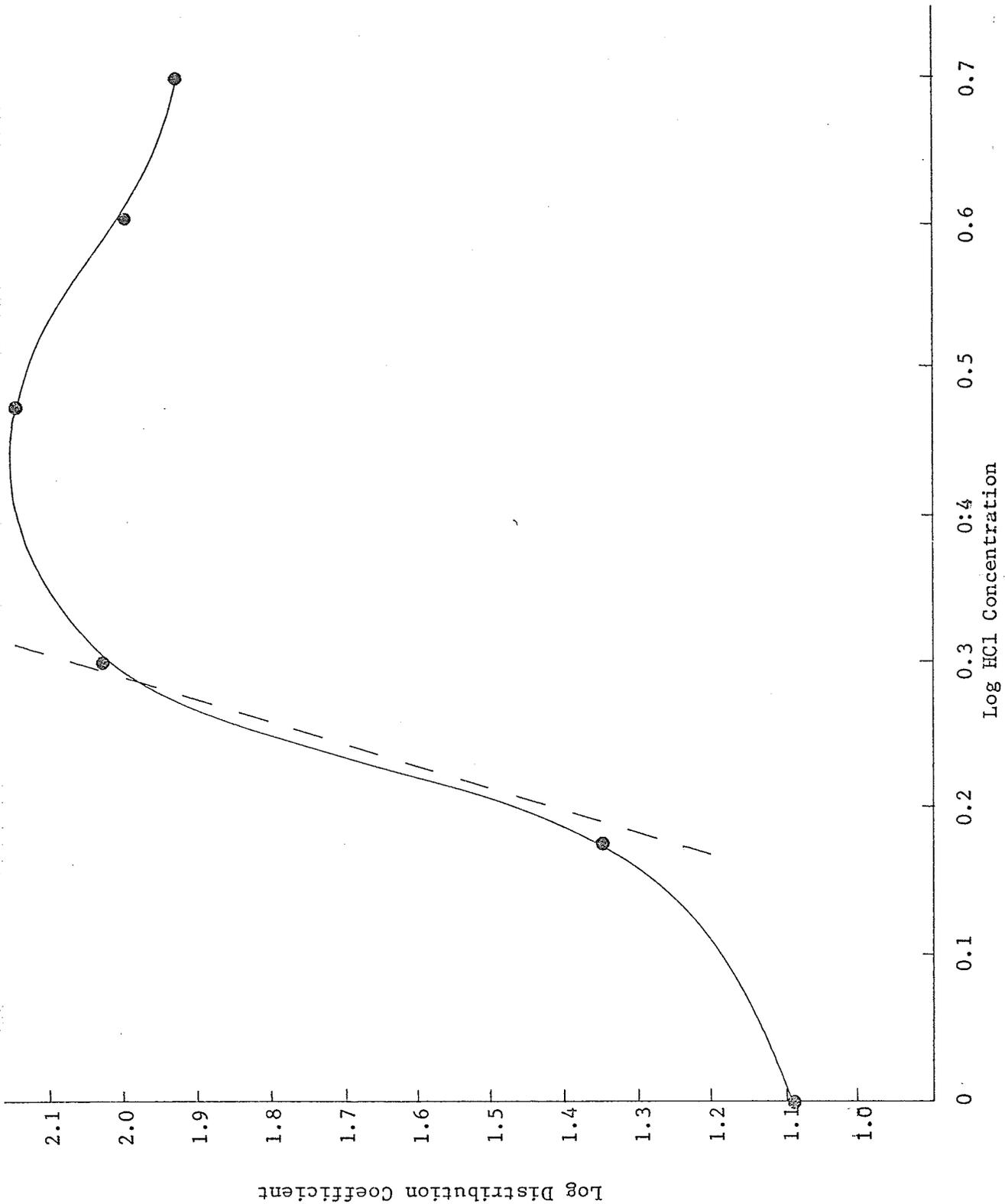
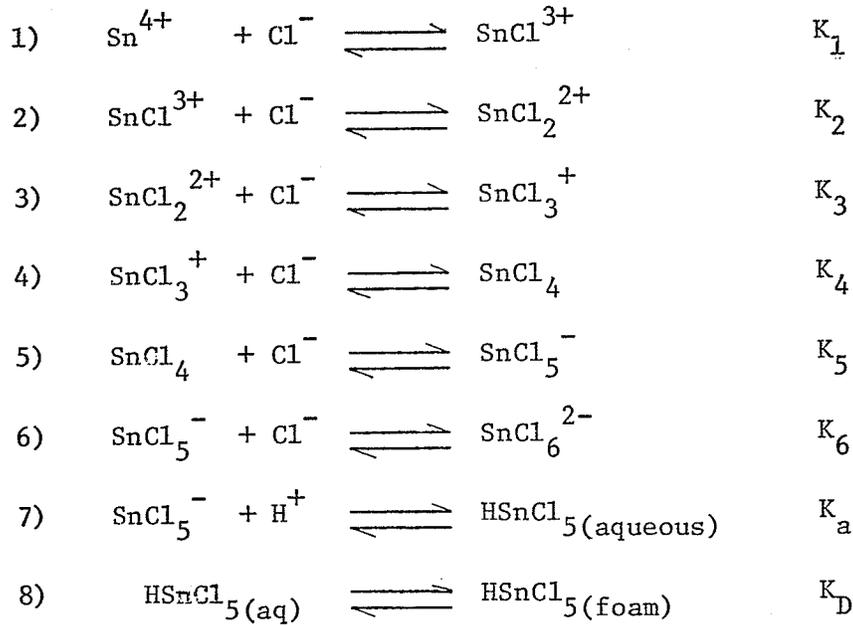


Figure 13a : Variation of Log D with Log HCl Concentration for  
Tin (IV) Tracer





where

$$9) \quad K_D = \frac{[\text{HSnCl}_5]_{\text{foam}}}{[\text{HSnCl}_5]_{\text{aqueous}}}$$

and

$$10) \quad K_a = \frac{[\text{HSnCl}_5]_{\text{aqueous}}}{[\text{SnCl}_5^-] [\text{H}^+]}$$

Let

$$\begin{aligned}
 K' &= K_1 K_2 K_3 K_4 K_5 \\
 &= \frac{[\text{SnCl}_5^-]_{\text{aqueous}}}{[\text{Sn}^{4+}] [\text{Cl}^-]^5}
 \end{aligned}$$

$$11) \quad K_D = \frac{[\text{HSnCl}_5]_{\text{foam}}}{K' K_a [\text{Sn}^{4+}] [\text{H}^+] [\text{Cl}^-]^5}$$

It is assumed that the extractable species is  $\text{HSnCl}_5$ .

The distribution coefficient,  $D$ , is the ratio of tin in the foam to all the tin in solution for the extraction process.

$$12) \quad D = \frac{[\text{HSnCl}_5]_{\text{foam}}}{[\text{Sn}^{4+}] + [\text{SnCl}^{3+}] + [\text{SnCl}_2^{2+}] + [\text{SnCl}_3^{\ddagger}] + [\text{SnCl}_4] + [\text{SnCl}_5^-] + [\text{SnCl}_6^{2-}] + [\text{HSnCl}_5]_{\text{aqueous}}}$$

$$13) \quad D = \frac{[\text{HSnCl}_5]_{\text{foam}}}{[\text{Sn}^{4+}] (1 + K_1[\text{Cl}^-] + K_1K_2[\text{Cl}^-]^2 + K_1K_2K_3[\text{Cl}^-]^3 + K_1K_2K_3K_4[\text{Cl}^-]^4 + K_1K_2K_3K_4K_5[\text{Cl}^-]^5 + K_1K_2K_3K_4K_5K_6[\text{Cl}^-]^6 + K_aK_1K_2K_3K_4K_5[\text{H}^+][\text{Cl}^-]^5)}$$

The stability constants (K's) are not available. Therefore, it is assumed that all the constants except,  $K_1$ , are much smaller than unity and may be neglected.

$$14) \quad D = \frac{[\text{HSnCl}_5]_{\text{foam}}}{[\text{Sn}^{4+}](1+K_1[\text{Cl}^-])} = \frac{K_D K'_a K_a [\text{H}^+][\text{Cl}^-]^5}{(1+K_1[\text{Cl}^-])}$$

$$15) \quad \log D + \log(1+K_1[\text{Cl}^-]) = \log K + \log [\text{H}^+] + 5\log[\text{Cl}^-]$$

where  $K = \text{constant}$

when  $[\text{H}^+] = [\text{Cl}^-]$ ,

$$16) \quad \log D + \log(1+K_1[\text{Cl}^-]) = \log K + 6\log[\text{HCl}]$$

A further approximation, the  $\log(1+K_1[\text{Cl}^-])$  term may be neglected, and a plot of  $\log D$  against  $\log [\text{HCl}]$  is shown in Fig. 13a where it is a curve compared with a slope of 6 expected.

The deviation is probably due to several factors such as the change in ionic strength studied over the wide range of acidity, a high hydrogen concentration is shown in the acid resistant foam section has a negative effect on the extraction, the unknown effect of hydrogen ion on the foam and the effect of hydrogen and chloride ions on the extractable species. It seems that the extraction relies more on the chloride ion for quantitative extraction with a minimum requirement of hydrogen

ion. Since both variables, namely the hydrogen and chloride ions are changing at the same time, it would be difficult to compare results to such a theoretical approximation.

Effect of Lithium Chloride on the Extraction of Tin (IV) by Regular Polyurethane Foam

Tin (IV) solutions were prepared at 100 ppm in 0.12 M HCl and different concentrations of lithium chloride. A 150 ml of solution was used and mixed well with the foam for 24 hours by squeezing with the multiple automatic squeezer at  $22.0 \pm 0.5^\circ\text{C}$ .

Figure 14 shows the effect of chloride concentration on the extraction of tin (IV).

The curve shows a gradual increase in extraction as the concentration of chloride goes up. It appears from this experiment that the extraction of tin (IV) is chloride dependent. The maximum distribution coefficient was calculated to be  $5630 \pm 120$ .

In another experiment with 50 ml of solution, it was found that  $98 \pm 2\%$  of tin (IV) was extracted and a squeezing time of 6 hours would be adequate.

Figure 14a shows a plot of log distribution coefficient against log chloride concentration.

The hydrogen concentration was 0.12 M. The assumption in the previous is again used. Since the hydrogen concentration is small and is therefore neglected. Equation 15) would become:  
 17)  $\log D + \log(1 + K_1 [Cl^-]) = \log K + 5 \log [Cl^-]$   
 and a further approximation, the  $\log(1 + K_1 [Cl^-])$  may be neglected and a plot of  $\log D$  against  $\log [Cl^-]$  is shown in figure 14a where

a slope of  $4.9 \pm 0.2$  is obtained from 4.12 to 7.12 M of chloride.

The extractable species would probably contain five chloride atoms which is  $\text{HSnCl}_5$ . The results seem to agree with the expected value which indicates that the extractable species is highly chloride dependent. The hydrogen ion does not affect the extraction at such low concentration.

Figure 14 : Effect of Chloride Concentration on the Extraction of Tin (IV) by Regular Polyurethane Foam

Tin (IV) Concentration : 100 ppm

Volume of Solution : 150 ml

Squeezing Time : 24 hours

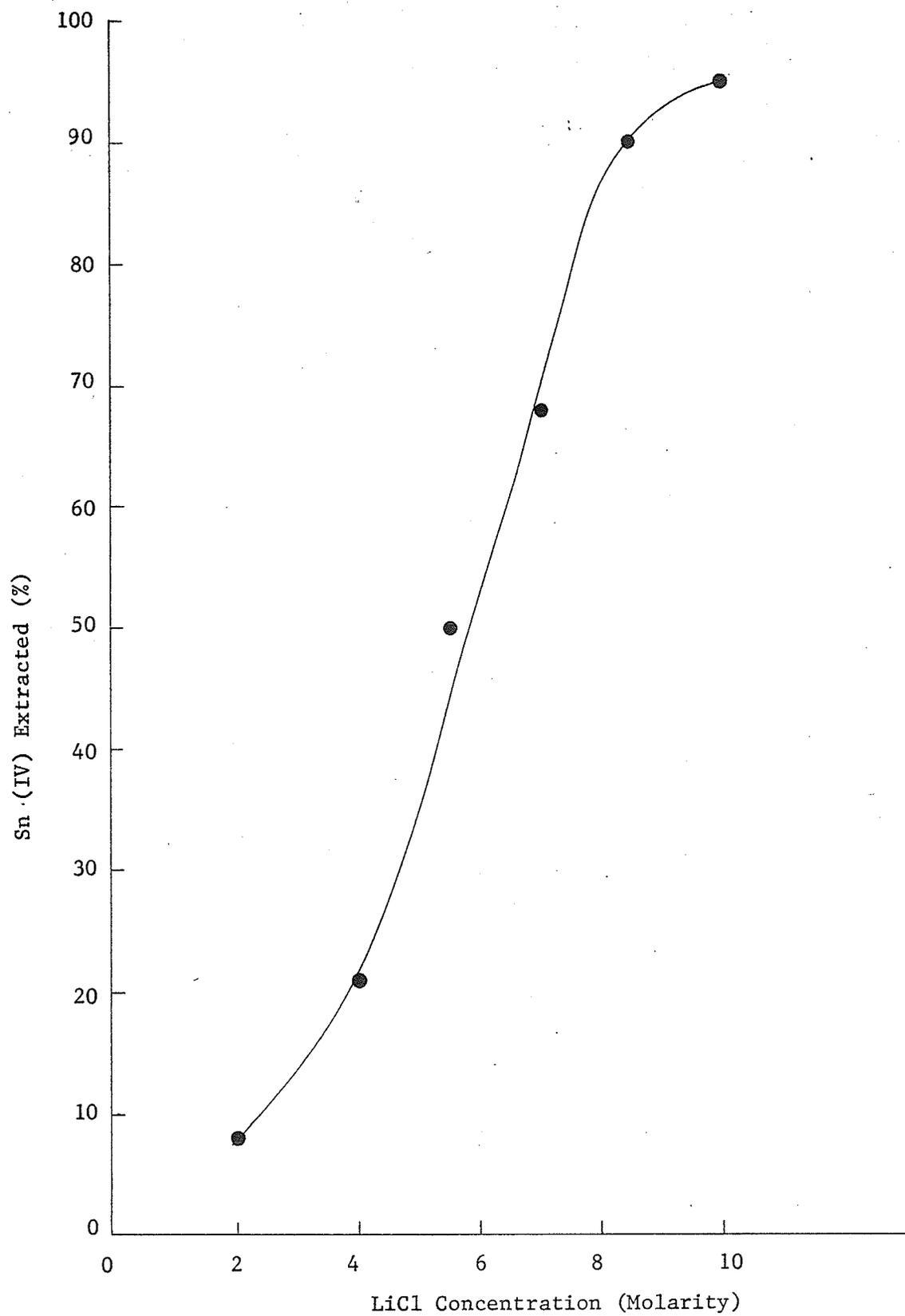
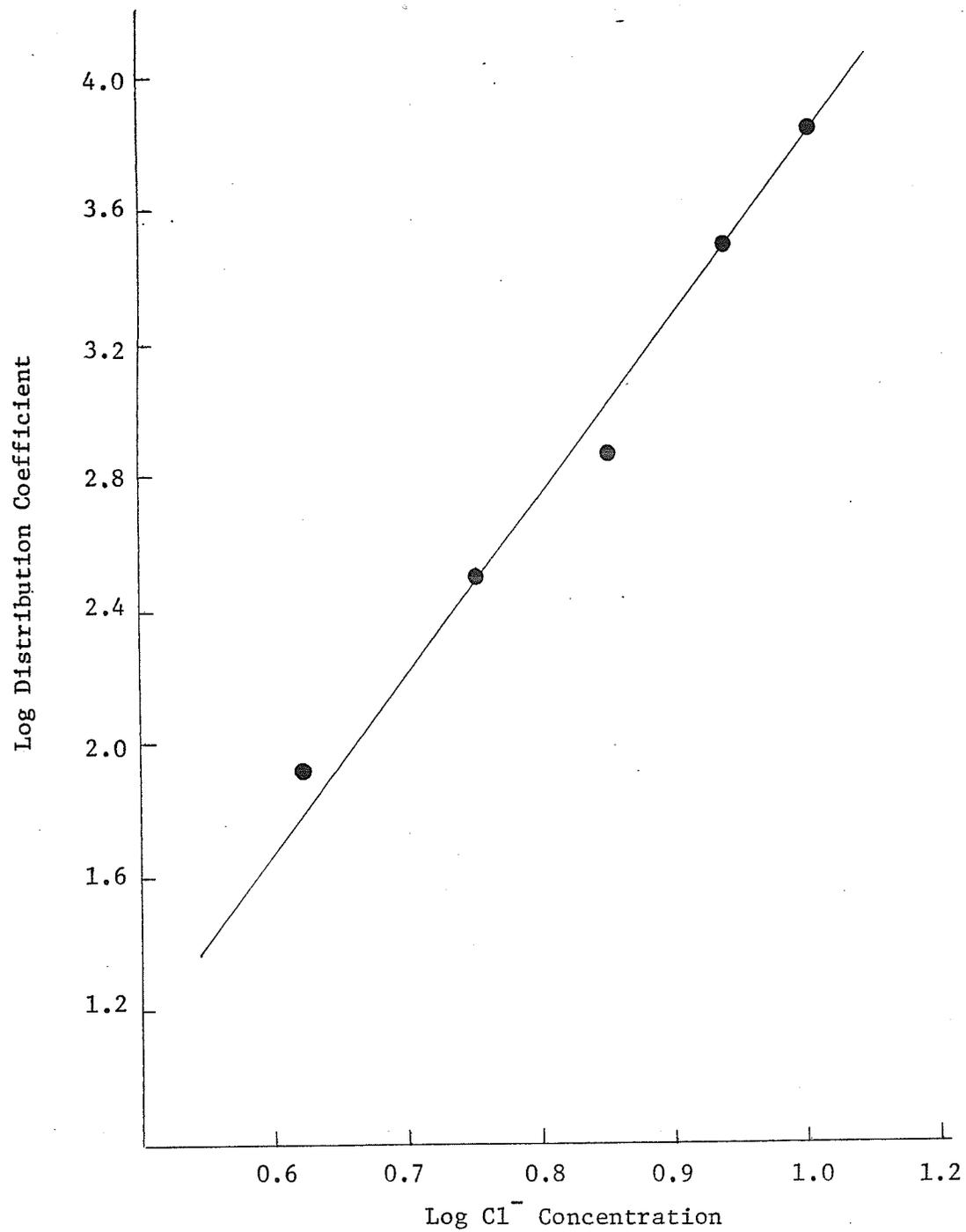


Figure 14 a : Variation of Log Distribution Coefficient with  
Log  $\text{Cl}^-$  Concentration for 100 ppm of Tin (IV) at  
0.12 M HCl



Recovery of Tin (IV) from Regular Polyurethane Foam

Tin (IV) at 100 ppm was first loaded on the foam from 0.12 M HCl and 10 M LiCl. A 50 ml of 0.1 M HCl was used to recover tin (IV) from the foam and squeezed for 6 hours.

A 95±3% of tin (IV) was recovered from the foam.

$$\% \text{ Stripping} = \frac{26620 \pm 160}{20440 \pm 140 \times 1.40 \pm 0.02} \times 100 = 93 \pm 2$$

$$\% \text{ Recovery} = \frac{93 \pm 2}{98 \pm 2} \times 100 = 95 \pm 3$$

Acetone was used to recover the tin and the percentage recovery determined by counting the residual activity on the foam. The procedures of loading and recovery of tin (IV) were the same as before except that the foam was now counted instead of the solution.

$$\begin{aligned} \% \text{ Recovery} &= \frac{71640 \pm 270 - 901 \pm 30}{71640 \pm 270} \times 100 \\ &= 98.7 \pm 0.5 \end{aligned}$$

It is found that acetone could recover more tin than 0.1 M HCl and the results showed better precision due to a smaller standard deviation in the determination of the unrecovered rather than the recovered radioactivity.

### The Capacity of Tin (IV) on the Extraction by Regular Polyurethane Foam

Different tin (IV) concentrations were prepared from stock solution in 0.12 M HCl and 10 M LiCl. Foams and 150 ml solution were accurately weighed and mixed for 24 hours by squeezing with the multiple automatic squeezer at  $22.0 \pm 0.5^\circ \text{C}$ .

Table 7 shows the capacity of tin (IV) on regular polyurethane foam.

The average of the three highest results was calculated to be  $81 \pm 9$  mg/g of foam. Therefore, a 8% by weight of tin could be extracted by regular polyurethane foam. This further confirms the previous proposed absorption hypothesis for tin extraction by polyurethane foam.

### Effect of Interfering Compounds on the Extraction of Tin (IV) by Regular Polyurethane Foam

Stock solutions at 10,000 ppm of  $\text{BiCl}_3$ ,  $\text{CuCl}_2$ ,  $\text{FeCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{SbCl}_3$ ,  $\text{SbCl}_5$  and  $\text{ZnCl}_2$  were prepared. A 100 ml of solution was made up containing 100 ppm of tin (IV) in 3 M HCl and with either 100 ppm or 1,000 ppm of the corresponding compound. Foams were weighed and mixed with the solution. It was squeezed for 2 hours.

Table 8 shows the effect of interfering compounds on the extraction of tin (IV) by regular polyurethane foam. The effect of interference was not significant for most of the compounds studied except for iron (III) at 1,000 ppm. It could be due to the fact that iron (III) was quantitatively extracted by the foam. The

Table 7 : The Capacity of Tin (IV) on Regular Polyurethane Foam

Tin (IV) Concentration (ppm)	1,000	800	600	400	200
Tin (IV) (mg)	150	120	90	60	30
Percentage Extracted	29±2	33±2	45±2	54±2	89±2
Weight of Tin (IV) Extracted (mg)	44±3	40±3	41±2	32±2	27±5
Capacity (Weight of Tin (IV) Extracted/ g of foam)	86±6	78±6	80±4	62±4	54±10
Weight of Foam (g)	0.5091	0.5169	0.5136	0.5135	0.5024

Density of Solution : 1.21 g/ml

Squeezing Time : 24 hours

Volume of Solution : 150 ml

HCl Concentration : 0.12 M

LiCl Concentration : 10 M

Table 8 : Effect of Interfering Compounds on the Extraction of Tin (IV) by Regular Polyurethane Foam

Added Compound	Concentration (ppm)	Percentage Extracted
None		31±2
BiCl <sub>3</sub>	100	27±2
	1,000	26±2
CuCl <sub>2</sub>	100	33±2
	1,000	30±2
FeCl <sub>2</sub>	100	33±2
	1,000	28±2
FeCl <sub>3</sub>	100	34±2
	1,000	18±2
SbCl <sub>3</sub>	100	32±2
	1,000	27±2
SbCl <sub>5</sub>	100	32±2
	1,000	32±2
ZnCl <sub>2</sub>	100	33±2
	1,000	27±2

HCl Concentration : 3 M

Sn(IV) Concentration : Tracer

iron (III) species compete with tin (IV) complexes for the sites available on the foam to be extracted. Thus, the extraction of iron (III) by the foam would lower the extraction of tin (IV). The other compounds studied were selected because they are usually present in tin ore which could interfere with the extraction of tin in other extraction and separation systems.

Effect of Different Acids on the Extraction of Tin (IV) by Regular Polyurethane Foam

Tin-119m tracer at 0.07 M was used

in 50 ml of HF and HCl which were prepared at 1 M.

Also, the tracer was used in 150 ml solutions of 3 M HF, HCl, HBr and HI.

Tin (IV) was not extracted from 1 M HF and had a  $15 \pm 1\%$  extraction from 1 M HCl. At 3 M acid concentration, 0% of tin (IV) was extracted from HF,  $32 \pm 2\%$  from HCl,  $18 \pm 4\%$  from HBr and  $32 \pm 1\%$  from HI. It appeared that at 3 M acid, tin (IV) was extracted about the same from HCl and HI and lower from HBr, none from HF. The solvent extraction system for diethyl ether in the extraction of tin (IV) was 17% from 6 M HCl and 85.4% from 4 M HBr. It was shown earlier in the acid resistant foam system that the HBr curve had a higher maximum extraction than the HCl system (60% at 7 M HBr vs 31% at 3 M HCl). In effect, tin is extracted better from HBr than from HCl, however, it is extracted better from HCl at 3 M. Therefore, one cannot say that the extraction increases or decreases as we go down the periodic table from fluoride to iodide after squeezing for 2 hours.

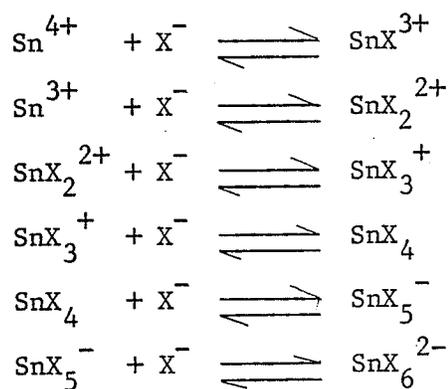
Effect of Metal Halides on the Extraction of Tin (IV) Tracer by Regular Polyurethane Foam

A 50 ml sodium fluoride and sodium chloride solution was prepared at 1 M. Also, the chloride, bromide and iodide of lithium, sodium and potassium were prepared at 3 M. A 150 ml volume at 3 M halide solution was made up and tracer was then added and squeezed for 2 hours.

For 1 M of NaF, a 1±1% of tin (IV) was extracted while a 15±1% was extracted from 1 M NaCl.

Table 9 shows the effect of halides on the extraction of tin (IV) tracer.

As from the table, it is observed as the size of the cation of the halide increases, the extraction increases as well. There is an increase in extraction as the size of the anion is increased from chloride to bromide. The extraction of tin (IV) tracer from the bromide and iodide are identical. When tin (IV) tracer was added into the solution of halides, the following equilibrium may be established:



where X is F, Cl, Br or I.

Table 9 : Effect of Metal Halides on the Extraction of Tin (IV) by Regular Polyurethane Foam

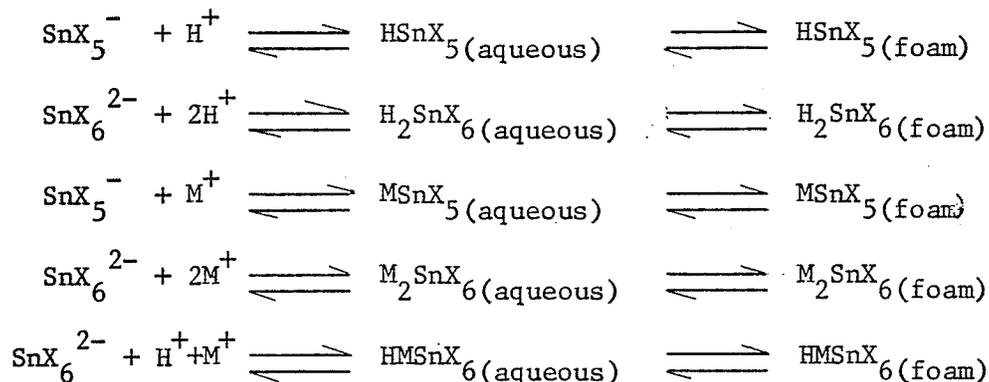
Metal Halide	LiCl	NaCl	KCl
Percentage Extracted	14±2	25±2	34±2
Metal Halide	LiBr	NaBr	KBr
Percentage Extracted	33±2	38±2	40±4
Metal Halide	LiI	NaI	KI
Percentage Extracted	28±2	37±2	39±4

Volume of Solution : 50 ml

Squeezing Time : 2 hours

Concentration of Metal Halides : 3 M

An extractable species could be formed when:



where C is Li, Na or K.

It could be that the formation of the heavier anion would be more favorable in the extraction of tin (IV) by the foam. Irving and Rossotti<sup>80</sup> has reported the possibility of finding the species  $\text{NaInBr}_4$  in the extraction of indium by isobutyl methyl ketone.

It could be possible that a species like  $\text{M}_2\text{SnX}_6$  is present.

## Part II

### Extraction of Antimony by Polyurethane Foams

The only previous report of the extraction of antimony by polyurethane foam was by Bowen<sup>5</sup> who examined briefly the extraction of antimony (V) from 6 M HCl. The distribution coefficient was found by Bowen to be between 75-500. The present study investigated the absorption of antimony (III) and antimony (V) by polyurethane foams from solutions of various HCl and LiCl concentrations.

Effect of HCl Concentration on the Extraction of Antimony by  
Acid Resistant Foam

Antimony<sup>124</sup> trichloride and antimony<sup>124</sup> pentachloride tracers at 0.006 M were used in various concentrations of HCl. A 150 ml volume was used and squeezed by the multiple automatic squeezer for 2 hours. Samples were taken at 30 minutes, 1 hour and 2 hours. The radio-activity was determined by the scintillation counter.

Table 10 indicates the extraction of antimony<sup>124</sup> trichloride tracer in various concentrations of HCl at different time intervals.

Table 11 indicates the extraction of antimony<sup>124</sup> penta-chloride tracer in various concentrations of HCl at different time intervals.

Figure 15 shows the plot of antimony (III) extracted (%) by regular polyurethane foam vs HCl concentration of solution.

Figure 16 shows the plot of antimony (V) extracted (%) by regular polyurethane foam vs HCl concentration of solution.

The time for antimony (III) and antimony (V) to reach equilibrium as shown in tables 10 and 11 is less than two hours. This was chosen to be the time for equilibrium because the percentage of extraction for most of the solutions did not change over the period from 1 hour to 2 hours. The exception was for both antimony (III) and antimony (V) solutions at 5 M HCl. However, it was considered that 2 hours should be adequate for all the solutions to reach equilibrium.

Figure 15 and figure 16 display the change in percentage extraction over different HCl concentrations for antimony (III) and

Table 10 : Effect of HCl Concentration and Squeezing Time on the Extraction of Sb (III) Tracer by Acid Resistant Foam

HCl Concentration (Molarity)	Percentage Extracted		
	30 minutes	1 hour	2 hours
4	6±2	6±2	6±2
5	17±1	23±1	28±1
6	46±1	51±1	52±1
7	62±2	61±2	60±2
8	44±1	44±1	46±1

Volume of Solution : 150 ml

Table 11 : Effect of HCl Concentration and Squeezing Time on the Extraction of SB (V) Tracer by Acid Resistant Foam

HCl Concentration (Molarity)	Percentage Extracted		
	30 minutes	1 hour	2 hours
4	3±1	4±1	6±2
5	15±1	20±1	26±1
6	49±1	54±1	53±1
7	65±1	66±1	66±1
8	55±2	55±2	54±2

Volume of Solution : 150 ml

Figure 15 : Effect of HCl Concentration on the Extraction of Antimony (III) Tracer by Acid Resistant Foam

Volume of Solution : 150 ml

Squeezing Time : 2 hours

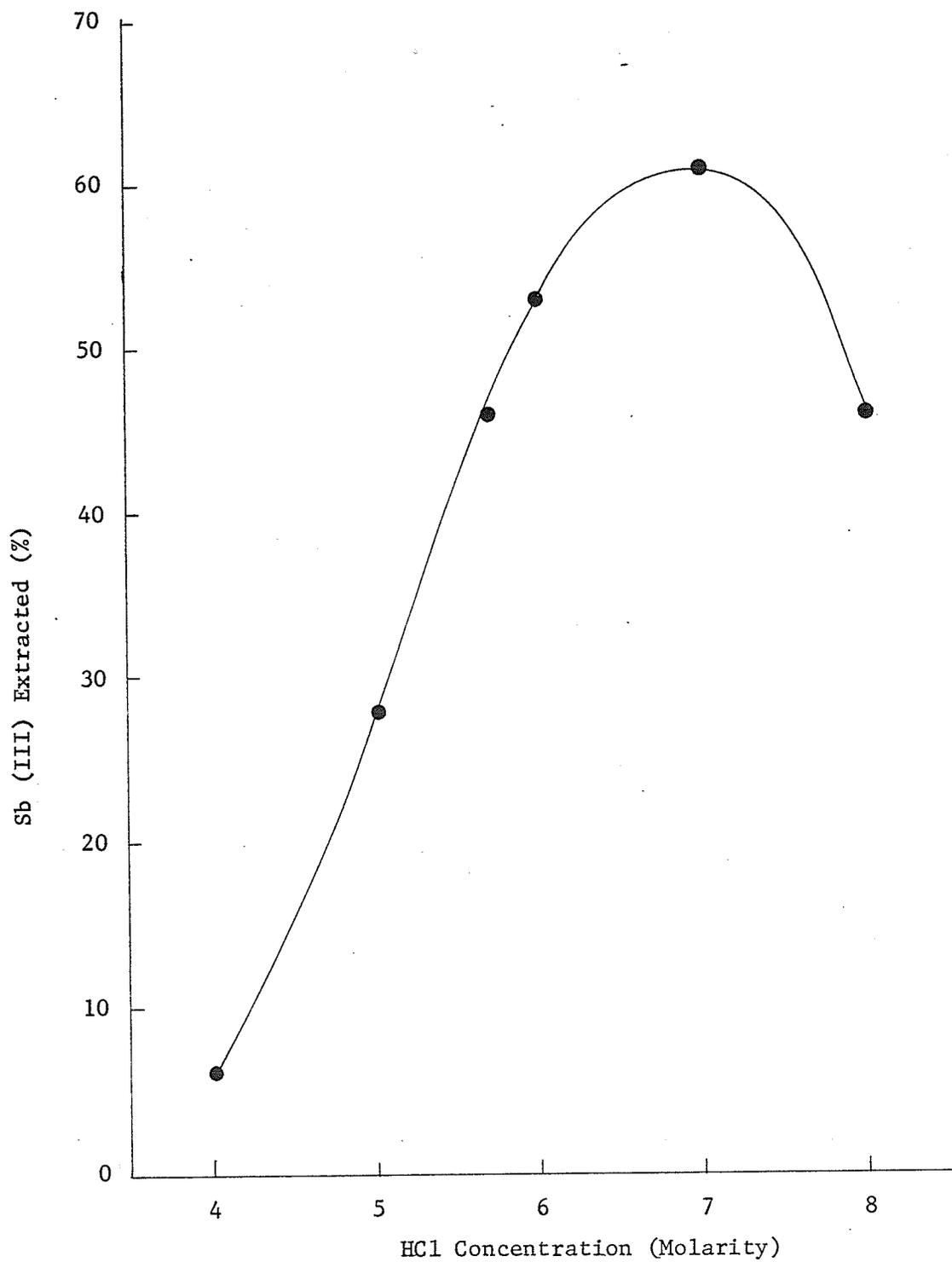


Figure 15a : Variation of  $\text{Log } D + \text{Log}(K_1 K_2 K_3 K_4 [\text{Cl}^-]^4 + K_1 K_2 K_3 K_4 K_5 [\text{Cl}^-]^5 + K_1 K_2 K_3 K_4 K_5 K_6 [\text{Cl}^-]^6)$  with  $\text{Log HCl}$  Concentration for Antimony (III) Tracer

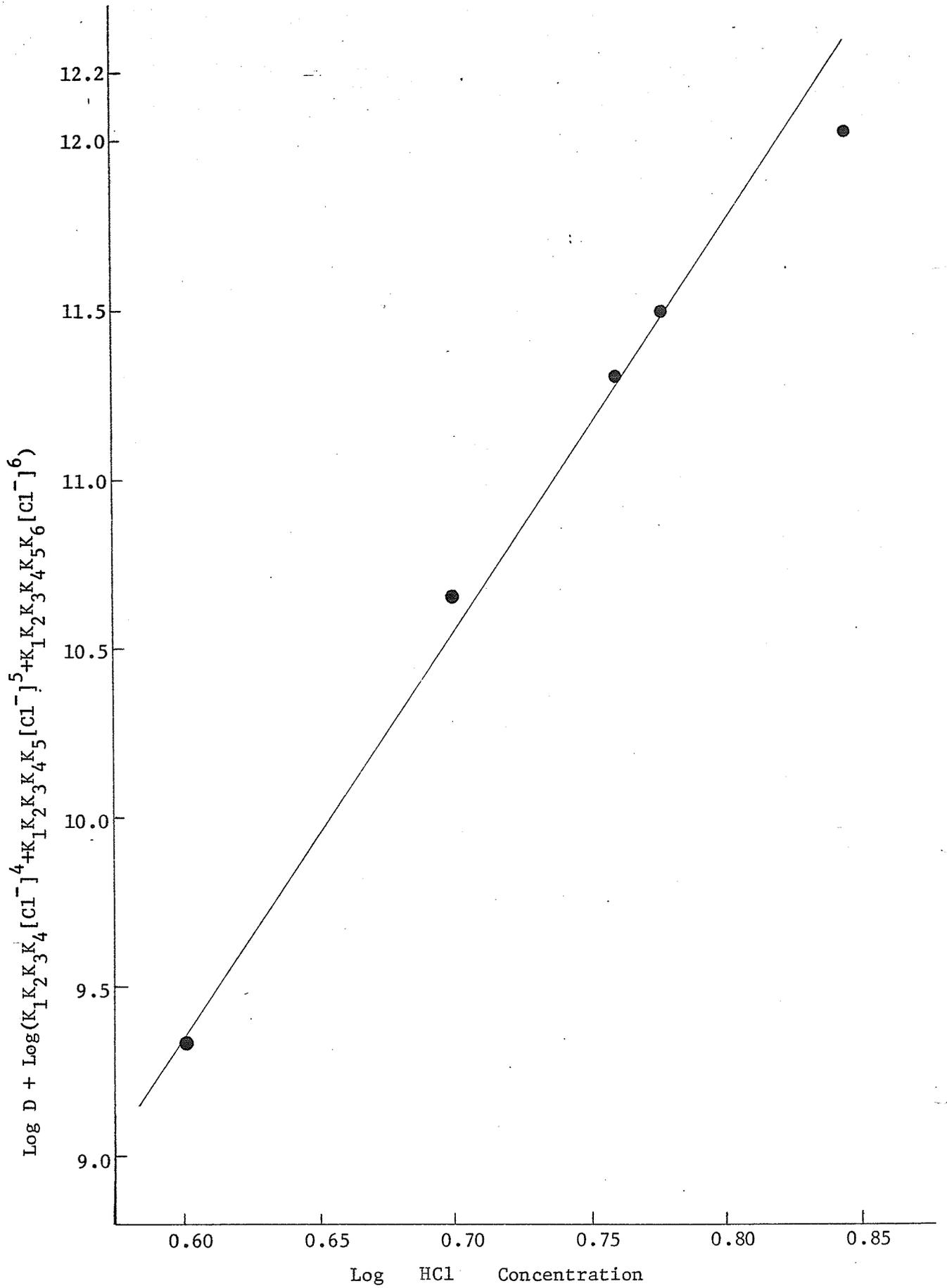


Figure 16 : Effect of HCl Concentration on the Extraction of Antimony (V) Tracer by Acid Resistant Foam

Volume of Solution : 150 ml

Squeezing Time : 2 hours

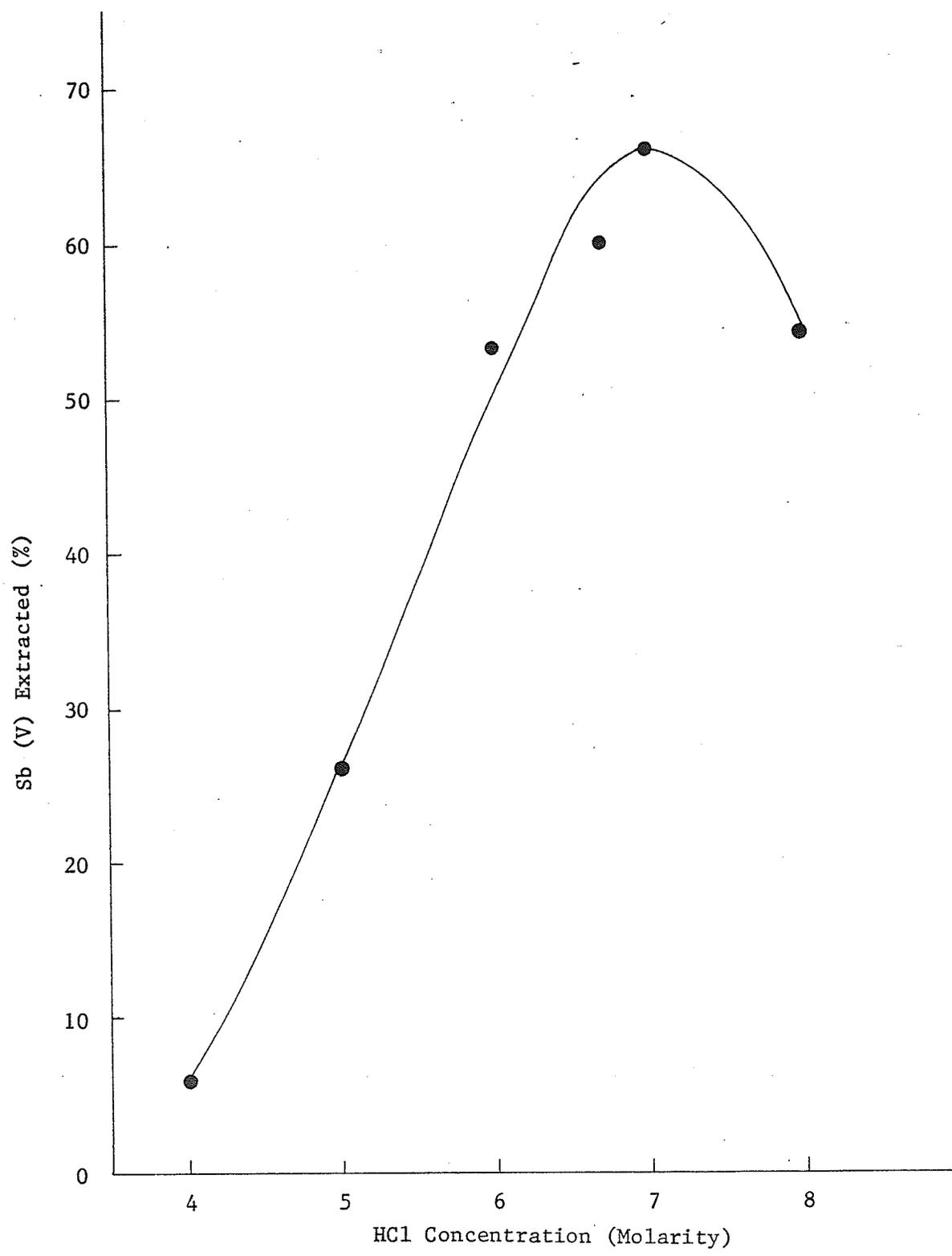
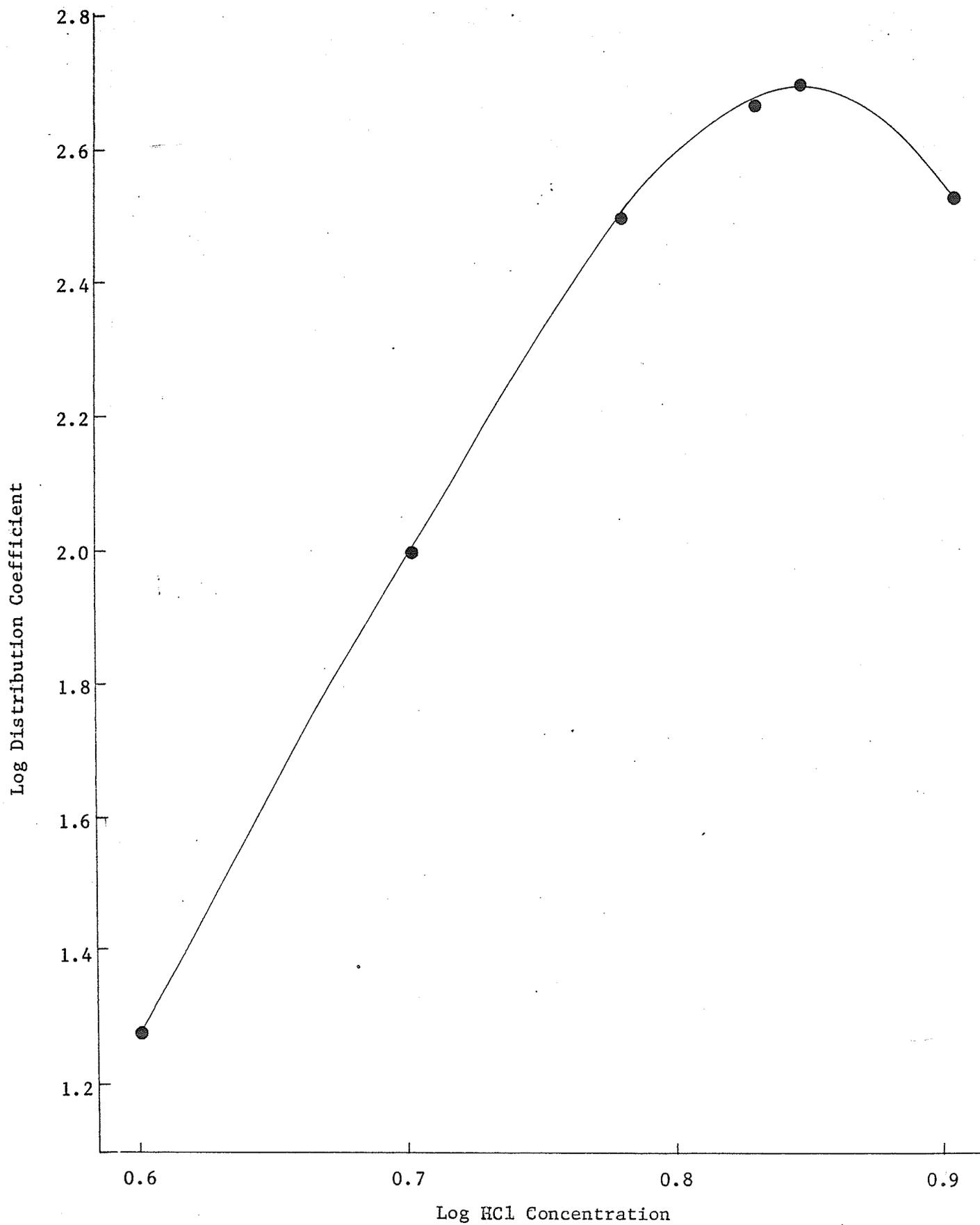


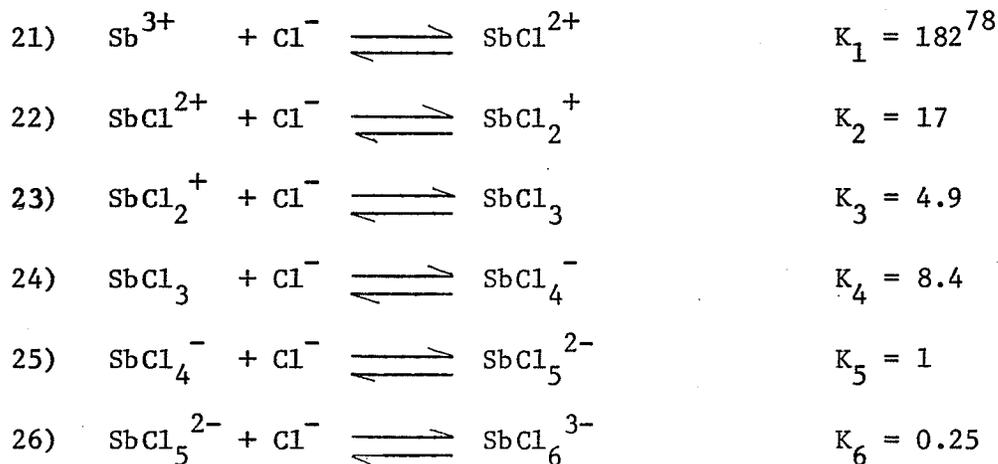
Figure 16a : Variation of Log D with Log HCl Concentration for Antimony (V) Tracer



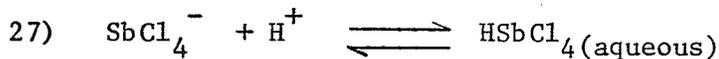
antimony (V). The maximum percentage extraction was observed to be at 7 M HCl for both antimony (III) and antimony (V).

The following equilibrium equations may explain the results:

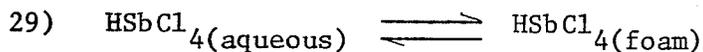
For antimony (III)



It is assumed that  $\text{HSbCl}_4$  is one of the extractable species.



$$28) \quad K_a = \frac{[\text{HSbCl}_4]}{[\text{H}^{+}] [\text{SbCl}_4^{-}]}$$



$$30) \quad K_D = \frac{[\text{HSbCl}_4]_{\text{foam}}}{[\text{HSbCl}_4]_{\text{aqueous}}}$$

$$31) \quad K' = K_1 K_2 K_3 K_4 = \frac{[\text{SbCl}_4^{-}]_{\text{aqueous}}}{[\text{Sb}^{3+}] [\text{Cl}^{-}]^4}$$

$$32) \quad K_D = \frac{[\text{HSbCl}_4]_{\text{foam}}}{K' K_a [\text{Sb}^{3+}] [\text{H}^{+}] [\text{Cl}^{-}]^4}$$

The distribution coefficient, D, representing the ratio of antimony in the foam to all the antimony in solution is given by

$$33) \quad D = \frac{[\text{HSbCl}_4]_{\text{foam}}}{[\text{Sb}^{3+}] + [\text{SbCl}^{2+}] + [\text{SbCl}_2^+] + [\text{SbCl}_3] + [\text{SbCl}_4^-] + [\text{HSbCl}_4]_{\text{aqueous}} + [\text{SbCl}_5^{2-}] + [\text{SbCl}_6^{3-}]}$$

$$34) \quad D = \frac{[\text{HSbCl}_4]_{\text{foam}}}{[\text{Sb}^{3+}] (1 + K_1 [\text{Cl}^-] + K_1 K_2 [\text{Cl}^-]^2 + K_1 K_2 K_3 [\text{Cl}^-]^3 + K_1 K_2 K_3 K_4 [\text{Cl}^-]^4 + K_a K_1 K_2 K_3 K_4 [\text{H}^+] [\text{Cl}^-]^4 + K_1 K_2 K_3 K_4 K_5 [\text{Cl}^-]^5 + K_1 K_2 K_3 K_4 K_5 K_6 [\text{Cl}^-]^6)}$$

The terms : 1,  $K_1 [\text{Cl}^-]$ ,  $K_1 K_2 [\text{Cl}^-]^2$ ,  $K_1 K_2 K_3 [\text{Cl}^-]^3$  and  $K_a K_1 K_2 K_3 K_4 [\text{H}^+] [\text{Cl}^-]^4$  are relatively small and may be neglected.

$$35) \quad D = \frac{[\text{HSbCl}_4]_{\text{foam}}}{[\text{Sb}^{3+}] (K_1 K_2 K_3 K_4 [\text{Cl}^-]^4 + K_1 K_2 K_3 K_4 K_5 [\text{Cl}^-]^5 + K_1 K_2 K_3 K_4 K_5 K_6 [\text{Cl}^-]^6)} \\ = \frac{K_D K_a [\text{H}^+] [\text{Cl}^-]^4 [\text{Sb}^{3+}]}{[\text{Sb}^{3+}] (K_1 K_2 K_3 K_4 [\text{Cl}^-]^4 + K_1 K_2 K_3 K_4 K_5 [\text{Cl}^-]^5 + K_1 K_2 K_3 K_4 K_5 K_6 [\text{Cl}^-]^6)}$$

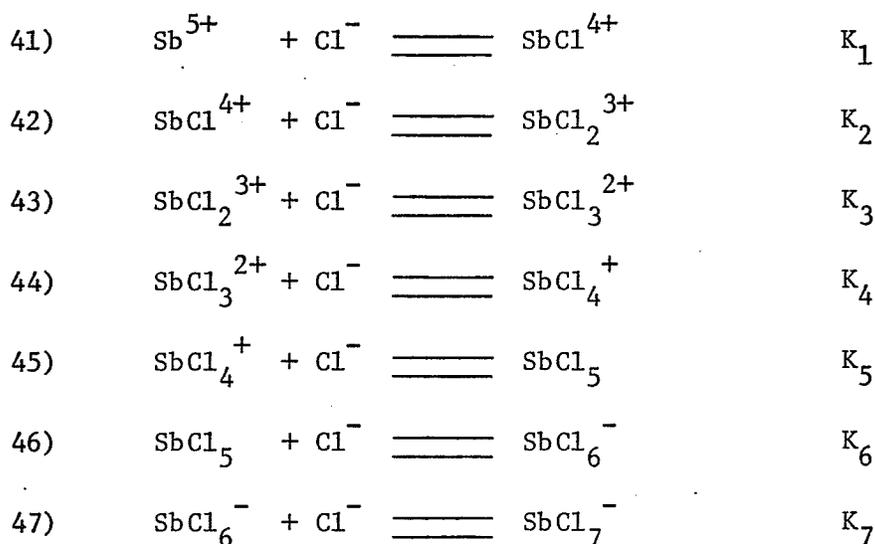
$$36) \quad \log D + \log (K_1 K_2 K_3 K_4 [\text{Cl}^-]^4 + K_1 K_2 K_3 K_4 K_5 [\text{Cl}^-]^5 + K_1 K_2 K_3 K_4 K_5 K_6 [\text{Cl}^-]^6) \\ = \log K + \log [\text{H}^+] + 4 \log [\text{Cl}^-]$$

where K is a constant, and when  $[\text{H}^+] = [\text{Cl}^-] = [\text{HCl}]$

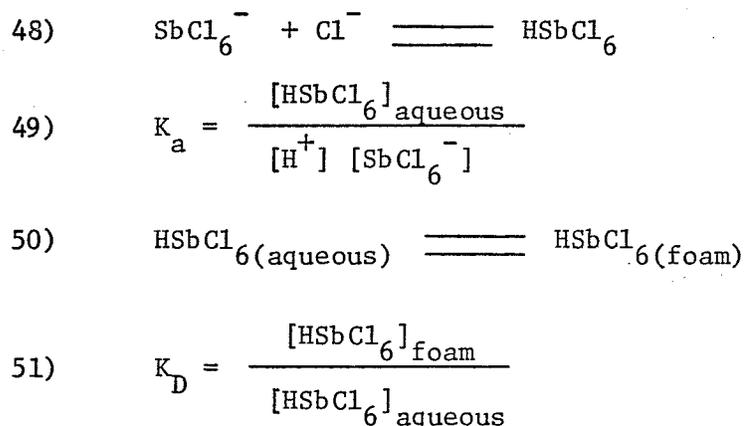
$$37) \quad \log D + \log (K_1 K_2 K_3 K_4 [\text{Cl}^-]^4 + K_1 K_2 K_3 K_4 K_5 [\text{Cl}^-]^5 + K_1 K_2 K_3 K_4 K_5 K_6 [\text{Cl}^-]^6) \\ = \log K + 5 \log [\text{HCl}]$$

A plot of  $\log D + \log (K_1 K_2 K_3 K_4 [Cl^-]^4 + K_1 K_2 K_3 K_4 K_5 [Cl^-]^5 + K_1 K_2 K_3 K_4 K_5 K_6 [Cl^-]^6)$  against  $\log [HCl]$  is shown in figure 15a, where the least square slope from 4 M to 7 M HCl of  $11.2 \pm 1.3$  is compared with a slope of 5 expected as deduced from the above assumptions. However, if another species is thought to be also extractable, the total effect might give a slope of about 11. More informations are required before any further predictions could be made.

For antimony (V)



It is assumed that  $HSbCl_6$  or  $SbCl_5$  is the extractable species.



$$52) \quad K' = K_1 K_2 K_3 K_4 K_5 K_6 = \frac{[\text{SbCl}_6^-]}{[\text{Sb}^{3+}][\text{Cl}^-]^6}$$

$$53) \quad K_D = \frac{[\text{HSbCl}_6]_{\text{foam}}}{K' K_a [\text{Sb}^{5+}] [\text{H}^+] [\text{Cl}^-]^6}$$

The distribution coefficient, D, representing the ratio of antimony in the foam to all the antimony in solution is given by

$$54) \quad D = \frac{[\text{HSbCl}_6]_{\text{foam}}}{[\text{Sb}^{5+}] + [\text{SbCl}^{4+}] + [\text{SbCl}_2^{3+}] + [\text{SbCl}_3^{2+}] + [\text{SbCl}_4^{3+}] + [\text{SbCl}_5] + [\text{SbCl}_6^-] + [\text{HSbCl}_6] + [\text{SbCl}_7^{2-}]}$$

$$55) \quad D = \frac{[\text{HSbCl}_6]_{\text{foam}}}{[\text{Sb}^{5+}] (1 + K_1 [\text{Cl}^-] + K_1 K_2 [\text{Cl}^-]^2 + K_1 K_2 K_3 [\text{Cl}^-]^3 + K_1 K_2 K_3 K_4 [\text{Cl}^-]^4 + K_1 K_2 K_3 K_4 K_5 [\text{Cl}^-]^5 + K_1 K_2 K_3 K_4 K_5 K_6 [\text{Cl}^-]^6 + K_a K_1 K_2 K_3 K_4 K_5 K_6 [\text{H}^+] [\text{Cl}^-]^6 + K_1 K_2 K_3 K_4 K_5 K_6 K_7 [\text{Cl}^-]^7)}$$

Unlike antimony (III), the stability constants (K's) for antimony (V) are not available in the literature, therefore, it is assumed that all other coefficients except  $K_1$  are smaller than 0.1 and may be neglected.

$$56) \quad D = \frac{[\text{HSbCl}_6]_{\text{foam}}}{[\text{Sb}^{3+}] (1 + K_1 [\text{Cl}^-])} = \frac{K_D K' K_a [\text{H}^+] [\text{Cl}^-]^6}{(1 + K_1 [\text{Cl}^-])}$$

$$57) \quad \log D + \log (1 + K_1 [\text{Cl}^-]) = \log K + \log [\text{H}^+] + 6 \log [\text{Cl}^-]$$

where K is a constant, and when  $[\text{H}^+] = [\text{Cl}^-] = [\text{HCl}]$

$$58) \quad \log D + \log (1 + K_1 [\text{Cl}^-]) = \log K + 7 \log [\text{HCl}]$$

A further approximation,  $\log(1+K_1[Cl^-])$  may be neglected and a plot of  $\log D$  against  $\log [HCl]$  is shown in figure 16a, where the least square slope from 4 to 7 M HCl of  $5.9 \pm 1.5$  is compared to a slope of 7 if  $HSbCl_6$  is the extractable species and 5 if  $SbCl_5$  is extracted. It would seem reasonable that  $SbCl_5$  and/or  $HSbCl_6$  are the extractable species.

Effect of Antimony Concentration on its Extraction by Acid Resistant Foam

Antimony trichloride was made up to 10 and 100 ppm from stock in 7 M HCl. Antimony pentachloride was prepared from stock as well. A 150 ml volume was used to mix with 50  $\mu$ l of tracer and squeezed by the multiple automatic squeezer for 2 hours. Samples were checked after 1 hour and the results indicated that extractions were the same at 2 hours.

Table 12 shows the distribution coefficients of antimony (III) at 10, 100 and 1,000 ppm.

Table 13 shows the distribution coefficients of antimony (V) at 10.6, 106 and 1,060 ppm.

This shows the capacity of the foam for antimony is quite good as for antimony (III), an increase of antimony (III) concentration by 100 times, the distribution coefficient only dropped about 20%. For antimony (V), the capacity is less and an increase of 100 times in metallic concentration resulted about 50% drop in distribution coefficient.

Table 12 : Effect of Antimony (III) Concentration on its Extraction by Acid Resistant Foam

Antimony (III) Concentration		Distribution Coefficient
(ppm)	(Moles l <sup>-1</sup> )	
10	$4.4 \times 10^{-5}$	538±18
100	$4.4 \times 10^{-4}$	478±15
1,000	$4.4 \times 10^{-3}$	413±12

Squeezing Time : 2 hours

Volume of Solution : 150 ml.

HCl Concentration : 7 M

Table 13 : Effect of Antimony (V) Concentration on its Extraction  
by Acid Resistant Foam

Antimony (V) Concentration		Distribution Coefficient
(ppm)	(Moles l <sup>-1</sup> )	
10.6	$3.4 \times 10^{-5}$	447±18
106.0	$3.6 \times 10^{-4}$	484±18
1,060.0	$3.6 \times 10^{-3}$	232±12

Squeezing Time : 2 hours

Volume of Solution : 150 ml.

HCl Concentration : 7 M

Figure 16b shows the plot of log D against log antimony (III) concentration, a least square slope of  $-0.003 \pm 0.001$  is obtained. This would indicate that there are no multinuclear species present for the antimony (III) concentration from tracer to 1,000 ppm.

Effect of Hydrogen Concentration on the Extraction of Antimony (III) by Acid Resistant Foam

A 150 ml of antimony trichloride at 162 ppm was prepared in 5 and 7 M chloride concentration. The solution were mixed well with the acid resistant foam for three hours by the multiple automatic squeezer.

Figure 16c shows the effect of hydrogen concentration on the extraction of antimony (III).

Figure 16d shows the plot of  $\log D + \log(K_1 K_2 K_3 K_4 [Cl^-]^4 + K_1 K_2 K_3 K_4 K_5 [Cl^-]^5 + K_1 K_2 K_3 K_4 K_5 K_6 [Cl^-]^6)$  against  $\log [H^+]$ .

The results may be explained by the following equations.

From equation 35)

$$D = \frac{[HSbCl_4]_{foam}}{[Sb^{3+}] (K_1 K_2 K_3 K_4 [Cl^-]^4 + K_1 K_2 K_3 K_4 K_5 [Cl^-]^5 + K_1 K_2 K_3 K_4 K_5 K_6 [Cl^-]^6)}$$

It is now assumed that  $H_2SbCl_5$  or  $H_3SbCl_6$  is the extractable species instead of  $HSbCl_4$ .

For  $H_2SbCl_5$ , equation 35) becomes

$$\begin{aligned} \log D + \log(K_1 K_2 K_3 K_4 [Cl^-]^4 + K_1 K_2 K_3 K_4 K_5 [Cl^-]^5 + K_1 K_2 K_3 K_4 K_5 K_6 [Cl^-]^6) \\ = \log K + 2\log[H^+] + 5\log[Cl^-] \end{aligned}$$

since  $[Cl^-]$  is constant, it can be included into the constant K and becomes

Figure 16b : Variation of Log D with Log Antimony (III) Concentration  
at 7 M HCl

Log Distribution Coefficient

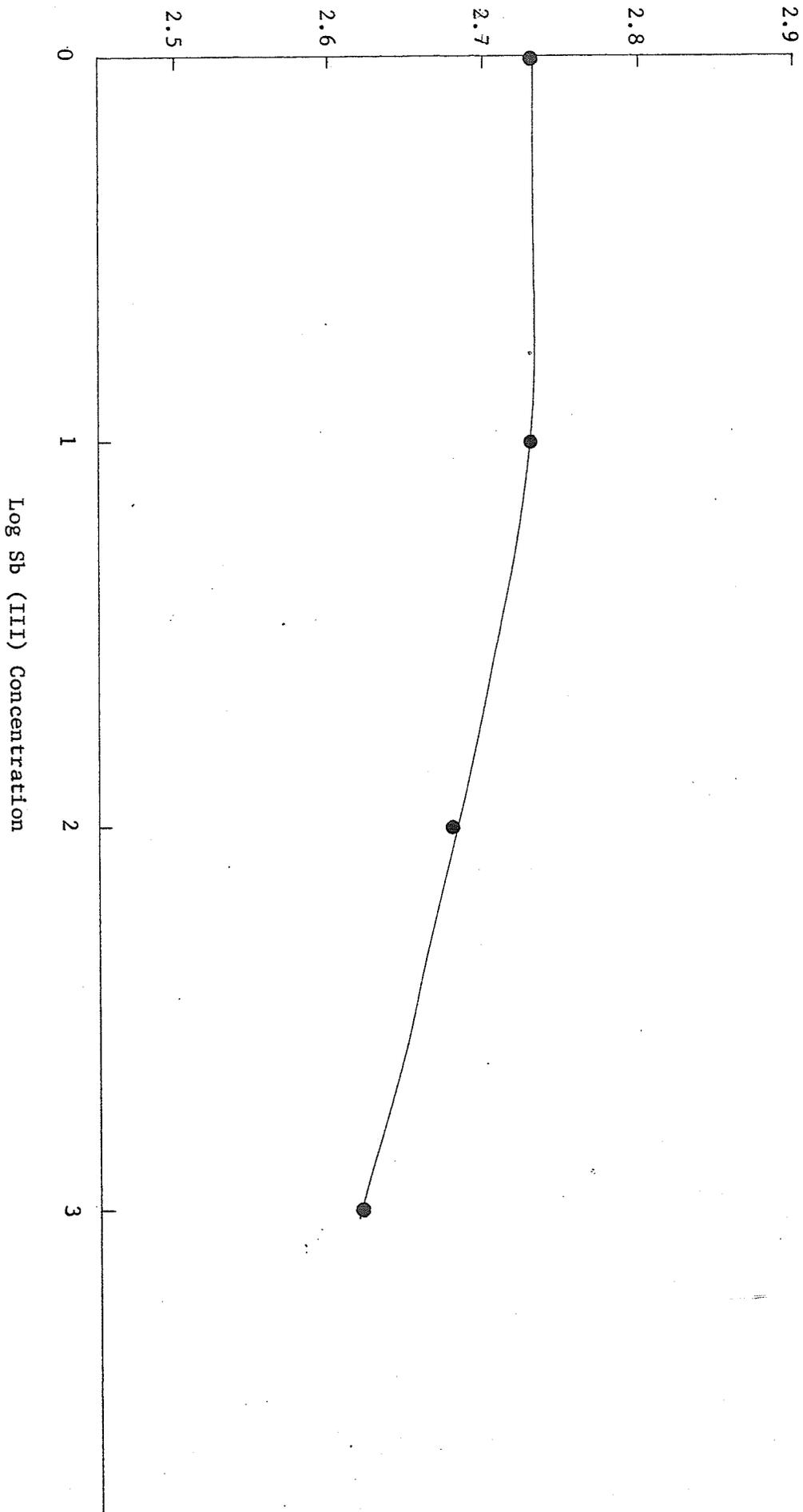


Figure 16c : Effect of  $H^+$  Concentration on the Extraction of Antimony (III) by Acid Resistant Foam at 7 M  $[Cl^-]$  (+) and 5 M  $[Cl^-]$  (o)

Antimony (III) Concentration : 162 ppm

Volume of Solution : 150 ml

Squeezing Time : 3 hours

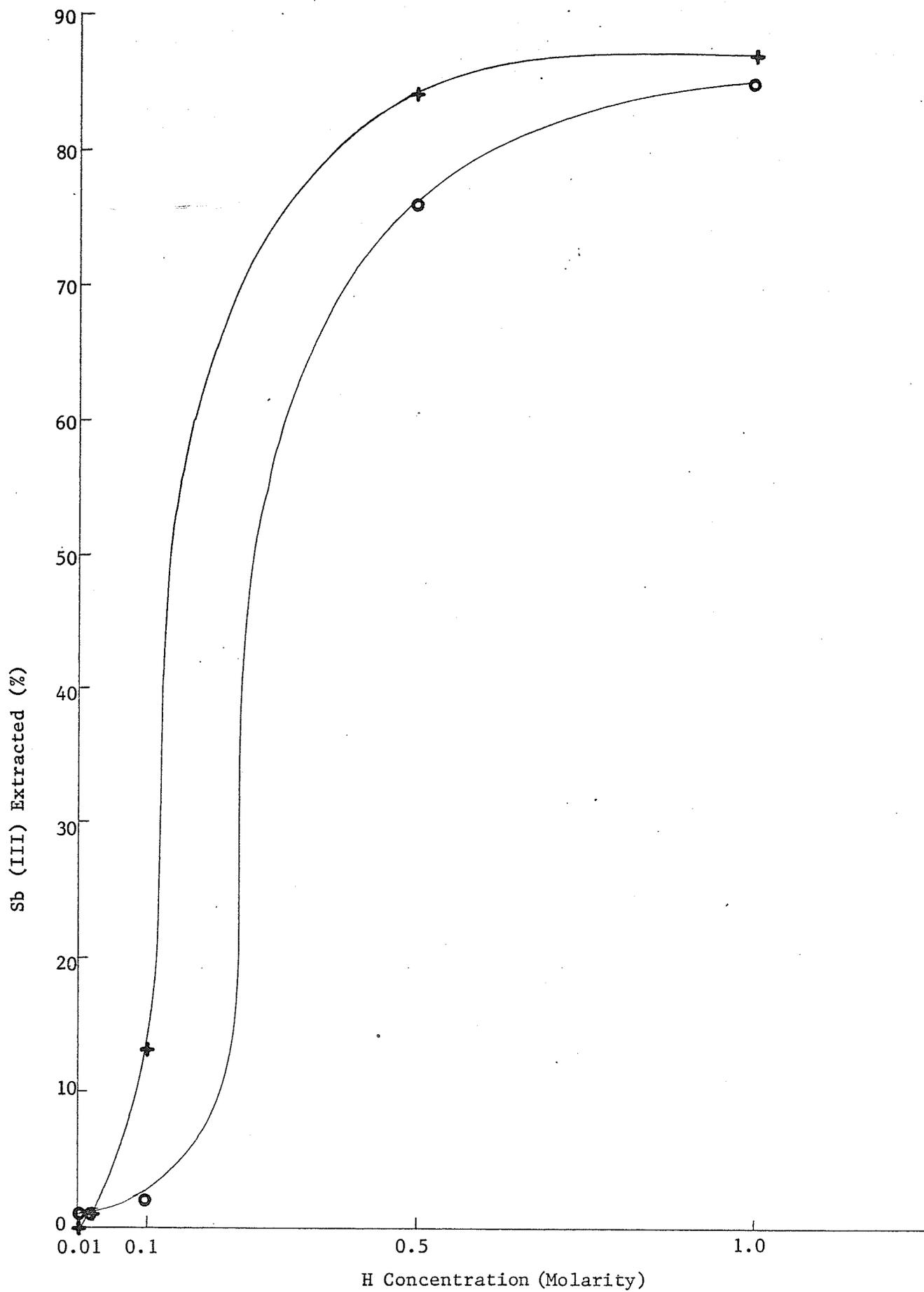
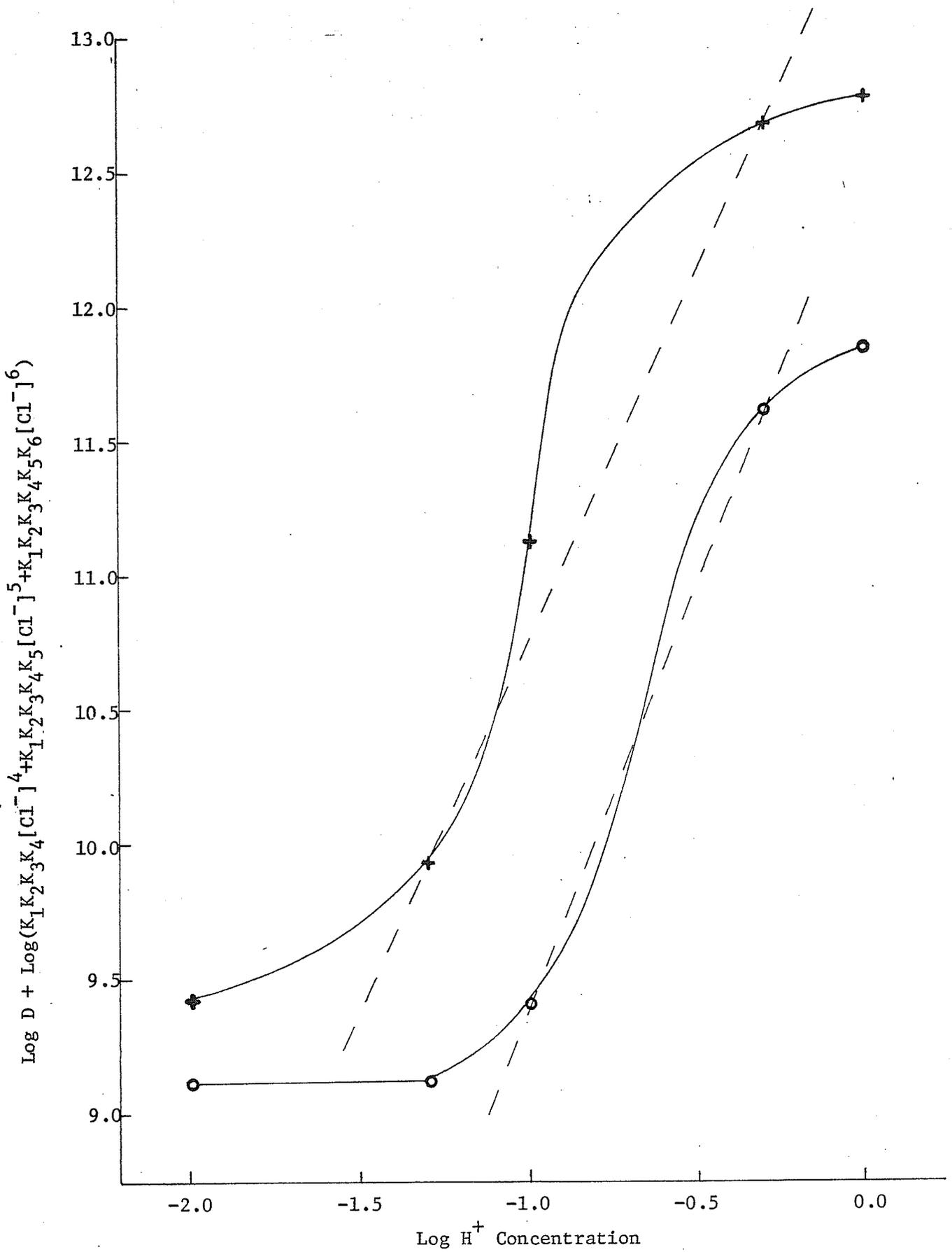


Figure 16d : Variation of  $\text{Log } D + \text{Log}(K_1 K_2 K_3 K_4 [\text{Cl}^-]^4 + K_1 K_2 K_3 K_4 K_5 [\text{Cl}^-]^5 + K_1 K_2 K_3 K_4 K_5 K_6 [\text{Cl}^-]^6)$  with Log Hydrogen Concentration for 162 ppm of Antimony (III) at 7 M  $[\text{Cl}^-]$  (+) and 5 M  $[\text{Cl}^-]$  (o)



$$\begin{aligned} & \log D + \log (K_1 K_2 K_3 K_4 [Cl^-]^4 + K_1 K_2 K_3 K_4 K_5 [Cl^-]^5 + K_1 K_2 K_3 K_4 K_5 K_6 [Cl^-]^6) \\ & = \log K^* + 2 \log [H^+] \end{aligned}$$

For  $H_3SbCl_6$ , equation 35) becomes

$$\begin{aligned} & \log D + \log (K_1 K_2 K_3 K_4 [Cl^-]^4 + K_1 K_2 K_3 K_4 K_5 [Cl^-]^5 + K_1 K_2 K_3 K_4 K_5 K_6 [Cl^-]^6) \\ & = \log K + 3 \log [H^+] + 6 \log [Cl^-] \end{aligned}$$

since  $[Cl^-]$  is constant, it can be included into the constant  $K$  and becomes

$$\begin{aligned} & \log D + \log (K_1 K_2 K_3 K_4 [Cl^-]^4 + K_1 K_2 K_3 K_4 K_5 [Cl^-]^5 + K_1 K_2 K_3 K_4 K_5 K_6 [Cl^-]^6) \\ & = \log K^* + 3 \log [H^+] \end{aligned}$$

A plot of  $\log D + \log (K_1 K_2 K_3 K_4 [Cl^-]^4 + K_1 K_2 K_3 K_4 K_5 [Cl^-]^5 + K_1 K_2 K_3 K_4 K_5 K_6 [Cl^-]^6)$  is shown in figure 16d which gives a least square slope of  $2.3 \pm 0.9$  for 5 M  $[Cl^-]$  and  $2.2 \pm 0.9$  for 7 M  $[Cl^-]$  from 0.05 to 1 M  $[H^+]$ . It seems that  $HSbCl_4$  or/and  $H_2SbCl_5$  or  $H_3SbCl_6$  are the extractable species in this study.

Effect of Lithium Chloride Concentration on the Extraction of Antimony by Acid Resistant Foam

A 150 ml of antimony trichloride at 100 ppm and antimony pentachloride at 100 ppm were prepared from stock in 0.7 M HCl and various LiCl concentrations. The solutions were mixed well with the acid resistant foam for three hours by the multiple automatic squeezer.

In a preliminary experiment, the rate of extraction for antimony (III) and antimony (V) at 100 ppm in 0.7 M HCl and 7 M LiCl was studied.

Figure 17 shows the rate of extraction of antimony (III) from aqueous solution.

Figure 18 shows the rate of extraction of antimony (V) from aqueous solution.

From the results it was noted that 3 hours should be adequate for the systems to reach equilibrium.

Figure 19 and 20 show the effect of lithium chloride on the extraction of antimony (III) and antimony (V).

The antimony (III) extraction curve shows an increase as the concentration of lithium chloride was increased until it reached a maximum at 7 M. It would therefore be possible that there are different species of antimony chloride present at different chloride concentration and that some of these species are not well extracted. The antimony (V) extraction curve was different, the extraction increased at first and then levelled off at LiCl

Figure 17 : Rate of Extraction of Antimony (III) from 0.7 M HCl  
and 7 M LiCl by Acid Resistant Foam

Antimony (III) Concentration : 100 ppm

Volume of Solution : 150 ml

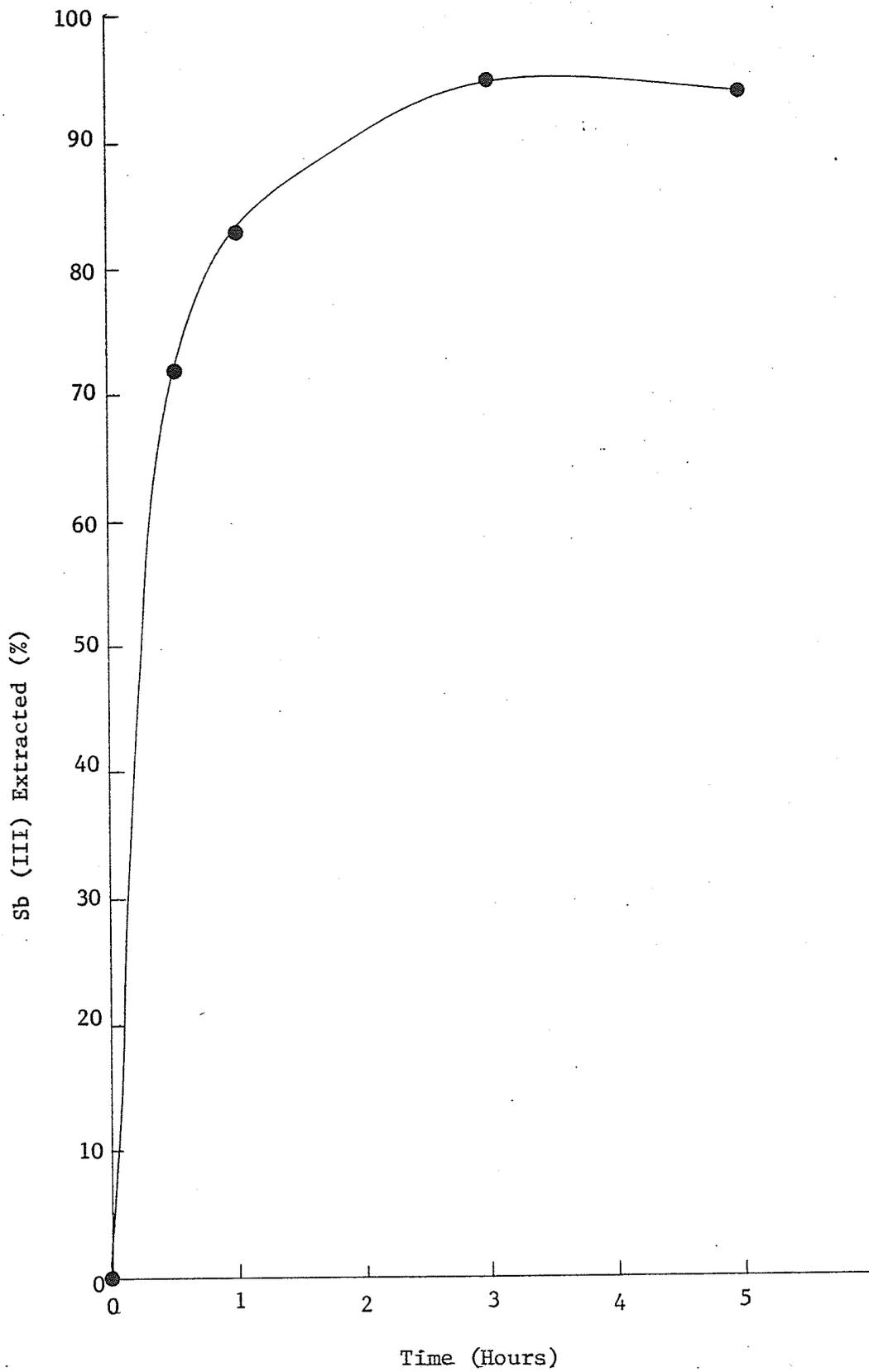
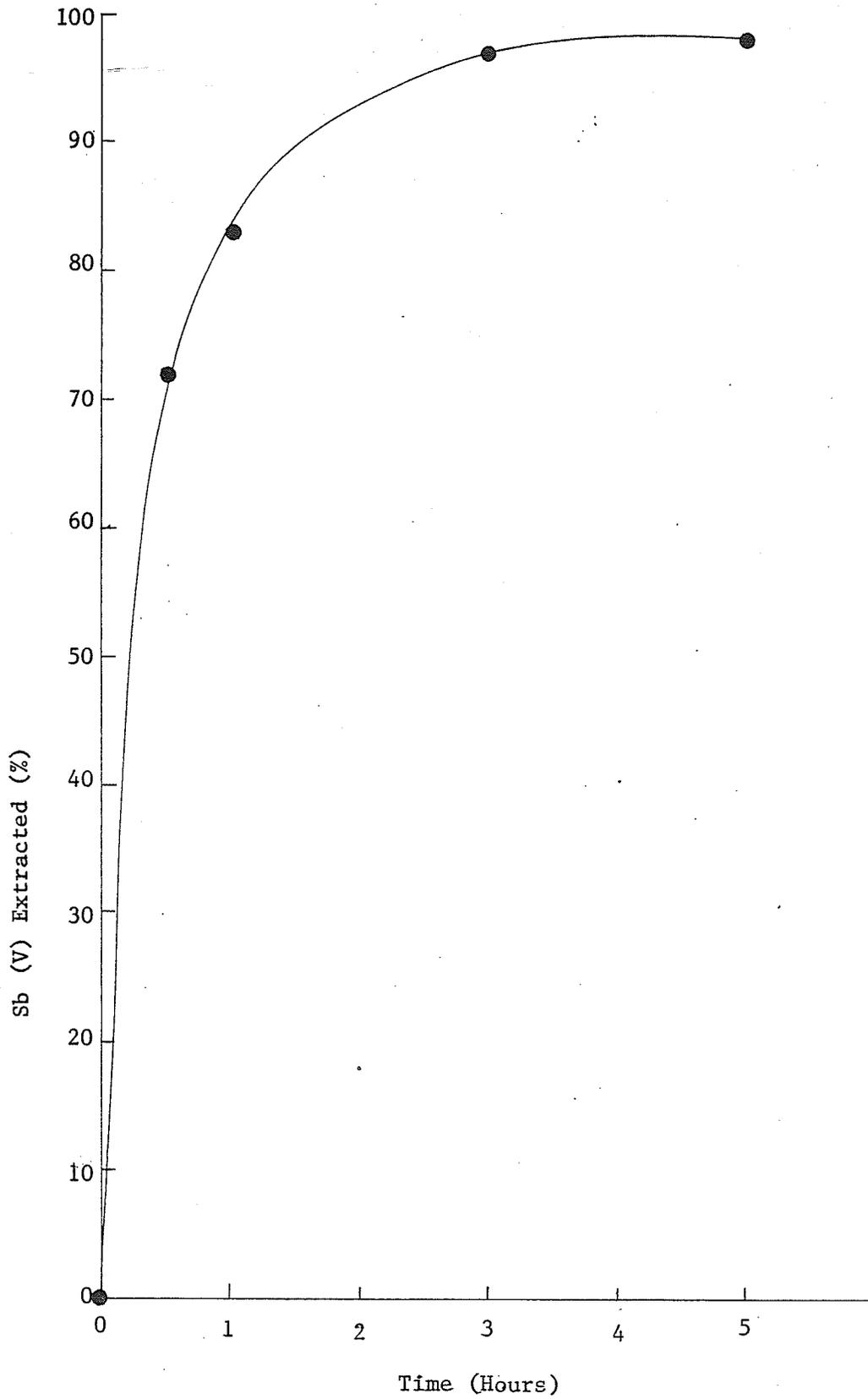


Figure 18 : Rate of Extraction of Antimony (V) from 0.7 M HCl  
and 7 M LiCl by Acid Resistant Foam

Antimony (V) Concentration : 100 ppm

Volume of Solution : 150 ml

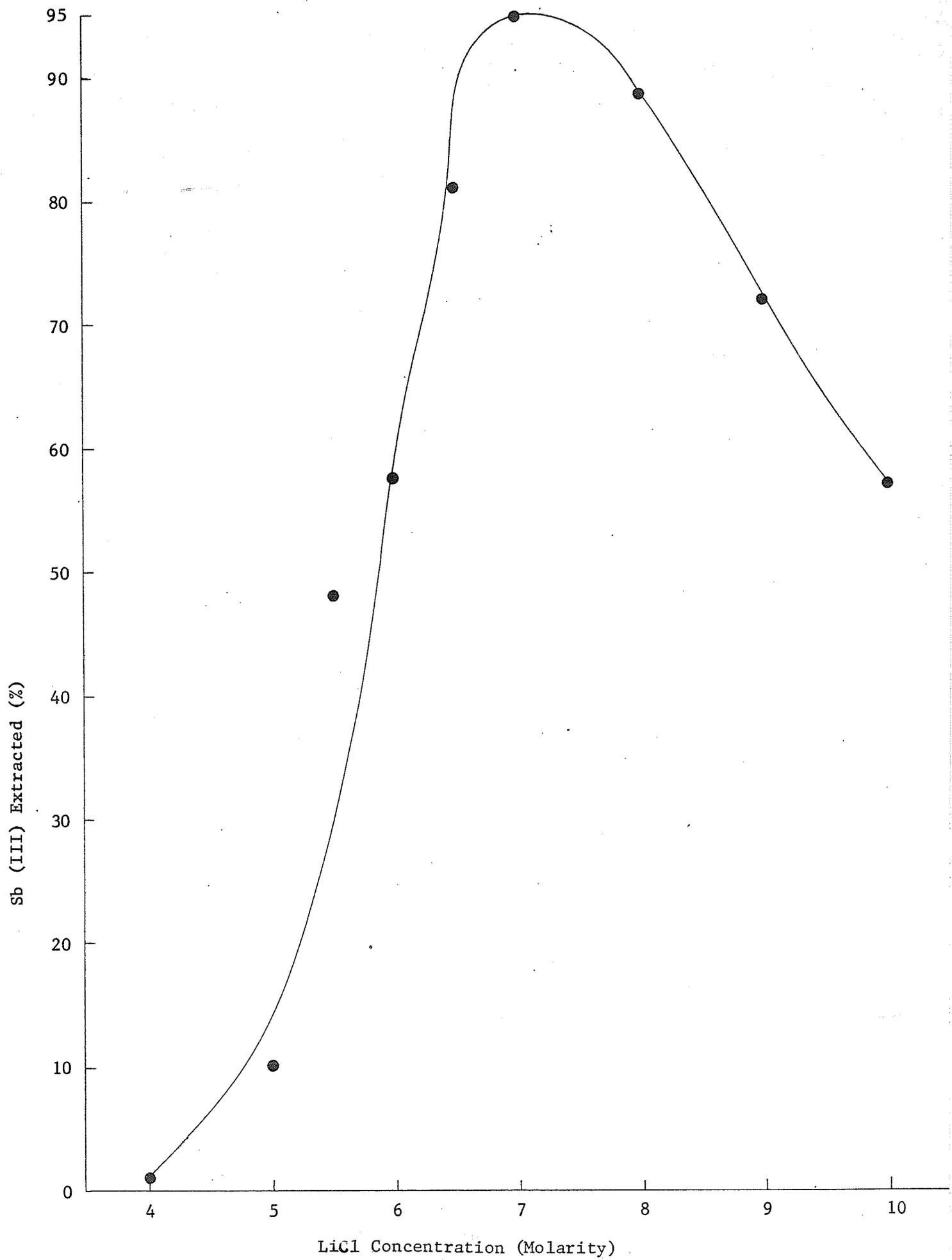


**Figure 19 : Effect of Lithium Chloride Concentration on the Extraction of Antimony (III) by Acid Resistant Foam**

Antimony (III) Concentration : 100 ppm

Volume of Solution : 150 ml

Squeezing Time : 3 hours



concentrations greater than 7 M. The species would still be well extracted at LiCl concentrations greater than 7 M.

The distribution coefficient for antimony (III) at 7 M LiCl and 0.7 M HCl was calculated to be  $6150 \pm 70$  and for antimony (V) at the same medium was  $35200 \pm 400$ .

Figure 20a shows the plot of log D against log chloride concentration for antimony (V).

From equation 57)

$$\log D + \log (1 + K_1 [Cl^-]) = \log K + \log [H^+] + 6 \log [Cl^-]$$

Figure 20 : Effect of Lithium Chloride Concentration on the  
Extraction of Antimony (V) by Acid Resistant Foam

Antimony (V) Concentration : 100 ppm

Volume of Solution : 150 ml

Squeezing Time : 3 hours

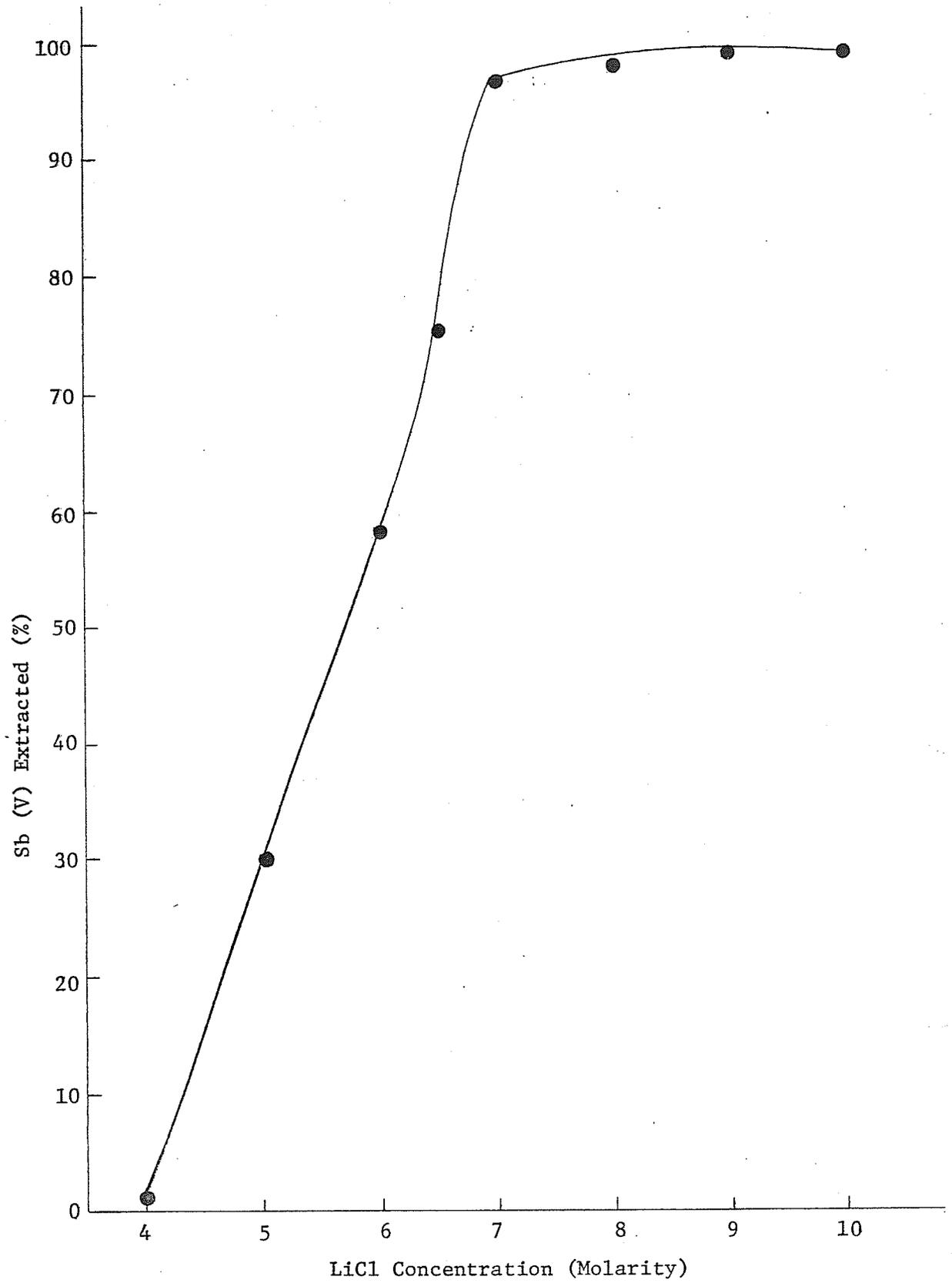
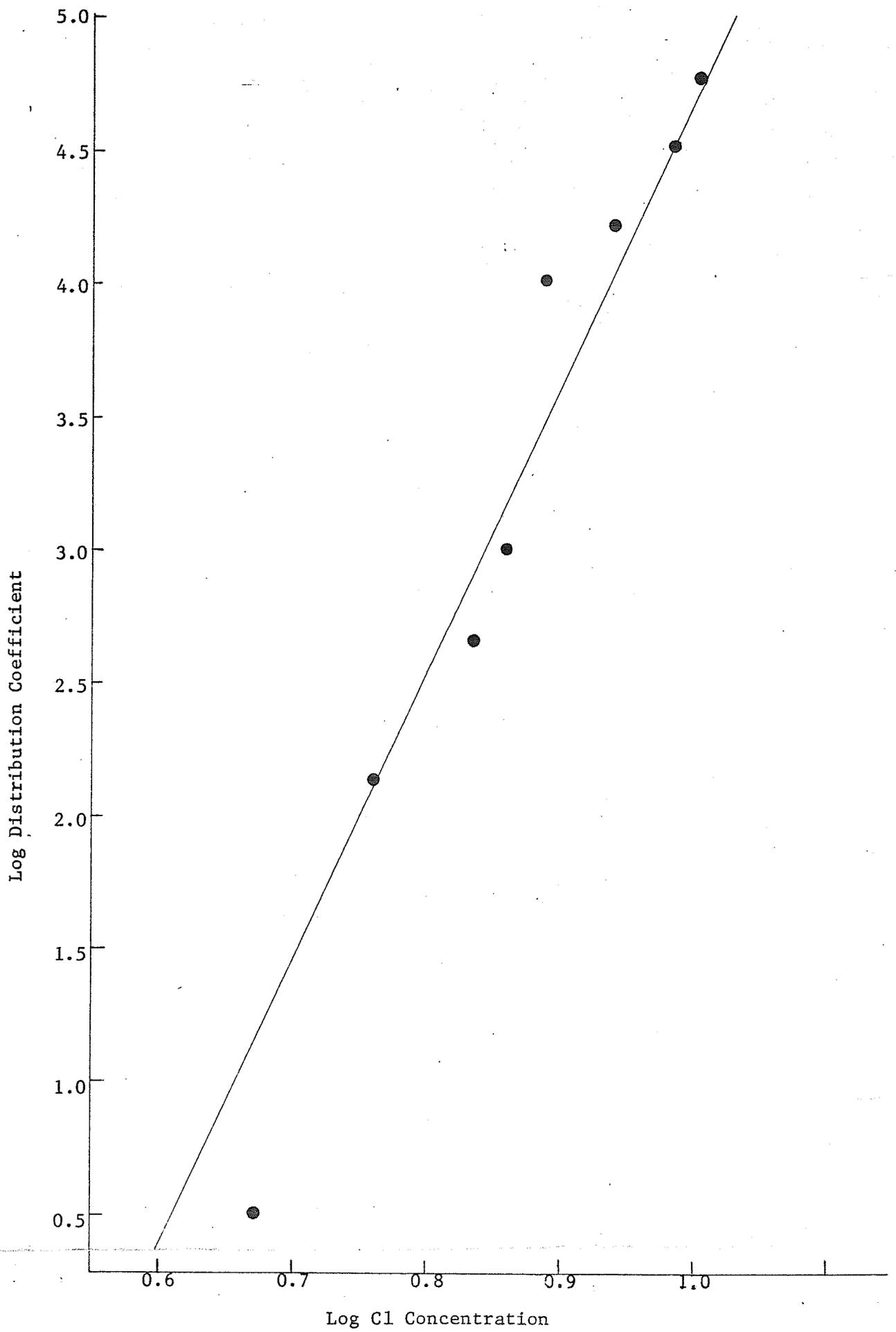


Figure 20a : Variation of Log D with Log Cl Concentration for 100 ppm of Antimony (V) at 0.7 M HCl



where  $K$  is a constant and  $[H^+]$  which is small and may be neglected.

A further approximation,  $\log(1+K_1[Cl^-])$  may be neglected and equation 57) becomes

$$\log D = \log K + 6\log[Cl^-]$$

The graphs shows a least square slope of  $14.7 \pm 4.5$  from 4.7 to 7.7 M chloride concentration and a slope of  $11.5 \pm 4.0$  from 4.7 to 10.7 M chloride concentration compared to the slope of 6 expected.

Many variables are involved in extraction from an aqueous solvent by means of an organic solvent. These variables are: the concentration of the metal itself and of other cations in the solution, the concentrations of the different anions present, the mechanism of extraction between the extractable species and the organic phase. It is assumed here that polyurethane foams behave like organic solvents, The assumptions made could apply to some aqueous/organic systems. Certain assumptions were applied here for the aqueous/polyurethane foam system in an attempt to explain the experimental results. It seems that the distribution of the metal between the phases depends on the variables mentioned in a very complicated way. It is not definitely known which are the extractable species and what are their relative extractabilities. The mechanism of the distribution of the metal between the aqueous phase and the foam may resemble that in aqueous/organic solvent extraction but is not necessarily exactly the same. Nevertheless, it is shown here that there is some resemblance of the two systems and that more evidence is required to provide a better explanation of the results.

### Recovery of Antimony from Acid Resistant Foam

Antimony (III) and (V) were loaded onto the foam using the optimum conditions obtained in previous extraction experiments.

Recovery was attempted to be recovered by water, 0.1 M HCl, 0.1 M NaOH and acetone. The recovery procedure was the same as the extraction procedure using the same volume of solution and squeezing time.

For antimony (III), only 21% was recovered by 0.1 M HCl, 9% by water, 91% by 0.1 M NaOH and 100% by acetone. For antimony (V), the recovery was better, 82% by 0.1 M HCl, 91% by water, 93% by 0.1 M NaOH and 100% by acetone. The standard deviation for the above percentages were  $\pm 2\%$

Acetone was used in the determination of the recovery of antimony. The technique by counting the foam was employed.

$$\begin{aligned} \text{Sb(III) \% Recovery} &= \frac{474261 \pm 689 - 1302 \pm 36}{474261 \pm 689} \times 100 \\ &= 99.7 \pm 0.3 \end{aligned}$$

$$\begin{aligned} \text{Sb(V) \% Recovery} &= \frac{462540 \pm 680 - 396 \pm 20}{462540 \pm 680} \times 100 \\ &= 99.9 \pm 0.3 \end{aligned}$$

This method for the percentage of recovery was shown to give more precise measurement than the method before due to the counting was done by directly counting the foam.

Extraction of Antimony (III) by Regular Polyurethane Foam

Antimony (III), 100 ppm in 0.7 M HCl and 4, 7, and 10 M LiCl were made up to 150 ml. The solutions were mixed with the foams by squeezing with the multiple automatic squeezer for 3 hours.

Table 14 shows the extraction of antimony (III) by regular polyurethane foam.

The regular polyurethane foam was found to extract about the same amount of antimony as the acid resistant foam at 7 M LiCl and 0.7 M HCl.

Table 14 : Effect of Lithium Chloride Concentration on the Extraction of Antimony (III) by Regular Polyurethane Foam

Lithium Chloride Concentration (Molarity)	Percentage Extracted	Distribution Coefficient
4	2±1	6±3
7	93±1	4360±47
10	21±1	95±5

Antimony (III) Concentration : 100 ppm

HCl Concentration : 0.7 M

Squeezing Time : 3 hours

Volume of Solution : 150 ml..

### Summary

Three types of foams have been used in this work. The results of the extraction of tin from hydrochloric acid suggest that regular polyurethane foam works better than acid resistant foam and diSPo plugs. Not only does it extract tin at a lower HCl concentration, it also extracts tin quantitatively from 0.12 M HCl and 10 M LiCl. The distribution coefficients of the three foams are shown in table 15.

The distribution coefficient for regular polyurethane foam is two and a half times better than acid resistant foam and seven and a half times better than diSPo plugs at 0.12 M HCl and 10 M LiCl.

It was also shown that the HCl-LiCl system is better than the HCl system, the reason could be due to the formation of more extractable species. It could also be due to the depressing effect of the hydrogen ion when its concentration is high.

The decrease after the maximum for all the acidity curves could be explained due to the formation of some species which were not well extracted by the foam. Moreover, the HCl could form ion pairs which require chloride competing with the extractable species which require chloride. A physical phenomenon which should not be overlooked is that at high acid concentrations, for example at 10 M HCl, the acid resistant foam swells about one and a half times its normal size.

Throughout most of this work, the static system was used. The flow-through system was briefly examined in the diSPO foam section. The use of static system works particularly well with the help of the automatic squeezer. For extractable species which are slow to equilibrate between the foam and aqueous phases, the static system allows flexibility in time without any interference in between while the flow-through system would probably require an extremely slow flow rate and then solutions have to repass through the column again in order to obtain quantitative extraction when one foam is used. However, the addition of more foams to the column would allow better and probably faster extraction to occur.

The acid resistant foam and regular polyurethane foam are shown to have high capacities for the extraction of tin (IV). Up to 8 % by weight of tin (IV) per gram of foam could be extracted. The surface area required for that amount of tin to be adsorbed would be about  $111 \text{ m}^2/\text{g}$  of foam compared to the available area  $0.081 \text{ m}^2/\text{g}$  of foam. This is clearly an absorption effect.

Acid resistant foam and regular polyurethane foam were used in the extraction of antimony from HCl and HCl-LiCl systems. Both types of foam work equally well in HCl-LiCl by quantitatively extracting antimony (III). Antimony (V) was also quantitatively extracted by acid resistant foam. The equilibrium was reached in about three hours. Extraction of  $95 \pm 2\%$  for antimony (III) and a  $98 \pm 2\%$  for antimony (V) were found.

Table 15 : The Distribution Coefficients of Tin (IV)

Foam Type	Distribution Coefficient	
	HCl System	HCl-LiCl System
DiSPo Plugs	120±8	732±23
Acid Resistant Foam	129±7	2280±48
Regular Polyurethane Foam	141±9	5630±119

HCl System	DiSPo Plugs	Acid Resistant Foam	Regular Polyurethane Foam
Tin (IV) Concentration (ppm)	100	100	Tracer
Volume of Solution (ml)	20	150	150
Squeezing Time (hour)	3/4	1	2
HCl Concentration (Molarity)	6	4	3

HCl-LiCl System	DiSPo Plugs	Acid Resistant Foam	Regular Polyurethane Foam
Tin (IV) Concentration (ppm)	100	100	100
Volume of Solution (ml)	150	50	150
Squeezing Time (hour)	24	6	24
HCl Concentration (Molarity)	0.12	0.12	0.12
LiCl Concentration (Molarity)	10	10	10

Recovery of tin (IV) was quantitative by the use of 0.1 M HCl or acetone. Antimony (III) and (V) were completely recovered by acetone. The foams were observed to be readily reusable.

### Conclusion

This work shows that tin (IV) and antimony (III) and (V) could be quantitatively extracted from aqueous solution by polyurethane foam. The foams have high capacity for tin (IV). Usually a 0.500 g of foam was used versus 150 ml of solution with a metal content from tracer to 150 mg. This suggests that the foam is very suitable for the preconcentration of tin (IV) and antimony (III) and (V).

The method is more effective than the conventional diethyl ether extraction system for tin (IV) and antimony (III) and (V) chlorides.

Adsorption and absorption have been used by researchers in the study of extraction by the use of polyurethane foam. It appeared here that some of the metal complexes could be adsorbed while most of them were absorbed.

Polyurethane foams have been shown to have great versatility in solvent extraction. It seems to act like a free ether or an ester in solution and yet offer itself as an inert solid support for various complexing agents like tri-n-butyl phosphate, dimethylglyoxime, dithizone and etc.. Selective extraction and separation of metal complexes by the use of coated polyurethane foams were reported. Foams could be adopted for field studies since they are easy to carry and relatively inexpensive. All these factors should lead to wide applications and more investigations in the

future for polyurethane foams.

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