PN ABU-162
93228

ANNUAL REPORT
Covering the period August 10, 1993 to August 31, 1994

POLYMER SUPPORTED LIGANDS FOR ECOLOGICAL PROBLEMS

Principle investigator: Prof. Abraham Warshawsky
Grantee Institution: Weizmann Institute of Science

Collaborator: Dr. Karel Jerabek
Institution: Czech Academy of Sciences
Institute of Chemical Process Fundamentals (ICPF)

Project No.: C13-985
Grant No.: TA-M04-C13-085

AID GRANT PROJECT OFFICER: Dr. David Moulinek

PROJECT DURATION: August 10, 1993 to August 31, 1997

TABLE OF CONTENTS

Executive Summary

Section I.

A, Research objectives

B. Research accomplishments

C. Scientific impact of collaboration

D. Description of project impact

E. Strengthening the development of co-country institutions

F. Future work

Section II

A. Managerial issues

B. Budget

C. Special concerns

D. Collaboration, travel, training and publications

E. Request for AID or BOSTID actions.

Executive Summary

The purpose of this project is to develop polymer-supported metal complexing ligands and applying them to solve industrial problems of heavy and toxic metal contamination in the Republic of Czechia, as a model for international application of this technology. The collaboration is based on the fact that the PI has pioneered solvent impregnated resins (SIR) technology, has the ability to design and invent new SIR systems and to establish the chemistry of the synthesis and application of such materials. The collaborating PI has expertise in physical methods of characterizing polymeric adsorbants and is aware of the industrial problems of metal contamination in his country.

The findings of the last year included systematic evaluation of the process of making SIR materials incorporating DTPA (dithiophosphoric acid) ligands and their performance in extracting two metals, copper and mercury. The relationship between method of impregnation, surface area, porosity and the thermodynamic and kinetic aspects of the metal extraction reactions were determined. The results were interpreted by mathematical calculations, based on the extraction model employed by Cortina et al.

The collaboration included the following steps

1. Synthesis and method of impregnation - WIS
2. Transfer of samples and determination of surface area and adsorption isotherms (ICPF).
3. Transfer of data from ICPF to WIS and back.
4. Measurement of extraction properties (WIS and ICPF). Selection of samples for systematic mathematical modelling (WIS).
6. Discussion of results, joint decisions in redirection of the research.

The contribution of WIS was to train the ICPF in the synthesis and application of SIR technology. The main contribution of ICPF was to produce in <u>real time</u> the

understanding of surface properties of SIR materials. Hence affecting the course of the research and direction of synthesizing improved materials.

SECTION I

A. Research Objectives

A.1. Overall

1. Synthesis and purification of DTPA ligands, particularly DEHTPA (di-2-ethylhexyldithiophosphoric acid) (WIS).
2. Determine stability of DEHTPA under extraction conditions (WIS).
3. Determine adsorption isotherms for DEHTPA from ethanol and other alcohols (ICPF).
4. Determine surface area and porosity of DEHTPA on various polymeric adsorbants (ICPF).
5. Develop a series of DEHTPA on XAD-2 (varying concentrations of DEHTPA) (WIS).
6. Determine extraction performance of SIR XAD-2-type resins (WIS).
7. Provide a preliminary model for understanding the metal extraction performance of DEHTPA-XAD-2 extractants.

A.2. At ICPF

For the team of the Institute of Chemical Process Fundamentals, Prague the main objective for the first year of the project was selection of perspective polymer carriers, characterisation of their morphology and investigation of the process of ligand immobilisation on the carriers. For application as carriers of DTPA ligand, two main types of the polymer carries were considered. Unfunctionalyzed styrenic polymers where the ligand would be immobilised purely physically, mainly by hydrophobic interaction and anion exchange resin where the ligand would be

bound by chemical interaction.

B. Research Accomplishments

B.1. At the W.I.S.

- A method was developed for binding DEHTPA to Amberlite XAD-2 (a commercial adsorbant produced by Rohm & Haas, U.S.A.), where the adsorption takes place from ethanol. The concentration of the ligand on the polymer (Cr) is dependent on the concentration in the impregnation solution ($C_{impr.s.}$) as shown in Fig. 1.
- The polarity of the solvent strongly influences the isotherm. In contradiction to anticipation, impregnation from the higher polarity solvent is stronger. This result needs to be investigated thoroughly, as it has very important theoretical and practical implications.
- The surface area of the DEHTPA-XAD-2 SIR resins is strongly dependent on ligand concentration, with a very steep falling off when $C_{impr.s.}$ increases (see Fig. 2).
- The distribution coefficients for metal extraction are larger than for the corresponding liquid-liquid extraction system log D for Cu(II) and Hg(II) reach levels higher than 3. The log D values for metal extraction are related to ligand concentration on the polymer. An optimal polymer of relatively low concentrations of C_{12} = 0.387 mol/μg is a very efficient material (see Fig. 3) and is cost-efficient.
- The loss of ligand by washup into the aqueous stream is related to concentration in the polymer phase. As shown in Fig. 4, for the optimal polymer discussed above the losses are less than 1 ppm.
- The pH of extraction has a marginal effect on its efficiency (expressed as log D) for copper (see Fig. 5). Hence, metal removal from highly acidic solutions

without pH adjustment is possible.

- The structure of the extracted complex, using the extraction reactions stochiometrically, was calculated. The structure proposed is:

$$CuCl_2(HL)_8$$

$$CuLCl_2(HL)_8$$

- Elution of metal from the SIR resin is related to the eluting ligand (thiourea) concentration. Separations between metals are possible (see Fig. 6), changing the acid to SM HBr allows elution of mercury as well.

B.2. At ICPF

Research Accomplishments: For bonding of the ligand by chemical interaction put together a selected group commercial ion exchanger resins varying both in the morphology of the polymer skeleton (gel and macroreticular) and type of the active group. For all materials of this group was obtained information on their working-state, swollen morphology using inverse steric exclusion chromatography. The obtained information will be used in the next year when the ligand immobilisation by ionic interaction will be investigated. For immobilisation of the ligand by physical forces was considered beside application of conventional high-surface area styrene-divinylbenzene copolymers (Amberlite XAD-2 and XAD-4) also novel hyper-crosslinked polymer adsorbents containing substantial volume of micropores. In the ICPF, Prague was prepared and characterised a series of these materials. It was expected that on conventional meso- and macroporous polymer carriers ligand immobilisation proceeds predominantly as surface adsorption while the presence of micropores could enhance bonding of the ligand to the carrier through the pore-filling mechanism. Investigation of the process of the covering of porous polymer carriers with liquid ligand from alcoholic solution shown that against the expectations by the liquid ligand can be completely filled even the

mesopores. Relatively easy formation of separate liquid ligand phase in alcohol, which is for ligand a good solvent, is very surprising. For kinetics of the ion separation using the SIR resins could be very important the area of the interface between the supported ligand and aqueous environment. By the chromatographic method, applicable to liquid-coated materials, was investigated influence of preparation condition on the surface area of the SIR resins. It was found that with increase of the ligand content in the SIR resin the surface area could drop from 775 m^2/g to as low as 66 m^2/g (Amberlite XAD-4). At present, investigation in this direction continue by studying of the influence of the carrier pore size distribution and the solvent from which the ligand is sorbed on the filling of the pore space of the polymer support with the liquid ligand.

C. Scientific impact of collaboration

Both partners of the collaboration made contributions from their sphere of expertise. The WIS team contributed to the methodology of synthesis of SIR materials, the analysis of the extraction chemistry, and the elution chemistry. The ICPF team added their expertise in measuring surface area and analyzing isotherms. The frequent exchange of information helped shape the direction of the work in both laboratories.

D. Description of project impact

The results obtained show how understanding polymer morphology and interaction between ligand and polymer, together with understanding the chemistry of the ion exchanges process, leads to development of an efficient system for metal recovery.

E. Strengthening the development of co-country institutions

A substantial part of the AID grant allocated for the Prague Laboratory was used for acquisition of the liquid chromatography equipment (pump and detector) together with computer data station. It is substantial boost of the analytical capabilities which helps to increase the precision of the experimental data.

F. Future work

The results obtained thus far show that very good progress was achieved. The material collected can be arranged into at least one major publication. Novel and surprising results on the importance of the polar solvent were discovered and require very basic study. The model of the extraction model was very well defined on the basis of these results. We need to revise the existing plan in only one direction: additional work on adsorption from different alcohols. This will be carried out at ICPF.

Continuation of the work in the second year will be as follows:

1. Describe a procedure for preparing a large sample of DEHDTPA/XAD-2 (at WIS) for application in industrial recovery of Hg(II) (at ICPF).
2. Continue work on the relation between resin morphology and SIR properties.
3. Start work on the synthesis of new DTPA reagents of improved affinity to polymeric matrix.
4. Start work on preparing acid-base (DEHDTPA-polymer)-type SIR and study its properties.
5. Start work on DTPA intermediates that could be covalently linked to polymers.

SECTION II

A. Managerial Issues

In the last Managerial Report were mentioned difficulties with waiving of the

value added tax for the bought equipment. This problem was successfully solved and the acquired experiences together with establishing of necessary working procedures will help with a smooth management of the project in the future.

B. Budget

A major increase in salaries in the last year at academic institutions in Israel required us shift funds to cover this expenditure. We did this by sacrificing purchase of equipment. The metal analysis was carried out on the Perkin Elmer atomic adsorption spectrometer 5100 PC. The chemical services at the WIS, and the ICF at Analytical Services, The Hebrew University of Jerusalem Faculty of Agriculture. Since our laboratory is in the Bergmann Building, which is undergoing major reconstruction, started in October 1993 and expected to be finished at the end of 1995, we will only purchase the equipment we need (HPLC, colorimeter or UV spectrophotometer) when conditions in this building allow proper maintenance of the new equipment.

C. Special concerns - nothing to report

D. Collaboration, travel, training and publication

Dr. D. Muraviev, originally scheduled to work on this project, visited us from Spain for a short discussion. Dr. K. Jerabek, attended the POC-'94 as part of his training in polymer chemistry. Two reports (one at WIS and one at ICPF) will be completed in October 1994; they will serve as a basis for a publication.

A visit of one of each to the lab of the other is anticipated within the next 6 months.

E. Request for AID or BOSTID actions - none.

Fig. 1 Dependence of the resin loadings (Cr) on the DEHTPA concentration (C EtOH) in the impregnation solution

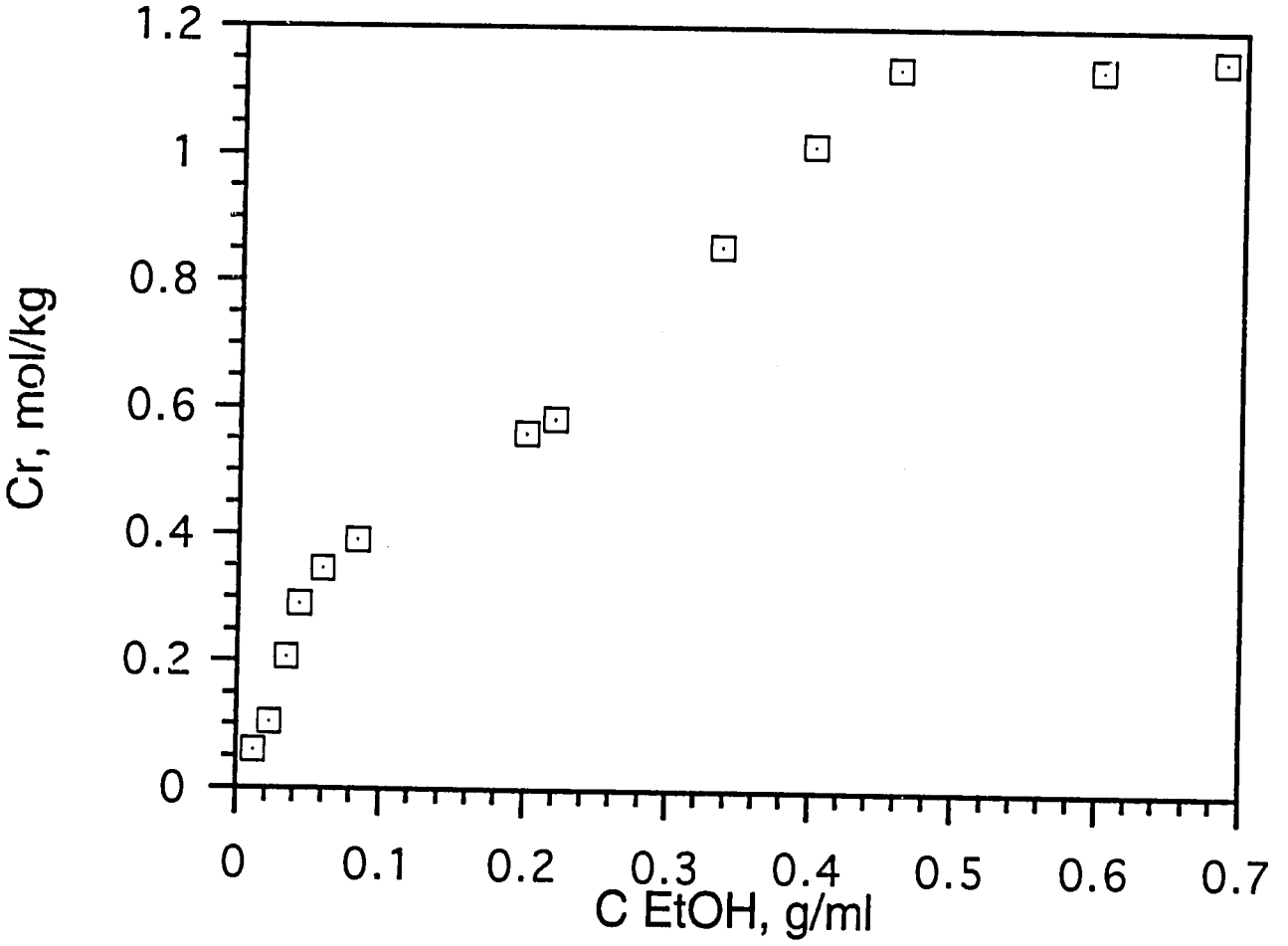
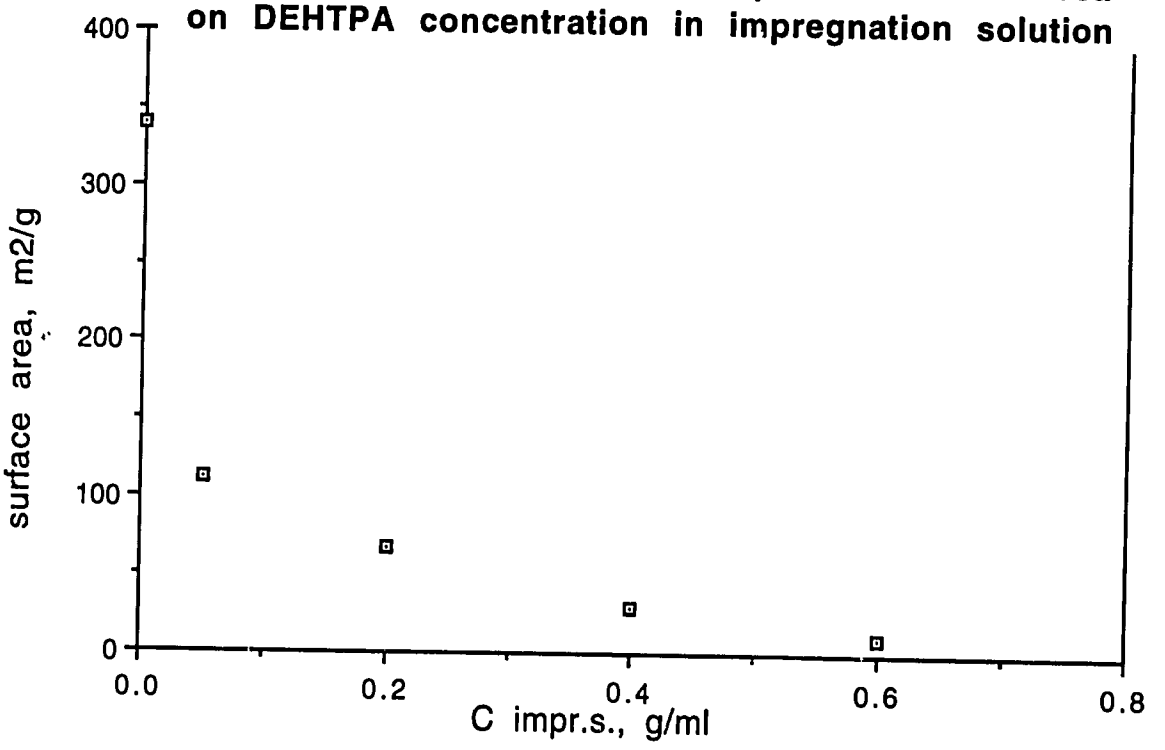


Figure 2. Dependence of the specific surface area on DEHTPA concentration in impregnation solution



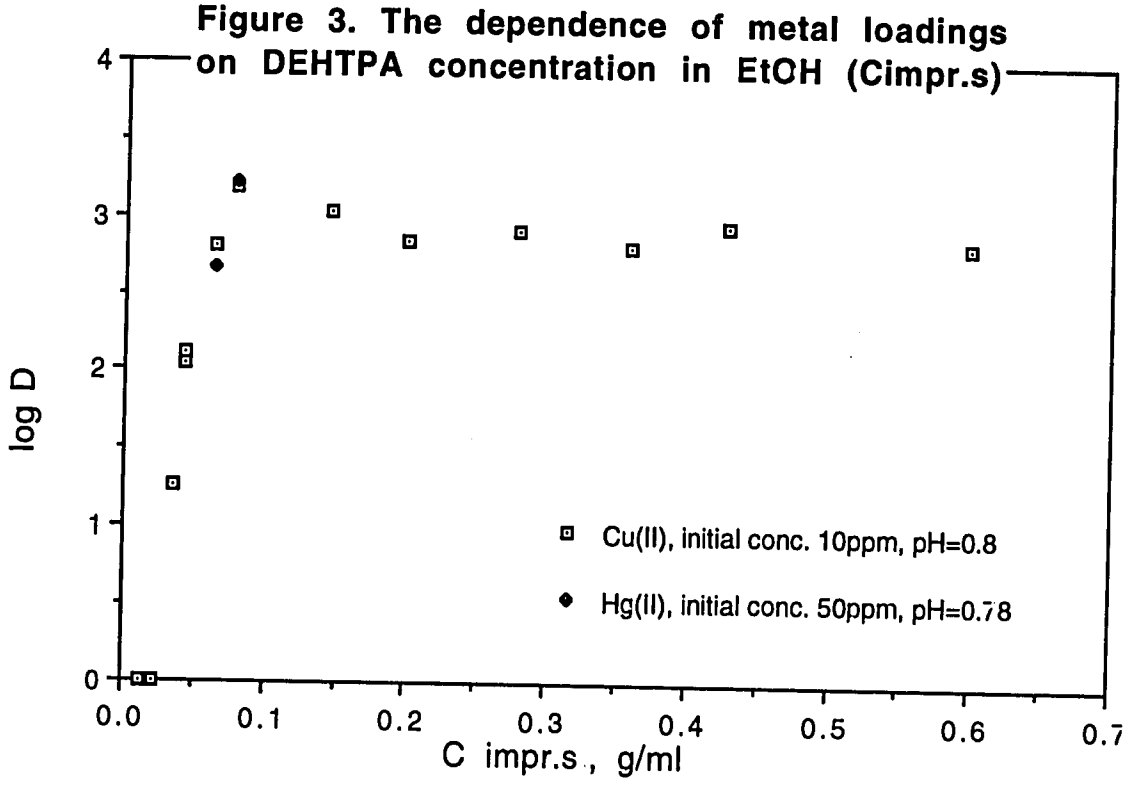


Figure 3. The dependence of metal loadings on DEHTPA concentration in EtOH (Cimpr.s)
log D
4
3
2
1
0
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
C impr.s., g/ml
Cu(II), initial conc. 10ppm, pH=0.8
Hg(II), initial conc. 50ppm, pH=0.78

Figure 4. The DEHTPA content in the aqueous phase (Caq) plotted as a function of DEHTPA concentration in the impregnation solution (Cimpr.s.); (24hrs contact time)

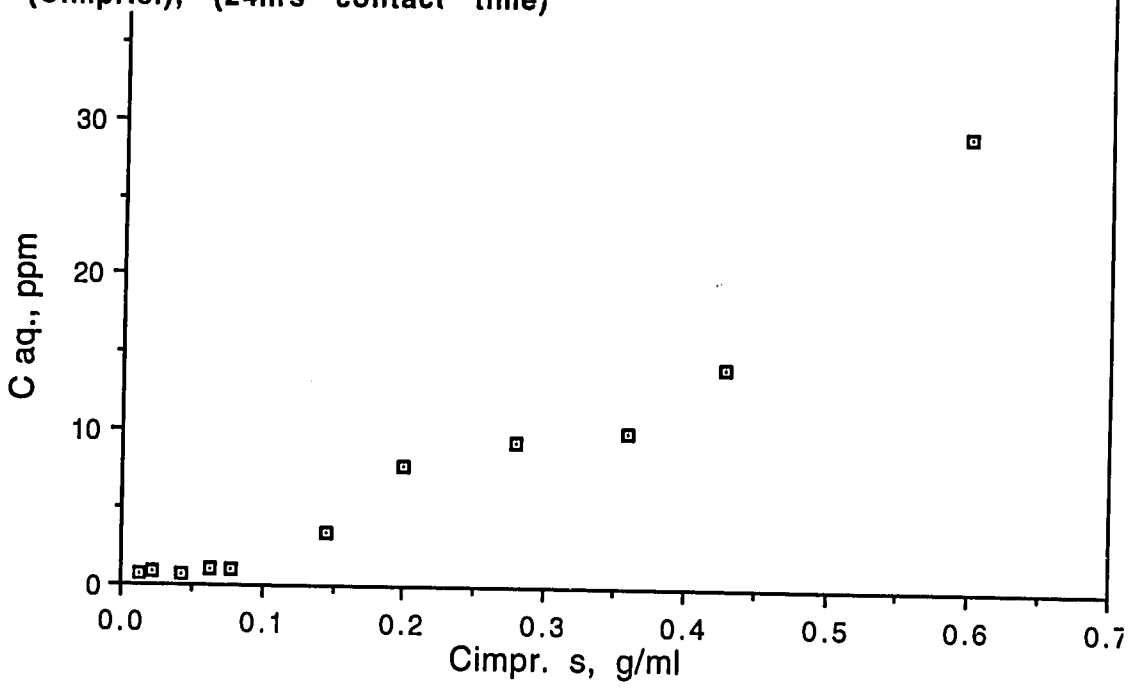
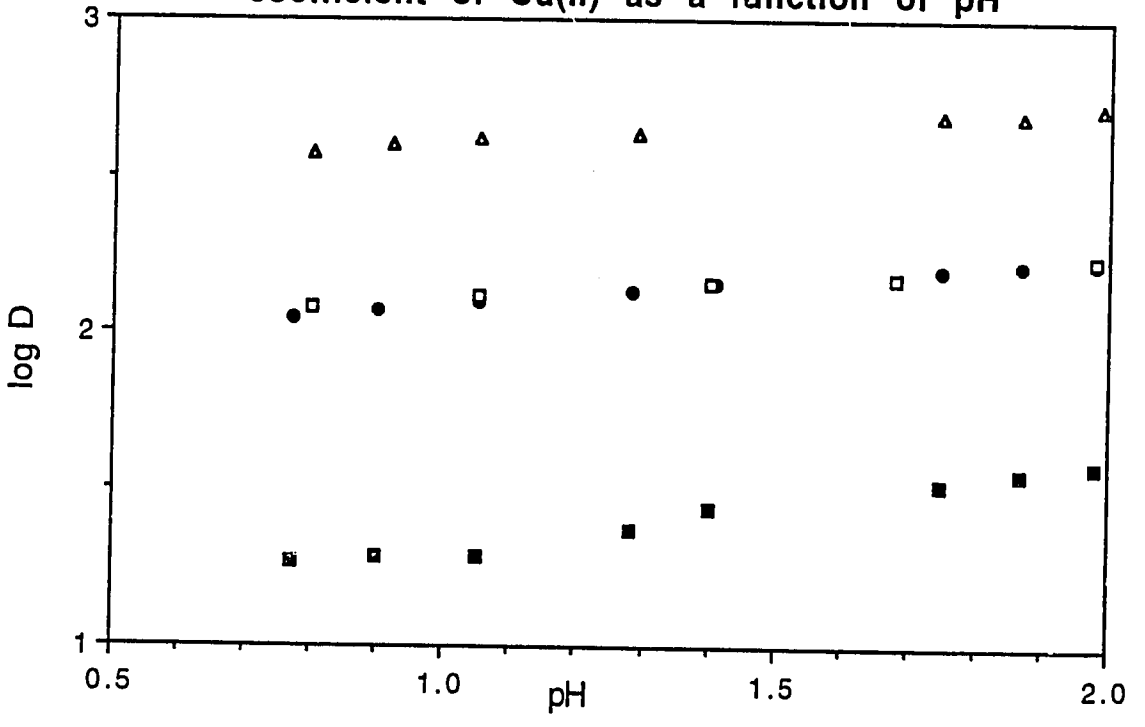


Figure 5. Variation of the distribution coefficient of Cu(II) as a function of pH



△ C_r = 0.298 mol/kg , 10ppm Cu(II) initial conc.

● C_r = 0.264 mol/kg , 10ppm Cu(II) initial conc.

■ C_r = 0.192 mol/kg, 10ppm Cu(II) initial conc.

□ C_r = 0.264 mol/kg, 20ppm Cu(II) initial conc.

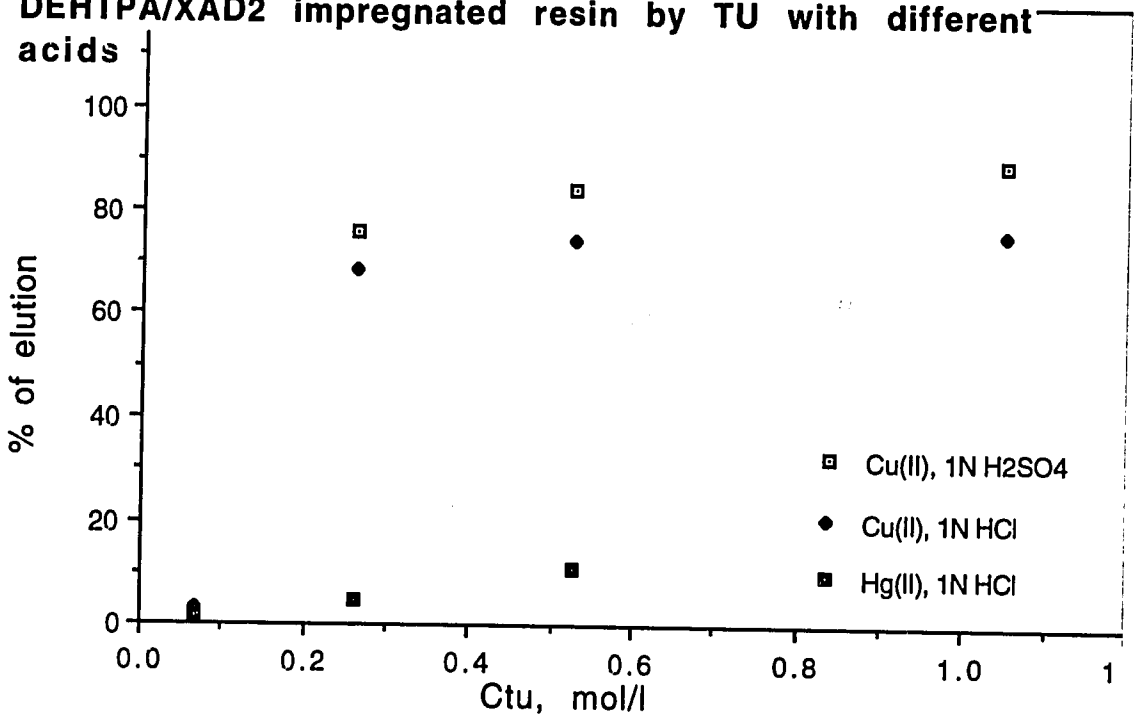



Figure 6. Elution efficiency of Cu(II) and Hg(II) from DEHTPA/XAD2 impregnated resin by TU with different acids