THE UNIVERSITY OF MANITOBA

THE EXTRACTION OF GALLIUM FROM ACID CHLORIDE SYSTEMS USING OPEN-CELLED POLYURETHANE FOAM

BY

GEORGE A. HORSFALL

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"THE EXTRACTION OF GALLIUM FROM ACID CHLORIDE SYSTEMS USING OPEN-CELLED POLYURETHANE FOAM"

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A dissertation submitted to the Faculty of Graduate Studies of the University of Manitoba in partial fulfillment of the requirements of the degree of

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Abstract

The extraction of gallium from acidic chloride solutions was examined, using open-celled polyurethane foam as the extracting medium. The chloride, hydrogen, and gallium ion concentrations were shown to influence the extraction process. An investigation of the diffusion of gallium through polyurethane membrane revealed the " active transport " of gallium. The diffusion rate was found to increase with increasing chloride and hydrogen ion concentration, consistent with the solubility of the gallium complex in polyurethane.

The Extraction of Gallium from Acid Chloride Systems using Open-Celled Polyurethane Foam

Introduction

Gallium(1)

Gallium was discovered in 1875 by Lecoq de Boisbaudran and named after the Latin name for France Gallia. Earlier, Mendeleev had predicted its existence and had described its properties under the name of eka-aluminum.

Gallium is in Group III, Period 4 of the periodic table, has atomic number 31 and atomic weight 69.72. Most notable of its physical properties is its low melting point 29.75°C. It also has a high boiling point 1983°C, giving it a long liquid range. In the solid state gallium is metallic grey and brittle; in the liquid state it resembles mercury. Gallium is one of the few metals in which the density of the liquid (6.095 g/cm^3) is greater than that of the solid (5.904 g/cm^3). It expands approximately 3.2 percent on solidification.

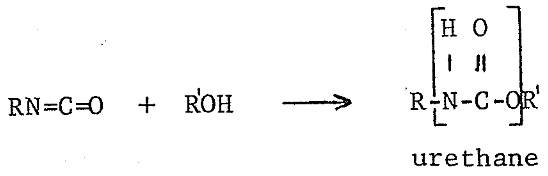
Its chemical properties are similar to those of aluminum. The metal usually forms a thin film of oxide on its surface when exposed to air. It slowly dissolves in mineral acids. Hot nitric acid will oxidize the metal and dissolve the oxide. Aqua regia also dissolves gallium. Sodium or potassium hydroxide solutions will dissolve gallium with the evolution of hydrogen. The normal valence state of gallium is three, although it is also found in mono and divalent states. Liquid gallium is particularly reactive with most solid metals, especially at elevated temperatures.

Gallium is quite widely distributed in the earth's crust, being present to about the same extent as lead and arsenic. It is, however, not usually found in concentrations greater than 0.01 percent of any material. It is found in small quantities in most claylike materials, as might be expected because of its similarity to aluminum. Most aluminum bearing minerals contain some gallium. It is present in small quantities in many coals and is often concentrated in the by-products of the coal combustion. Gallium also is present in trace amounts in copper and zinc sulphide ores.

Gallium, alloyed with arsenic, antimony or phosphorus, is used in intermetallic compounds for semiconductors. Intermetallic compounds containing gallium also have applications as high temperature rectifiers and transistors (2). Gallium arsenide is recommended for making diodes, which convert electrical energy into modulated infrared radiation to be used for multichannel line-of-sight communications. Gallium is used in many low melting point alloys, as well as in "cold soldering" for heat sensitive instruments. It has also been suggested that liquid gallium, or one of its low melting alloys, be used as a heat exchange medium for nuclear power plants. Its long liquid range, low vapour pressure and relatively high thermal conductivity are advantageous in this application. Drawbacks include high cost, an appreciable absorption of thermal neutrons and a tendency to react with many metals at high temperatures. As a result, it is difficult to find a satisfactory container which will resist attack by gallium. In medicine, radioisotope ^{72}Ga has been suggested as an aid in the study of bone cancer. Various gallium salts are absorbed by bone cancer, facilitating detection and observation.

Polyurethane Foam(3)

The reaction of an isocyanate with an alcohol to form a urethane was discovered by Wurtz in 1848.

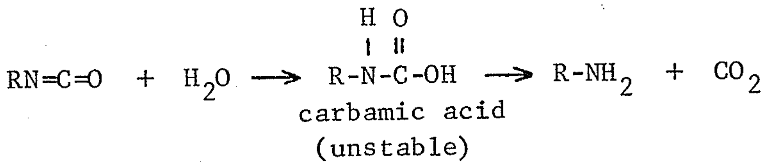


$$RN{=}C{=}O \;+\; R'OH \longrightarrow R\left[-\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-O\right]R'$$

urethane

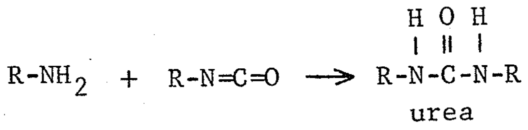
In 1937 Bayer realized the possibility of reacting diisocyanates and diols to produce a polymer. Today the diisocyanate used extensively is toluene diisocyanate (TDI). It is reacted with polyols such as polyesters or polyethers to form polyurethane.

The reaction of isocyanate with water to produce ureas and evolve CO_2 gas, is also important in polyurethane production.



$$RN{=}C{=}O \;+\; H_2O \longrightarrow R-\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-OH \longrightarrow R-NH_2 \;+\; CO_2$$

carbamic acid
(unstable)

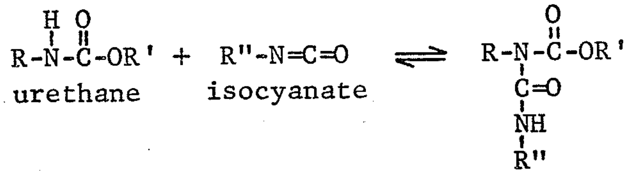


$$R-NH_2 \;+\; R-N{=}C{=}O \longrightarrow R-\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-R$$

urea

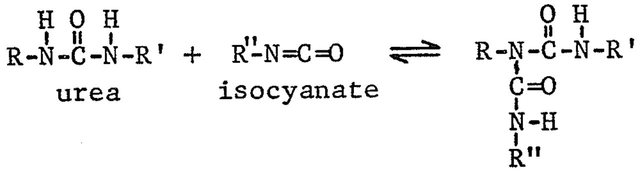
The urea reaction results in chain extension by introducing polyether chains into the polymer structure. The nature of the polyether introduced in the urea reaction will determine the degree of cross linking in the final product. The greater the number of functional groups of the polyether and the lower its molecular weight, the greater will be the degree of cross linking in the polymer. This determines the rigidity of the foam. In addition, the CO_2 gas formed from the decomposition of the carbamic acid creates bubbles in the polymerizing material, helping to form the cellular structure of the foam.

Of less significance are the reactions of isocyanate with urethanes to form allophanates and with urea to form biurets.



$$R-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-OR' + R''-N=C=O \rightleftharpoons R-N(C(=O)-NH-R'')-\overset{O}{\overset{\|}{C}}-OR'$$

allophanate



$$R-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-R' + R''-N=C=O \rightleftharpoons R-N(C(=O)-N(H)-R'')-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-R'$$

biuret

The rates of these reactions are much slower than the catalyzed rates of the primary reactions. They also become reversible at the temperatures at which the foam is produced (4).

The technology of manufacturing polyurethane foams is quite complex with several other materials being required in order to produce a suitable product. These include silicone emulsifiers, metallo-organic and amine catalysts, auxiliary blowing agents, fillers, flame retardants, colorants and stabilizers. The rates of the gas production and polymer formation must be balanced using catalysts so that the gas pressure is just enough to open the cells. The struts must not be broken as this would cause split or collapse of the foam. The opening of the cells is required to let air flow in on cooling to prevent foam shrinkage as well as to increase the resiliency of the foam (5).

In general polyurethane foams are quite stable and inert. They degrade when heated to 200°C and slowly turn brown in u.v. light. They are for the most part unaffected by water, 6M hydrochloric acid, 4M sulfuric acid, 2M sodium hydroxide, 2M nitric acid, glacial acetic acid, 2M ammonia, benzene, carbon tetrachloride, chloroform, diethyl ether, di-isopropyl ether, acetone, isobutyl methyl ketone, ethyl acetate, isopentyl acetate and alcohols (6).

The foams used in this study were provided by Union Carbide and were prepared from a mixture of polyols (60% oxypropylene/ oxyethylene copolymer of 5000 number average molecular weight and 40% a mixture of 20 percent by weight styrene/acrylonitrile copolymer in the 5000 number average molecular weight polyol) and a mixture of diisocyanates (80/20 blend of TDI and polymethylene polyphenyl isocyanate).

Solvent Extraction

The solvent extraction of metals is a rapidly expanding field as evidenced by the volume of work published in this area (7-9). The phenomenon of solvent extraction depends on the affinity of a solute for two phases which are in intimate contact. The affinity or total interaction energy of the solute to each phase depends on several factors including: solvation energy, electrostatic interaction energy among ions, dipole interaction energy, hole formation energy and entropy factors. Qualitatively the factors which cause a low affinity for the aqueous phase are:

a) zero or low charge - resulting in decreased hydration.

b) large size - resulting in decreased hydration and increased hole formation energy.

c) nonpolar - resulting in lower interaction with the water dipoles.

d) lack of electronegative atoms at the surface - reduces hydrogen bonding.

e) low water activity and highly ordered water structure - decreases availability of water for interaction with the solute; often caused by salting-out agents.

The various extraction systems have been classified on the basis of the nature of the extractable species; either "molecular" or "ionic"; or on the mechanism of the extraction process (10,11). Classification according to the type of extraction process includes: physical distribution of inert systems, distribution involving solvation in either or both phases, distribution of ion association complexes involving dissociation at least in the aqueous phase, distribution involving reaction with excess ligand, distribution involving aggregation, and ion exchange reactions (10-12). In most cases more than one reaction occurs; for example ionic dissociation is usually accompanied by solvation and may also involve reaction with excess ligand or aggregation.

The theory of ion association complexes was developed by N. Bjerrum and expanded by the work of Fuoss and Krauss (13). In general the theory relates the ion pair formation constant to the dielectric constant of the solvent, the temperature, and the size of the ions involved. If the ionic size and temperature remain constant the association will depend only on the dielectric constant of the solvent.

Hasted *et al.*(14) examined the effect of various solutes on the dielectric constant of aqueous solutions. The marked decrease in dielectric constant with increasing HCl and LiCl concentration, was illustrated.

The extraction of metal halides from aqueous halide solution involves the extraction of protonated metal complex anions, usually singly charged. Higher charged complexes are not extracted even into relatively high dielectric constant solvents (11). In spite of their usually high solubilities in these solvents, the high charge increases their affinity for the aqueous phase. Only a few metals form extractable complexes with fluoride ions because the small ion tends to form polynegative anions such as FeF_6^{3-} as compared to $FeCl_4^-$. In addition, should a mononegative fluoride complex be formed, it would be small and therefore generally less extractable.

Much work has been done on the extraction of metal from chloride solutions (15-18), with the extraction of iron (III) chloride being extensively studied. The behaviour of several tervalent metal halides is similar to that of iron (12, 19-22). In the extraction of these metals from aqueous hydrogen halide solutions there is an initial steep rise in percentage extraction with increasing acid concentration. The point at which this occurs depends on the formation constant of the metal complex. In some solvents the extraction curves show a maximum, although this phenomenon is not present in all cases (12,22). Where a maximum does occur it appears to be a property of the solvent-acid system and is independent of the metal involved as long as the metal concentration is small (19,22,23). It has been shown (24,25) that as the solvents become less soluble in the aqueous phase, the point where the maximum occurs is shifted to higher acid concentrations. Where the solvent is insoluble in the aqueous phase, there is no maximum in the distribution curve (12,22).

Spectroscopic evidence indicates that for the iron chloride system the extracting species is the $HFeCl_4$ complex (28,32-35,39). Further studies have indicated that this form of extracted complex applies generally for the tervalent halides in any oxygenated solvent (36-38,40).

It has been shown that the concentration of the metal affects the distribution ratio (D) in many extraction systems (21,26,27,29), although the effect may differ at different acid concentrations, or with different metals in any given solvent. Evidence indicates that the dielectric constant of the solvent is primarily responsible for the manner in which D varies with concentration, presumably because of changes in the dissociation-association equilibrium. With solvents of high dielectric constant at relatively high metal concentrations, D decreases with increasing metal concentration (30,31). In the case of solvents of low dielectric constant, D becomes independent or in fact increases (12,26,27,29,31) with increasing metal concentration.

The effect of various chloride salts on the extraction of ferric chloride from hydrochloric acid solution was examined by Morrison (41). For extractions into ethyl ether it was found that adding a salting agent significantly increased the percentage extraction. The extraction depended to a certain extent on the nature of the cation used. The salting agent increases the concentration of the extractable complex by decreasing the dielectric constant of the aqueous phase, by mass action effect, and by decreasing the water activity (10).

From acid-alkali chloride solutions the species extracted is mainly the protonated species even when the alkali halide concentration predominates. For proton deficient systems, other complexes such as $LiFeCl_4$ and $Ca(FeCl_4)_2$ have been identified in the organic phase (11).

Extraction into Polyurethane Foam

In recent years the use of polyurethane foam in separation systems has been investigated extensively. It is used both as a solid support for other active agents and as the extractive medium itself.

Ross and Jefferson (42) first used open-pore polyurethane foam as a support for chromatographic separations. The foam was prepared "in-situ" and the column was then used to separate various aliphatic hydrocarbons. Ross (43) later examined this application to gas and liquid chromatography in greater detail. Lynn, Rushneck and Cooper (44) have varied the isocyanate-polyol ratio in "in-situ" formed polyurethane foam, and have examined the effect of excess NCO or OH groups in liquid chromatography.

A number of workers have coated polyurethane foam with various reagents in order to achieve the desired separation. Uthe, Reinke, and Gesser (45) coated polyurethane foam with various chromatographic greases to extract organochlorine pesticides from water. Similarly prepared foam plugs have been used by Uthe, Reinke and O'Brodovich (46) as field monitors for pesticides and polychlorinated biphenyls.

Musty and Nickless (47) have examined various foams, both coated and uncoated, in the extraction of organochlorine pesticides and polychlorinated biphenyls. Various flow rates and pH's were investigated.

Braun and Farag have performed extensive studies using polyurethane foam as a solid support for reversed phase partition chromatography. Nickel and palladium were separated using polyurethane foam as a support for tri-n-butyl phosphate (48). The separation of nickel, bismuth and palladium was also described using a similar system (49).

Braun and Farag also used tri-n-butyl phosphate loaded foams to quantitatively extract gold (III) from acidic solutions of thiourea (50). Separation from higher concentrations of Zn^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}, Sb^{3+}, Cu^{2+}, Bi^{3+} and Pd^{2+}, was attained. Extraction of the gold-thiourea complex with tri-n-butyl phosphate loaded foam was also compared to that of active carbon (51). Evidence was presented indicating the foam acts only as an inert support in the loaded state.

Iron was separated from cobalt, copper and nickel in hydrochloric acid systems using tri-n-butyl phosphate loaded polyurethane foam (52). The distribution of the metals was dependent on the HCl concentration with only iron being retained by the foam at 4M HCl.

Tri-n-octylamine was used by Braun _et al._ (53) to treat foams used to separate trace amounts of cobalt from nickel in hydrochloric acid media.

Lypka, Gesser and Chow (54) used polyurethane foam coated with benzoylacetone to extract copper and cadmium from aqueous solutions. Separation of the two metals was also achieved.

Diphenylthiocarbazone treated foams were used by Chow and Buksak (55) for the extraction of mercury and methylmercury from aqueous solutions.

Polyurethane foams have also been loaded with inorganic reagents. A precipitate of finely divided silver sulphide has been used in the isotope exchange separations of radio silver (56). Isotope exchange separations of radio iodide and radio silver on plasticized iodine and silver dithizonate foams have also been demonstrated (57).

Braun and Farag also used plasticized foams containing zinc dithizonate to quantitatively extract trace amounts of silver from aqueous solutions (58). The effects of different plasticizers, dithizone concentrations and pH's were examined. Dithizone and diethyldithiocarbamate foams were used to collect and preconcentrate trace concentrations of mercury (59). A similar system was used in the preconcentration of cobalt (60).

Braun and Farag have used polyurethane foams treated with chromogenic organic reagents in a plasticizer solution for the detection and semiquantitative determination of metal ions from dilute aqueous solutions (61). The detection of zinc, lead, copper and cobalt at concentrations in the ppb range was illustrated.

Braun has also chemically altered the foam by introducing ion exchange groups into the structure of the polymer (62). Using polyurethane - Varion KS heterogeneous cation exchange foam, distribution coefficients were determined for cadmium (II), zinc (II), iron (III) and calcium (II) (63).

Mazurski, Chow and Gesser (64) incorporated sulfhydryl groups in polyurethane foam by exposing foam plugs to an electrical discharge in a hydrogen sulfide atmosphere. The foams were then used to absorb mercury (II) chloride and methylmercury (II) chloride from aqueous solutions.

Although the applicability of unloaded foams is lessened somewhat by their limited selectivity, they have been used successfully for the separation and concentration of a number of inorganic and organic components.

Bowen (6) was the first to use polyurethane foam to extract a number of substances from dilute aqueous solutions. The foam performed in a similar manner to diethyl ether in extracting iodine, benzene, chloroform, and phenol from water; mercury (II) and gold (III) from 0.2M hydrochloric acid; iron (III), antimony (V), thallium (III), molybdenum (VI) and rhenium (III) from 6M - hydrochloric acid and uranium (VI) from saturated aluminum nitrate solution. From surface area measurements it was concluded that absorption rather than adsorption was the process involved.

Gesser et al.(65) used untreated polyurethane foam to extract polychlorinated biphenyls (PCB) from water. The PCB were recovered by eluting with acetone and hexane, and then analyzed by gas chromatography. A similar method was used to monitor river and municipal drinking water for organic matter (66).

Polyurethane foams have also been used by Bidleman and Olney (67,68) to measure PCB and chlorinated insecticide levels in the atmosphere.

Gough and Gesser (69) used treated and untreated polyurethane foam to remove various phthalates from aqueous solution. It was found that untreated foams were as efficient for removing most phthalates as foams coated in D.C.-200 silicone oil.

Braun and Farag found that gold-thiourea complex is extracted by unloaded foams almost to the same extent as the tri-n-butyl phosphate loaded polyurethane. Similar results were obtained with palladium-thiourea complex although elution from the unloaded foam proved more difficult.

Lypka (70) used untreated foam to extract copper and cadmium from aqueous solution. The extraction was pH dependent with extraction curves similar to acetylacetonate systems.

Previous work (71) in this laboratory has shown that gallium and iron may be extracted from aqueous solutions using untreated polyurethane foam. A flow-through system was used and the equilibrium between the foam and the solution was not examined.

This study was undertaken to investigate the extraction of gallium by polyurethane foam under equilibrium conditions, and to determine the extent to which the extraction by polyurethane foam is similar to the extraction of gallium by organic ether solvents.

Membrane Transport

The term membrane has been defined as a phase, usually heterogeneous, which acts as a barrier to the flow of molecular and ionic species, present in the liquids or vapors in contact with the two surfaces (72). Membranes may be either solid or liquid. They are classified as natural or synthetic, with the greater emphasis being placed on the study of natural membranes in biological systems.

The properties of membranes generally include some interaction with the solute. Most membranes carry ionogenic groups fixed to the structure which give properties of selectivity or semipermeability to the membrane. Often membranes will swell and imbibe water when in contact with aqueous solutions. Permeability has been related to the degree of swelling by a number of workers (73). The degree of cross linking of the membrane is another characteristic which has been found to affect the rates of diffusion. In general the diffusion rate decreases as the extent of cross linking increases (73).

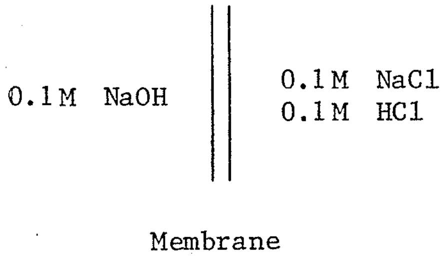
The driving forces for the transport of solutes across a membrane may include gradients of chemical potential, electric potential, pressure or temperature. Often more than one factor will be involved.

Expressions have been developed (74) describing the process of diffusion through a membrane under various conditions. Experimental methods for determining the various coefficients have also been documented (75,76).

An interesting phenomenon, not uncommon in biological systems (77), involves the movement of a solute across a membrane in the absence of, or against a difference in concentration or electrical potential. Such movement is called "active transport". It is generally believed that a carrier mechanism is involved in this type of diffusion process. The transport of alkali metal cations through a liquid membrane by macrobicyclic carriers has recently been reported (78).

Choy, Evans and Cussler (79) have developed a liquid membrane system which will transport sodium ions against a concentration gradient. The mechanism of transport involves a mobile carrier, the macrocyclic antibiotic monensin, which is dissolved in the membrane and reacts selectively with sodium.

The experiment was set up as shown below:



The monensin forms a complex with sodium ion on the basic side of the membrane. This complex then diffuses down its concentration gradient across the membrane. At the membrane-acid interface the sodium is replaced by a proton and the monensin diffuses back across the membrane. The net result is that sodium ions are moved in one direction and protons are moved in the other. Though the sodium is transferred against a concentration gradient with respect to the two solutions, within the membrane itself diffusion always occurs from a region of high concentration to a region of low concentration. It seems probable that once the mechanism has been established in other cases of active transport, it will be shown that Fick's Laws are not contravened.

Based on earlier results demonstrating the solubility of the $HGaCl_4$ complex in open-celled polyurethane foam, it became apparent that gallium would diffuse through polyurethane film. This thesis reports the results of some preliminary experiments which indicate "active transport" of gallium.

Experimental

Apparatus and Reagents

Model 306 Perkin Elmer Atomic Absorption Spectrophotometer

Varian Techtron Hollow Cathode Lamps

Beckman Electromate pH Meter

Radiometer - Conductivity Meter - Type CDM 2d.

Haake Temperature Controller model - E 12

Fisher Scientific Certified Buffer Solutions

Gallium metal, 99.9999%, Research Inorganic Chemical Co.

Silver Nitrate, Baker Analyzed Reagent, J. T. Baker Chemical Co.

Sodium Hydroxide, Certified Reagent, Fisher Scientific Co.

Lithium Chloride, Certified Reagent, Fisher Scientific Co.

Potassium Chloride, Certified Reagent, Fisher Scientific Co.

Potassium Sulphate, Reagent, Anachemia Chemical Ltd.

Sodium Hydroxide, Acculute Standard Volumetric Solution,
Anachemia Chemicals Ltd.

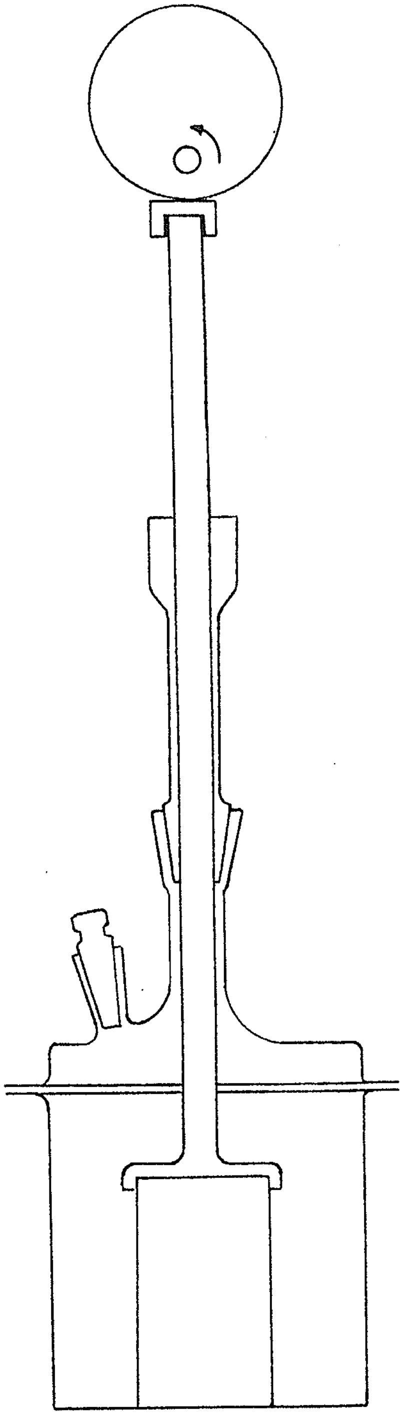
Polyurethane Foam, Union Carbide type "A",(surface area 0.081 m^2/g by
B.E.T. method using krypton.) Dr. C.G. Seefried,
Union Carbide Corp., Chemicals and Plastics,
P.O. Box 8361, South Charleston, W. Virginia,
U. S. A., 25303

Polyurethane Film, 0.127mm,MP1880 Natural
J. P. Stevens and Co., Inc.,
Elastomeric and Plastic Products Dept.,
Easthampton, Mass. 01027

Pyrex batch extractor and diffusion cells were made (figs. 1 and 2)

Figure 1

Batch Extraction Apparatus



General Procedure

Part I Polyurethane Foam

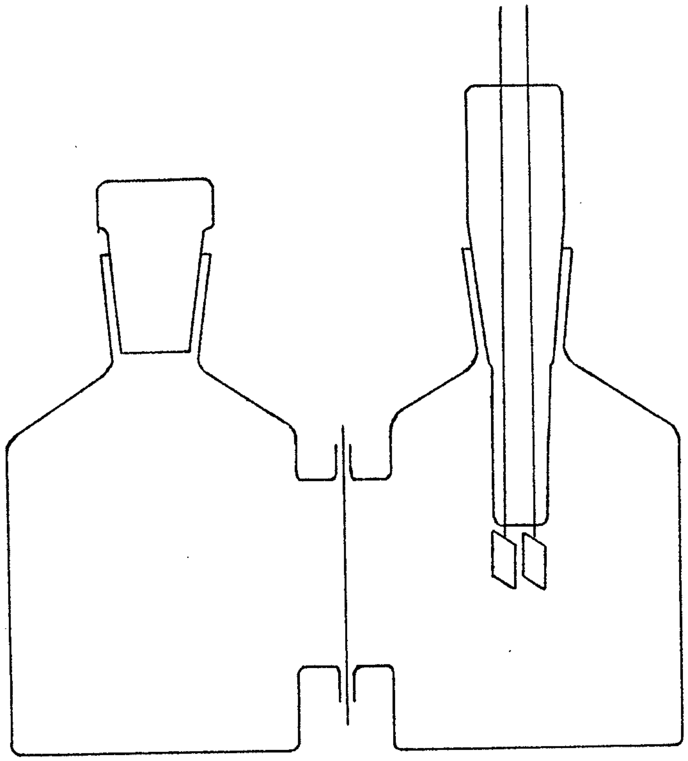
Foam plugs, 4.0 cm. in diameter and 5.3 cm. in length, average weight 2.1535 ± 0.0608 gm. were cut from sheets of polyurethane foam. Prior to use, the plugs were soxhlet extracted with acetone for 6 hours, washed with distilled water, 1 M HCl, distilled water and then air dried.

Experiments were carried out by placing a foam plug in the batch extractor shown in fig. 1, and equilibrating, usually for a period of 30 minutes. The equilibration was accomplished by using an off-centre circular cam which converted the rotary motion of an electric motor to a linear motion, resulting in cycles of compression and expansion of the foam plug. The plunger period was 7.5 seconds and the length of the compression stroke was 2.2 cm. The volume of solution used was 150 ml. determined by the size of the apparatus and the requirement to keep the foam plug completely immersed at all times.

The amount of gallium extracted was determined by measuring the concentration of the metal in solution after exposure to the foam and comparing it to the original concentration. The calculation of the distribution ratio (D) is illustrated in appendix B. Solutions were analyzed in accordance with instructions in the Perkin-Elmer Handbook(80), except that a nitrous oxide-acetylene flame was used in order to increase the

Figure 2

Membrane Diffusion Apparatus



sensitivity (81). A two or ten second integration period was used depending on the stability of the readout. The average of five or more instrument readings was reported.

Part II Membrane Studies

Polyurethane membrane was cut from sheets provided by J. P. Stevens & Co., Inc. It was clamped between two glass diffusion cells and the joint sealed with Dow Corning High Vacuum silicone grease to prevent leakage (fig. 2). The initial cross sectional area of the membrane was 9.1 $cm.^2$. Both 0.127mm and 0.0254mm polyurethane was tested although the 0.0254mm membrane proved too fragile to successfully complete an experiment.

Trials were carried out by putting various solutions on one side of the diffusion cell and double distilled deionized water on the other. The volume of solution used, as dictated by the cell size, was 130 ml. The cells were stirred and kept at 25.0 ± 0.5°C. in a water bath and the conductivity of the water side was monitored using a Radiometer-conductivity meter. The conductivity readings indicated when diffusion had begun and at what rate it was taking place and samples were taken accordingly. The samples were then analyzed to determine how the concentration of the various ions varied with time.

Preparation of Standard and Sample Solutions

A 1000 ppm Ga^{3+} stock solution was prepared by dissolving Ga metal 99.9999%, Research Inorganic Chemical Co., in a minimum amount of concentrated hydrochloric acid and then diluting to volume with distilled water.

Stock solutions of HCl were standardized with standard NaOH solution (Acculute Standard Volumetric Solution, Anachemia Chemicals Ltd.).

Stock solutions of LiCl were made by dissolving the salt (Certified Reagent, Fisher Scientific Co.) in distilled water and then standardizing using Fajan's method.(87)

Sample solutions were made up by diluting the above solutions to give the required concentrations.

Part I Polyurethane Foam

A. Preliminary Experiments

Introduction

Previous work on the absorption of gallium (71) by polyurethane foam had been carried out on a flow-through system and equilibrium between the solution and the foam had not been examined. In order to do this it was necessary to determine the length of time required for the equilibrium to be established. It was decided to use a solution of 2.5×10^{-3} M (174 ppm) Ga and 5.4M HCl, as the gallium concentration was within the expected capacity of the foam and the HCl concentration was close to that required for optimum absorption (based on previous work).

In addition, as it was planned to re-use the foams, a method of washing the gallium off the foam had to be developed.

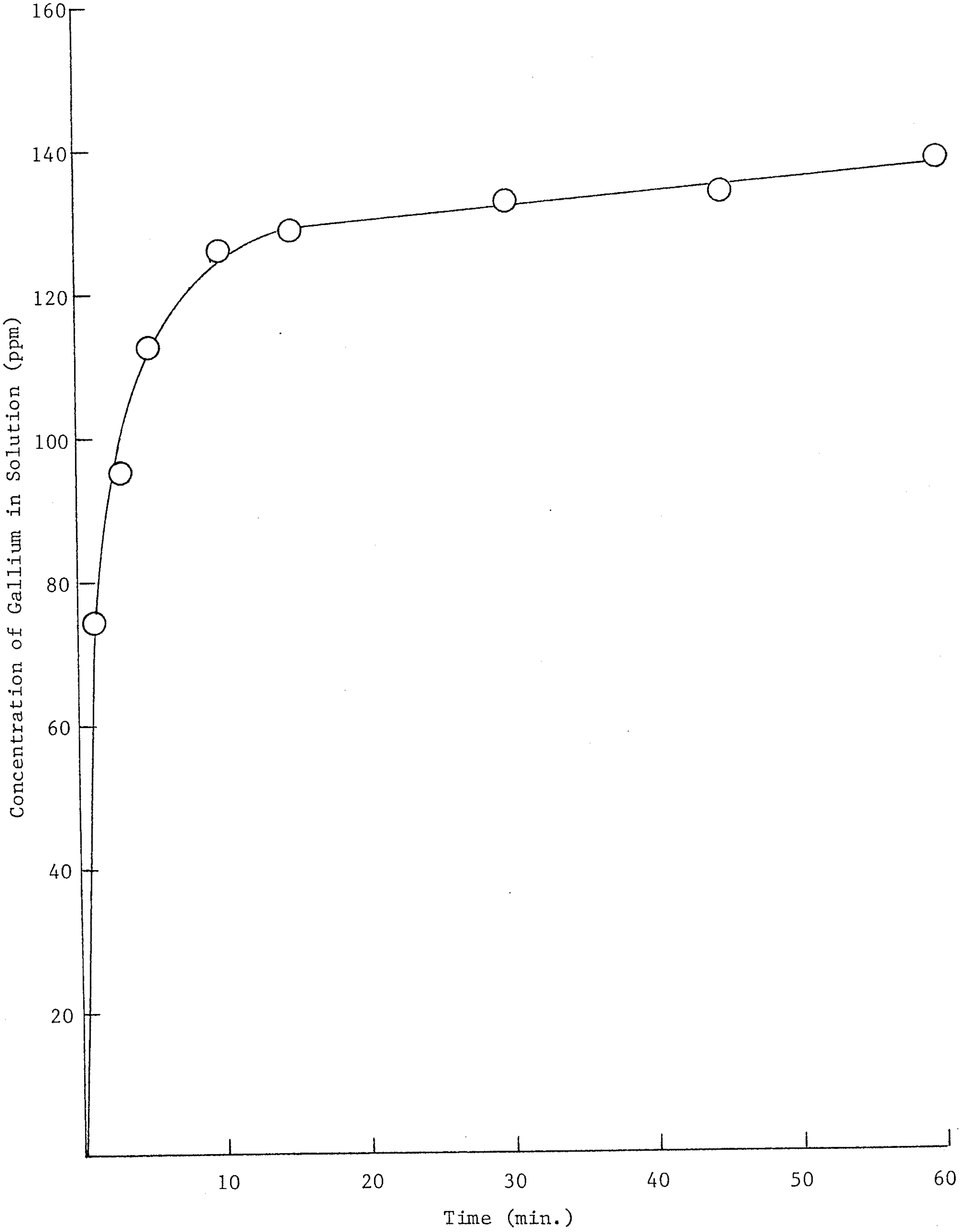
Experimental

A solution of 5.4 MHCl containing 174 ppm Ga was equilibrated for 90 minutes with a polyurethane foam plug. Samples were taken at 15 minute intervals and were analyzed for Ga.

The foam was squeezed dry and equilibrated for 60 minutes with 150 mls. of distilled water. Samples were taken and the

Figure 3

Time Dependence for the Desorption into Distilled Water of Gallium from Loaded Polyurethane Foam (Appendix A, Table A-I)


160
140
120
100
80
60
40
20
Concentration of Gallium in Solution (ppm)
10
20
30
40
50
60
Time (min.)

results are shown in fig. 3.

The foam was then washed with three 100 ml. aliquots of 2M NaOH. Each aliquot was run for 15 minutes with samples being taken at 5 minute intervals.

Results and Discussion

The results of the first run indicated that the foam and solution had reached equilibrium within the first 15 minutes. The amount of gallium absorbed on the foam was 25.06 mg.

From fig. 3 it can be seen that the removal of gallium from the foam requires longer than 1 hour to come to equilibrium. The total amount of Ga extracted was 20.81 mg. or 83.0%. The solution was titrated at the completion of the run and was found to be 0.185 M HCl, mainly as a result of the residual acid left on the foam after the first run. The removal of Ga would have been somewhat more efficient had the solution remained approximately neutral.

The gallium remaining on the foam was removed with successive NaOH washes as shown in Table I.

A mass balance indicated that 107% of the Ga was removed from the foam. It was later learned that Na^+ enhances the absorbance of gallium in a NO_2 - C_2H_2 flame (81), accounting

Table 1 : Removal of Residual Gallium from Polyurethane Foam using Three 100 ml Aliquots of 2 M NaOH

Aliquot no.	Time (min.)	Concentration of Gallium in Solution (ppm)
1	5	40.9
	10	41.3
	15	58.0
2	5	1.6
	10	1.8
	15	2.3
3	5	0.6
	10	0.4
	15	0.6

for the excess recovery. Though the absolute values are no doubt inflated, the relative magnitudes from Table I can be used to show at what stage the Ga is removed.

Based on the above results a procedure for removing Ga from the foam was developed. It consisted of washing the loaded foam with distilled water for 5 minutes, then with two 100 ml. aliquots of 2M NaOH for 30 minutes each, and then again in distilled water for 5 minutes. During the water washes the foam plug was compressed and allowed to expand using a glass rod, while distilled water was continuously run into the beaker.

The above procedure was used to wash a foam plug which had been equilibrated with three successive 30 minute runs at 1000 ppm Ga (3.15M HCl). After the washing was completed, the foam was equilibrated with 150 mls. of distilled water. Analysis of the solution showed no gallium present at the end of 30 minutes. Thus the cleaning procedure appears adequate.

B. Effect of HCl Concentration

Introduction

The concentration of HCl was varied to determine the optimum concentration for the absorption of Ga. As it was thought that the time required to attain equilibrium might change with different HCl concentrations,the change in gallium concentration with time was also examined. The effect of reusing the foam plugs was investigated by repeating two runs after the experiments in which the HCl concentration was varied had been completed.

Experimental

A polyurethane foam plug was equilibrated in solutions of 200 ppm Ga and various HCl concentrations. Samples were taken at 1, 3, 5, 10, 15, 30, 45 and 60 minute intervals. The foam plug was cleaned between runs. The results are shown in figs. 4 and 5.

Results and Discussion

As can be seen from fig. 5 there is a marked dependance of the percentage extracted on the HCl concentration. The maximum absorption occurs at 7M HCl and it appears to decrease slightly at higher acid concentrations. The general shape of the extraction curve is characteristic of the extraction of

Figure 4 a

Time Dependent Curves for the Extraction of Gallium by Open Celled Polyurethane Foam at various HCl Concentrations

(Appendix A, Table A-II)

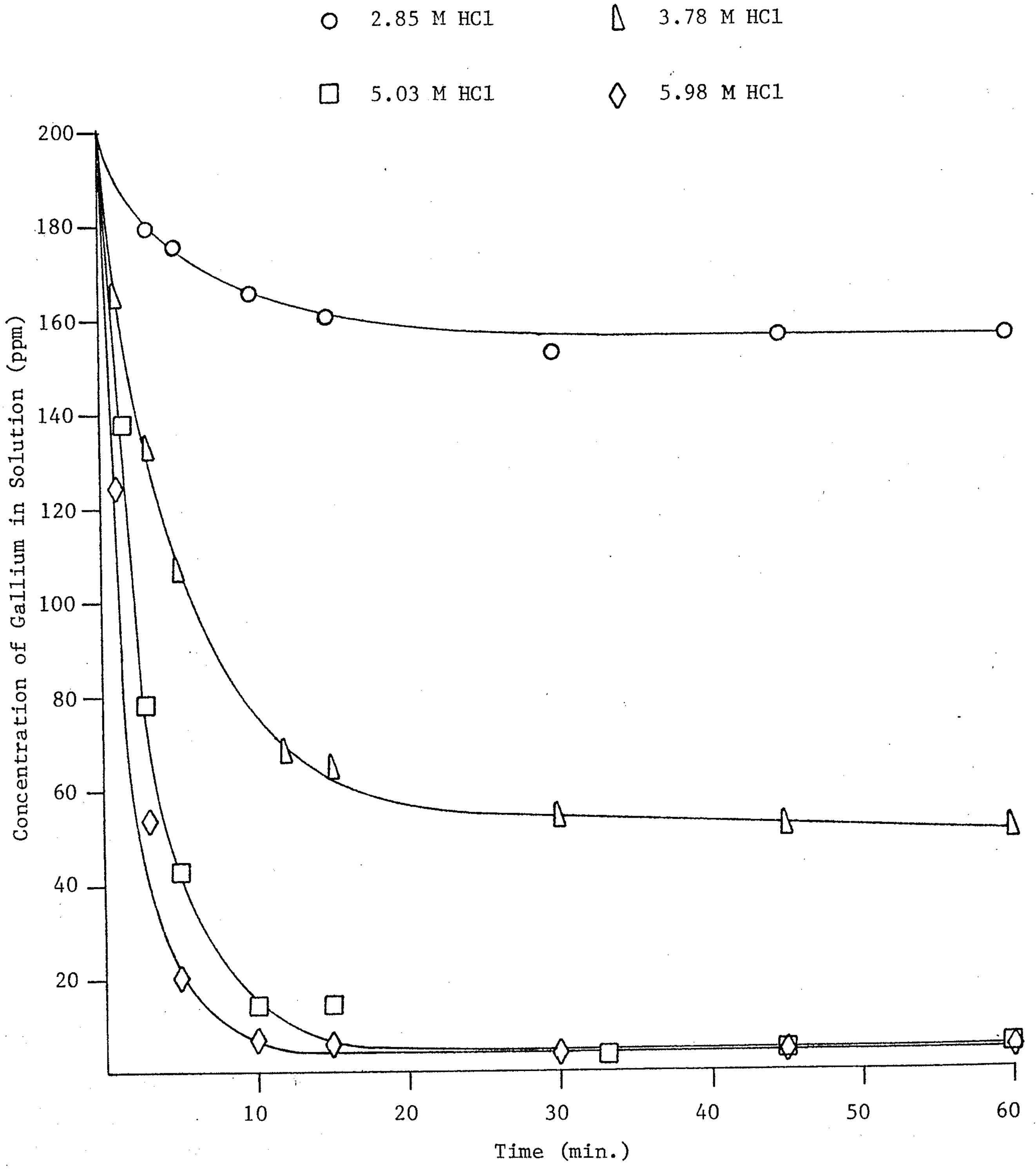

○ 2.85 M HCl
Δ 3.78 M HCl
□ 5.03 M HCl
◇ 5.98 M HCl
200
180
160
140
120
100
80
60
40
20
Concentration of Gallium in Solution (ppm)
10
20
30
40
50
60
Time (min.)

Figure 4 b

Time Dependent Curves for the Extraction of Gallium by Open Celled Polyurethane Foam at various HCl Concentrations

(Appendix A, Table A-II)

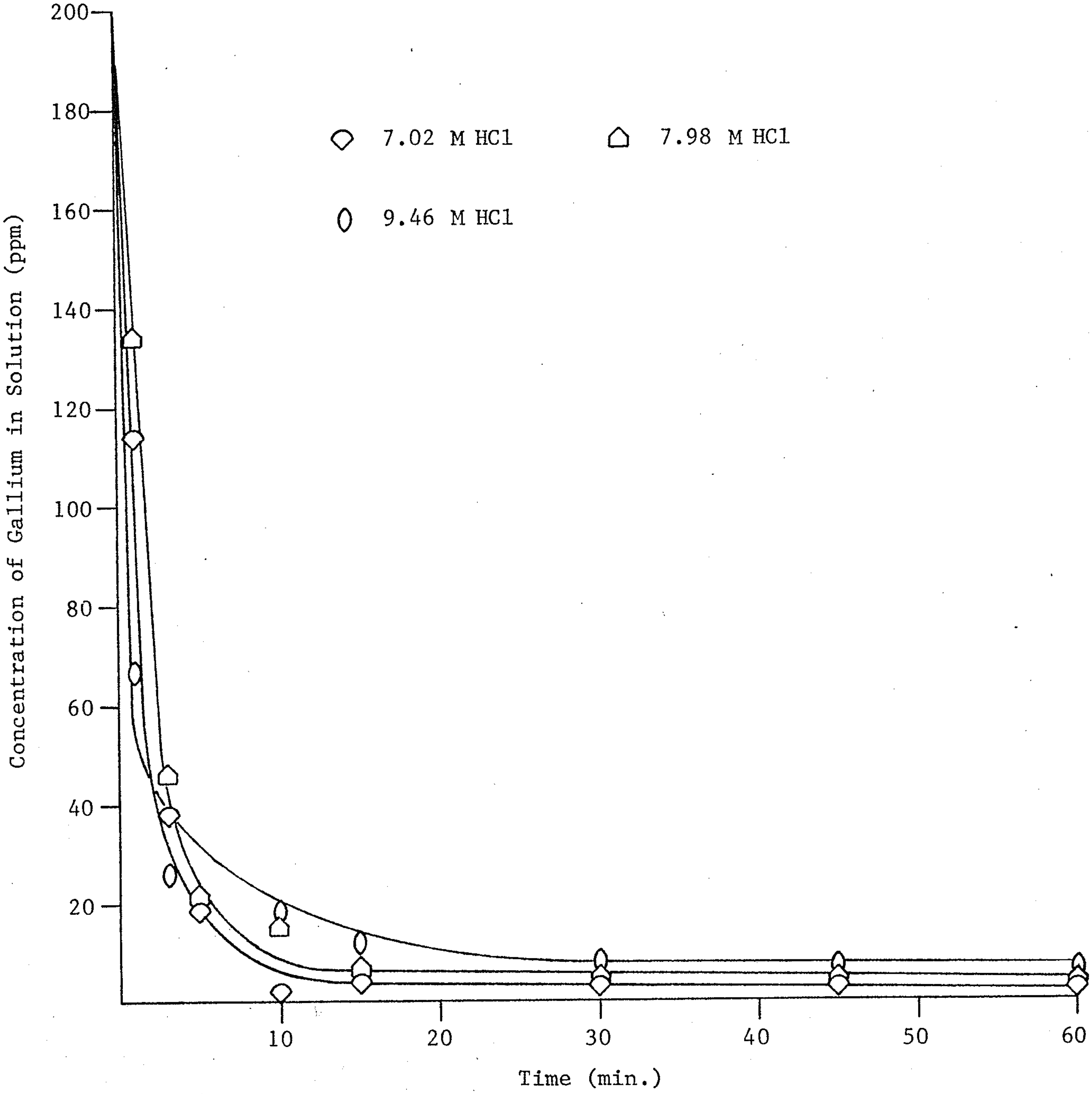
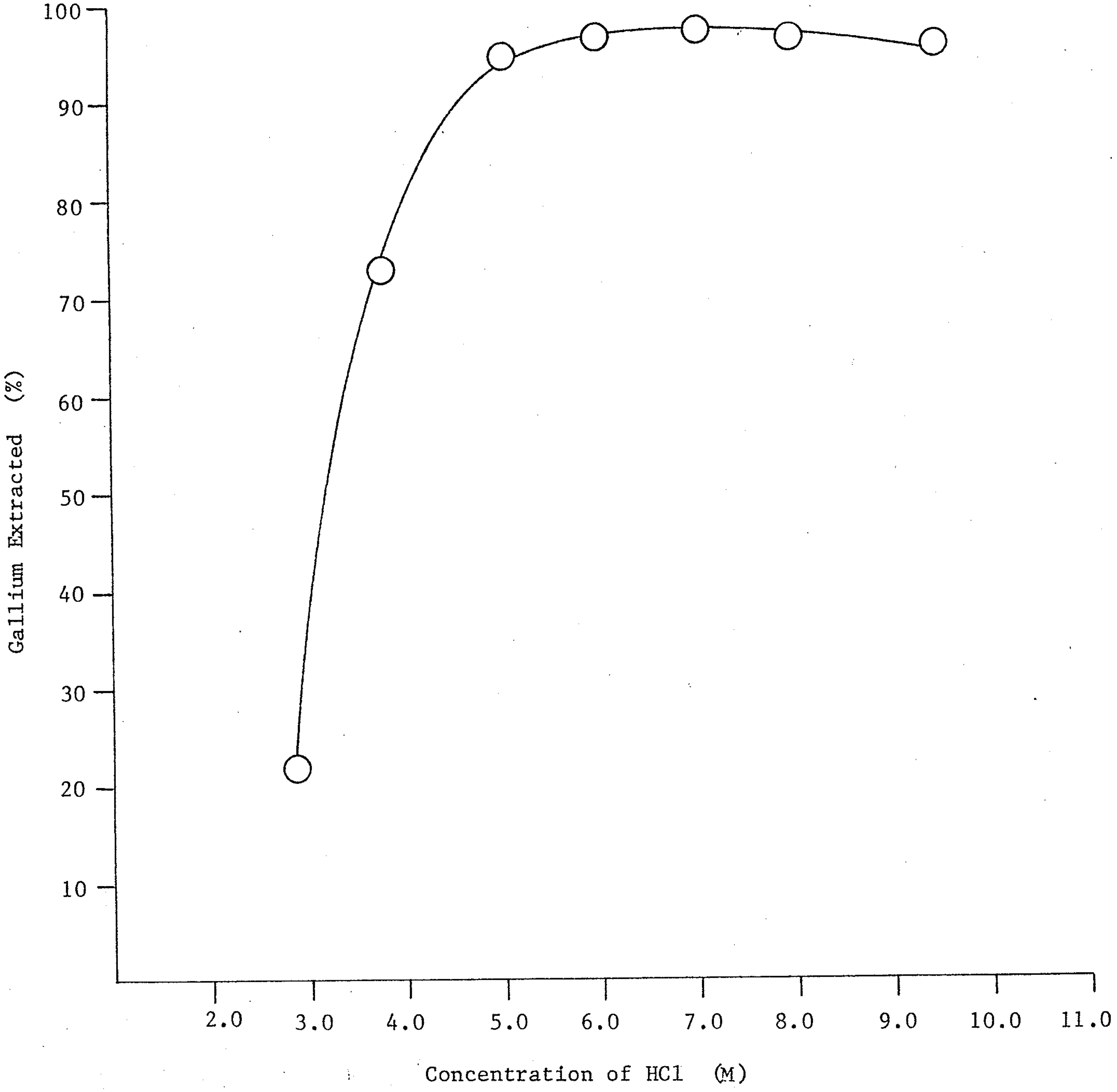

◇ 7.02 M HCl
⌂ 7.98 M HCl
0 9.46 M HCl
Concentration of Gallium in Solution (ppm)
200
180
160
140
120
100
80
60
40
20
10
20
30
40
50
60
Time (min.)

Figure 5

HCl Concentration Dependence for the Extraction of Gallium by Open Celled Polyurethane Foam

(Appendix A, Table A-III)


100
90
80
70
60
50
40
30
20
10
Gallium Extracted (%)
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
Concentration of HCl (M)

many metal halide complexes as previously discussed.

Several attempts have been made to quantitatively describe the extractive behaviour of halometal complexes (12, 19-21,30,82), however in the majority of practical solvent extraction systems the deviations from ideality in one or both phases are too great for the experimental data to be fitted to the derived equations.

Given the above considerations, the following may be taken as a simplified representation of the extraction process. Such factors as ion solvation in both phases and aggregation or dissociation of the complex in the organic phase have been ignored. Solvation no doubt occurs to varying degrees, however at moderate complex concentrations and considering the low dielectric constant of the organic phase, aggregation and dissociation may not be significant.

Formation of the $GaCl_4^-$ anion

1) $Ga^{3+} + Cl^- \overset{k_1}{\rightleftharpoons} GaCl^{2+}$ $k_1 = 0.25$ l/mole (85)

2) $GaCl^{2+} + Cl^- \overset{k_2}{\rightleftharpoons} GaCl_2^+$ $k_2 = 0.02$ l/mole

3) $GaCl_2^+ + Cl^- \overset{k_3}{\rightleftharpoons} GaCl_3$ $k_3 = 0.006$ l/mole

4) $GaCl_3 + Cl^- \overset{k_4}{\rightleftharpoons} GaCl_4^-$ $k_4 = 0.05$ l/mole

Formation of the Extractable Complex

5) $H^+ + GaCl_4^- \overset{k_5}{\rightleftharpoons} (HGaCl_4)_a$

Distribution of the Complex

6) $(HGaCl_4)_a \overset{k_D}{\rightleftharpoons} (HGaCl_4)_f$

Thus

$$k_D = \frac{[HGaCl_4]_f}{[HGaCl_4]_a} \quad ; \quad k_5 = \frac{[HGaCl_4]_a}{[H^+][GaCl_4^-]} \quad ; \quad k' = k_1k_2k_3k_4 = \frac{[GaCl_4^-]}{[Ga^{3+}][Cl^-]^4}$$

7) $$k_D = \frac{[HGaCl_4]_f}{k_5k'[Ga^{3+}][H^+][Cl^-]^4} \quad ; \quad \text{ie.} \quad \frac{[HGaCl_4]_f}{[Ga^{3+}]_a} = k_Dk_5k'[H^+][Cl^-]^4$$

The distribution ratio for the extraction process may be written as follows:

8) $$D = \frac{[HGaCl_4]_f}{[Ga^{3+}] + [GaCl^{2+}] + [GaCl_2^+] + [GaCl_3] + [GaCl_4^-] + [HGaCl_4]_a}$$

9) $$D = \frac{[HGaCl_4]_f}{[Ga^{3+}](1+k_1[Cl^-]+k_1k_2[Cl^-]^2+k_1k_2k_3[Cl^-]^3+k_1k_2k_3k_4[Cl^-]^4+k_1k_2k_3k_4k_5[H^+][Cl^-]^4)}$$

Because all the coefficients, except k_1, are much smaller than unity the above expression may be reduced to:

10) $$D = \frac{[HGaCl_4]_f}{[Ga^{3+}](1+k_1[Cl^-])} = \frac{k_Dk_5k'[H^+][Cl^-]^4}{(1+k_1[Cl^-])}$$

11) Therefore $\log D + \log(1+k_1[Cl^-]) = K + \log[H^+] + 4\log[Cl^-]$ (K=constant)

To a further approximation, the $(1+k_1[Cl^-])$ term may be neglected.

12) ie. $D = k_Dk_5k'[H^+][Cl^-]^4$

and $\log D = K + \log[H^+] + 4\log[Cl^-]$

In this case $[H^+] = [Cl^-]$ (as only HCl is used), therefore the above eqn. may be

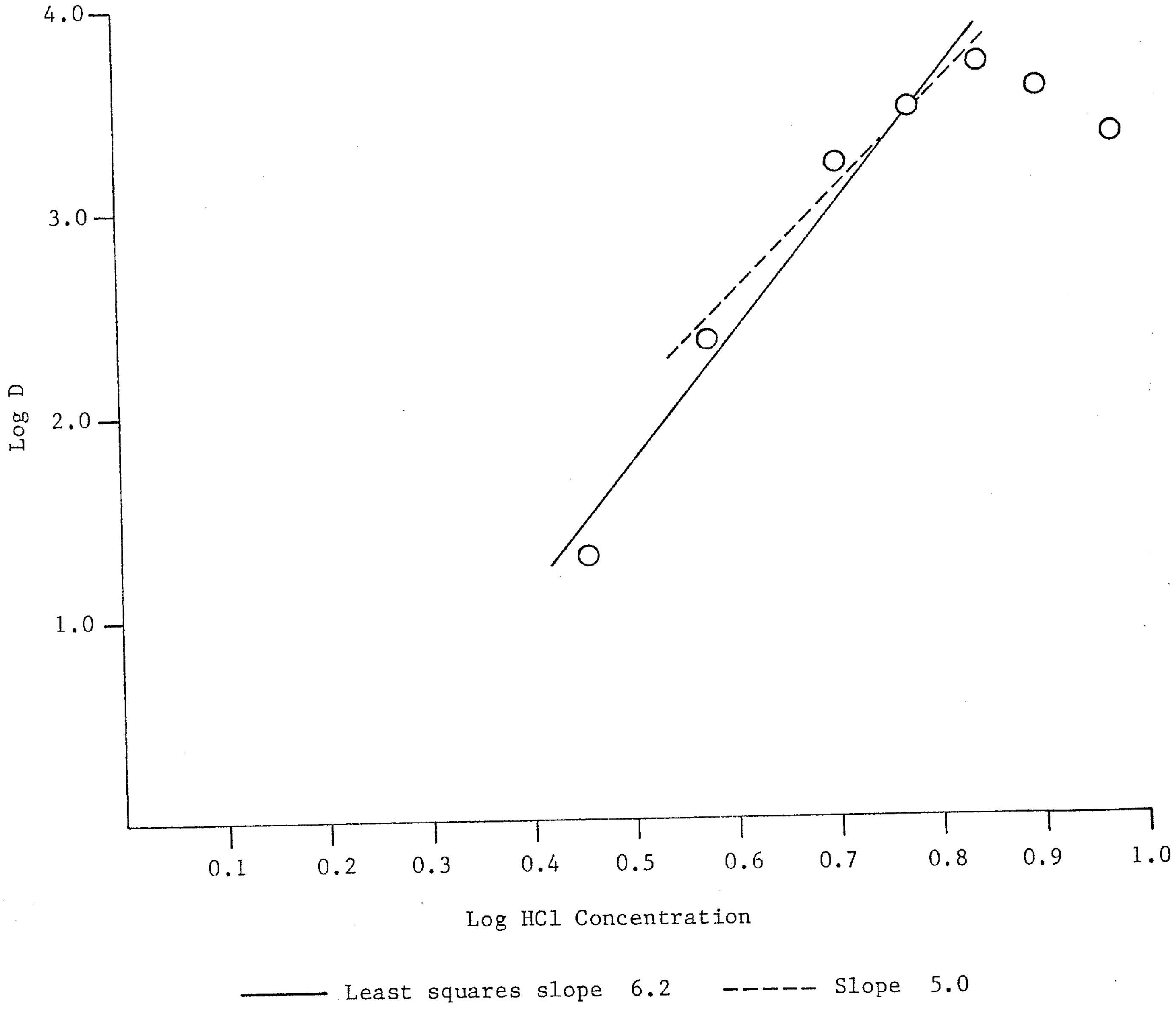
13) written: $\log D = K + 5\log[HCl]$

Thus a plot of log D vs log[HCl] should be a straight line with a slope of 5. Fig. 6 shows that the experimental results approximate this value at moderate concentrations. The least squares plot through the first five points has a slope of 6.2. When the log $(1+k_1[Cl^-])$ term is included, the disagreement

Figure 6

Variation of Log D with Log HCl Concentration at 200 ppm Gallium

(Appendix A, Table A-IV)


4.0
3.0
2.0
1.0
Log D
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
Log HCl Concentration
Least squares slope 6.2
Slope 5.0

between the experimental and the theoretical values of the slope, increases by approximately 0.5 for $k_1 = 0.25$(85). Information concerning the medium in which this value was measured is not available however. Morris and Andrews (86) obtained a value of $k_1 = 1.02$ in 0.691 M. $HClO_4$. When this value is used, the disagreement increases by approximately 0.8. It seems probable that the value of k_1 is dependent on the acid concentration and perhaps on the concentration of other ions in solution.

From equation (12) it is evident that an increase in HCl concentration will result in an increase in the percentage extraction. Qualitatively it seems reasonable to expect an increase in the concentration of the extractable complex with increasing HCl concentration (based on mass action arguments) and thus a corresponding increase in the distribution ratio. The addition of HCl also causes a significant decrease in the water activity. By binding the water dipoles into an oriented shell around the ions, they become unavailable as "free solvent". Hydrochloric acid also greatly reduces the dielectric constant of the aqueous phase. Both these effects stabilize the ion association complex resulting in increased extraction.

The decrease in extractability at high acid concentrations for some metal halide systems is not predicted by the various mass action equations which have been developed and certainly not the above semi-quantitative approach. This behaviour is usually explained as a result of the organic phase dissolving in the aqueous phase, thus diluting the acid strength and affecting the complex formation equilibrium. Evidence has been presented showing that in systems where the phase volumes do not change or equilibration, there is no maxima in the distribution curves of metal halides.

This argument, however, does not apply to extractions into polyurethane foam, as there is no noticeable tendency for the foam to dissolve into the aqueous phase (at least not in proportions required to dilute the acid strength significantly). It has also been noted in the extraction of $FeCl_4$ into low dielectric constant ethers, that at acidities higher than about 8 M HCl the HCl:$FeCl_3$ ratio is frequently higher than unity (32,33). A similar result has been reported for the extraction of $HGaCl_4$ into isopropyl ether (40). Absorption spectrum data on the iron system suggest that the excess HCl is only loosely associated with the complex if at all. It was thought that the dissolution of HCl into foam at high acid concentrations could result in a sufficient decrease in acid strength in the aqueous phase to lower the distribution ratio. A titration of the aqueous phase after equilibrium however, revealed no significant decrease in acid concentration.

Perhaps at high HCl concentrations, a higher ordered chloride complex is formed which is less extractable than the $HGaCl_4$ complex.

This could explain the decrease in extraction which is observed.

The effect of HCl concentration on the time to reach equilibrium is shown in fig. 4. No marked trend is apparent. All runs have come to equilibrium after approximately 20 minutes.

In order to examine the effect of reusing the foam plugs two runs were repeated. It was thought that any change in the performance of the foam would be most evident at HCl concentrations where the extraction is less efficient. The run at approximately 4 M HCl was repeated first and essentially the same percentage extraction (70.6% compared to 72.9%) was achieved indicating that the foams could be reused without affecting the extraction efficiency. When the first run at 3 M HCl was repeated, only about one-half of the original percentage extraction was attained (11.7% compared to 21.8%). This difference exceeds the experimental error and could not have been caused by HCl damage to the foam as the run at 4 M HCl was not affected.

It appears as though some gallium is irreversibly bound to the foam the first time it is used and then remains on the foam. If this were the case, it would become apparent only by repeating the first run. This possibility was examined in greater detail in section C.

During this set of experiments it was noticed that undiluted samples gave significantly lower absorption on the Atomic Absorption Spectrophotometer than diluted samples.

Tests on standard solutions showed that HCl reduced the absorbance of Ga in solution. This effect has been documented by Lypka and Chow (83). To avoid preparing sets of standard solutions at each acid concentration studied, the method of standard addition was used whenever practicable.

C. Reversibility of Gallium Absorption

Introduction

The results of the previous section indicated that some gallium may be irreversibly absorbed on the foam the first time it is used. This possibility was investigated further in part a). In addition, the redistribution of gallium from a loaded foam was also examined in part b).

Experimental

a) New foams were equilibrated for 30 minutes with 150 mls. of 3 M HCl solution containing 100 ppm Ga. Samples were taken and analyzed by the method of standard addition. The foams were then cleaned and the procedure was repeated. The results are shown in Table II.

b) In order to determine if the distribution ratio would be the same whether the gallium was initially in the foam (desorption) or initially in solution (absorption), the following procedure was carried out:

Step 1 A foam plug was loaded with Ga by equilibrating with 150 mls. of 3.30 M HCl solution containing 100 ppm Ga. After 30 minutes samples of the solution were taken.

Step 2 The foam was then squeezed dry and

Table II : Variation of Extraction Efficiency for Gallium using a Polyurethane Foam Cleaned between successive Experiments

Experiment no.	Trial A		Trial B	
	Initial Conditions: 150 mls 2.92 M HCl, 100 ppm Ga		Initial Conditions: 150 mls 3.16 M HCl, 100 ppm Ga	
	% Extracted	D	% Extracted	D
1	32.7	33.9	50.3	72.5
2	23.9	21.9	35.4	39.1
3	30.9	31.2	44.9	58.2
4			40.2	48.0
5			35.8	39.8
6			38.8	45.3

Table III : Comparison of Distribution of Gallium (between Polyurethane Foam and HCl Solution) on Absorption and Desorption

Trial	Step	Initial Conditions	Equilibration Time (min.)	% Gallium in Foam	D
A	1	150 mls, 3.30 M HCl, 100 ppm Ga	30	57.1	92.9
	2	150 mls, 3.30 M HCl	30	64.3*	125.6*
	3	150 mls, 3.29 M HCl 57.1 ppm Ga	30	52.5	77.2
B	1	150 mls, 3.34 M HCl 100 ppm Ga	30	53.3	79.7
	2	150 mls, 3.34 M HCl	90	57.6	94.8
	3	150 mls, 3.30 M HCl 53.7 ppm Ga	30	44.1	55.1

* not equilibrium values

equilibrated for 30 minutes with 150 mls. of 3.30 M HCl containing no gallium. Samples of solution were again taken and analyzed by standard addition.

Step 3 The foam was then cleaned and equilibrated with 150 mls. of 3.30 M HCl solution containing the same amount of gallium as was absorbed on the foam in step 1. Thus step 2 and step 3 are comparable systems.

The procedure was repeated as above except a time study was carried out on the removal of the gallium from the foam to see if equilibrium was established within 30 minutes. Results are shown in Table III and fig. 7.

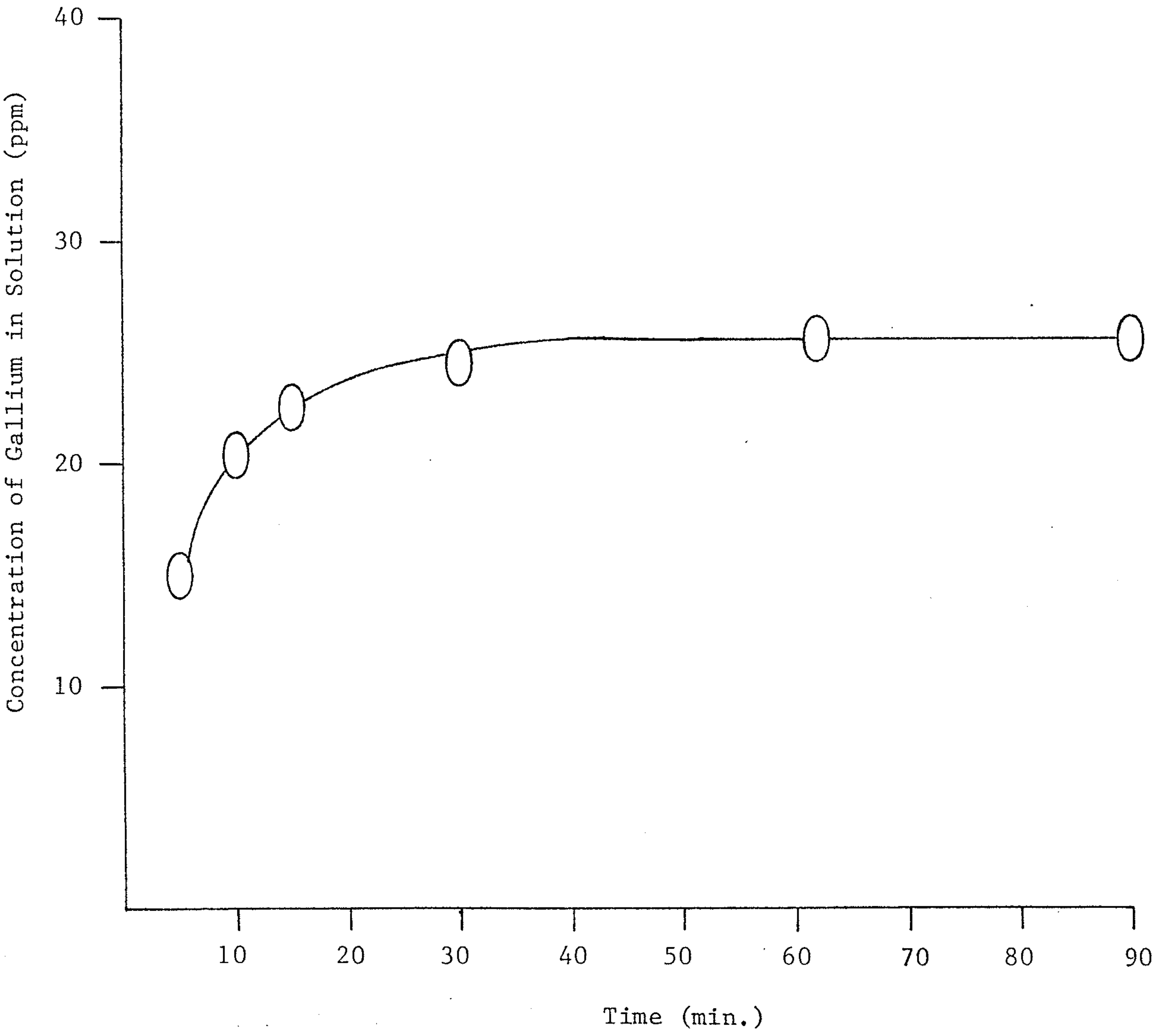
Discussion and Results

a) As noted in Table II, the first trial showed a significant drop in percentage extraction for the second run. However, for the third run the extraction efficiency increased almost to the original value. The second trial shows a similar trend, but although the repeatability is not good, the results for the last few runs fluctuate around a lower percentage extraction than was initially attained. More data is required before definite conclusions can be made, however, it

Figure 7

Time Dependence for the Desorption of Gallium from a Loaded Polyurethane Foam into 3.34 M HCl Solution

(Appendix A, Table A-V)


40
30
20
10
Concentration of Gallium in Solution (ppm)
10
20
30
40
50
60
70
80
90
Time (min.)

appears as though the extraction efficiency is a maximum the first time the foam is used. One explanation could be that the foam absorbs a certain amount of gallium irreversibly on the first equilibration and that this gallium remains on the foam causing less efficient extraction for subsequent runs.

b) By comparing the results of steps 2 and 3 in Table III, it appears that the absorption-desorption process is not reversible. In the second trial, the time study (fig. 7) shows that the desorption appears to take longer, coming to equilibrium after a period of approximately 1 hour. In spite of the longer equilibration period, the distribution ratio is still greater for the desorption of gallium from the foam.

From the results in steps 1 and 3 there is an apparent dependance of the distribution ratio on the gallium concentration. This is examined in more detail in section D.

D. Effect of Gallium Concentration

Introduction

The effect of gallium concentration on the distribution between the solution and the foam was investigated. It was decided to use approximately 3 M HCl in order to attain comparable amounts in each phase, thus improving the accuracy of the calculation of the distribution coefficient. One disadvantage of working in this range is that small changes in acid concentration could cause significant changes in percentage extraction (fig. 5).

Experimental

Solutions of 3 M HCl containing various concentrations of gallium were equilibrated with a foam plug for a period of 30 minutes. Samples were then taken and analyzed by the method of standard addition. Two or more runs were carried out at each gallium concentration. The foam plug was cleaned after each run.

The effect of ionic strength was examined by adding K_2SO_4 to make the ionic strength at 20 ppm the same as at 1000 ppm gallium. Results are shown in figs. 8 and 9.

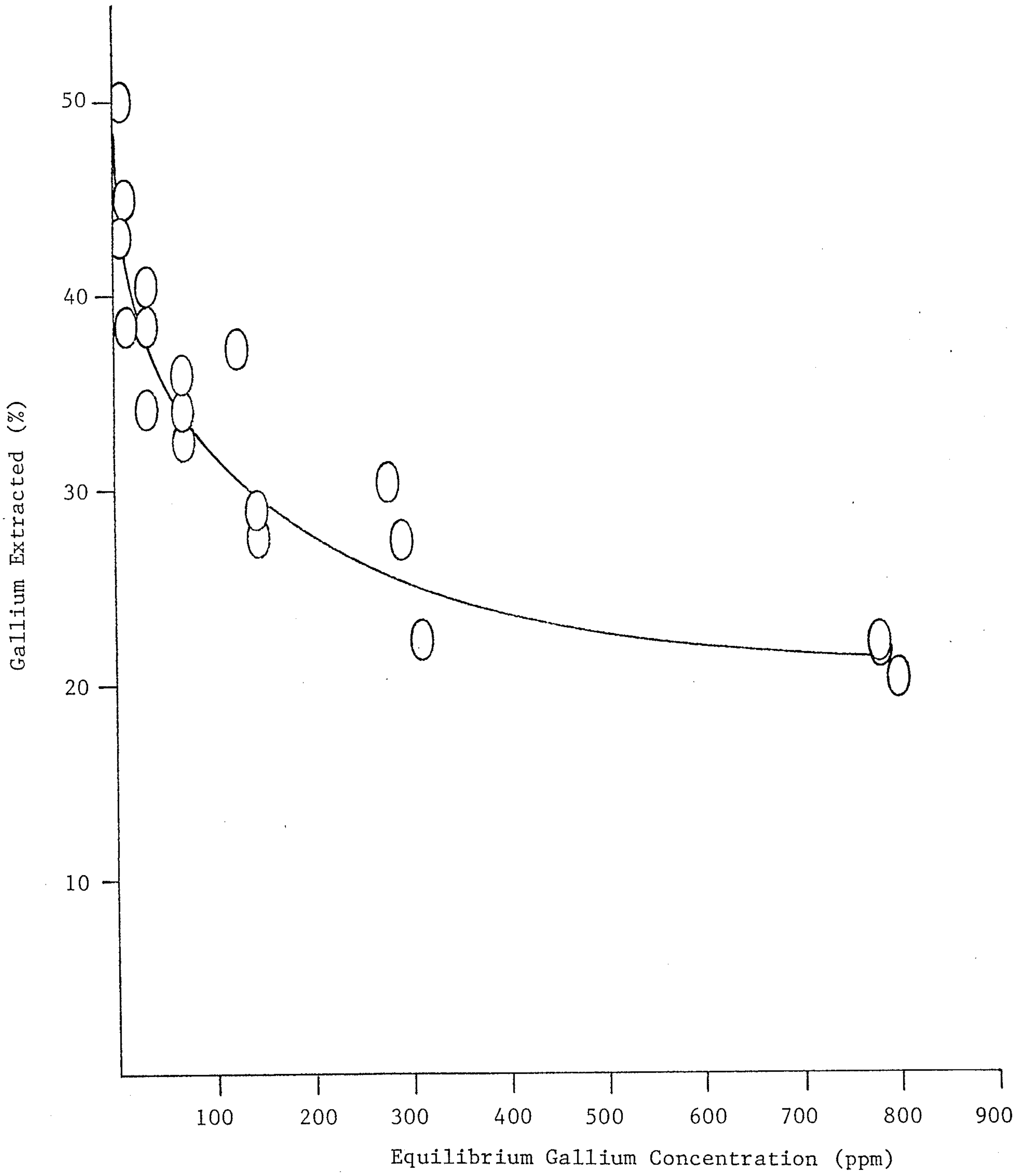
Results and Discussion

Fig. 8 shows a decrease in percentage extraction as the concentration of gallium increases. This is somewhat unexpected

Figure 8

Variation of Percentage Extraction with Equilibrium Gallium Concentration at 3.15 M HCl

(Appendix A, Table A-VI)


50
40
30
20
10
Gallium Extracted (%)
100
200
300
400
500
600
700
800
900
Equilibrium Gallium Concentration (ppm)

as extractions into isopropyl ether are independent of $[Ga]$ at low concentrations and increase with increasing $[Ga]$ at concentrations exceeding 0.01 molar (40). In addition, the expression for the distribution ratio developed in section B suggests that it should be independent of Ga concentration.

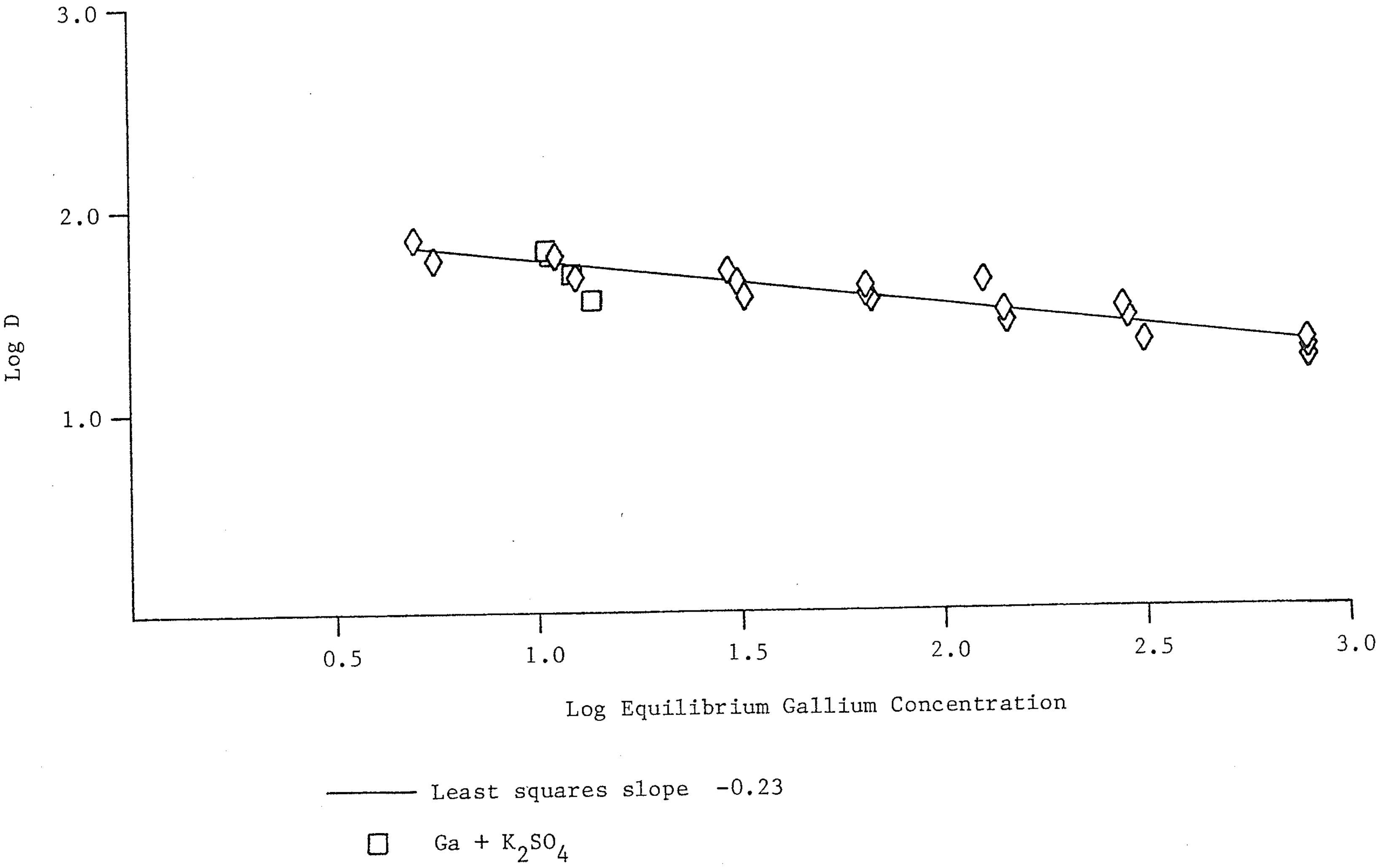
The increased ionic strength at high $[Ga]$ was ruled out as a probable cause of the reduction in percentage extraction. Fig. 9 shows no marked effect of ionic strength at the concentrations involved.

The foam capacity at 3 M HCl was examined to ensure that the reduction in absorbance was not a result of a capacity limitation. The results of these experiments are reported in section F. It was found that the foam capacity at 3 M HCl was much lower than that at 7 M HCl (which had been previously determined). At 3 M HCl, the amounts of gallium absorbed are no longer on the "capacity plateau" shown for 7 M HCl in fig. 12. On this "plateau" the percentage extraction is independent of the amount of gallium on the foam. In order to determine the effect of gallium concentration on the distribution, one should operate within the confines of this region where the foam capacity does not limit the percentage extraction. As this criterion has not been met, it is probable that the results shown in figs. 8 and 9 arise from the limited foam capacity at 3 M HCl, and do

Figure 9

Variation of Log D with Log Equilibrium Gallium Concentration at 3.15 M HCl

(Appendix A, Table A-VII)


3.0
2.0
1.0
Log D
0.5
1.0
1.5
2.0
2.5
3.0
Log Equilibrium Gallium Concentration
Least squares slope -0.23
Ga + K2SO4

not reflect the true dependance of the distribution ratio on gallium concentration. In order to verify this, the effect of Ga concentration at higher acidities should be examined.

E. Effect of Chloride Concentration

Introduction

The effect of chloride (LiCl) concentration on the percentage extraction was investigated.

Experimental

Solutions of various LiCl concentrations containing either 1.0 or 0.1 M HCl and 100 ppm gallium, were equilibrated for 30 minutes with a foam plug. Samples were then taken and analyzed by the method of standard addition. The foam plug was cleaned after each run.

Results and Discussion

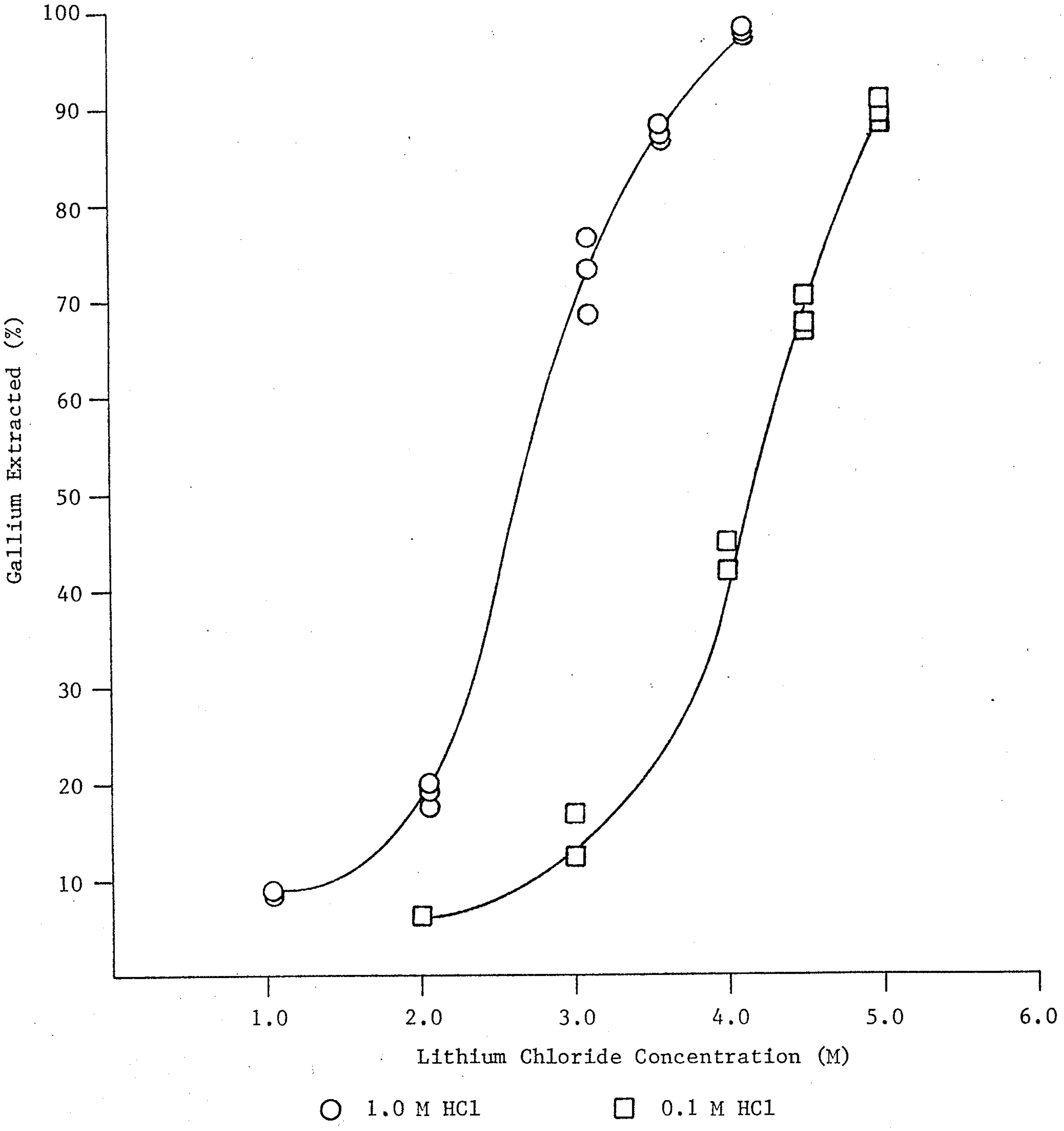
As shown in fig. 10, increasing the chloride concentration at constant acid concentration, increases the percentage of gallium extracted. It is thought that the LiCl affects the extraction in three ways:

1) by mass action effect - increasing the concentration of the anion resulting in a higher concentration of the extractable complex;
2) by reducing the water activity and developing a highly ordered water structure. This is accomplished by binding the water dipoles in an oriented shell around the ions making them

Figure 10

Variation of Percentage Extraction of Gallium with Lithium Chloride Concentration for different HCl Concentrations

(Appendix A, Table A-VIII)


100
90
80
70
60
50
40
30
20
10
Gallium Extracted (%)
1.0
2.0
3.0
4.0
5.0
6.0
Lithium Chloride Concentration (M)
○ 1.0 M HCl
☐ 0.1 M HCl

unavailable as "free solvent". The Li ion is small enough to fit into the existing structure of the water and enhance its stability through its charge (84); and

3) by lowering the dielectric constant of the aqueous phase which favors formation of the ion association complex.

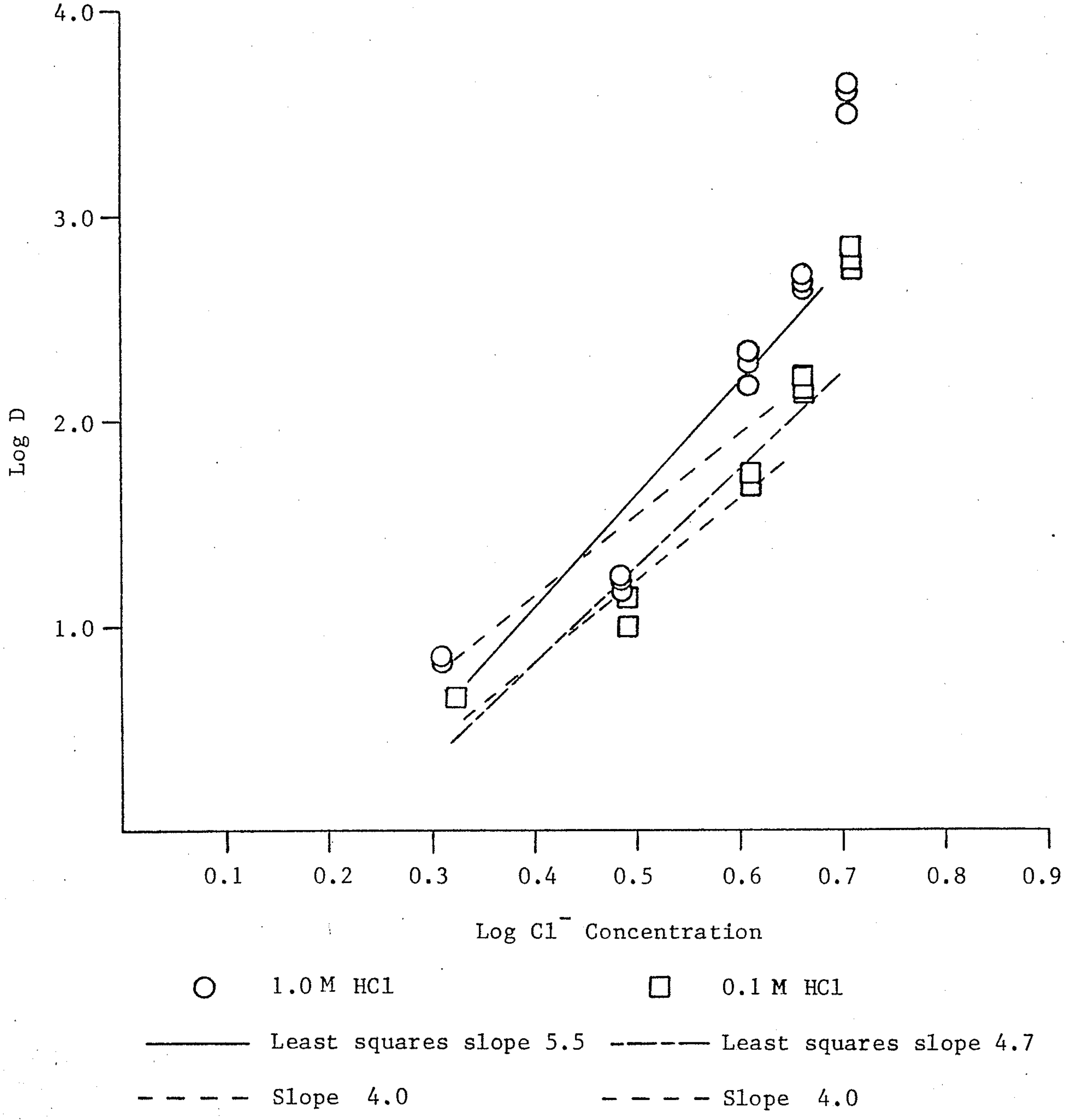
All three effects increase the concentration of the extractable complex in solution which results in an increase in the amount of gallium on the foam, thus giving a higher percentage extraction. It is expected that different chlorides would affect the distribution ratio to different degrees, as their influence on the activity coefficients of the ions participating in the formation of the complex would vary somewhat.

Equation (12) developed in section B predicts an increase in percentage extraction with increasing chloride concentration, however, the plot of log D versus log $[Cl^-]$ should be a straight line with a slope of four. As seen in fig. 11, the experimental results deviate considerably from this value, especially at high chloride concentrations. The least squares slope, excluding the highest chloride concentration, is 5.5 for 1.0 M HCl and 4.7 for 0.1 M HCl. The inclusion of the $(1+k_1[Cl^-])$ term, eqn. 11), would increase the experimental slope by 0.5 to 0.8 depending on the value chosen for k_1.

Figure 11

Variation of Log D with Log Chloride Ion Concentration at 1.0 M and 0.1 M HCl

(Appendix A, Table A-IX)


4.0
3.0
2.0
1.0
Log D
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
Log Cl$^-$ Concentration
○ 1.0 M HCl
□ 0.1 M HCl
——— Least squares slope 5.5
— — — Least squares slope 4.7
- - - - Slope 4.0
- - - - Slope 4.0

F. Capacity Studies

Introduction

It was desired to determine the capacity of the foam to absorb gallium. At first it was thought that the optimum capacity would occur in approximately 7 M HCl where the extraction efficiency was a maximum. This determination was made, however later experiments indicated that the foam capacity was dependent on several factors. Further studies were then performed to determine the effect of HCl, chloride ion, and Ga concentration on the capacity of the foam.

Experimental

A foam plug was equilibrated with 150 mls. of 7.05 M HCl containing 100 ppm Ga for 30 minutes. Samples were taken and analyzed by the method of standard addition. The foam plug was then squeezed dry but not cleaned, and the procedure was repeated with fresh solution.

A similar procedure was performed at 3 M HCl with various H^+, Cl^-, and Ga concentrations.

Results and Discussion

The effect of HCl concentration on foam capacity is shown in fig. 12. Limited capacity curves shown in fig. 13 indicate the effect of H^+ and Cl^- ion concentration on the foam capacity. Fig. 14 shows the dependance of foam capacity on

Figure 12

Variation of Extraction Efficiency of Polyurethane Foam for Gallium as a function of Amount of Gallium on the Foam at 3.16 M and 7.05 M HCl and 100 ppm Gallium in Solution

(Appendix A, Table A-X)

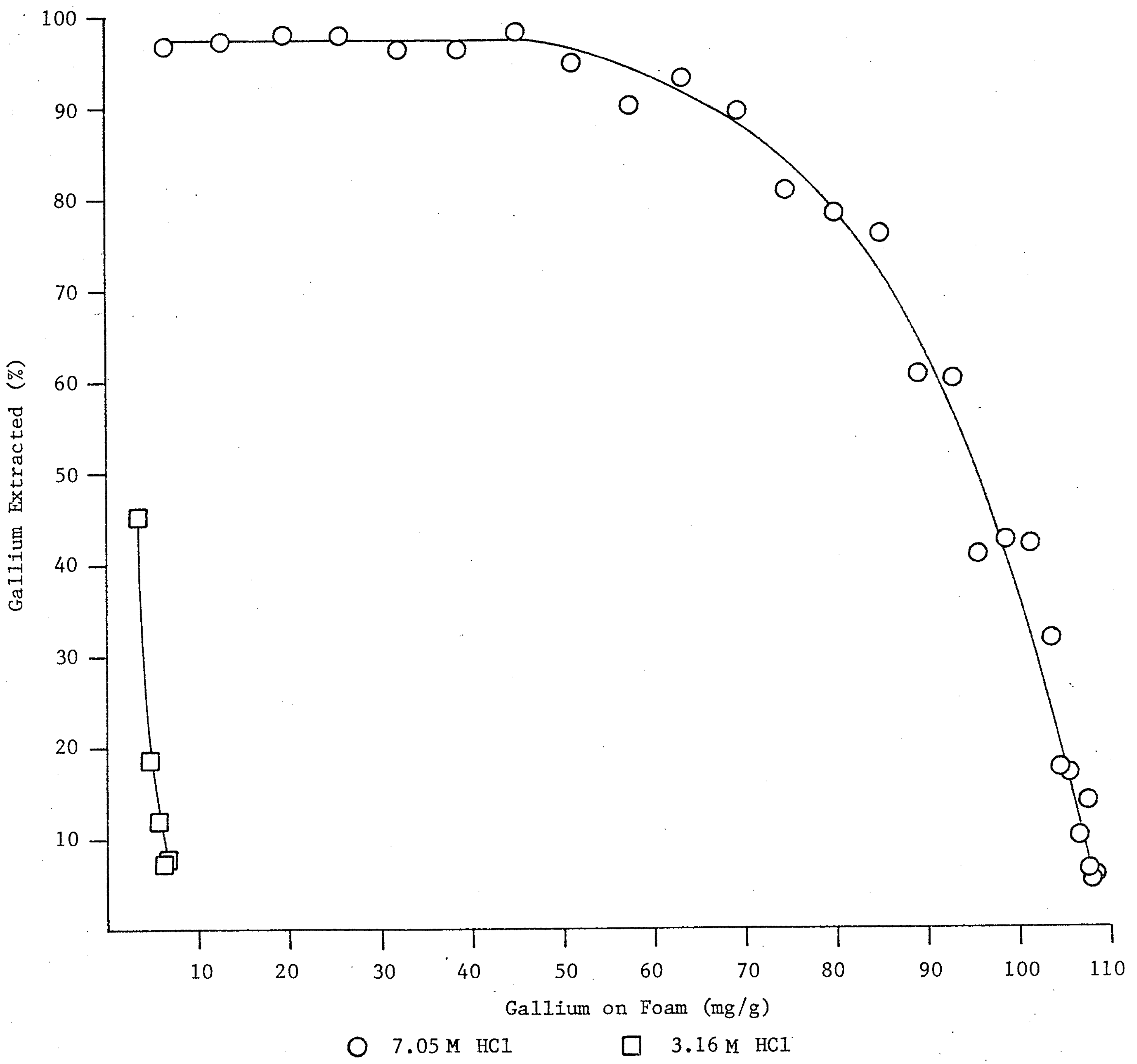
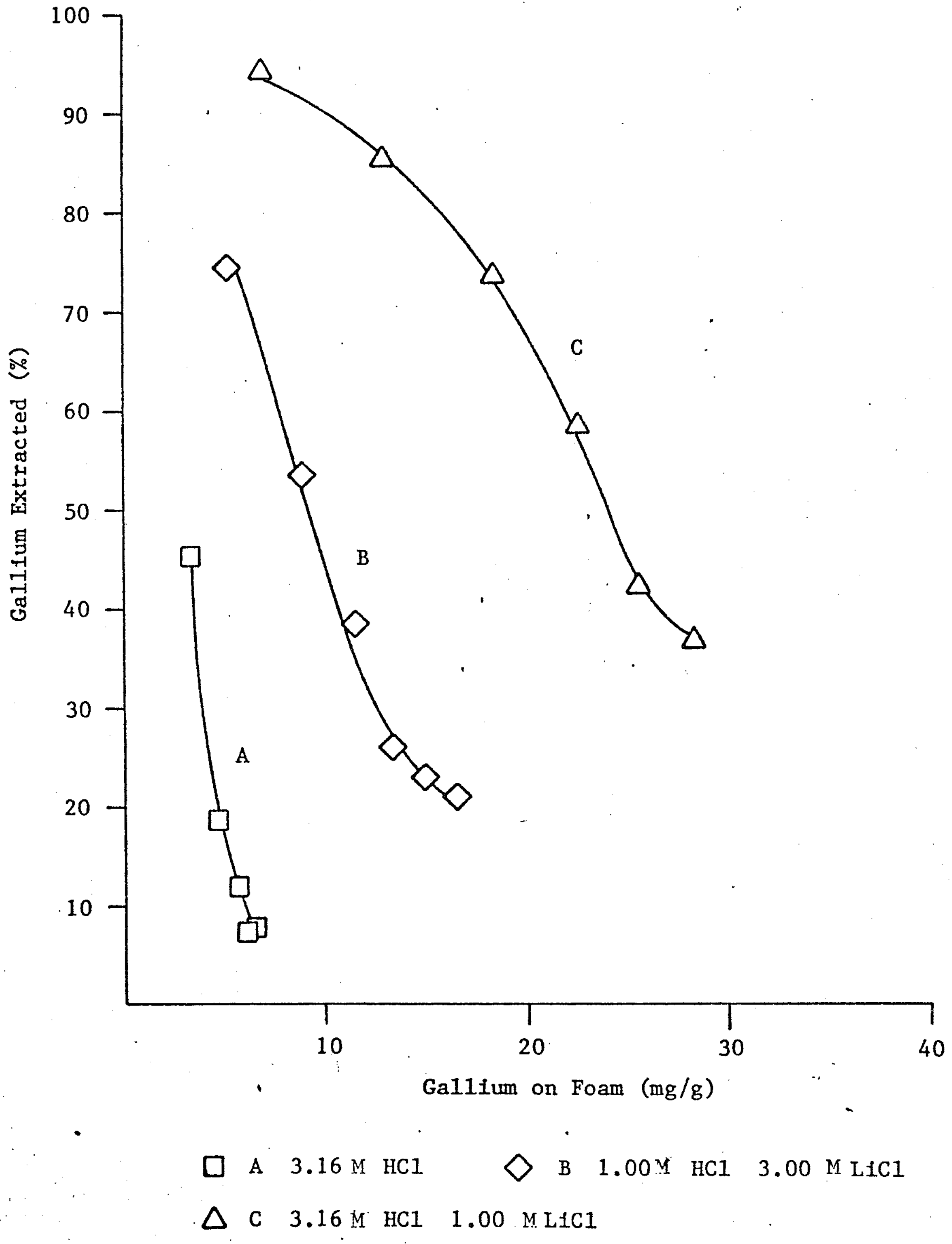

Gallium Extracted (%)
100
90
80
70
60
50
40
30
20
10
10
20
30
40
50
60
70
80
90
100
110
Gallium on Foam (mg/g)
○ 7.05 M HCl
□ 3.16 M HCl

Figure 13

Variation of Extraction Efficiency of Polyurethane Foam for Gallium as a function of the Amount of Gallium on the Foam at various H^+ and Cl^- Concentrations and 100 ppm Gallium in Solution (Appendix A, Table A-X)


100
90
80
70
60
50
40
30
20
10
Gallium Extracted (%)
10
20
30
40
Gallium on Foam (mg/g)
A
B
C
□ A 3.16 M HCl
◇ B 1.00 M HCl 3.00 M LiCl
△ C 3.16 M HCl 1.00 M LiCl

gallium concentration.

As shown in figs. 12 - 14, the percentage extraction decreases as the foam becomes saturated with gallium. The point at which the foam does not absorb any more gallium may be taken as the foam capacity. Fig. 12 indicates that the capacity of the foam at 7.05 M HCl is approximately 110 mg. Ga/g. The capacity at 3.16 M HCl can be seen to be significantly lower, approximately one-tenth the former value. Thus the capacity increases greatly with an increase in HCl concentration.

The effect of the individual H^+ and Cl^- ions is shown in fig. 13. Curves A and C show that at constant $[H^+]$, increasing the chloride concentration increases the foam capacity. Curves B and C show that increasing the hydrogen ion concentration at constant chloride concentration, also increases the foam capacity. The effect of chloride ion is seen to be greater than that of H^+ ion.

It is worth noting that the effect of H^+ and Cl^- ions on the foam capacity is the same as their effect on the distribution coefficient. It is thought that the foam capacity, like the distribution ratio, is determined by the concentration of the extractable complex in the aqueous phase. As previously discussed, H^+ and Cl^- ions increase the concentration of the complex in solution by mass action effect as well as by decreasing the dielectric constant and activity of the water.

The successive extractions involved in determining the foam capacity may be thought of as proceeding in the following manner. The concentration of the extractable complex in solution is a maximum prior to contact with the foam, and this concentration is a function of the initial concentration of ions present. When equilibrated with a foam plug the complex concentration in solution will begin to decrease as the complex distributes itself between the foam and aqueous phases. The various equilibria represented in section B will shift to account for the loss of complex in solution. When equilibrium is once again established the amount of complex going onto the foam will equal the amount of complex coming off the foam. The total amount of gallium in the aqueous phase will be less than that originally present, resulting in a certain percentage extraction.

When other aliquots of solution are equilibrated with the foam, the original complex concentration in the aqueous phase will be the same as for the first trial. However, as the foam already has some gallium absorbed in it, the concentration of complex in the aqueous phase, when equilibrium is established, will be higher than for the first trial. The more gallium in the foam, the higher will be the concentration of the complex in the aqueous phase at equilibrium. This results in a higher total gallium concentration in the aqueous phase and thus a lower percentage extraction.

Eventually the concentration of complex in the aqueous phase at equilibrium will equal the initial concentration of complex. Thus there will be no net increase in the amount of gallium in the foam and a zero percentage extraction. The amount of gallium in the foam may be termed the foam capacity (for that particular set of initial concentrations).

This capacity however, is determined by the maximum or initial concentration of complex in the aqueous phase. As increasing the concentration of either H^+ or Cl^- ions increases the concentration of complex in the aqueous phase, it results in an increase in the foam capacity.

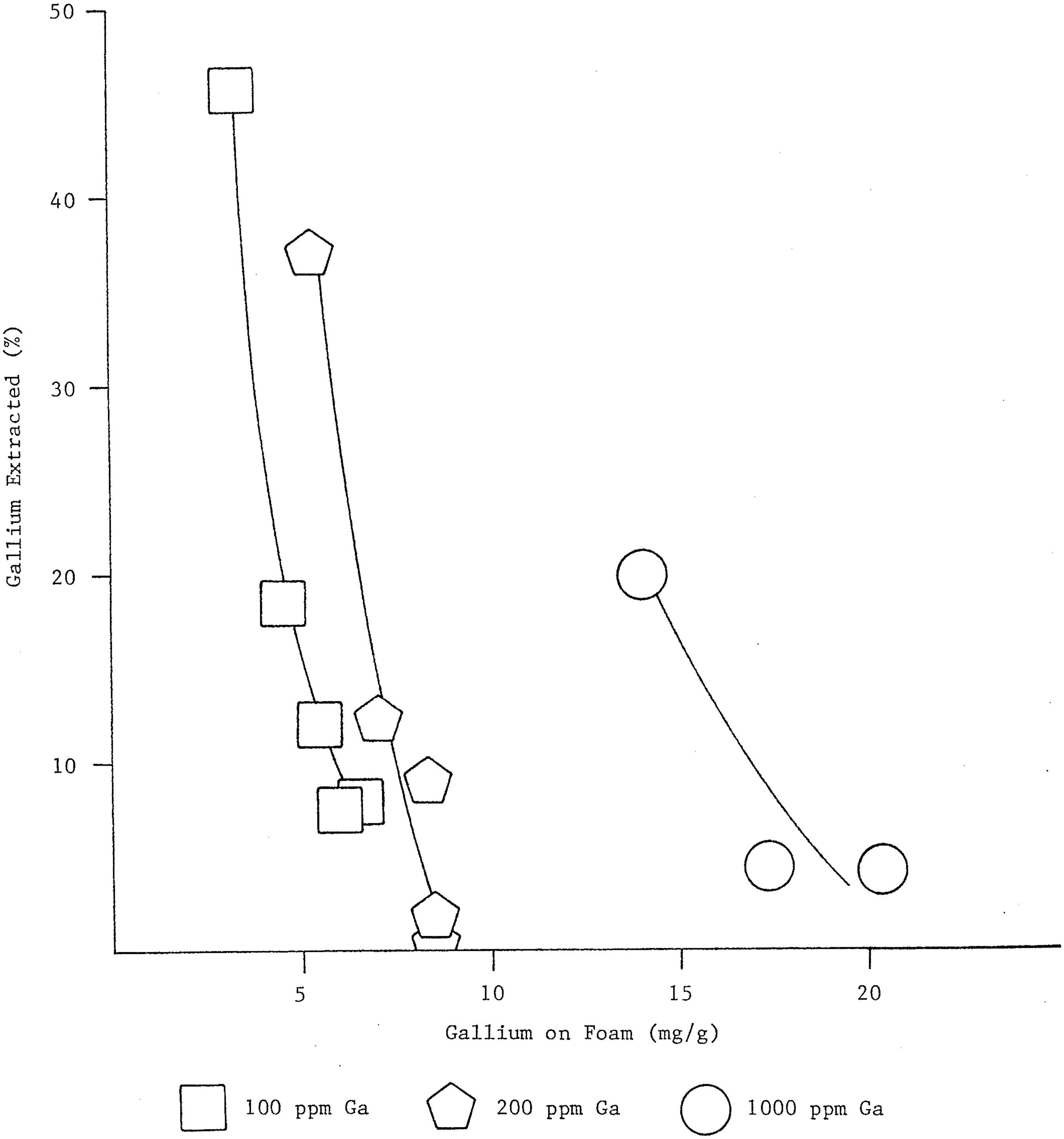
The following equation from section B

$$\left[HGaCl_4 \right]_a = k_5 k' \left[H^+\right] \left[Ga^{3+}\right] \left[Cl^-\right]^4$$

predicts a greater influence of chloride on the concentration of the complex in the aqueous phase. Therefore it is not surprising that the chloride concentration is more important than $\left[H^+\right]$ in determining foam capacity. It is also probable that the effect of chloride on the activity and dielectric constant of the water in solution is greater than the H^+ ion.

Figure 14

Variation of Extraction Efficiency of Polyurethane Foam for Gallium as a function of the Amount of Gallium on the Foam at various Gallium Concentrations in Solution and 3 M HCl (Appendix A, Table A-XI)


50
40
30
20
10
Gallium Extracted (%)
5
10
15
20
Gallium on Foam (mg/g)
100 ppm Ga
200 ppm Ga
1000 ppm Ga

The effect of gallium concentration on the foam capacity is shown in fig. 14. As the concentration of gallium increases the capacity of the foam increases. The reason for the increase is because the increasing concentration of gallium in solution increases the concentration of the extractable complex.

A preliminary experiment involved saturating a foam plug at 200 ppm gallium and then equilibrating it with a 1000 ppm solution. Although the foam would no longer extract gallium from a 200 ppm solution, approximately 10 percent was extracted from the 1000 ppm solution. When the same foam was then equilibrated with another 200 ppm solution, the concentration of gallium in the solution rose to approximately 290 ppm after 30 minutes. This example illustrates how the rates of absorption and desorption shift for various changes in complex concentration.

The concentration of gallium in solution affects the complex concentration mainly by mass action. Unlike Cl^- and H^+ ions, the amount of Ga added is probably too low to affect significantly the dielectric constant or activity of the water in solution. Based on mass action arguments alone one would expect capacity $\propto \left[HGaCl_4 \right]_a \propto \left[H^+\right] \left[Cl^-\right]^4 \left[Ga^{3+}\right]$

From fig. 14 it can be seen that a tenfold increase in gallium concentration increases the capacity from approximately 10 mg./g.

foam to approximately 20 - 25 mg./g. Fig. 13 shows that a threefold increase in hydrogen ion concentration (B to C) increases the capacity from about 25 mg./g. to about 40 mg./g. A threefold increase in $[Cl^-]$ (1.3^4) increases it from approximately 10 mg./g. to approximately 40 mg./g. It is of interest to note that a tenfold increase in the gallium concentration does not increase the capacity by as much as a proportionally lower increase in $[H^+]$ or $[Cl^-]$. Though the data are limited, it would appear that the effects of decreasing the dielectric constant and activity of the water are of at least comparable importance to the mass action effect.

In addition, unlike the $[H^+]$ and $[Cl^-]$ effects, increasing the concentration of Ga does not necessarily increase the distribution ratio even though it does increase the capacity. The reason for this is that increasing $[H^+]$ and $[Cl^-]$ increases the concentration of the complex in the aqueous phase (and therefore in the foam) without adding any additional Ga to the solution. Increasing the gallium concentration, while increasing the complex concentration in both phases, also increases the total gallium concentration in the aqueous phase. Thus both the numerator and denominator of the distribution ratio increase and there is not necessarily any significant change in the value of D.

As noted in section D, the decrease in percentage extraction with increasing gallium concentration, shown in fig. 8, does not reflect the true behaviour, but rather is a result of the low foam capacity at 3 M HCl. It is worth noting however, that the reason the curve levels off instead of continuing to decrease, is the result of an increase in foam capacity at high gallium concentrations.

Part II Membrane Studies

Introduction

Based on the results of the polyurethane foam work, it was decided that the separation of gallium using a polyurethane membrane should be investigated.

Preliminary experiments demonstrated that gallium would pass through the membrane and that the rate of diffusion depended on the temperature. In order to compare the extraction and diffusion results, the effect of H^+ and Cl^- ions on the rate of diffusion was examined.

Experimental

A solution of 6.07 M HCl containing 200 ppm Ga was placed on one side of the diffusion apparatus and double distilled deionized water was placed on the other side. The two cells were separated by a piece of .127mm polyurethane membrane. The cells were kept at $25.0 \pm 0.5^\circ C$ in a water bath and the conductivity(*) of the water side was monitored. Samples of the water side were taken at intervals in accordance with the change in conductivity. The samples were analyzed for gallium using the standard solution method, and for HCl by titration with standard base. The acid side was analyzed for gallium at the completion of the experiment.

The above procedure was repeated for solutions containing 3 M HCl and 3 M HCl, 3 M LiCl. For the last trial the samples

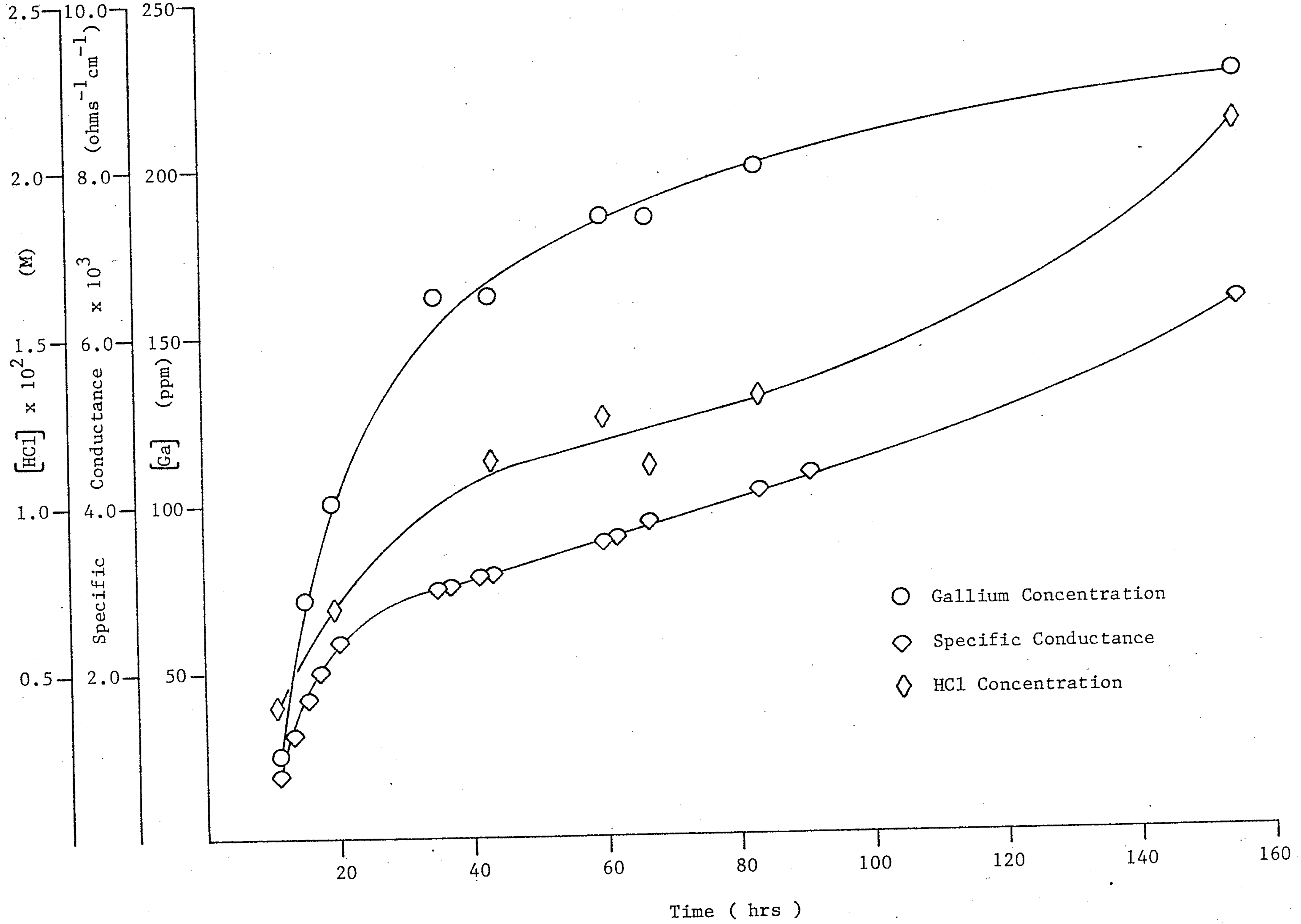
(*) cell constant = 2.59 cm

Figure 15

Time Dependence of Specific Conductance and Diffusion of Gallium and HCl into Double Distilled Water through a Polyurethane Membrane

Initial Conditions - 130 mls 6.07M HCl, 200 ppm Ga

(Appendix A, Table A-XII)


2.5
2.0
1.5
1.0
0.5
[HCl] x 10^2 (M)
10.0
8.0
6.0
4.0
2.0
Specific Conductance x 10^3 (ohms^{-1}cm^{-1})
250
200
150
100
50
[Ga] (ppm)
20
40
60
80
100
120
140
160
Time (hrs)
Gallium Concentration
Specific Conductance
HCl Concentration

were also analyzed for lithium by atomic absorption.

Results and Discussion

Fig. 15 shows the relationship between the specific conductance, acid concentration, and gallium concentration on the water side of the diffusion apparatus. As shown, the curves follow the same general shape allowing the conductance to be used as an indication of changes in gallium concentration. The acid concentration can also be seen to increase slowly. The analysis of the acid side at the conclusion of the experiment indicated that there was no longer any gallium present. An osmotic effect also became apparent at the end of this trial with the volume on the acid side increasing and that on the water side decreasing. This would result in the gallium concentration on the water side increasing to a higher value than would be expected had no water transfer taken place. The resistance across the membrane was measured at the completion of the trial and was found to be 20 K ohms.

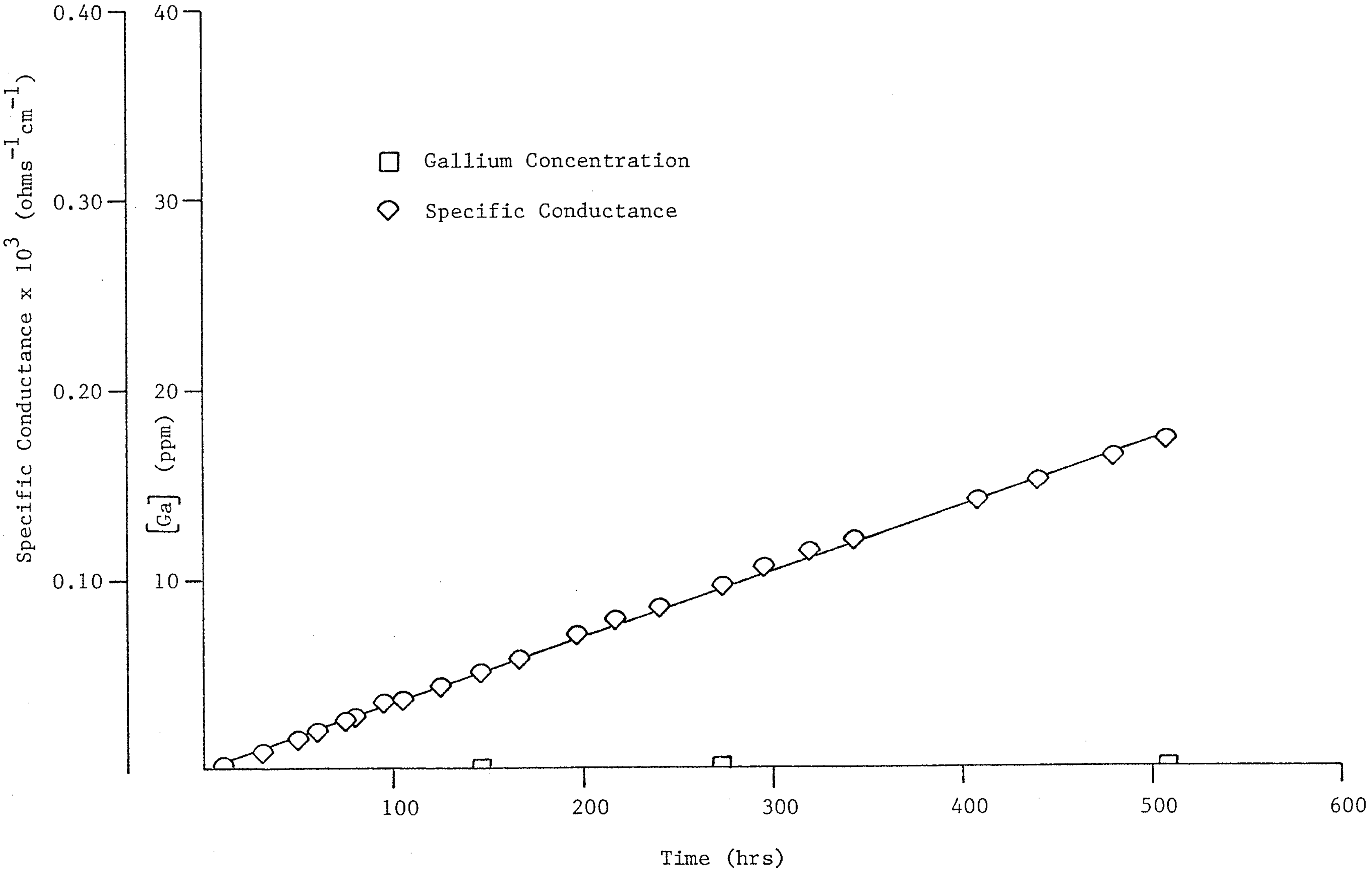
Fig. 16 shows that for a 3.10 M HCl solution containing 200 ppm Ga, no significant transfer of Ga across the membrane takes place within 400 hours. The increase in conductivity indicates that the transfer would occur but at a very slow rate. The acid concentration on the water side was 0.0030 M when the

Figure 16

Time Dependence of Specific Conductance and the Diffusion of Gallium into Double Distilled Water through a Polyurethane Membrane

Initial Conditions - 130 mls 3.10 M HCl, 200 ppm Ga

(Appendix A, Table A-XIII)


Gallium Concentration
Specific Conductance
Specific Conductance x 10^3 (ohms^{-1}cm^{-1})
0.40
0.30
0.20
0.10
[Ga] (ppm)
40
30
20
10
100
200
300
400
500
600
Time (hrs)

experiment was terminated. The acid side was analyzed for gallium and essentially all remained in the acid solution. Approximately 1.4 percent was unaccounted for and may have been absorbed in the membrane. The volumes in both cells indicated that no osmotic water transfer had occurred.

Fig. 17 shows the typical relationship between specific conductance, HCl concentration and Ga concentration. The curves are similar, although the HCl concentration and thus the conductivity continue to increase at the end of the experiment, while the Ga concentration tends to level off somewhat. The analysis for Li on the water side indicated that no significant transfer occurred. Analysis of the acid side for gallium indicated that only trace amounts remained at the end of the run.

Fig. 18 shows the increase in gallium concentration with time for the three trials. It indicates that the diffusion rate increases with increasing H^+ and Cl^- concentration. The effect of the chloride ion appears greater than that of the H^+ ion. It is thought that the reason for these effects is that the gallium is diffusing through the membrane as the $(HGaCl_4)$ complex. As previously discussed, the additional H^+ and Cl^- ions increase the concentration of the complex. Thus the concentration gradient of the diffusing species and therefore the rate of diffusion is increased.

Figure 17

Time Dependence of Specific Conductance and Diffusion of Gallium and HCl into Double Distilled Water through a Polyurethane Membrane

Initial Conditions - 130 mls 3.12 M HCl, 3.00 M LiCl, 200 ppm Ga

(Appendix A, Table A-XIV)

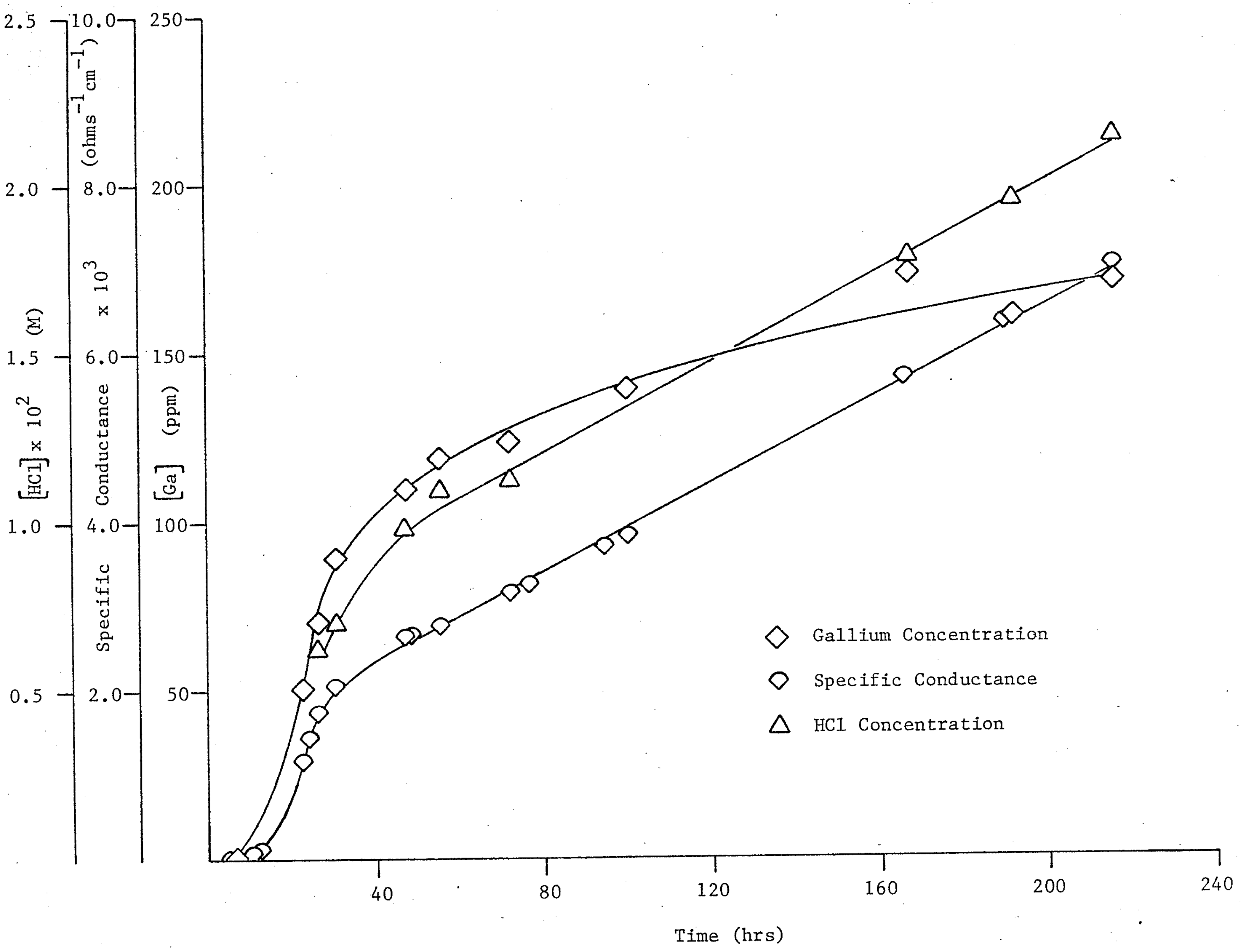
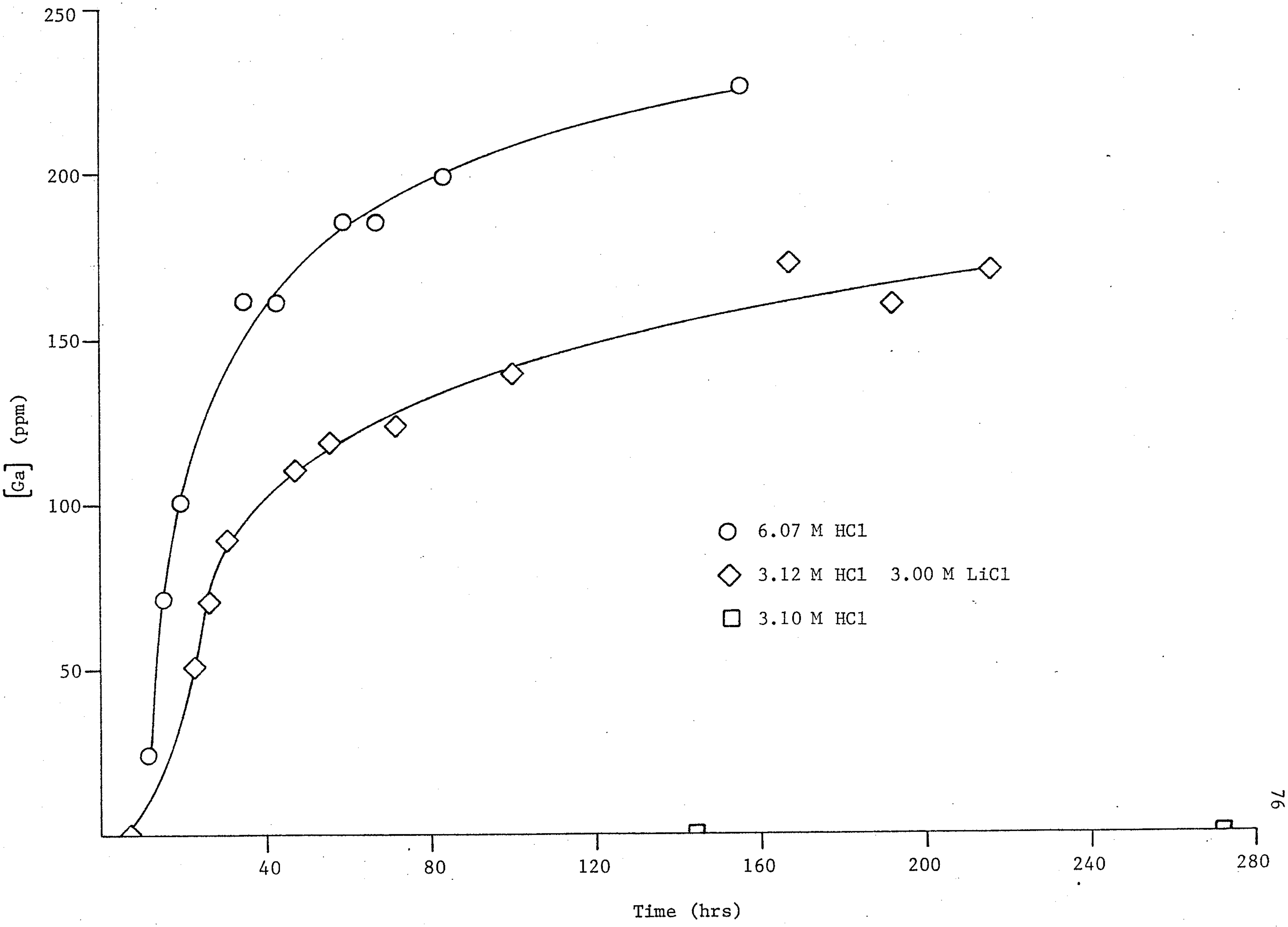

2.5
2.0
1.5
1.0
0.5
[HCl] x 10^2 (M)
10.0
8.0
6.0
4.0
2.0
Specific Conductance x 10^3 (ohms^{-1}cm^{-1})
250
200
150
100
50
[Ga] (ppm)
40
80
120
160
200
240
Time (hrs)
Gallium Concentration
Specific Conductance
HCl Concentration

Figure 18

Variation of Diffusion of Gallium through a Polyurethane Membrane with various Initial Concentrations of H^+ and Cl^- Ions

(Appendix A, Tables A-XII, A-XIII, A-XIV)


250
200
150
100
50
[Ga] (ppm)
40
80
120
160
200
240
280
Time (hrs)
○ 6.07 M HCl
◇ 3.12 M HCl 3.00 M LiCl
☐ 3.10 M HCl

It is of interest to note that while the concentration of gallium increases to a maximum on the water side, it falls essentially to zero on the acid side of the diffusion apparatus. One might expect the mass transfer to stop when the gallium concentrations on both sides of the membrane were equal. Although the gallium is transferred against a concentration gradient with respect to the two solutions (active transport), the gradient within the polyurethane membrane always favors transfer to the water side.

This may be explained as follows. It is known that there is a net absorption of gallium complex into polyurethane from HCl solutions at the concentrations used in these experiments. It is also known that polyurethane containing gallium complex will undergo a net desorption when in contact with water. Thus the gallium on the acid side of the membrane associates to form the complex ($HGaCl_4$). This complex is absorbed into the polyurethane membrane and diffuses through the membrane in this form. At the water side the complex is desorbed from the membrane and dissociates into H^+, Ga^{3+}, and Cl^- ions. Within the membrane itself, the concentration of gallium complex is a maximum at the membrane-acid interface and a minimum at the membrane-water interface. In spite of the increase in total gallium concentration on the water side, the low HCl concentration will keep the gallium for the most part in the dissociated form. Thus the complex concentration on the water side will remain at a low level resulting in a net desorption from the membrane until the acid side becomes depleted.

It is expected that if the solutions were left long enough, the HCl concentration on the water side would continue to increase and eventually the gallium would redistribute itself back across the membrane. Recent unpublished results(88) using the $HFeCl_4$ complex indicate that this redistribution does take place.

Diffusion occurs at a rate proportional to the concentration gradient within the membrane. As the gallium on the acid side is depleted the concentration gradient will decrease. As shown in figs. 15 - 18, the diffusion rate decreases as the experiment progresses.

The osmotic transfer of water noted in these experiments appears to depend on the diffusion of gallium through the membrane. Not until the gallium is almost completely transferred to the water side, does the change in volume associated with osmosis become apparent. During the 3 M HCl trial, no change in volume was noticed even though the experiment was run twice as long as the other two trials. There was no significant transfer of gallium for this trial however. Experiments with no gallium present in solution also resulted in no osmotic effect. Thus the gallium diffusion appears to "condition" the membrane to allow the solvent transfer to occur.

Quantitative information describing the diffusion process is not readily available from the experimental results as some of the basic assumptions used in determining the various parameters, are not valid in this case. For example, it is generally assumed that the concentration change on one side of the membrane is sufficiently small that it does not affect the equilibrium concentration at the solution-membrane interface. The gallium concentrations used in these experiments, however, are too low and it is doubtful that a steady state concentration gradient is established. Secondly, during the diffusion of gallium the membrane swells, increasing in thickness and cross sectional area. Though attempts have been made to account for these changes in other systems, the assumptions of purely unidirectional or isotropic swelling do not apply. In addition, recent unpublished results(88) have indicated that the ferric chloride complex undergoes hydrolysis on diffusing through the membrane. Ferric hydroxide is formed and precipitates at the membrane-water interface. The iron is not released into solution until the pH drops to a level at which the hydroxide dissolves. A similar process may be occurring with gallium. If this were the case, gallium would not be detected until the solution reached a pH of 3.2; the point at which $Ga(OH)_3$ dissolves. During the various trials, the pH was below this value before gallium was detected in solution. Thus the possibility that gallium hydroxide is formed cannot be ruled out. If this is in fact occurring, the initial portion of the curve would not accurately describe the diffusion process, but would be displaced somewhat along the time axis.

Conclusion

This work has examined the use of polyurethane foam as a medium for the extraction of gallium from acidic chloride solutions. It was found that the equilibrium between the foam and the solution was established relatively quickly, with the time required being essentially independent of the concentration of HCl (from 3 - 10 M HCl). The rate of absorption is greater than the rate of desorption however, and the two processes do not appear to be reversible in terms of the amount of gallium in the two phases at equilibrium.

In general the foam extraction is characteristic of extraction into liquid ethers, with a similar dependence on HCl concentration for both systems. It was noted however, that explanations for the decrease in percentage extraction in the liquid solvent above 7 M HCl, are not applicable to similar behaviour in polyurethane foam.

Increasing the concentration of the chloride and hydrogen ions resulted in increased extraction, with the influence of chloride concentration being the predominant effect. The decrease observed in percentage extraction with increasing gallium concentration is thought to be a result of the limited foam capacity at 3 M HCl and not an indication of the actual effect of gallium concentration.

The capacity of the foam to extract gallium was shown to increase as the concentration of chloride, hydrogen, and gallium ions increase, with the influence of chloride concentration having the greatest effect.

The diffusion of the gallium complex through a polyurethane membrane illustrated the phenomenon of " active transport ". The diffusion rate was found to increase with increasing chloride and hydrogen ion concentration, consistent with the solubility of the gallium complex in polyurethane.

Appendix A Data Summary

Table A-I : Time Dependence for Desorption into Distilled Water of Gallium from Loaded Polyurethane Foam (see fig. 3)

Time (min)	Conc of Gallium in Soln. (ppm)
1	75
3	96
5	113
10	126
15	129
30	133
45	134
60	138

Table A-II : Time Dependence for the Extraction of Gallium by Open Celled Polyurethane Foam at various HCl Concentrations (see fig. 4)

Time (min)	Conc. of Gallium in Soln. (ppm)						
	2.85 M.	3.78 M.	5.03 M.	5.98 M.	7.02 M.	7.98 M.	9.46 M.
1		166	138(i)	125	115	134	67
3	180	133	79	54	38	47	26
5	175	108	43	20	19	22	
10	166	68(iii)	15	7	2	16	19
15	162	64	15	7	4	7	12
30	154	56	3(ii)	6	4	5	8
45	157	53	6	5	3	4	7
60	157	51	6	5	3	4	6

(i) - 1.5 min (ii) - 33 min (iii) - 12 min

Table A-III : HCl Concentration Dependence for the Extraction of Gallium by Open Celled Polyurethane Foam (see fig. 5)

Conc. HCl (M)	Gallium Extracted (%)
2.85	21.8
3.78	72.9
5.03	94.4
5.98	96.4
7.02	97.5
7.98	96.7
9.46	96.0

Table A-IV : Variation of Log D with Log HCl Concentration at 200 ppm Gallium (see fig. 6)

Log HCl Concentration	Log D
0.455	1.29
0.577	2.36
0.702	3.22
0.777	3.48
0.846	3.70
0.902	3.58
0.976	3.34

Table A-V : Time Dependence for the Desorption of Gallium from a Loaded Polyurethane Foam into 3.34 M HCl Solution (see fig. 7)

Time (min)	Conc. of Gallium in Soln. (ppm)
5	15
10	20
15	23
30	25
60	26
90	26

Table A-VI : Variation of Percentage Extraction with Equilibrium Gallium Concentration at 3.15 M HCl (see fig. 8)

Gallium Conc. (ppm)	Gallium Extracted (%)	Gallium Conc. (ppm)	Gallium Extracted (%)
5.0 ± 0.2	50	125.6 ± 2.8	37.2
5.7 ± 0.2	43	142.0 ± 1.2	29.0
11.0 ± 0.1	45.0	145.0 ± 0.9	27.5
12.3 ± 0.1	38.5	278.4 ± 6.0	30.4
29.7 ± 0.3	40.6	290.8 ± 5.4	27.3
30.9 ± 0.6	38.2	311.5 ± 5.4	22.1
32.9 ± 0.1	34.2	779.2 ± 4.6	22.1
64.1 ± 1.1	35.9	780.5 ± 11.8	21.9
65.1 ± 1.0	34.9	797.5 ± 7.6	20.2
67.7 ± 1.2	32.3		

Table A-VII : Variation of Log D with Log Equilibrium Gallium Concentration at 3.15 M HCl (see fig. 9)

Log Gallium Conc.	Log D	Log Gallium Conc.	Log D
0.70	1.85	1.81	1.58
0.75	1.73	1.83	1.53
1.03*	1.80	2.10	1.63
1.03*	1.79	2.15	1.47
1.08*	1.68	2.16	1.43
1.13*	1.54	2.44	1.49
1.04	1.77	2.46	1.43
1.09	1.65	2.47	1.31
1.47	1.69	2.89	1.31
1.49	1.64	2.89	1.30
1.51	1.57	2.90	1.26
1.81	1.60		

* Ga + K_2SO_4

Table A - VIII : Variation of Percentage Extraction of Gallium with Lithium Chloride Concentration at 1.0 and 0.1 M HCl (see fig. 10)

1.0 M HCl		0.1 M HCl	
Conc. LiCl (M)	Gallium Extracted (%)	Conc. LiCl (M)	Gallium Extracted (%)
1.03	8.7 ± 1.6	2.00	6.2 ± 0.6
1.03	8.9 ± 1.6	3.00	17.0 ± 3.7
2.05	17.6 ± 1.3	3.00	12.3 ± 1.7
2.05	19.4 ± 1.2	3.99	44.9 ± 0.4
2.05	20.0 ± 1.7	3.99	42.0 ± 0.9
3.08	76.6 ± 0.6	4.50	67.9 ± 1.3
3.08	73.5 ± 0.5	4.50	70.7 ± 0.9
3.08	68.4 ± 0.8	4.50	67.3 ± 1.2
3.59	86.8 ± 0.9	5.00	91.1 ± 0.1
3.59	87.5 ± 0.4	5.00	89.7 ± 0.4
3.59	88.2 ± 0.3	5.00	88.8 ± 0.4
4.10	97.8 ± 0.0		
4.10	98.4 ± 0.0		
4.10	98.4 ± 0.0		

Table A - IX : Variation of Log D with Log Chloride Ion Concentration at 1.0 M and 0.1 M HCl (see fig. 11)

1.0 M HCL		0.1 M HCl	
Log Chloride Conc.	Log D	Log Chloride Conc.	Log D
0.307	0.83	0.322	0.67
0.307	0.84	0.491	1.16
0.484	1.23	0.491	1.00
0.484	1.18	0.613	1.76
0.484	1.25	0.613	1.71
0.611	2.36	0.663	2.17
0.611	2.29	0.663	2.23
0.611	2.18	0.663	2.16
0.662	2.66	0.708	2.86
0.662	2.69	0.708	2.79
0.662	2.72	0.708	2.75
0.708	3.50		
0.708	3.63		
0.708	3.65		

Table A - X : Variation of Extraction Efficiency of Polyurethane Foam for Gallium as a function of the Amount of Gallium on the Foam at various Hydrogen and Chloride Concentrations and 100 ppm Gallium in Solution (see fig. 12 and 13)

Gallium on Foam (mg/g)	Gallium Extracted (%)	Gallium on Foam (mg/g)	Gallium Extracted (%)
7.05 M HCl		107.32	14.0 ± 0.8
6.43	97.1 ± 0.1	107.76	6.6 ± 1.6
12.88	97.5 ± 0.1	108.12	5.5 ± 0.3
19.36	98.0 ± 0.0	108.53	6.2 ± 0.4
25.84	98.0 ± 0.0	3.16 M HCl	
32.23	96.5 ± 0.1	3.30	45.6 ± 0.2
38.61	96.5 ± 0.2	4.63	18.5 ± 1.6
45.13	98.5 ± 0.1	5.50	12.0 ± 1.4
51.40	94.8 ± 0.3	6.04	7.4 ± 1.0
57.37	90.2 ± 1.7	6.60	7.8 ± 0.9
63.56	93.6 ± 0.4	1.00 M HCl 3.00 M LiCl	
69.48	89.3 ± 0.4	5.17	74.3 ± 0.3
74.83	80.9 ± 2.7	8.89	53.5 ± 0.4
80.02	78.4 ± 0.3	11.55	38.3 ± 0.2
85.06	76.2 ± 0.1	13.36	26.1 ± 0.7
89.08	60.7 ± 0.8	14.96	23.0 ± 1.2
93.07	60.3 ± 2.0	16.43	21.2 ± 1.5
95.76	40.7 ± 2.9	3.16 M HCl 1.00 M LiCl	
98.56	42.4 ± 0.6	6.81	94.3 ± 0.1
101.34	42.0 ± 1.2	12.99	85.6 ± 0.3
103.44	31.8 ± 1.7	18.32	73.9 ± 0.4
104.61	17.7 ± 0.3	22.55	58.5 ± 0.3
105.72	16.8 ± 1.1	25.60	42.3 ± 0.9
106.39	10.1 ± 17.4	28.24	36.6 ± 0.5

Table A - XI : Variation of Extraction Efficiency of Polyurethane Foam for Gallium as a function of the Amount of Gallium on the Foam at various Gallium Concentrations in Solution and 3 M HCl (see fig. 14)

Gallium on Foam (mg/g)	Gallium Extracted (%)
100 ppm Ga	
3.30	45.6 ± 0.2
4.63	18.5 ± 1.6
5.50	12.0 ± 1.4
6.04	7.4 ± 1.0
6.60	7.8 ± 0.9
200 ppm Ga	
5.29	37.0 ± 0.7
7.04	12.3 ± 0.7
8.33	9.0 ± 2.0
8.56	1.6 ± 1.9
8.56	0.0 ± 2.7
1000 ppm Ga	
14.14	19.8 ± 0.3
17.28	4.4 ± 0.2
20.35	4.3 ± 1.4

Table A - XII : Time Dependence of Specific Conductance and Diffusion of Gallium and HCl into Double Distilled Water through a Polyurethane Membrane (see fig. 15) Initial Conditions - 130 mls 6.07M HCl, 200 ppm Ga

Time (hrs)	Specific Conductance $\times 10^3$ (ohms^{-1}cm^{-1})	Gallium Conc. (ppm)	HCl Conc. $\times 10^2$ (M)
11	0.77	25	0.39
13	1.27		
15	1.66	72	
17	2.01		
19	2.24	101	0.68
20	2.36		
35	2.97	162	
37	3.01		
41	3.13		
43	3.17	162	1.13
60	3.55	186	1.26
62	3.59		
67	3.75	186	1.11
84	4.13	200	1.32
91	4.32		
156	6.33	227	2.13

Table A - XIII : Time Dependence of Specific Conductance and the Diffusion of Gallium into Double Distilled Water through a Polyurethane Membrane (see fig. 16)
Initial Conditions - 130 mls 3.10 M HCl, 200 ppm Ga

Time (hrs)	Specific Conductance $\times 10^3$ (ohms^{-1}cm^{-1})	Gallium Conc. (ppm)
10	0.0024	
32	0.0099	
50	0.0169	
59	0.0204	
71	0.0259	
79	0.0286	
95	0.0367	
104	0.0375	
124	0.0436	
145	0.0510	0.0
167	0.0579	
196	0.0714	
216	0.0784	
239	0.0865	
272	0.0977	0.0
296	0.106	
320	0.114	
343	0.121	
407	0.141	
440	0.151	
479	0.164	
508	0.172	0.0

Table A - XIV : Time Dependence of Specific Conductance and Diffusion of Gallium and HClinto Double Distilled Water through a Polyurethane Membrane (see fig. 17)
Initial Conditions - 130 mls 3.12 M HCl, 200 ppm Ga

Time (hrs)	Specific Conductance x 10^3 (ohms^{-1}cm^{-1})	Gallium Conc. (ppm)	HCl Conc. x 10^2 (M)
5	0.038		
6	0.051	0.0	
10	0.105		
12	0.127		
23	1.18	51	
24	1.46		
27	1.77	72	0.63
31	2.05	90	0.70
47	2.63	110	0.98
49	2.66		
55	2.78	118	1.10
72	3.17	123	1.13
77	3.28		
95	3.71		
99	3.82	140	
167	5.71	173	1.78
191	6.37		
192	6.41	160	1.95
216	7.03	171	2.13

Appendix B Calculation of the Distribution Ratio

See Table A-III and Table A-IV p. 84

Initial conc. of Ga in solution = 200 ppm (ug/g or ug/ml)
Volume of solution used = 150 mls
Weight of polyurethane foam used = 2.1307g

At 2.85 M HCl, percent gallium extracted = 21.8% *

Equilibrium conc. of Ga in solution = 156 ppm

Weight of gallium extracted = (initial conc.)(volume)(fraction extracted)

= (200 ug/ml)(150 ml)(0.218)

= 6540 ug

$$\text{Conc. of gallium in foam} = \frac{6540 \text{ ug Ga}}{2.1307 \text{ g foam}} = 3070 \text{ ppm}$$

$$\text{Distribution Ratio (D)} = \frac{\text{Conc. of gallium in foam}}{\text{Conc. of gallium in soln.}}$$

$$= \frac{3070 \text{ ppm}}{156 \text{ ppm}} = 19.7$$

As noted in Table A-IV, the Log D = 1.29.

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* The amount of gallium removed in the various samples taken, as well as the amount of gallium remaining in solution at equilibrium, was considered in calculating the percentage extracted.

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