

SOLVENT EXTRACTION OF TUNGSTEN AND MOLYBDENUM  
FROM ACIDIC SOLUTIONS

A THESIS  
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This work is dedicated to my wife, Kyung,

to my son, Joon Sung,

to my daughters, Sungmin and Jinmin

For their belief in the value of learning,

For their patience and encouragement for three years.

ABSTRACT

Solvent extraction of tungsten and molybdenum has been investigated using tri-n-octylamine (TOA) and di-2-ethylhexyl phosphoric acid (D2EHP) in benzene. Tungsten and molybdenum were very well extracted by TOA and no problem was encountered from the point of view of the industrial application of the method.

The lack of extraction of tungsten from acidified tungstate solutions using D2EHP as the extractant confirmed that tungsten does not exist as a cationic form in the acidic solution.

The extraction of molybdenum from acidic solutions using D2EHP as the extractant confirmed that molybdenum exists in acidic solutions as both anion and cation species in equilibrium. The results show that the anionic species are much more predominant in the aqueous phase.

The extractability of molybdenum with D2EHP suggested the possibility of separating tungsten and molybdenum by a solvent extraction method.

The extraction of molybdenum in the presence of tungsten concentrations of zero, 10, 20, 40 g/l with 10% D2EHP in benzene was investigated. Full extraction of molybdenum in a simple extraction system with D2EHP was not achieved with the higher concentrations of tungsten present.

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## 1. INTRODUCTION

Tungsten is a metal of great industrial and strategic importance. It is valued, in particular, for the hardness and wear resistance of its carbide and as an additive in the manufacture of tool steels to which it imparts high temperature hardness and tensile strength.

The metal tungsten does not occur in its elemental state in nature. The principal raw material for the production of metallic tungsten is scheelite ( $\text{CaWO}_4$ ) and Wolframite  $\left[ (\text{Fe, Mn}) \text{WO}_4 \right]$ .

These minerals are found in many countries. The main sources are China, U.S.A., South Korea, U.S.S.R., Canada, Bolivia, Australia and Portugal.

Molybdenum is obtained principally from molybdenite ( $\text{MoS}_2$ ) ore. Wulfenite ( $\text{PbMoO}_4$ ) and powellite  $\left[ \text{Ca}(\text{Mo, W}) \text{O}_4 \right]$  are also minor commercial ores. Molybdenum is also recovered as a by-product of copper and tungsten mining operations.

Scheelite is very abundant in South Korea. It is essentially calcium tungstate and is the main source of tungsten for the industry today.

Briefly the process for the recovery of tungsten from its ore in the Korea Tungsten Mining Company can be divided into two parts.

Firstly the mineral dressing plant where a large bulk of useless materials is removed from scheelite by using conventional mineral dressing procedures such as crushing, comminution, flotation and tabling, etc. In this plant the differences in the inherent physical properties of the

minerals such as specific gravity and surface chemical reactivity are exploited.

Scheelite has a high specific gravity (S.G. 6.06) hence particles of it are readily separated from the large bulk of less dense gangue minerals (S.G. < 3) by a simple gravity concentrator such as a table. The gravity method, however, is not adequate for the separation of individual heavy minerals from each other because of the small difference in their specific gravities.

The case of the removal of molybdenum, if present in the form of a chemical combination with tungsten and calcium [powellite:  $\text{Ca}(\text{Mo,W})\text{O}_4$ ], presents the most difficulty and so far as is known it is not removable except by chemical treatment. Molybdenum, if present as molybdenite, can be removed by the sulphide flotation method.

Molybdenum is recovered as a by-product in the Korea Tungsten Mining Company. It occurs in ore mainly as Molybdenite ( $\text{MoS}_2$ ) which is easily recovered by a sulphide flotation process. (Fig. 1.1) and powellite, which it is impossible to remove in the mineral dressing plant.

The product of the mineral dressing plant is called Natural scheelite or scheelite A which is basically concentrated by physical methods and contains a fairly high % of molybdenum (Table 1.1). This is used for the manufacture of high speed tool steel or ferro-tungsten where molybdenum is either required or is quite acceptable.

Fig. 1.1. Flow sheet for natural scheelite production processes in the Korean Tungsten Mining Company.

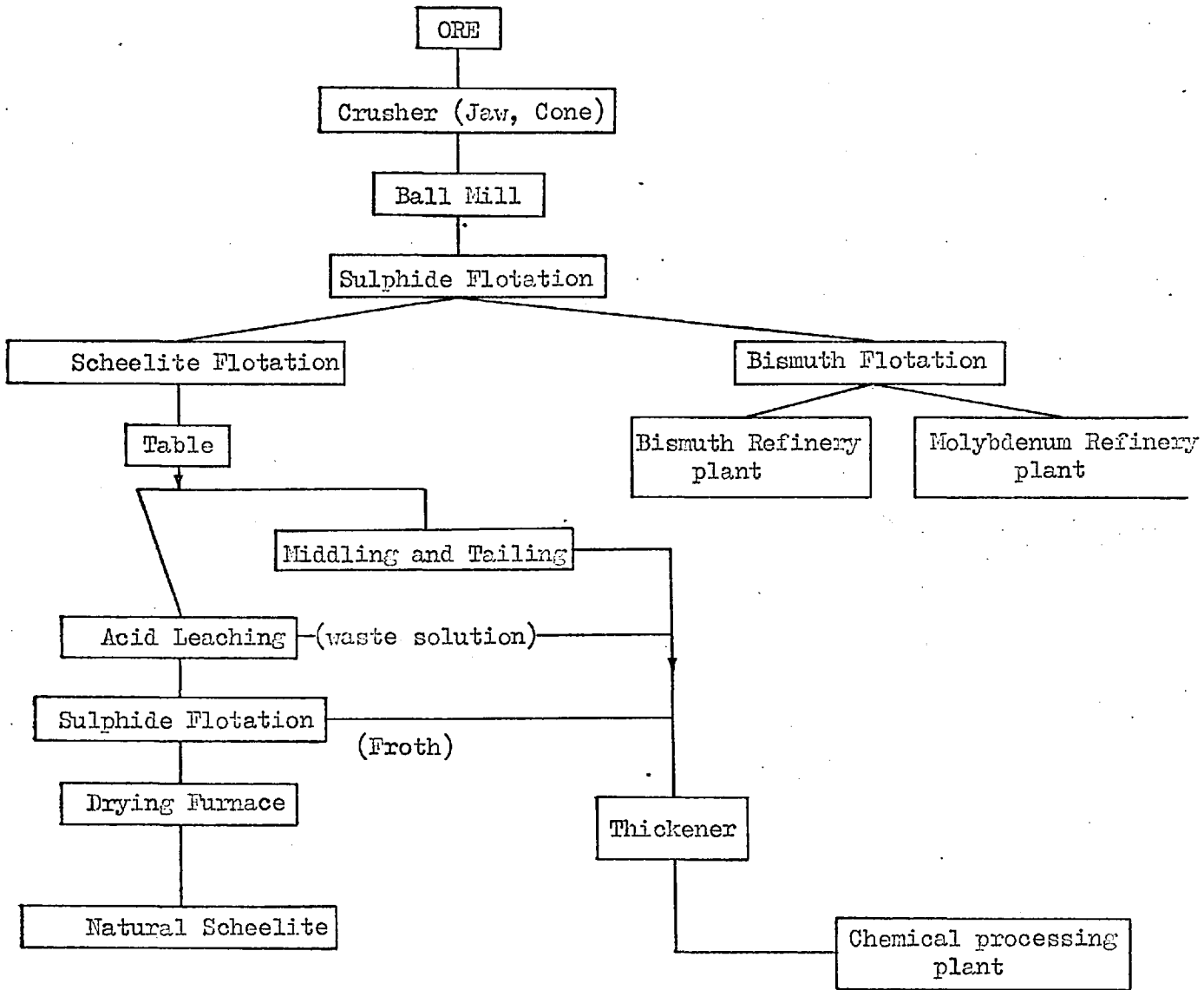




Table 1.1. Chemical composition of natural scheelite produced by Korean Tungsten Mining Company.

<u>Element</u>	<u>Typical</u>	<u>Guaranteed</u>
WO <sub>3</sub>	71.00 %	70.00 %
Sn	Trace %	0.01 %
As	0.01 %	0.01 %
S	0.03 %	0.05 %
Cu	Trace	0.01 %
P	0.01 %	0.03 %
Sb	Trace	0.01 %
Mo	1.50 %	1.70 %
<hr/>		
Mn	0.03 %	0.075 %
Bi	0.01 %	0.02 %
Pb	Trace	0.01 %
Zn	0.02 %	0.02 %
Fe	1.00 %	1.20 %
Ca	22.14 %	24.05 %
SiO <sub>2</sub>	2.68 %	3.82 %

If scheelite and powellite are present it is necessary to use chemical methods to separate the molybdenum from the tungsten.

Secondly in the chemical processing plant a synthetic scheelite (scheelite B) and high purity ammonium paratungstate  $[5(\text{NH}_4)_2\text{O} \cdot 12\text{WO}_3 \cdot 5\text{H}_2\text{O}]$ ; hereinafter this will be referred to as APT] is produced by chemical methods (Fig. 1.2.).

The chemical processing plant in the Korea Tungsten Mining Company is basically designed for recovering tungsten and molybdenum from low grade middling and tailings from the mineral dressing plant and solution and froth produced during production of scheelite A (Fig. 1.1).

Briefly the chemical processing treatment consists of digestion of tungsten ore with sodium carbonate under 200 psi pressure, converting tungsten and molybdenum into soluble sodium tungstate and sodium molybdates whereas iron and manganese are precipitated as hydrated oxide. Impurities are removed by a series of chemical treatments, finally resulting in a mixture of tungsten and molybdenum in the pregnant solution. This usually contains  $\text{WO}_3$  40 - 60 g/l, Mo 1-2 g/l.

In most cases, the element presenting the most serious problem in the tungsten industry is molybdenum. To remove this the strongly alkaline pregnant solution is acidified to pH 2-3 with sulphuric acid and the molybdenum is removed by precipitation with the sodium sulphide in the conventional manner.

Molybdenum is separated extremely well from the tungsten by the sulphide precipitation method (Table 1.2.). However, the author very reluctantly accepted the post of supervisor in this section when he was

working as a foreman in the chemical processing plant in 1961. In order to precipitate insoluble molybdenum tri-sulphide, the solid hydrated sodium sulphide is added to the acidic pregnant solution while the solution is being heated to about 80°C. Hydrogen sulphide gas is evolved during this process. It is time consuming tedious work to filter the fine molybdenum trisulphide precipitate, and since then the author has been trying to find an improved alternative for separating molybdenum from the tungsten solution. This is the main reason for the present work reported here. It would be beneficial to the tungsten industry if the separation of both metals could be carried out in a commercial plant by solvent extraction methods.

Molybdenum-free pregnant solution is made alkaline (pH 9-10) again by adding sodium hydroxide and then tungsten is precipitated and recovered as artificial scheelite by adding calcium chloride. This is used for the raw material for the manufacture of high-purity metal powder and is exported to foreign countries, i.e. Japan, U.S.A., France, England, West Germany, Sweden, Austria, etc.

During the last few years, attention has been given to the recovery of APT from the purified pregnant solution and eventually a commercial operation for the recovery of tungsten by solvent extraction was successfully installed at Sang Dong Mine, Korea Tungsten Mining Company, in 1973. This was developed entirely by the engineers of the company and has great advantages and the alternative process of taking scheelite, treating it with a mixture of hydrochloric and nitric acids, washing the tungstic acid very thoroughly to remove all calcium, dissolving the tungstic acid in ammonia, filtering off solid impurities, and crystallising APT. The savings in reagent and labour costs is very considerable.

In addition to a solvent extraction process for producing APT from

the molybdenum-free pregnant solution, it would also be desirable to separate the molybdenum from the tungsten by a solvent extraction process.

An important application of solvent extraction is its use in separating a number of metals occurring together. At the present time, commercial plants are in operation for the extraction and separation of Hafnium-Zirconium (Group IV a periodic table); Niobium-tantalum (Group V a periodic table) and why should one not be used for Molybdenum-Tungsten (Group VI a periodic table)? This was another reason for carrying out this work.

Fig. 1.2. Flow sheet for synthetic scheelite and A.P.T. production processes in Korea Tungsten Mining Company.

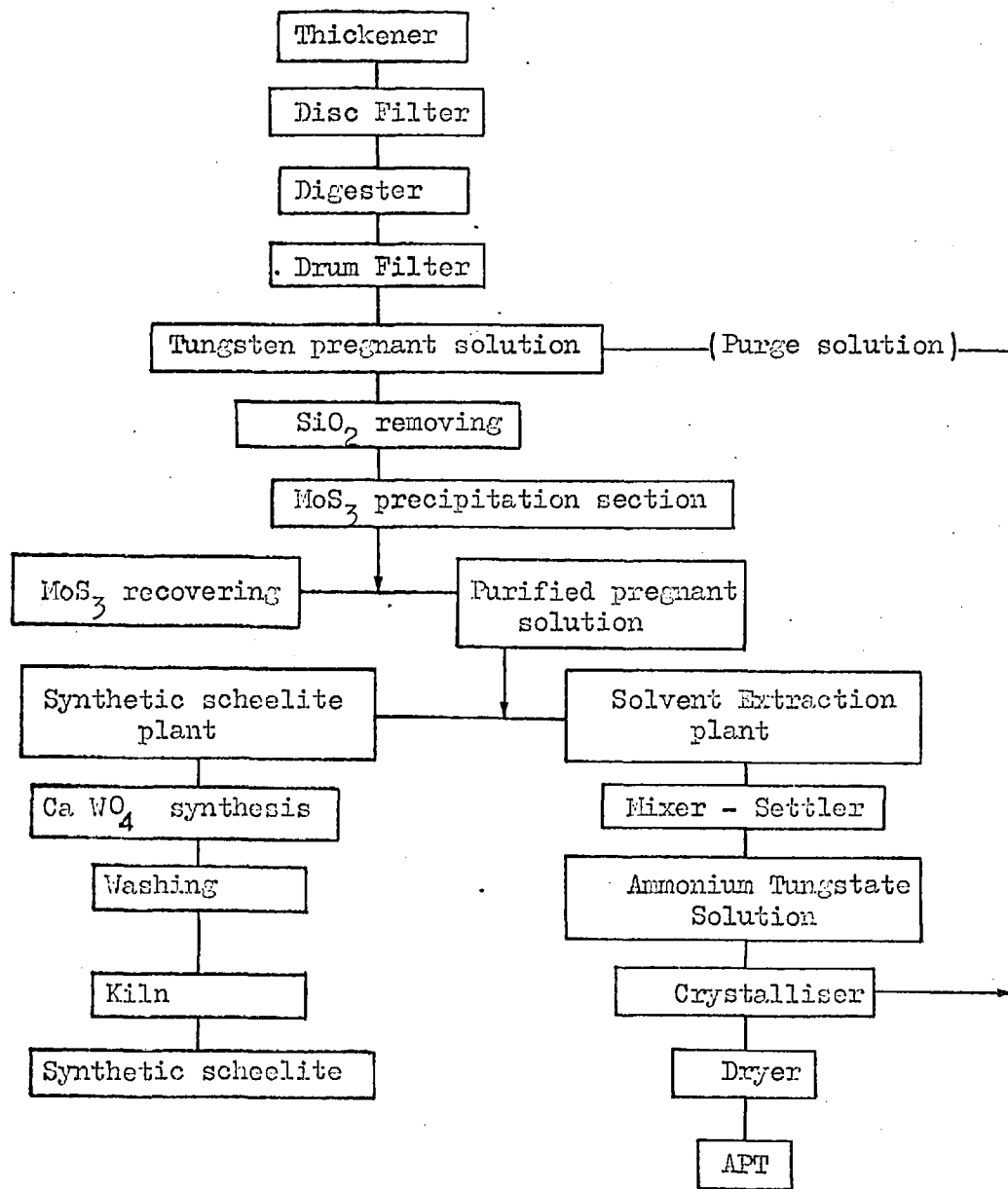


Table 1.2. Chemical composition of synthetic scheelite produced by Korea Tungsten Mining Company

<u>Element</u>	<u>Typical</u>	<u>Guaranteed</u>
WO <sub>3</sub>	71.00 %	70.00 %
Sn	Trace	0.01 %
As	0.01 %	0.01 %
S	0.30 %	0.35 %
Cu	trace	0.01 %
P	0.03 %	0.04 %
Sb	Trace	0.01 %
Mo	0.02 %	0.03 %
<hr/>		
Mn	Trace	0.01 %
Bi	0.01 %	0.02 %
Pb	Trace	0.01 %
Zn	0.01 %	0.01 %
Fe	0.30 %	0.35 %
CaO	22.25 %	24.82 %
SiO <sub>2</sub>	0.40 %	0.70 %

Table 1.3. Chemical composition of APT produced by Korea Tungsten Mining Company.

<u>Element</u>	<u>Typical</u>	<u>Guaranteed</u>
Ignition loss	11.0 %	11.5 %
Moisture	1.0 %	1.0 %
WO <sub>3</sub>	89.0 %	88.5 %
NH <sub>3</sub>	5.4 %	5.4 %
Si	30 p.p.m.	40 p.p.m.
Mo	40 "	50 "
<hr/>		
Al	10 p.p.m.	20 p.p.m.
Fe	30 "	50 "
Cu	5 "	10 "
Ca	10 "	20 "
Ni	5 "	10 "
Na	30 "	50 "
Cr	5 "	10 "

The tungsten market today may be considered as requiring

- a) very pure tungsten metal for wire in incandescent bulbs and in other applications where high ductility is necessary.
- b) a reasonably pure tungsten for production of cast or sintered tungsten carbide for such items as oil well tools and high-grade cutting tools, and
- c) a relatively impure tungsten for use in high-speed tool steel production.

It can also be pointed out that the element molybdenum is the most important impurity separating the three grades of tungsten. Specifications for the tungsten oxide from which the high-purity tungsten metal is produced usually require less than one ppm molybdenum in the tungsten oxide; the intermediate oxide for carbide production may specify from 50 to 200 ppm maximum molybdenum content; whereas for high-speed tool steel production, a tungstic oxide containing as much as 0.10 to 2.5% molybdenum may be quite acceptable.

Depending upon the end use, therefore, research effort for improving tungsten winning technology may be directed in different ways but it is clear that as far as the tungsten industry is concerned improved technology of separating the two metals is needed.

At this point, together with the operation of the commercial solvent extraction plant in the Korea Tungsten Mining Company, it is hoped that the principal impurity, molybdenum, could be removed from the pregnant solution by solvent extraction methods which takes all the potential advantages of a completely hydraulic system.

The present work is an attempt to understand some of the aspects of a



commercial operation to separate both metals and to find out difficulties which have arisen from the practical experimental results.

In the work described in the remainder of this thesis particular attention has been given to the mechanism of the extraction of cationic molybdenum with organophosphoric acid in weakly acidic solution. It seems difficult to separate molybdenum from tungsten by solvent extraction without utilizing the fact that there exists a cationic form of molybdenum.

The principal parameters of the extraction of pure tungsten or molybdenum in weakly acidic solution were studied using tri-n-octylamine and Di-2-ethylhexylphosphoric acid respectively as a first investigation. Then tungsten and molybdenum were mixed together in the solution to a ratio near that of pregnant solution ( $W/Mo = 20 - 40$ ), extraction was carried out by Di-2-ethylhexylphosphoric acid. It was found that the molybdenum distribution coefficient was significantly decreased in the presence of tungsten; the more tungsten concentration was increased the more the molybdenum distribution coefficient was decreased.

It was beyond the scope of this work to investigate quantitatively the decrease in molybdenum distribution coefficient in the presence of tungsten. This effect was qualitatively explained in terms of tungsten concentrations derived from tungsten and molybdenum heteropoly anion complexes.

The present work was concerned only with the separation of the two metals by a solvent extraction process from the point of view of industrial application. No further theoretical treatment of the data obtained can be carried out because the system proved to be highly complex and the lack of data and literature available.

## 2. LITERATURE SURVEY

### 2.1. Extraction of sulphuric acid in the tertiary amine-benzene system

The use of long chain tertiary amines for the extraction of various acids was first reported by Smith and Page (1). They were primarily concerned with the development of a method for the separation of strong and weak acids, but it was also suggested that the acidified amine solutions might find other uses as liquid anion exchangers, e.g. "in the recovery of metals, such as chromium or vanadium, after oxidation to anions".

Some time later, further tests of amines were made by F.L. Moore of the O.R.N.L. Analytical Division to determine the general applicability of these reagents to analytical separation problems (2).

A number of papers concerning the extraction of nitric, hydrochloric and sulphuric acids by amines have appeared since then (3), (4) and (5).

Because of the frequent use of sulphuric acid in processing tungsten raw materials, most of the literature survey was concerned with the sulphate system.

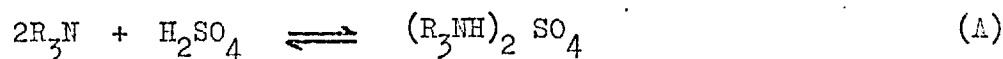
The first quantitative study of sulphuric acid extraction by tri-n-octylamine was made by Allen (6). The extraction of sulphuric acid by long-chain amines has since been studied extensively by various workers (7), (8), (9), (10), (11).

The transformation of a tertiary amine to the corresponding amine salt, which is accomplished by the equilibration of the free amine with a sulphuric acid solution, may give rise to either the amine normal sulphate or the amine bisulphate. The nature of amine salt present in the organic phase in the

extraction of sulphuric acid by tri-n-caprylamine was studied by Kim and Chiola (12). They found that the tri-n-caprylamine in the concentration range of 0.05 - 0.25 M extracted sulphuric acid to form either the normal sulphate or the bisulphate salt, depending on the concentration of acid in the aqueous phase. The amine salt formed was studied by vapour-pressure osmometry, by the extraction isotherm, and by its infra-red spectrum. To determine which salt form predominated in the organic phase, extraction isotherms of 0.05, 0.10, 0.15, 0.22, and 0.25 amine in benzene were constructed. The extraction isotherms of the 0.15 M solution is shown in Fig. 2.1.1. This shows three regions in which the magnitude of the acid-extraction coefficients differ significantly. Very high extraction coefficients of acid are obtained when the equilibrium concentration of acid in the aqueous phase does not exceed about 0.02 M. This is the region where the amine sulphate exists predominantly. The average equilibrium constant (K) was  $3.24 \times 10^8$  when the amine concentration was 0.05 - 0.22 M. When the amine concentration was 0.25 M, K values were unusually high ( $K = 6.78 \times 10^9$ ).

Allen (6), using tri-n-octylamine, reported K values of  $1.90 \times 10^8$ . Wilson (12) also obtained K values of  $1.4 \times 10^8$  for tri-n-octylamine. Versteegen and Ketelaar (10), using tri-n-octyl and tri-n-hexylamine, found K values of  $1.87 \times 10^7$  and  $0.45 \times 10^7$ , respectively.

Logarithmic plots of  $A_{H_2SO_4}$  versus  $(R_3NH)_2SO_4 / (R_3N)^2$  for all of the amine concentrations examined resulted in essentially straight lines having slopes equal to about 1. Fig. 2.1.2 shows typical plots for 0.05 and 0.10 M amine in benzene. From these data, it was concluded that (a) the reaction takes place according to equation (A)



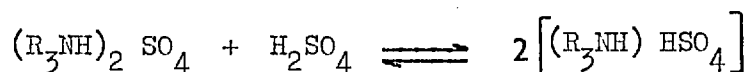
(b) the predominant species which exists in the region is the amine normal sulphate.

It can be seen that there is a systematic break in the line when the acid concentration in the equilibrium aqueous phase exceeds about 0.02 M. This is the point where amine bisulphate is thought to start to form.

Allen (6) demonstrated that a logarithmic plot of  $A_{H_2SO_4}$  versus  $(R_3NH)_2 SO_4 / (R_3N)^2$  gave a straight line having a unit slope when sulphuric acid was extracted by tri-n-octylamine of 0.05, 0.1, 0.25 and 0.5 M concentration in benzene. He found also that the formation of normal sulphate occurs when the acidity of the aqueous phase at equilibrium is less than 0.02 M. Above 0.02 M, it was considered that aggregation of the salt begins. The conclusion was based on the evidence of the systematic break in the logarithmic plot of  $A_{H_2SO_4}$  versus  $(R_3NH)_2 SO_4 / (R_3N)^2$ .

Verstegen and Ketelaar (10) also found that tri-n-octylamine normal sulphate forms predominantly at low acidities, that is, when the sulphuric acid concentration of the aqueous phase after equilibration is less than 0.02 M.

Following the region of very efficient acid extraction, the extraction coefficient decreases gradually (Fig. 2.1.1). This is the region where an additional acid molecule is extracted and amine bisulphate starts to form. The reaction may be represented as follows :



Examination of the extraction isotherms show two regions where straight lines may be drawn. One of these corresponds to the region where the amine sulphate exists predominantly and another to the region where amine bisulphate

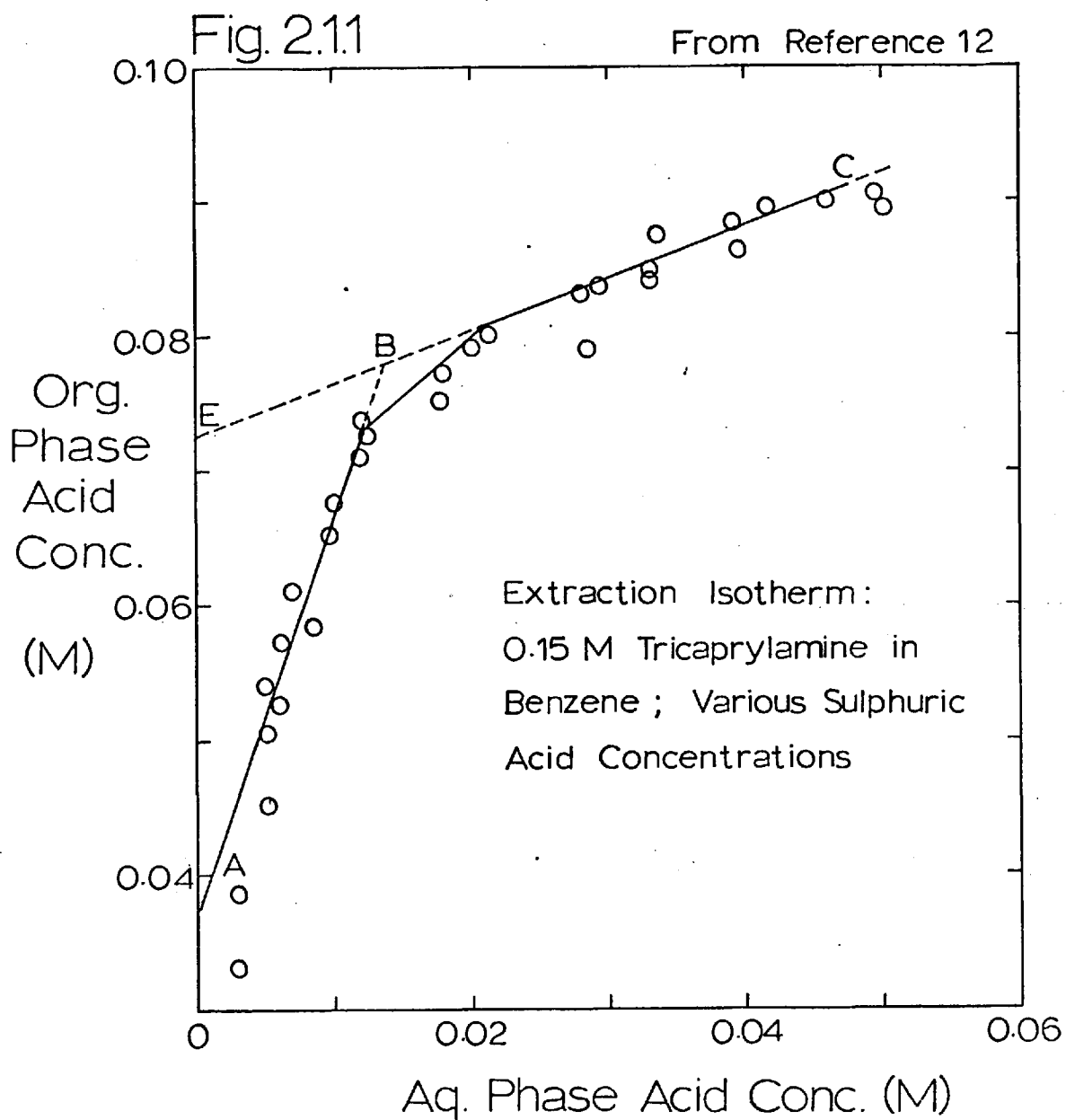
is forming.

The mole ratio of amine to acid in the organic phase as determined from the point of intersection (B) (Fig. 2.1.1) was found to be 2:1 in all cases. Beyond the intersection point the extraction coefficient decreases until the mole ratio of acid to determine in the organic phase approaches 1.

It has been reported by Allen (13), on the basis of a light-scattering technique, that tri-n-octylamine sulphate is monomeric, while the tri-n-octylamine bisulphate is dimeric.

Fig. 2.1.3 shows the relationship between aggregation number and the ratio of acid concentration to the amine concentration.

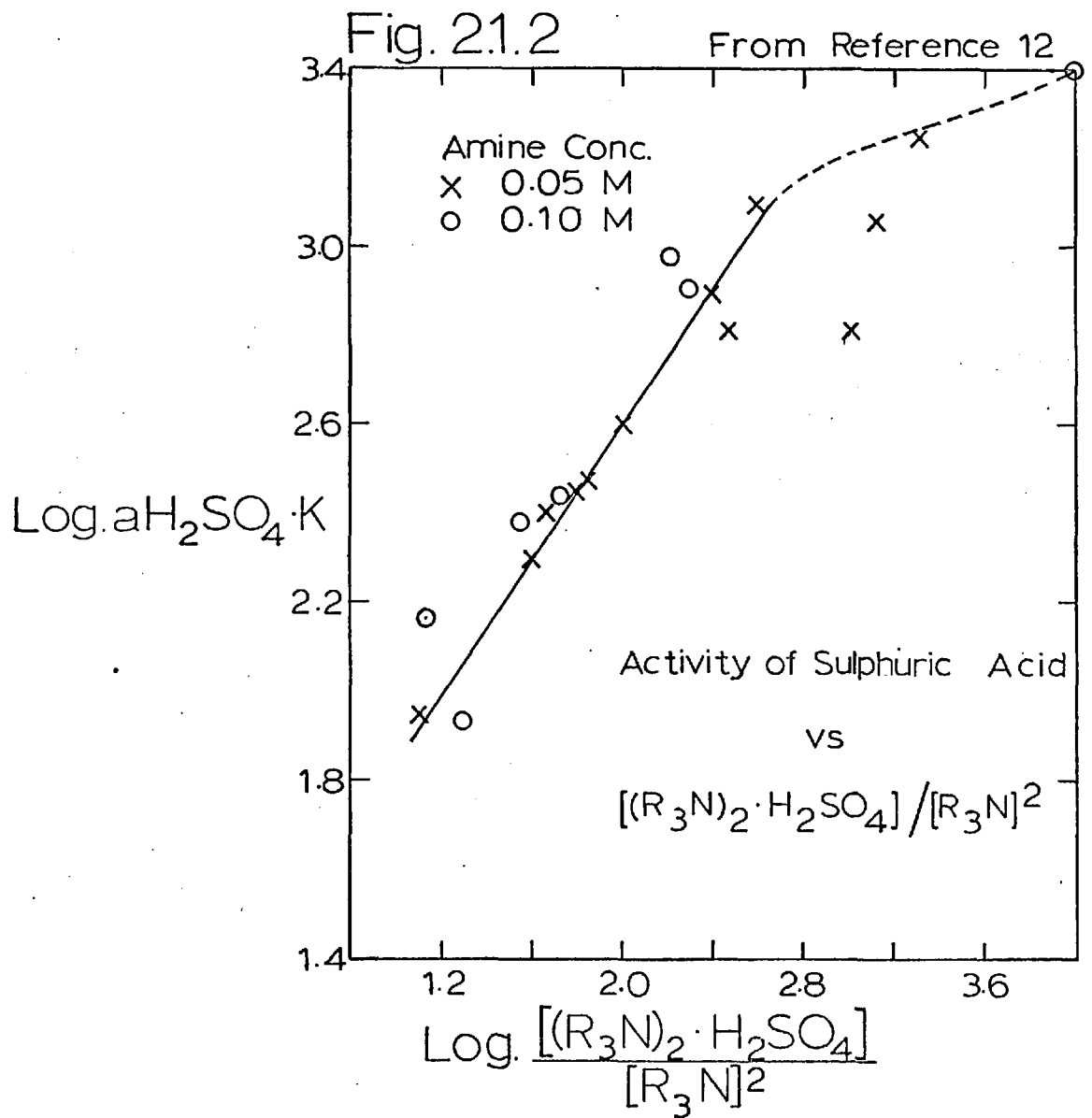
Marcus (14) suggested that symmetrical tertiary amine normal sulphates are usually monomeric, while the bisulphate form is dimeric. On the other hand, nonsymmetrical tertiary amine normal sulphates tend to exhibit larger aggregation numbers, indicating the presence of polymeric forms.

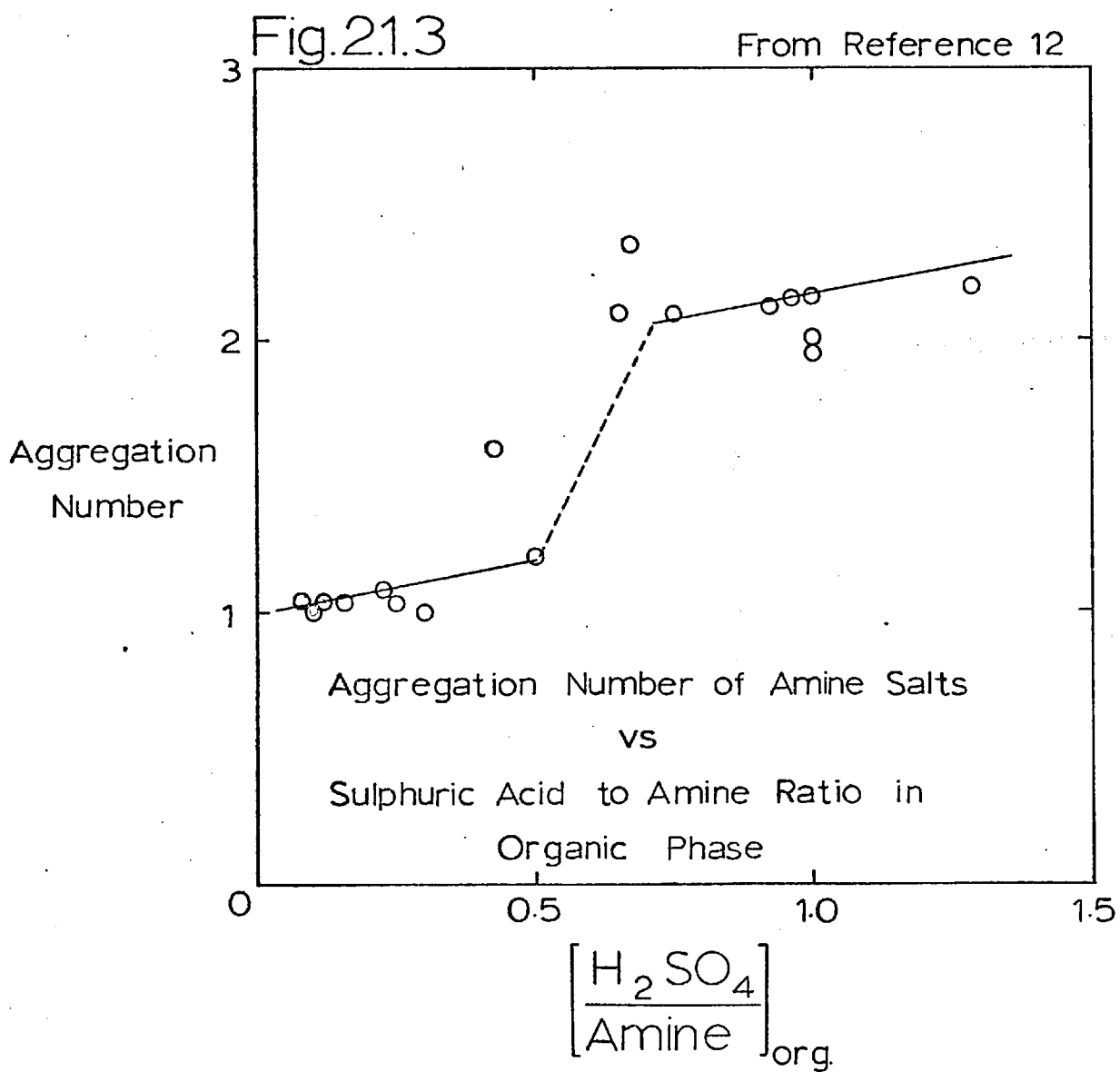


Point B: Amine completely transformed to amine salt, and no free amine available.

Line AB: Amine sulphate exists predominantly.

Line BC: Amine bisulphate exists







## 2.2. Solvent extraction of tungsten and molybdenum

The extraction of metals by amines has been investigated by many workers. Very little solvent extraction data concerning tungsten are recorded in the literature. In the published literature, the extraction of molybdenum is often considered in conjunction with the extraction of uranium. Brown and Coleman (15) noted that all long-chain amines extract molybdenum from sulphate solutions. Its distribution coefficients were higher than those of uranium.

Laskorin (16) and co-workers compared the extraction of molybdenum and tungsten, emphasizing the extractability of molybdenum.

Petrov et al. (17) investigated the extraction of tungsten and molybdenum with tri-n-butylphosphate from strong HCl solutions with emphasis on the separation of molybdenum from tungsten.

Kim et al. (18) investigated the study of soluble tungstate species by solvent extraction. Distribution data derived from solvent extraction are interpreted in terms of the predominating tungsten species present in the aqueous phase. The nature of the tungstate species extracted by tri-n-caprylamine changes markedly with the pH of the system. (Fig. 2.2.1). The aqueous phase they used was prepared to contain a countable quantity of radioisotope  $^{181}\text{W}$  (half-life 140 days), in a concentration of the order of  $10^{-7}\text{M}$ .

The amine extraction process has been applied recently on a commercial scale in the tungsten industry. Molybdenum is removed during acidification by the conventional sulphide precipitation methods (19), (20).

Sylvania Electric Products Inc. have recently installed a solvent extraction plant for tungsten (21). Patents have been granted to the company for solvent extraction processes for purification of molybdenum by selective extraction with a trialkylamine (22) and for the separation of molybdate values from tungstate by selective extraction at pH 2.0 with a di-2-ethylhexylphosphoric acid-tributyl phosphate modified organic phase (23). Another patent cites the use of a 10 to 11% solution of monohexadecyl phosphoric acid for the recovery of molybdenum from aqueous mineral acid solutions (24). In both cases the molybdenum is recovered from the organic phase by stripping with ammonia.

Drobnick and Lewis (26) have reviewed the extraction and purification of tungsten by a liquid ion exchange method in expectation of an increase in tungsten, tungsten carbide and tungsten alloy consumption. They conclude that Aliquat 336 chloride is the most promising reagent for extraction of tungsten from alkaline solutions while Alamine 336 is the best extractant from acid solutions and permits partial removal of molybdenum from tungsten during re-extraction with ammonia.

The extraction of tungsten from tungstate solutions by trialkylamines and the effect of fluoride ion on the extraction has been reported by Zelikman et al. (27).

The nature of the heteropoly complex molybdenum and tungsten species in acid solutions, which are extractable by amines, have been described by Petrov et al. (28).

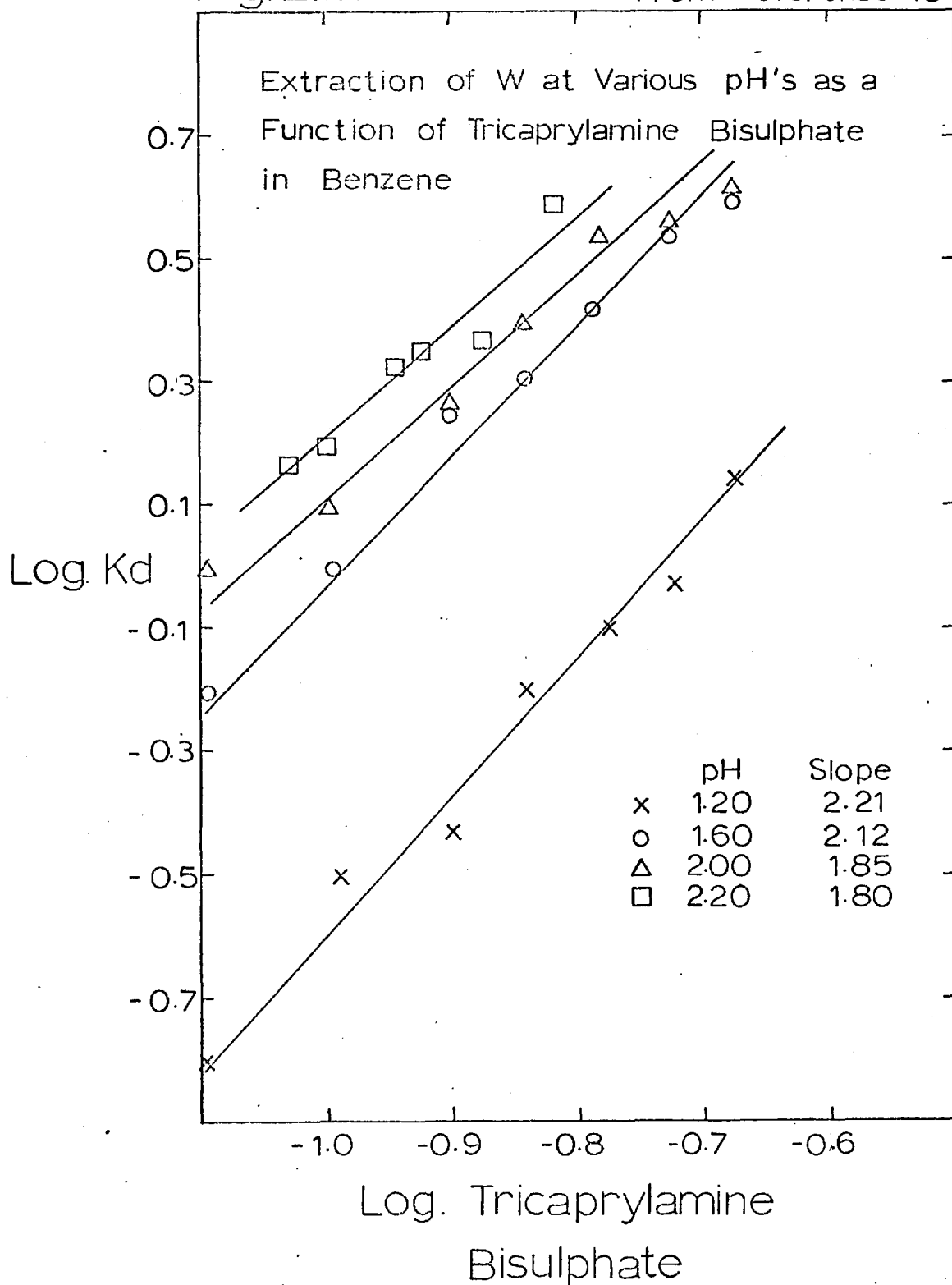
A process for separating molybdenum from tungsten was carried out on a laboratory scale by Esnault et al. (29). It includes acidifying the ammonium tungstate solution containing a small amount of molybdenum with HCl to

pH 3-3.5, then contacting with D2EHP diluted in kerosene in the presence of 2-ethyl-1-hexanol to extract molybdenum. The molybdenum is then stripped by an aqueous ammonia solution. The mother liquor, free from molybdenum, is contacted with a primary amine dissolved in kerosene to form a tungsten amine complex, then tungsten is stripped by aqueous ammonia.

The mechanism of the extraction of molybdenum from weakly acidic solutions (pH range 0.5 - 5) by D2EHP has been studied by Zelikman and Nerezov (30).

Fig. 2.21

From Reference 18



### 3. EXPERIMENTAL

#### 3.1. Tungsten-Sulphate system

##### 3.1.1. Materials

###### (a) Tri-n-octylamine (TOA)

Technical grade tri-n-octylamine was obtained from B. Newton Maine Ltd. The purity was checked by dissolving appropriate amounts in ethanol and titrating against standard 0.1 M hydrochloric acid. The end point was determined by measuring the pH of the solution after 1 ml. additions of acid (or 0.1 ml. additions near the end point) and plotting  $\text{pH}/\Delta V$  versus the volume of solution added. pH values were measured using a Pye "Dynacap" pH meter fitted with an Ingold composite glass and saturated calomel electrode.

The molecular weight of the amine was found to be 334 compared with a theoretical value of 353.7, so the TOA was used with no further purification.

The appropriate quantity of amine, based on the measured equivalent weight, was dissolved in A.R. grade benzene and made up to 1 litre. Amine solutions were pre-equilibrated, using a mechanical shaker, for 10 minutes with an equal volume of 0.9 M sulphuric acid, which is the optimum concentration to convert the whole of the amine into the bisulphate form (12) and the optimum concentration from the corrosion point of view (31).

###### (b) $^{185}\text{W}$ isotope

2.02 m Ci  $^{185}\text{W}$  ( $\beta^-$  emitter of half-life 75.8 days) contained in 5.6 ml. of 0.08 M NaOH solution was obtained from the Radiochemical Centre, Amersham. This was mixed with a solution containing sodium tungstate and the volume was made up to 1 litre with distilled water. The resulting

$^{185}\text{W}$  stock solution had the following composition:

W 200  $\frac{\text{g}}{\text{l}}$       Activity = 2.02  $\mu\text{Ci } ^{185}\text{W}$  per ml.

(c) Other reagents

All other reagents used were standard A.R. grade reagents.

### 3.1.2. Equilibration

Working solutions were prepared by acidifying stock solution with 0.9 M sulphuric acid. Very slow addition of acid was necessary in order to avoid precipitation of tungsten.

20 ml. of aliquots of working solution and pre-equilibrated TOA in benzene were placed in 100 ml. cylindrical separating funnels and shaken, using a mechanical shaker, at ambient temperature which was usually within the range 18 to 25°C. The contact time with amine sulphate was 5 minutes. When extracting tungsten with tri-n-octylamine sulphate this contact time was found to be sufficient for the attainment of equilibrium.

After equilibration the phases were allowed to settle overnight, and were then separated and samples of each were taken for counting.

### 3.1.3. Analysis of tungsten

The distribution of tungsten was determined by liquid scintillation counting of the beta emission of  $^{185}\text{W}$ . The principles of scintillation counting and the statistics of counting are adequately dealt with in the relevant literature (32), (33), (34), (35), (36), (37), (39), (40).

Very little work has been done on solvent extraction of tungsten using radioactive isotopes as tracers. Only one reference has been found which deals with  $^{181}\text{W}$  (half-life 140 days) in the study of soluble tungstate species by solvent extraction (18).

When a minute amount of  $^{185}\text{W}$  is added to some of its normally

occurring isotope solutions, its radioactivity ( $\beta^-$ ) acts as an indicator of the concentration of the tungsten in the solutions before and after solvent extraction.

The equipment used for measuring the radioactivity of  $^{185}\text{W}$  was an Ekco N612 liquid scintillation counter, coupled with an Ekco N530G scaler. The scintillation counter comprises a specially chosen fourteen stage photo-multiplier tube which, together with a novel source coupling unit, is contained in a lead shield fitted with a spring counter-balance lid. The shielded counter assembly is mounted in a steel case, which also contains a five valve wide band linear amplifier. The source coupling unit is an aluminium alloy casting fitted with a Pyrex glass window in its lower face. Immediately above the window is a light-proof shutter and above this a tray to hold the special Pyrex glass sample holder. A light-proof lid covers the sample holder and interlocks with the shutter to prevent extraneous light from reaching the P.M. tube. To improve the light collecting efficiency, MS.200 silicone fluid was used between the sample holder and the window as a liquid coupling medium.

The principle (32) of operation is that the energy of the beta particles emitted by the test sample is converted to light energy by the liquid phosphor solution. The resulting light photons impinge upon the cathode of the P.M. tube and release photo-electrons, which are then accelerated towards the first dynode. Each dynode emits some three or four secondary electrons for each primary electron reaching it. This results in an overall gain of about one hundred million between the photo cathode and the collector. The signal at the collector is then amplified still further, by the built-in linear amplifier, to a level sufficient to operate any conventional scaler or counting rate meter requiring a positive going input signal of five volts minimum.



The phosphor solution (34), (35), (36) consisted of 8g of 2,5 diphenyl oxazole (P.P.O) and 0.36 g of 1,4-bis-(2 -[5-phenyloxazolyl] ) - benzene (P.O.P.O.P) dissolved in a litre of sulphur-free toluene. The function of the P.P.O. was that of primary scintillator whilst P.O.P.O.P. acted as a wavelength shifter to alter the wavelength of the fluorescence nearer to that of the maximum sensitivity of the photomultiplier tube (35), (38), (41). Sulphur-free toluene was used because sulphur compounds have the effect of quenching the energy transfer process in the scintillator. These scintillation solutions are sensitive to light so that it was necessary to acclimatise them in the dark of the sample chamber for several minutes before counting. To avoid deterioration of the scintillation solutions, they were stored in the dark.

The Ekco 530G automatic scaler which is coupled with the scintillation counter performs as a complete counting instrument. It is a combined six-decade scaler and timer. It may be used to time a pre-determined count, to count a pre-determined time, or as a manually operated scaler. For recording the time taken to achieve a count, the instrument can be set to the following ranges: 100, 300, 1000, 3000, 10,000, 30,000, 100,000, 300,000 and 1,000,000 counts. When counting for a pre-determined time, the settings available are: 100, 300, 1,000, 3,000, 10,000, 30,000 and 100,000 seconds.

External connections between counter and scaler are as follows. The 'HV' plug on the N612 counter to the 'HV' plug on the rear of N530 G scaler, with one of the coaxial connectors. The 'output' plug on the counter to the 'Direct INPUT' on the scaler with the second coaxial connector. The 'power' plug on the counter to the 'probe' plug on the scaler.

The counter was refrigerated at  $-20^{\circ}\text{C}$  to reduce thermal noise and all samples were equilibrated to this temperature before counting.

It was found necessary to test the scaler by using main frequency to count 5000 pulses per 100 seconds before every counting. The reason was that some decades in the scaler sometimes jumped which led to incorrect results, seems as abnormal mass balances. When this was found, the electronic bulbs were changed.

Counting was actually performed by timing a pre-determined count of 10,000 to give 96% chance of the percentage error being less than  $\pm 2\%$ . For the more concentrated samples, background counts were neglected.

The best operating condition of the counter was that which would determine the activity of any sample to a given accuracy, in the shortest possible time. It has been shown that the optimum signal to noise ratio is obtained when  $R_s^2/R_B$  is a maximum (32), (39). (Fig. 3.1.3.1. and 3.1.3.2.).

Where  $R_s$  is the count rate from the sample alone and  $R_B$  is the background count rate. The most favourable operating conditions will differ according to the energy of the isotope being used and once the settings have been determined for one isotope, they are independent of the amount of activity present (32).

Optimum instrument settings for  $^{185}\text{W}$  were found to be E.H.T = 1200 V, discriminator bias = 20 V and amplifier gain = 250 X.

When a solution for counting was made up with an aqueous phase containing tungsten the quenching effect reduced counting efficiency

by about 50% compared with the same amount of tungsten added in an organic phase.

Hence, all the counting solutions were made up in single homogeneous organic phases so that the background, reference and sample solutions of each phase were of similar compositions except for the tungsten content.

The concentration of amine sulphate was not the same in each counting solution, but the difference was shown to have no effect on the counting efficiency for  $^{185}\text{W}$ .

After each equilibration experiment the concentration of tungsten was determined in both phases. The organic phase is identified below as the equilibrated organic phase. A sample of the aqueous phase was treated with 0.1 M amine sulphate, the pH being between 2 and 3, so as to extract the whole of the tungsten into the organic phase. This organic solution was added to the scintillation solution for the determination of tungsten in the equilibrated aqueous phase.

The counting solutions were made up as follows :

Aqueous background

10 ml. scintillation solution, 1 ml. amine sulphate.

Aqueous reference

10 ml. scintillation solution, 1 ml. amine sulphate containing tungsten extracted from a sample of the aqueous phase before equilibration.

Aqueous sample

10 ml. scintillation solution, 1 ml. amine sulphate containing tungsten extracted from the aqueous phase after equilibration.

Organic background

10 ml. scintillation solution, 1 ml. amine sulphate.

Organic reference

10 ml. scintillation solution, 1 ml. organic reference solution.

Organic sample

10 ml. scintillation solution, 1 ml. organic phase after equilibration.

An organic reference solution was prepared by extracting known concentrations of tungsten with amine sulphate and diluting to appropriate concentrations.

Fig. 3.1.3.1

Data from Tables 3.1.31 a&b

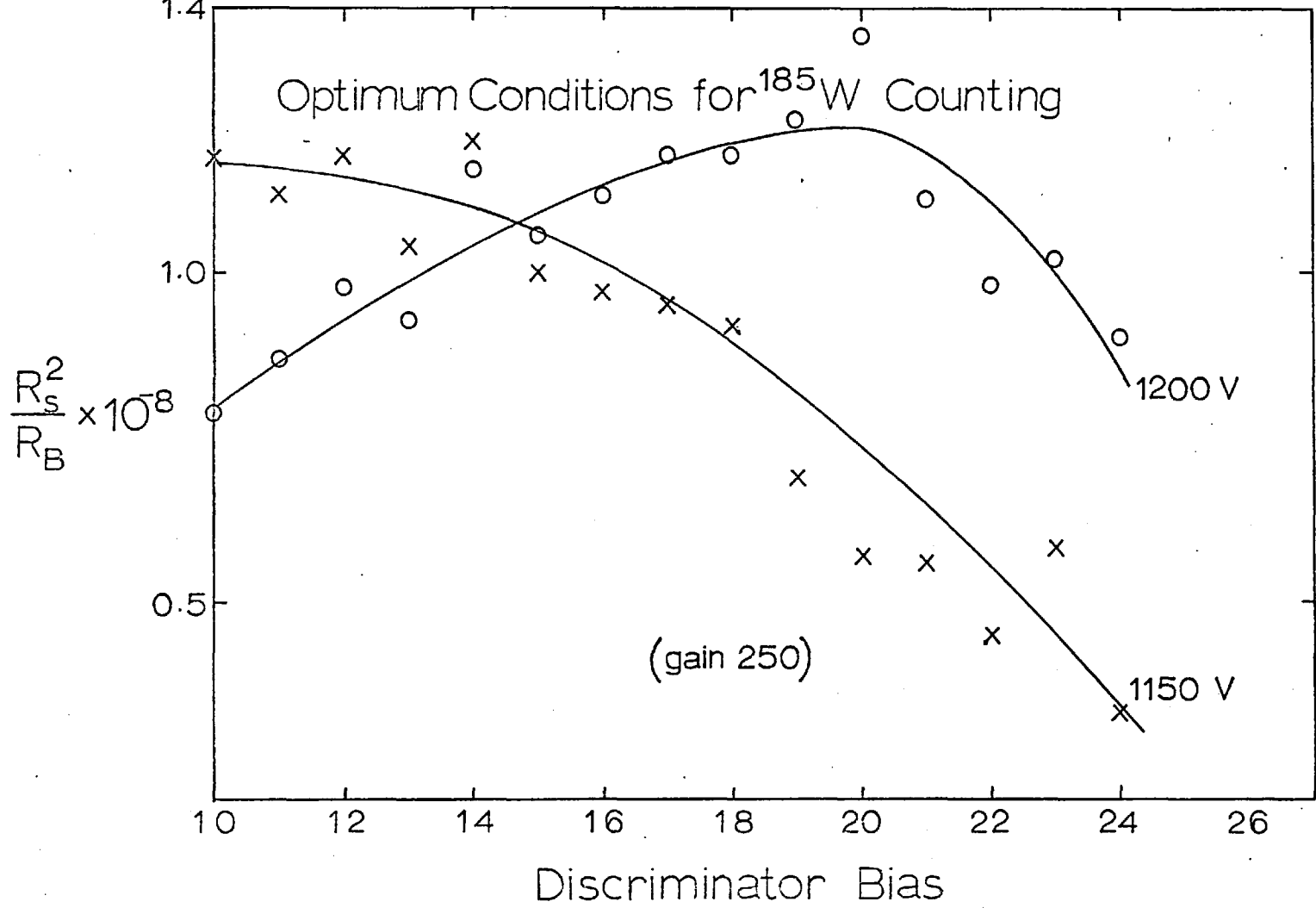


Fig. 3.1.3.2

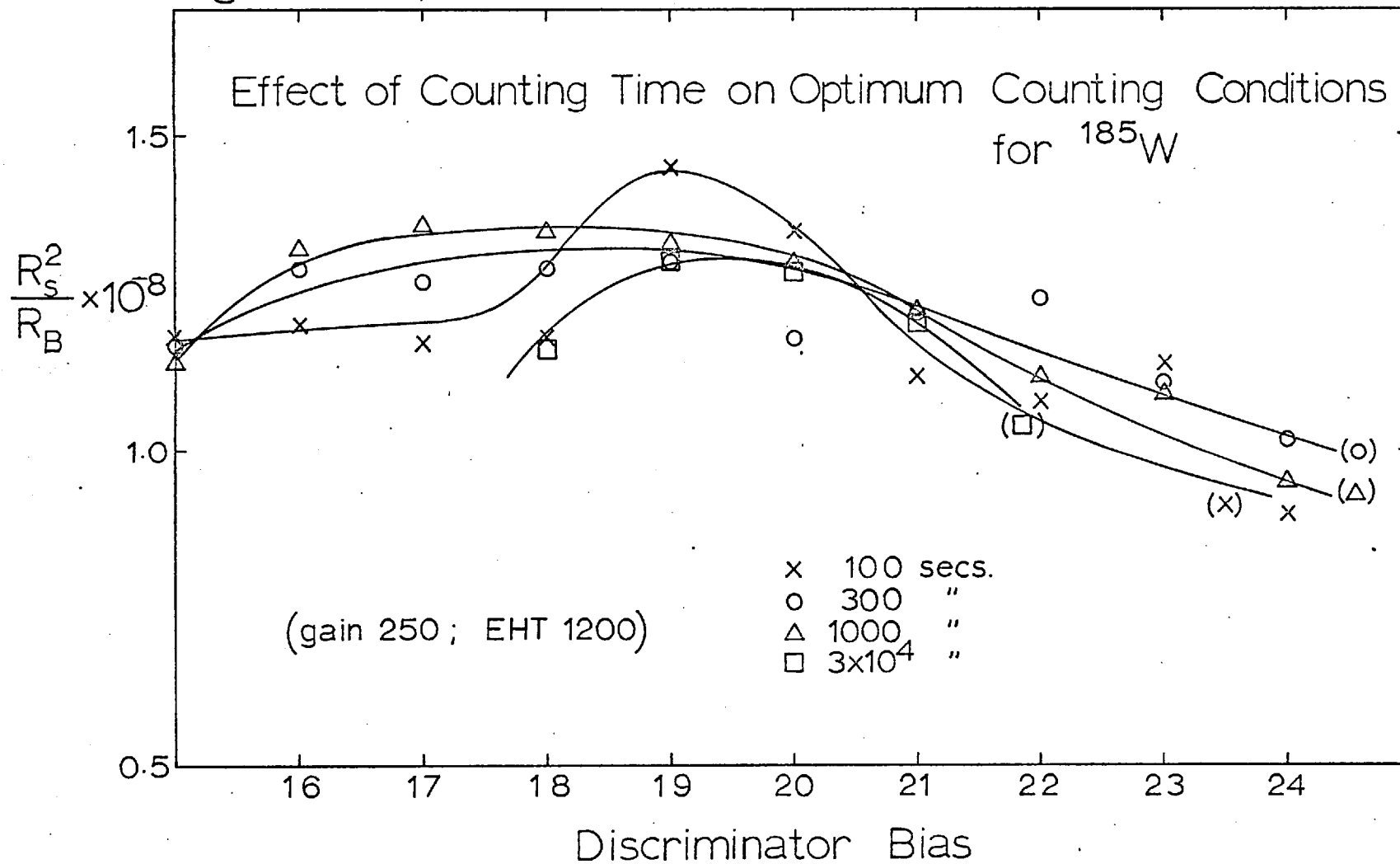


Table 3.1.3.1 (a) Countings of  $R_B$  and  $R_S$ 

Conditions: Amplifier Gain = 250 x

E. H. T. = 1200 V

Discriminator Bias	$R_B$ (C.P.S.)	$R_S$ (C.P.S.)	$R_S^2$	$R_S^2/R_B \times 10^{-8}$
10	8.27	25,706	$6.60 \times 10^8$	0.79
11	6.94	24,630	$6.06 \times 10^8$	0.87
12	5.63	23,584	$5.56 \times 10^8$	0.98
13	5.51	22,727	$5.18 \times 10^8$	0.93
14	4.02	21,739	$4.72 \times 10^8$	1.17
15	4.07	20,790	$4.32 \times 10^8$	1.06
16	3.49	19,801	$3.92 \times 10^8$	1.12
17	3.00	18,832	$3.54 \times 10^8$	1.18
18	2.72	17,953	$3.22 \times 10^8$	1.18
19	2.36	17,064	$2.91 \times 10^8$	1.23
20	1.91	16,181	$2.61 \times 10^8$	1.36
21	2.07	15,197	$2.30 \times 10^8$	1.11
22	2.05	14,184	$2.01 \times 10^8$	0.98
23	1.78	13,513	$1.82 \times 10^8$	1.02
24	1.75	12,610	$1.59 \times 10^8$	0.90
25	1.82	11,834	$1.40 \times 10^8$	0.76
30	1.21	8,368	$0.70 \times 10^8$	0.57
35	1.04	5,868	$0.34 \times 10^8$	0.32
40	0.96	4,625	$0.21 \times 10^8$	0.21

Table 3.1.3.1 (b) Counting of  $R_B$  and  $R_S$

Conditions: Amplifier Gain = 250 x

E. H. T. = 1,150 V

Discriminator Bias	$R_B$ (C.P.S.)	$R_S$ (C.P.S.)	$R_S^2$	$R_S^2/R_B \times 10^{-8}$
10	3.77	21,141	$4.46 \times 10^8$	1.18
11	3.32	19,379	$3.75 \times 10^8$	1.12
12	2.83	18,348	$3.36 \times 10^8$	1.18
13	2.75	16,949	$2.87 \times 10^8$	1.04
14	2.08	15,822	$2.50 \times 10^8$	1.20
15	2.17	14,749	$2.17 \times 10^8$	1.00
16	1.86	13,458	$1.81 \times 10^8$	0.97
17	1.62	12,437	$1.54 \times 10^8$	0.95
18	1.55	11,325	$1.28 \times 10^8$	0.82
19	1.55	10,438	$1.08 \times 10^8$	0.69
20	1.36	9,596	$0.92 \times 10^8$	0.67
21	1.32	8,613	$0.74 \times 10^8$	0.56
22	1.34	7,849	$0.61 \times 10^8$	0.45
23	0.86	7,097	$0.50 \times 10^8$	0.58
24	1.15	6,293	$0.39 \times 10^8$	0.33
25	1.03	5,711	$0.32 \times 10^8$	0.31
30	0.74	3,168	$0.10 \times 10^8$	0.13
35	0.63	1,751	$0.03 \times 10^8$	0.04
40	0.62	-	-	-



#### 3.1.4. Statistical analysis of $\beta^-$ counting

A statistical analysis was carried out on some results obtained for liquid scintillation counting of  $^{185}\text{W}$  at the beginning of the experimental work. At that time attempts were being made to determine the tungsten concentration in aqueous solutions directly, by adding samples together with absolute alcohol to the scintillation solution. The results are presented here to show that satisfactory results were obtained, even though the subsequent development of complete extraction of tungsten and use of wholly organic counting solutions gave considerable improvement.

10 ml. of scintillation solution and 10 ml. of absolute alcohol were placed in a sample holder with 1 ml. of aqueous 0.232 M  $^{185}\text{W}$  solution and made fifty observations of 100 seconds duration. The observations were taken in a continuous series without long interruptions, and the source, counter, and the conditions of the experiment were not disturbed throughout. The total count in each observation, uncorrected for background, dead-time, etc., was used to compute the standard deviation.

Table 3.1.4.1 Counting of  $^{185}\text{W}$ 

Number of counts	$d_i$ $= x_i - \bar{x}$	$(d_i)^2$ $= (x_i - \bar{x})^2$	Number of counts	$d_i$ $= x_i - \bar{x}$	$(d_i)^2$ $= (x_i - \bar{x})^2$
124,032	121	14,641	124,133	222	49,284
123,626	-285	81,225	124,442	531	281,961
123,322	-589	346,921	123,884	-27	729
124,083	172	29,584	124,888	977	954,529
123,934	23	529	123,953	42	1,764
124,259	348	121,104	124,307	396	156,816
123,874	-37	1,369	123,946	35	1,225
123,415	-496	246,016	124,051	140	19,600
123,853	-58	3,364	123,838	-73	5,329
123,950	39	1,521	124,735	824	678,976
124,489	578	334,084	123,856	-55	3,025
123,663	-248	61,504	123,337	-574	329,476
123,559	-352	123,904	123,788	-123	15,129
123,338	-573	328,329	123,522	-389	151,321
124,382	471	221,841	123,757	-154	23,716
124,314	403	162,409	123,541	-370	136,900
124,106	195	38,025	123,927	16	256
124,596	685	469,225	123,400	-511	261,121
122,875	-1036	1,073,296	123,714	-197	38,809
125,071	1160	1,345,600	124,329	418	174,724
123,311	-600	360,000	124,067	156	24,336
124,135	224	50,176	123,318	-593	351,649
123,526	-385	148,225	123,965	54	2,916
123,135	-776	602,176	123,640	-271	73,441
124,075	164	26,896	124,300	389	151,321

a) POISSON distribution tests

1) Square Root of Mean Value and the Standard Deviation

From the Table 3.1.4.1.

The sum of all the counts obtained in all the observations is

$$\sum_{i=1}^N x_i = 6,195,561$$

The mean count  $\left( \frac{1}{N} \sum_{i=1}^N x_i \right) = \bar{x} = 123,911$

The sum of all the squares of deviations

$$d_i^2 = \sum_{i=1}^N [x_i - \bar{x}]^2 = 10,080,317$$

Hence,

$$\begin{aligned} \text{Standard deviation } \sigma &= \sqrt{\frac{1}{N} \sum_{i=1}^N d_i^2} = \sqrt{\frac{1}{N} \sum_{i=1}^N (x_i - \bar{x})^2} = 449 \\ \text{The square root of the mean value} &= \sqrt{\bar{x}} = \sqrt{\frac{1}{N} \sum_{i=1}^N x_i} = 352 \end{aligned}$$

In this case, the standard deviation does not equal to the square root of the mean, and the question arises whether the difference is significant or merely due to the finite number of observations used. This is ascertained from the theory of statistics using  $\chi^2$ -distribution in section b).

2) The ratio of the mean deviation to the standard deviation should be approximately four fifths (0.7979)

From the Table 3.1.4.1.

The mean deviation,  $a = \frac{1}{N} \sum_{i=1}^N |d_i| = \frac{1}{N} \sum_{i=1}^N |x_i - \bar{x}| = 351$

$$\frac{a}{\sigma} = 0.7817 \text{ which is in reasonable agreement with}$$

the theoretical value of 0.7979.

3) The average of the error should be zero

$$\frac{1}{N} \sum_{i=1}^N d_i = \frac{1}{N} \sum_{i=1}^N (x_i - \bar{x}) = \frac{1}{N} \sum_{i=1}^N x_i - \bar{x} = 0$$

From Table 3.1.4.1,

$$\sum_{i=1}^N d_i = 11$$

Hence  $\frac{1}{N} \sum_{i=1}^N d_i = 0.22$  which is in reasonable agreement with the theoretical value of zero.

- 4) The number of counts in which the deviations are greater than twice the standard deviation should be about one observation in twenty (4.6%)

$$\bar{x} \pm 2\sigma = 123,911 \pm 898$$

that is the number of counts which are larger than 124,809 and the number of counts which are smaller than 123,013. The number of the former is 2 and that of the latter is 1, of which total numbers are 3.

Hence  $3/50 \times 100 = 6\%$  which is in reasonable agreement with the theoretical value of 4.6%.

- 5) The number of counts which the deviations are greater than the standard deviation should be approximately one third of the observations (31.8%)

$$\bar{x} \pm \sigma = 123,911 \pm 449$$

that is the numbers of counts which are larger than 124,360 and the numbers of counts which are smaller than 123,462. The number of the former is 7 and that of the latter is 9, the total being 16 counts.

Hence  $16/50 \times 100 = 32\%$  which is very close to the theoretical value of 31.8%.

From the above tests we can conclude that the observations follow the Poisson distribution well.

b)  $\chi^2$  - distribution tests

The significance of the difference obtained between the standard deviation and the square root of the mean value can be assessed from the statistical theory of  $\chi^2$ - distribution which is used for comparing the deviations from the average value obtained experimentally with those predicted from theory (37), (42), (43), (44). This may be done for a Poisson distribution by determining the frequency of occurrence of deviations within given intervals which may be chosen as desired.

In radioactive counting it is usually convenient to choose six intervals equal to the standard deviation. Thus in the range from  $\bar{x}$  to  $\bar{x} + \sigma$  (or  $\bar{x}$  to  $\bar{x} - \sigma$ ) the theoretical frequency is 34.1%, from  $\bar{x} + \sigma$  to  $\bar{x} + 2\sigma$  (or  $\bar{x} - \sigma$  to  $\bar{x} - 2\sigma$ ) it is 13.6%, and for greater than  $\bar{x} + 2\sigma$  (or less than  $\bar{x} - 2\sigma$ ) it is 2.3%. The differences between the theoretical ( $f_t$ ) and observed ( $f_o$ ) frequencies are determined in each case, squared, and divided by the theoretical frequency. The value of

$$\chi^2 = \sum \frac{(f_o - f_t)^2}{f_t} \quad \text{is then calculated from the}$$

Table 3.1.4.2, from which the value of P is interpolated from Fig. 3.1.4.1. P is the probability of a similar set of observations giving a value of  $\chi^2$  as great as or greater than that obtained from the set used to compute  $\chi^2$ . In practice, if P lies between 5 and 95%, the difference between the observed and the theoretical distribution (and consequently the difference between the standard deviation and the square root of the average number of counts) may be regarded as reasonable.

In the experiment given here,  $\bar{x} = 123,911$  and  $\sigma = \sqrt{\bar{x}} = 352$ . Hence we take intervals of 352 on both sides of the mean, as shown in Table 3.1.4.2.

Table 3.1.4.2. Calculation of  $\chi^2$  Value

Range	Observed frequency ( $f_o$ )	Theoretical frequency ( $f_t$ )	$ f_o - f_t $	$ f_o - f_t ^2 / f_t$
<123,207	2	1.15 (2.3%)	0.85	0.628
123,207 - 123,559	11	6.80 (13.6%)	4.2	2.594
123,559 - 123,911	11	17.05 (34.1%)	6.05	2.147
123,911 - 124,263	15	17.05 (34.1%)	2.05	0.246
124.263 - 124,615	8	6.8 (13.6%)	1.2	0.212
> 124,615	3	1.15 (2.3%)	1.85	2.976
Total	50	50 (100%)	-	8.803

Thus  $\chi^2 = 8.803$ , and from Fig. 3.1.4.1, P is seen to be equal to 19%, i.e. there is a 19% chance that a similar set of 50 observations of the same counting rate would have given a value of  $\chi^2$  greater than or equal to 8.803. Hence the discrepancy between the observed results and theoretical expectation cannot be regarded as significant, and the difference obtained between the standard deviation and the square root of the mean is not unreasonable. If P had been less than 5%, it would have been likely that spasmodic fluctuations in the counting rate had occurred, probably due to some fault in the operation of the scintillation assembly. If P had been greater than 95%, a systematic variation in counting rate throughout the experiment would have been suggested (37), (42), (43), (44).

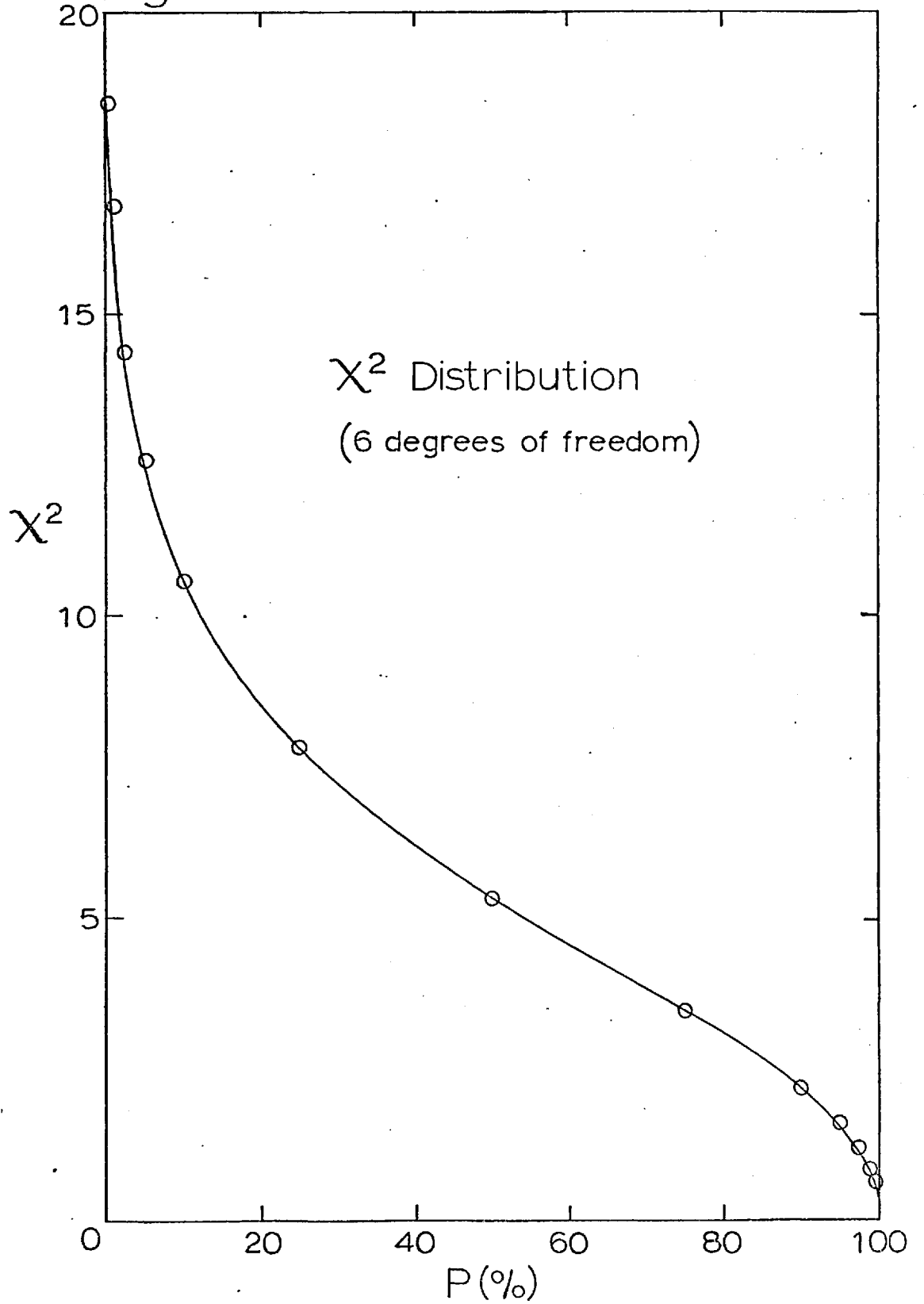
Table 3.1.4.3. Percentage points of  $\chi^2$ -Distribution

$\nu \backslash \alpha$	.995	.990	.975	.950	.900	.750	.500	.250	.100	.050	.025	.010	.005
6	.676	.872	1.24	1.64	2.20	3.45	5.35	7.84	10.6	12.6	14.4	16.8	18.5

Where  $\nu$  is the number of degrees of freedom and  $\alpha$  the probability of exceeding the tabular value (45).

Fig. 3.1.4.1

Data from Table 3.1.4.3



### 3.2. Molybdenum - Sulphate system

#### 3.2.1. Materials

(a) Tri-n-octylamine (TOA)

The TOA used has been described in section 3.1.1.(a)

(b) Di-2 - ethylhexylphosphoric acid (D2EHP)

Pure grade D2EHP was obtained from Koch-Light Laboratories Ltd.

A sample of the acid was weighed out and diluted with ethanol. 10 ml. aliquots were titrated with standard 1N sodium hydroxide solution (B.D.H.) and the end point was detected using a Pye "Dynacap" pH meter fitted with an Ingold composite glass and saturated calomel electrode. A purity of 99% was measured and the D2EHP was used without any further purification.

(c) Molybdenum solution

$\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ , anular grade was used for the experiments. A stock solution containing 100  $\text{gMo/l}$  was made up and analysed by atomic absorption spectrophotometry.

(d) Other reagents

All other reagents used were standard A.R. grade reagents.

#### 3.2.2. Equilibration

Stock solution was acidified with 0.9M sulphuric acid. 20 ml. aliquots of working solution and pre-equilibrated TOA or D2EHP in benzene were placed in 100 ml. cylindrical separating funnels and shaken using a mechanical shaker at ambient temperature which was usually within the range 18 to 25°C. Contact time with TOA was 5 minutes and with D2EHP 10 minutes. When working solutions were equilibrated with D2EHP emulsification were often encountered.

When the pH of a working solution was less than 3, emulsification hardly



occurred. Around pH 5, when two phases were mixed together, complete emulsion occurred immediately shaking was started. This problem was overcome by adding appropriate amounts of a salt. For example, when the D2EHP and working solution were completely emulsified, addition of ammonium sulphate to the system produced a separation into two clear phase layers.

### 3.2.3. Stripping of organic phase

Extraction and stripping of molybdenum working solution with TOA always produced two clear phase layers.

Stripping of Mo-loaded D2EHP, however, produced a stable emulsion.

With the cation extracting solvents, like D2EHP, stripping takes place generally in strong acidic media to replace  $M^{n+}$  in the organic phase by  $H^+$ . In the case of molybdenum, the mechanism can be more complex and acids do not seem to be very good stripping reagents. Stripping of Mo-loaded D2EHP with basic solution was rapid and complete. The species  $MoO_2^{2+}$  was not able to exist in basic media. But if D2EHP was stripped with 5%  $NH_4OH$ , as soon as the two phases were contacted, they emulsified. This problem can be completely overcome by stripping with 1M ammonium carbonate solution. Modification of the organic phase with 2% (V/V) ethyl 2-hexanol 1 caused good phase separation.

### 3.2.4. Analysis of Molybdenum

A Perkin-Elmer (Model 290B) Atomic Absorption Spectrophotometer with Perkin-Elmer Multi-Element Hollow-Cathode lamp (Co, Cu, Fe, Mn, Mo) was used for analysis of molybdenum.

The instrument conditions used throughout were: slit width, 7Å;

Wavelength, 3133Å (259 in Perkin-Elmer Model 290B instrument settings); lamp current 10 mA. As the hollow-cathode lamp is stamped with a maximum current rating, it should not exceed this limit.

The usual air-acetylene burner was replaced by a nitrous oxide burner head. This system requires more acetylene consumption to provide fuel-rich reducing conditions compared with an air-acetylene burner and flame. The acetylene cylinder should be renewed when the cylinder pressure reaches 80 psi.

Nitrous oxide pressure was regulated to 40 psi by a cylinder regulator which was connected to the Model 290B through a T junction valve.

Under no circumstances should nitrous oxide be introduced into gas lines or equipment contaminated with oil. Like oxygen, nitrous oxide can cause spontaneous combustion of oil, with dangerously explosive results. Acetylene and copper form an explosive combination. Copper tubing or fittings for acetylene gas must therefore be stringently avoided.

The nitrous oxide flow was controlled by a flow controller to produce the maximum height of red "feather" in the flame without luminosity. The burner height was adjusted so that as much as possible of the converging light beam from the hollow-cathode lamp passed through the red "feather" above the primary reaction zone. The strongest absorbance for molybdenum is always obtained in this band, which is highly characteristic of the nitrous oxide-acetylene flame.

The flame was first ignited using an air-acetylene mixture, and the air was immediately replaced by nitrous oxide via the T-junction valves.

When first ignited, the flame split and produced a high pitched

noise, forming a "V" along the entire slot. As the burner head warmed up and the fuel flow was adjusted, the "V" configuration closed up and formed a normal flame suitable for analysis. Continuous operation of the nitrous oxide burner head produced deposits near the slot which caused a ragged flame. A badly clogged slot may cause a flashback with possible damage to the mixing chamber. In this case, with the flame off, the surface of the slot was scraped with sharp edged knives.

### 3.3. Tungsten - Molybdenum Mixed System

#### 3.3.1. Materials

##### (a) Di-2-ethylhexylphosphoric acid (D2EHP)

The D2EHP used has been described in section 3.2.1(b).

##### (b) Tungsten solutions

$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ , analar grade was used for the experiments. A stock solution containing 100g W/l was made up and analysed gravimetrically by precipitation with cinchonine solution from acidic tungsten solution, followed by ignition to  $\text{WO}_3$ .

This stock solution was used for mixing tungsten and molybdenum together to investigate the effect of the presence of tungsten on the extraction of molybdenum with D2EHP.

As molybdenum was analysed by atomic absorption spectrophotometry, non-radioactive tungsten stock solution was added to the molybdenum working solution.

##### (c) $^{185}\text{W}$ isotope

The use of  $^{185}\text{W}$  was described in section 3.1.1.(b)

##### (d) Molybdenum solutions

The molybdenum solutions used were described in section 3.2.1.(c)

##### (e) Other reagents

All other reagents used were standard A.R. grade reagents.

### 3.3.2. Preparation of working solution of tungsten and molybdenum mixed system.

Appropriate quantities of tungsten solution and molybdenum were placed in 100 ml. flasks and 0.9M  $H_2SO_4$  was added very slowly to adjust the pH of the mixed solution to pH 2-3.

The investigation of the extraction of tungsten in acidic solution by D2EHP was carried out with  $^{185}W$  isotope.

The investigation of the effect of the presence of tungsten in the extraction of molybdenum with D2EHP was carried out with normal tungsten solution.

### 3.3.3. Equilibration

20 ml. aliquots of tungsten-molybdenum sulphate solution and D2EHP in benzene were placed in 100 ml. cylindrical separating funnels and shaken using a mechanical shaker at ambient temperature of 18 to 25°C for 10 minutes. As the pH of working solutions was between 2 and 3, no emulsions were encountered.

### 3.3.4. Stripping

Molybdenum-loaded D2EHP solutions were stripped with 1M ammonium carbonate solution and produced very clear phase separation. No emulsion occurred.

### 3.3.5. Analysis of Tungsten in W-Mo-sulphate system

The analysis of tungsten was described in section 3.1.3. The presence of molybdenum in the organic phase did not interfere with the counting of  $^{185}W$ . However, samples and standards were prepared using exactly the same backgrounds throughout the work.

3.3.6. Analysis of molybdenum in W-Mo-sulphate system

The analysis of molybdenum was described in section 3.2.4. Tungsten at concentration in the range 1-2 g/l did not interfere with the absorbance of molybdenum using the nitrous oxide-acetylene flame.

Higher concentrations of tungsten, however, did cause interference. The same amount of molybdenum in a mixed solution gave a different absorbance compared with that of a standard molybdenum solution.

Depending upon the other ions present, the interference was either an enhancement or a depression in the molybdenum absorption.

The best results were obtained when the standard solutions and working solutions had the same background composition, regardless of whether the absorbance-concentration plot line is straight or curved. The strict adherence to Beer's law in a highly concentrated background solution was not necessary for successful analytical utilization.

#### 4. Experimental Results

##### 4.1. Tungsten Extraction

##### 4.1.1. Extraction of Tungsten with TOA-Sulphate (TOAS)

The extraction isotherm of tungsten with 0.01M TOAS in benzene is plotted in Fig. 4.1.1.1. The extraction reaction was rapid and complete. TOAS proved to be an excellent extractant for tungsten.

Fig. 4.1.1.2 shows a plot of TOAS concentration versus  $\log D_W$ , the cause of the non linearity can be ascribed to the pH change due to the extraction.

The saturation of various strengths of TOAS in benzene with respect to tungsten is plotted in Fig. 4.1.1.3. Regardless of concentration of TOAS in the benzene it can be seen that they all reach the same value of  $\frac{[TOAS]}{[W]_{org}}$  on saturating.

##### 4.1.2. Extraction of tungsten with D2EHP

Extraction of tungsten in acidic solutions with 10% D2EHP in benzene are recorded in Table 4 (p. 107 ), and it was confirmed that tungsten does not exist as an extractable cationic form in acidic solutions. The distribution coefficients of tungsten were very low and were less than the % error of the analytical accuracy.

Laskorin (16) and co-workers found that in contrast to molybdenum, tungsten is not extracted to any appreciable extent by D2EHP at  $pH = 2$ .

They found that the distribution coefficient of tungsten with D2EHP at pH 2-3 is 0.005 - 0.003, which is in good agreement with the results shown here. It was given by them an approximate value, as small distribution coefficients were difficult to determine by analytical methods at the time their work was carried out.



## 4.2. Molybdenum Extraction

### 4.2.1. Extraction of Molybdenum with TOAS

Extraction isotherm of molybdenum from sulphate solutions by TOAS in benzene is plotted in Fig. 4.2.1.1.(a).

It is noted that the isotherms are S-shaped.

This is attributed to a change in the chemical state of molybdenum in the organic phase.

$\log D_{Mo}$  versus  $\log [Mo]_{aq.initial}$  is plotted in Fig. 4.2.1.1.(b). Up to the saturation point, the molybdenum distribution coefficient increases with the increase of molybdenum concentration in initial aqueous solutions. After the saturation point,  $\log D_{Mo}$  decreases very sharply.

Coleman, Brown et al. (46) note that at complete saturation of the organic phase, the molybdenum-amine mole ratio is 2 : 1. The saturation of TOAS with molybdenum is plotted in Fig. 4.2.1.2 in terms of  $\frac{[TOAS]}{[Mo]_{org}}$ .

In the case of 0.1 M TOAS, at the saturation point the value of  $\frac{[TOAS]}{[Mo]_{org}}$  is 0.437, which is equivalent to a molybdenum-amine ratio of 2.28 : 1, in good agreement with the literature value.

The extraction of molybdenum was lowered by addition of sulphate ions to the initial working solutions. The distribution coefficients are plotted against the sulphate concentrations in Fig. 4.2.1.3. The distribution coefficients should decrease with increasing sulfate concentration because any increase in the sulphate ion concentration of the solution shifts the equilibrium toward formation of the amine sulphate, and thus lowers the molybdenum concentration in the organic phase.

The hydrogen ion concentration of the aqueous phase is the major factor influencing the distribution of molybdenum between the two phases. The distribution coefficients of molybdenum are plotted against the aqueous pH (after extraction) in Fig. 4.2.1.4. The main reason for the decrease of the distribution coefficients in the pH range of 3 - 6 is hydrolysis of the amine salt, which begins at 3 (16). The extraction maximum is in the pH range 2 - 3.

In strongly acidic media (pH = 1) the concentration of molybdenum in the cationic form increases (especially in nitrate solutions), as does that of the non extractable polymerized uncharged molecules (16). This accounts for the decreased extraction of molybdenum in acid solutions.

At high acid concentrations molybdenum can be extracted in the form of negatively charged complexes, e.g. with sulphate ions. This could account for the first slope of the distribution coefficient - pH curve in the acid region for sulphate solutions. This extraction mechanism is probably analogous to that of uranium (47).

#### 4.2.2. Extraction of molybdenum with D2EHP

Elements present as cations in solutions can be extracted by D2EHP. Fig. 4.2.2.1 and Fig. 4.2.2.2. show that the extraction isotherm for distribution of molybdenum between the aqueous and organic phases. Fig. 4.2.2.1, where concentration of molybdenum are very low, shows that the slope of the molybdenum extraction isotherm in the region far from saturation is close to 1. This indicates that under these conditions virtually only one type of molybdenum cation is extracted, otherwise the isotherm would be concave or convex (this refers to the initial regions of the isotherm, when saturation of the organic phase does not influence the concentration of

free D2EHP). It is most probable that the extracted cation is  $\text{MoO}_2^{2+}$ .

Fig. 4.2.2.3 shows that concentrations of sulphates have virtually no effect on the extraction of molybdenum by D2EHP. In Fig. 4.2.2.4 and Fig. 4.2.2.5, the molybdenum distribution coefficients are plotted against the equilibrium pH of the aqueous solutions. In the strongly acid region the distribution coefficient decreases. With an increase in pH the distribution coefficient curve passes through a maximum around  $\text{pH} = 2$ . With a further fall of the hydrogen ion concentration the distribution coefficients decrease sharply owing to the predominance of the anionic form of molybdenum which is not extracted by D2EHP.

pH changes of aqueous phase before and after extraction with various strengths of D2EHP and TOAS are tabulated in Table 14. When they were plotted against the ideal line (i.e. same pH before and after extraction), D2EHP deviates positively and TOAS negatively and both the deviations were random because the pH changes were a function of molybdenum concentration and of the strength of the organic phases. The pH change was divided by the molarity of the initial molybdenum concentration and plotted in terms of  $\Delta\text{pH}/(\text{Mo})_{\text{initial}}$  against initial molybdenum concentrations ( $\text{Mol}/\text{l}$ ). Fig. 4.2.2.6 shows that the lower the concentration of molybdenum in the initial working solution, and the higher the strength of the extractants in the organic phase, the larger the deviation is from the ideal line.

$\log D_{\text{Mo}}$  versus  $\log \text{D2EHP}$  were plotted in Fig. 4.2.2.7 and Fig. 4.2.2.8. The slope varied according to the pH of the initial working solutions, with an initial pH2, the slopes were 1.4 - 2 and with initial pH3, the slopes were 1.

The effects of initial pH and initial molybdenum concentration on the distribution coefficient are plotted in Fig. 4.2.2.9.  $D_{\text{Mo}}$  values for

initial pH2 are always higher than  $D_{Mo}$  for initial pH3.

Saturation of D2EHP with molybdenum from solutions with initial pH2 is plotted in terms of  $(D2EHP)/(Mo)_{org}$  versus  $(Mo)$  initial in Fig. 4.2.2.10. At complete saturation, the value of  $(D2EHP)/(Mo)_{org}$  approaches 4 regardless of the strength of organic phase. This is in good agreement with the work done by A.N. Zelikman and V.M. Nerezov (30).

The values  $(D2EHP)/(Mo)_{org}$  from initial working solutions of pH3 are much higher and the saturation point cannot be reached, due to the decrease in the hydrogen ion concentration and thus a decrease of the value of the distribution coefficient. Fig. 5.2.2.11 shows this effect.

#### 4.3. Separation of Tungsten and Molybdenum with D2EHP

Fig. 4.3.1 shows that % extraction of molybdenum decreases with an increase of the W/Mo ratio in the initial working solution.

Fig. 4.3.2 shows that the molybdenum distribution coefficient decreases with the increase of W/Mo ratio.

Figs. 4.3.3, 4.3.4, 4.3.5 show the effect of the presence of tungsten on the extraction power of D2EHP for molybdenum. Extraction isotherms are shown for molybdenum with various background concentrations of tungsten; the effect of the presence of tungsten on the saturation of D2EHP with molybdenum is also shown.

The effect of tungsten on the molybdenum distribution coefficient with 10% D2EHP is plotted in Fig. 4.3.6.

Fig. 4.3.7 shows the effect of various background concentration of tungsten on the distribution coefficient of molybdenum with 10% D2EHP. Tungsten-free and 10 g W/1 and 20g W/1 solutions were used and showed distribution coefficients of molybdenum which decreased with increasing initial molybdenum concentration.

With 40g W/1 background concentration of tungsten, however, the molybdenum distribution coefficient increased with increasing molybdenum concentration up to around 5g/1 in the initial working solution and then very slowly decreased. This effect is amplified in Fig. 4.3.8.

The effect of tungsten concentration (40g W/1) on the % extraction of molybdenum with 10% D2EHP is plotted in Fig. 4.3.9.

Fig. 4.3.10 and 4.3.11 show the results of successive batchwise

extractions of molybdenum in the presence of 40 g W<sub>1</sub> background concentration of tungsten.

Addition of fluorine (F<sup>-</sup>) did not improve the molybdenum distribution coefficient.

Fig. 4.11.1

Data from Table 1

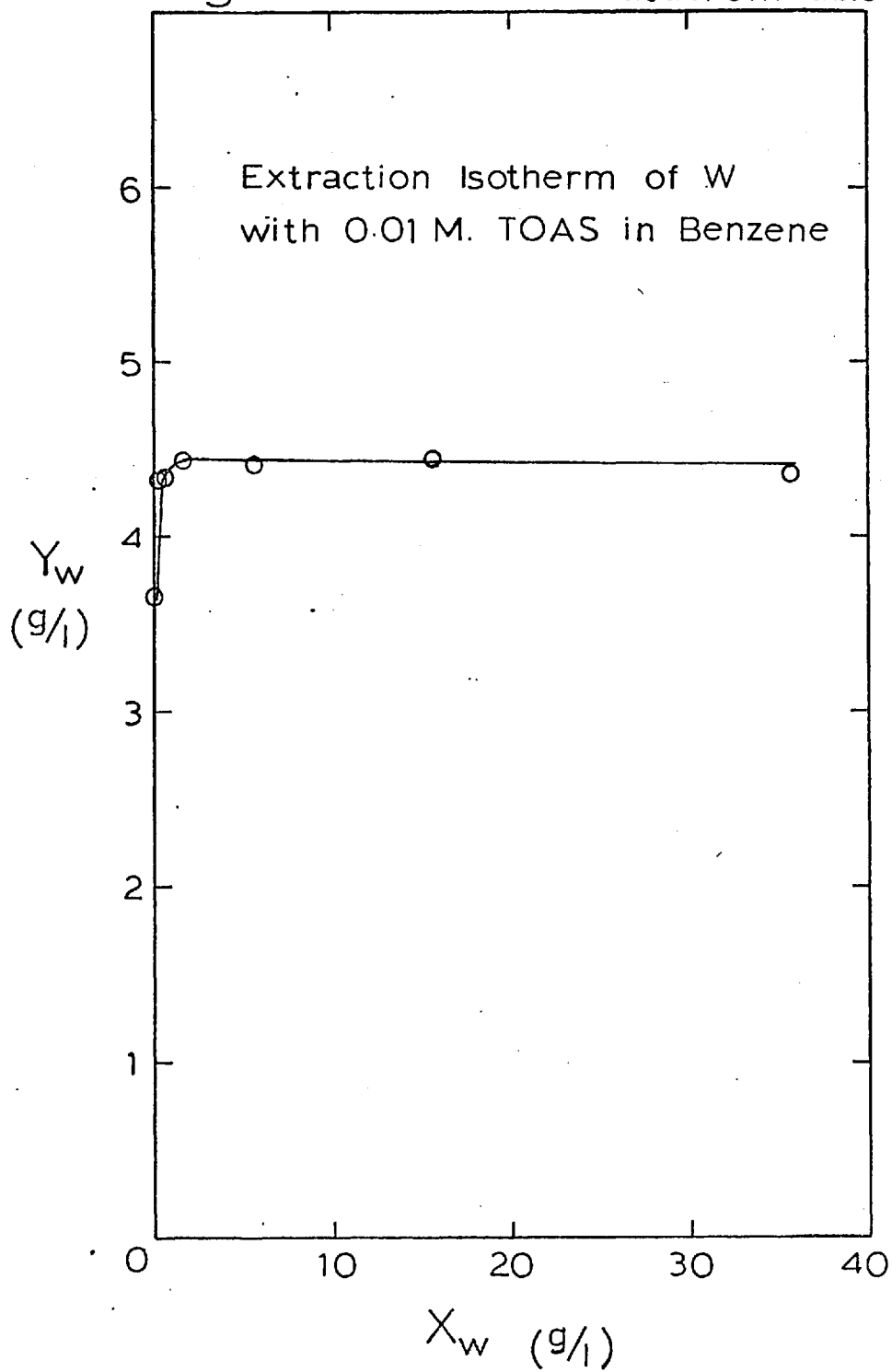
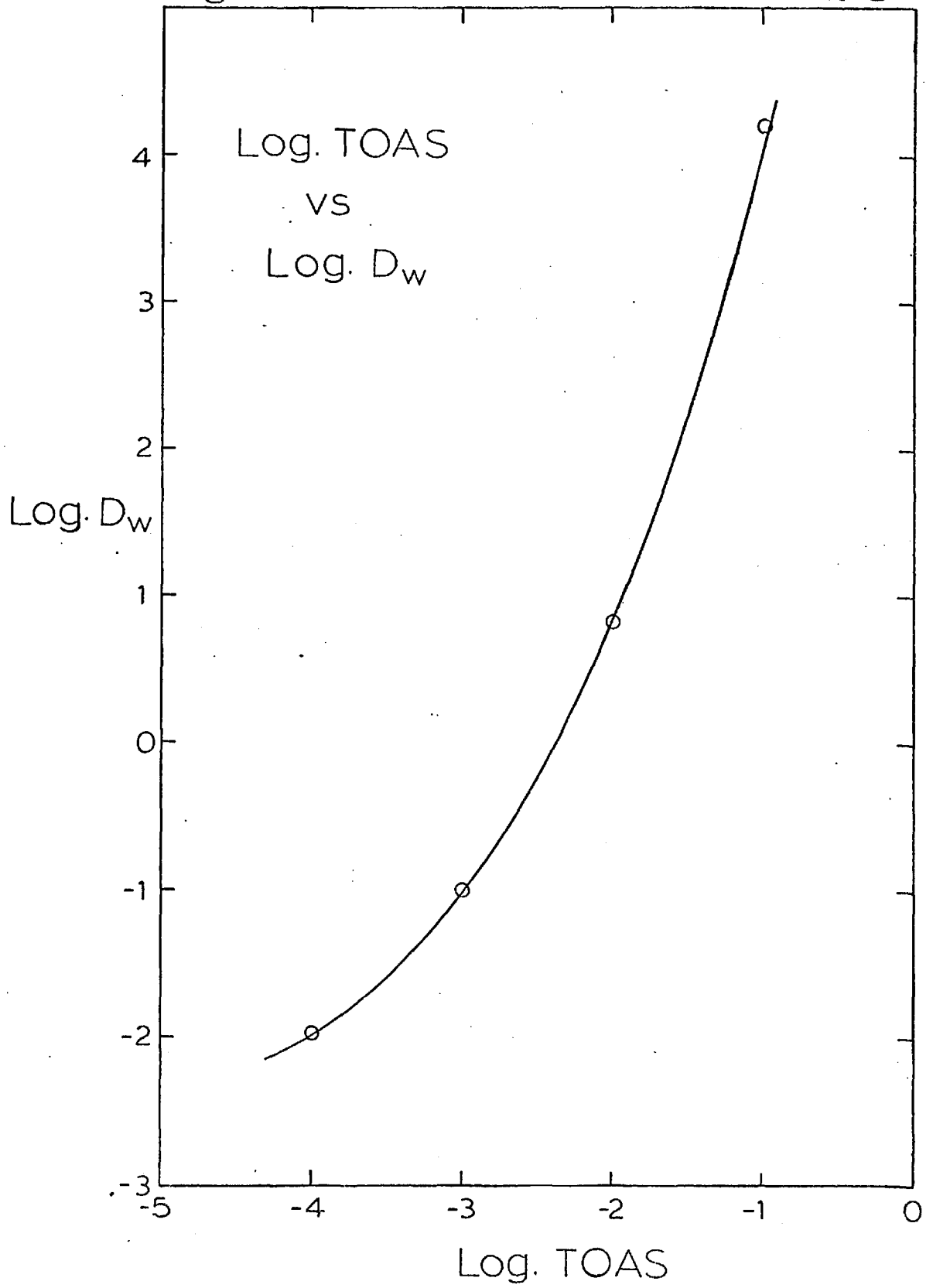


Fig. 4.11.2

Data from Table 2





### Saturation of TOAS with W

Fig. 4.11.3

Data from Table 3

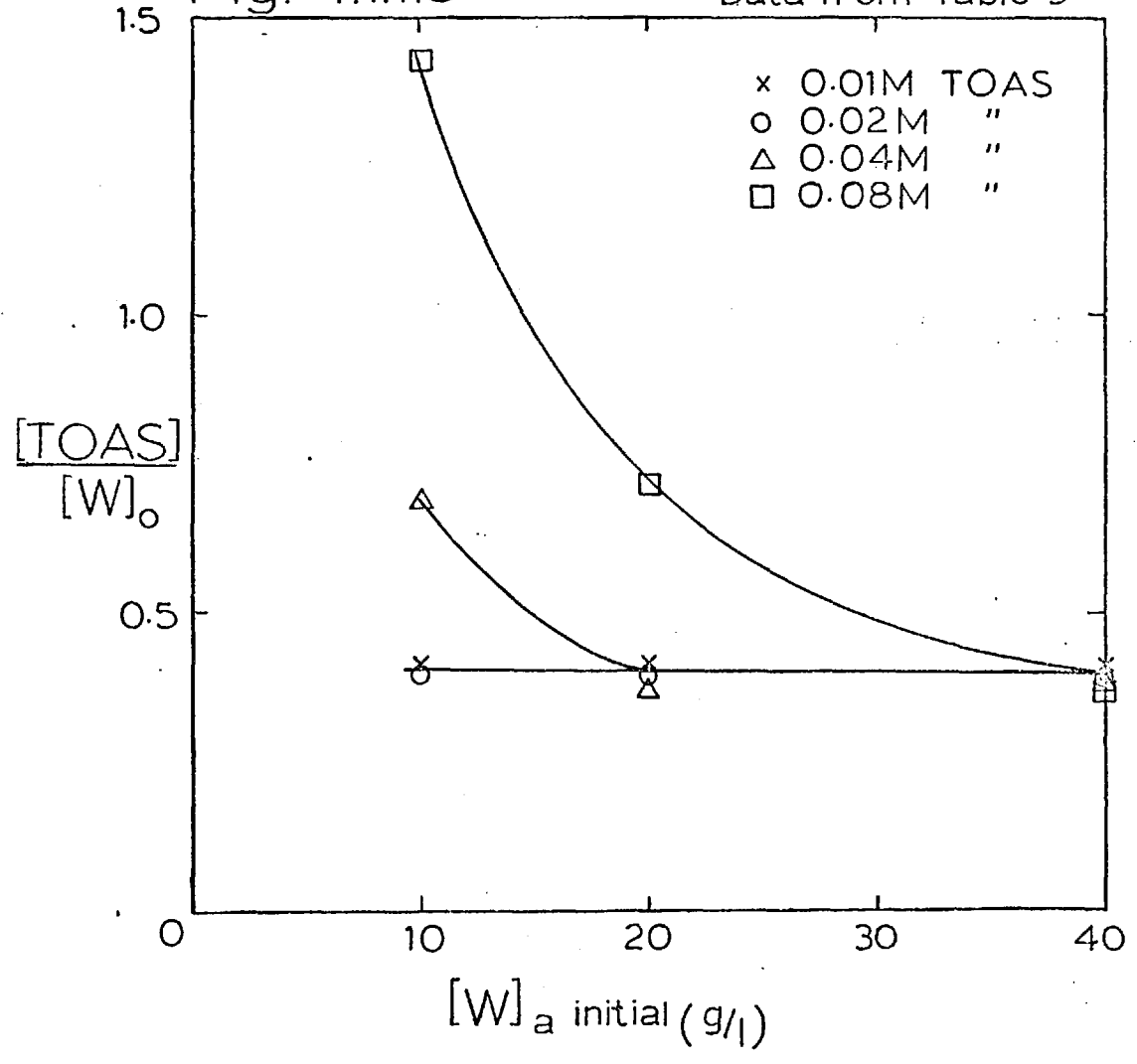
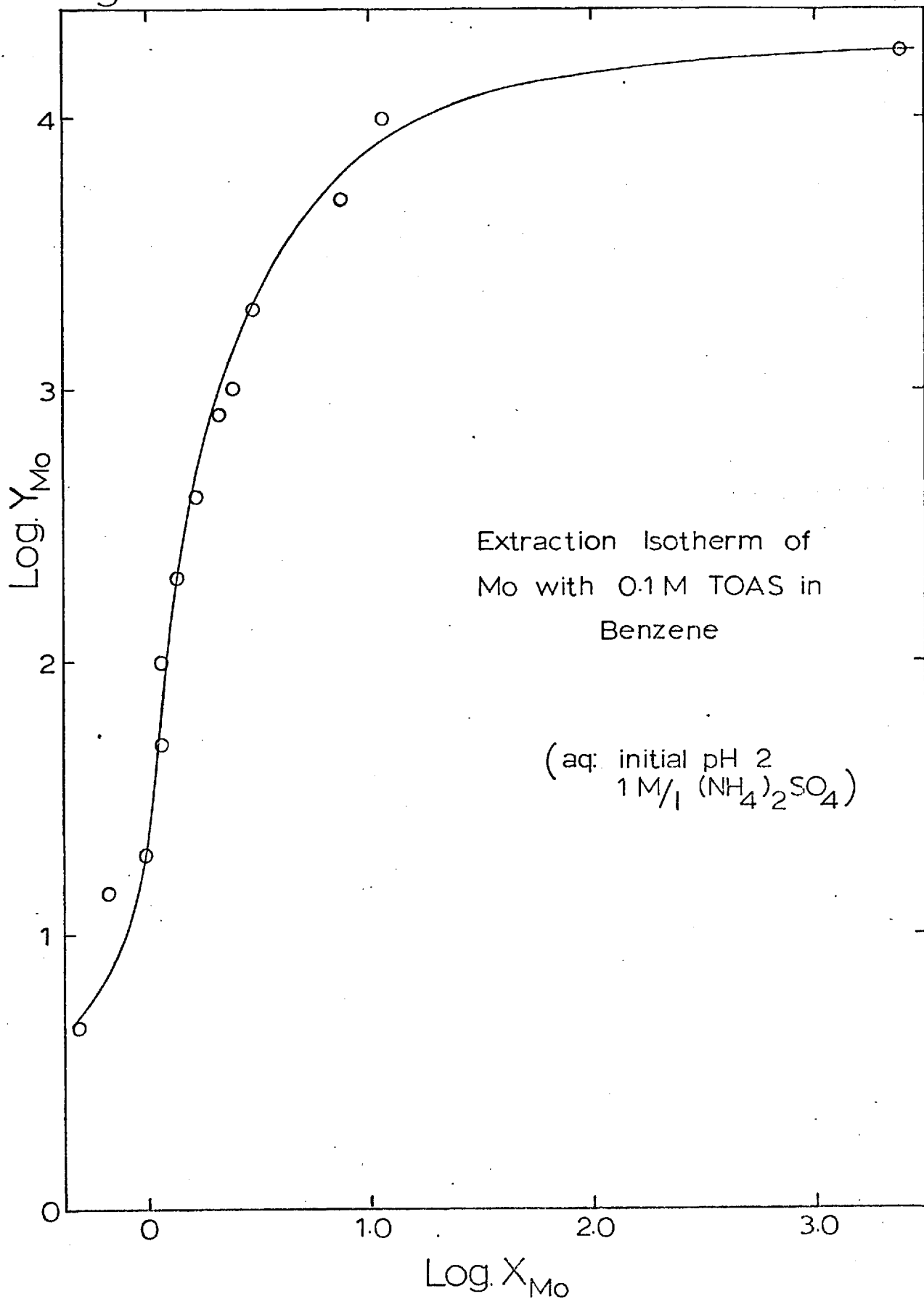


Fig. 4.2.11a

Data from Table 5.



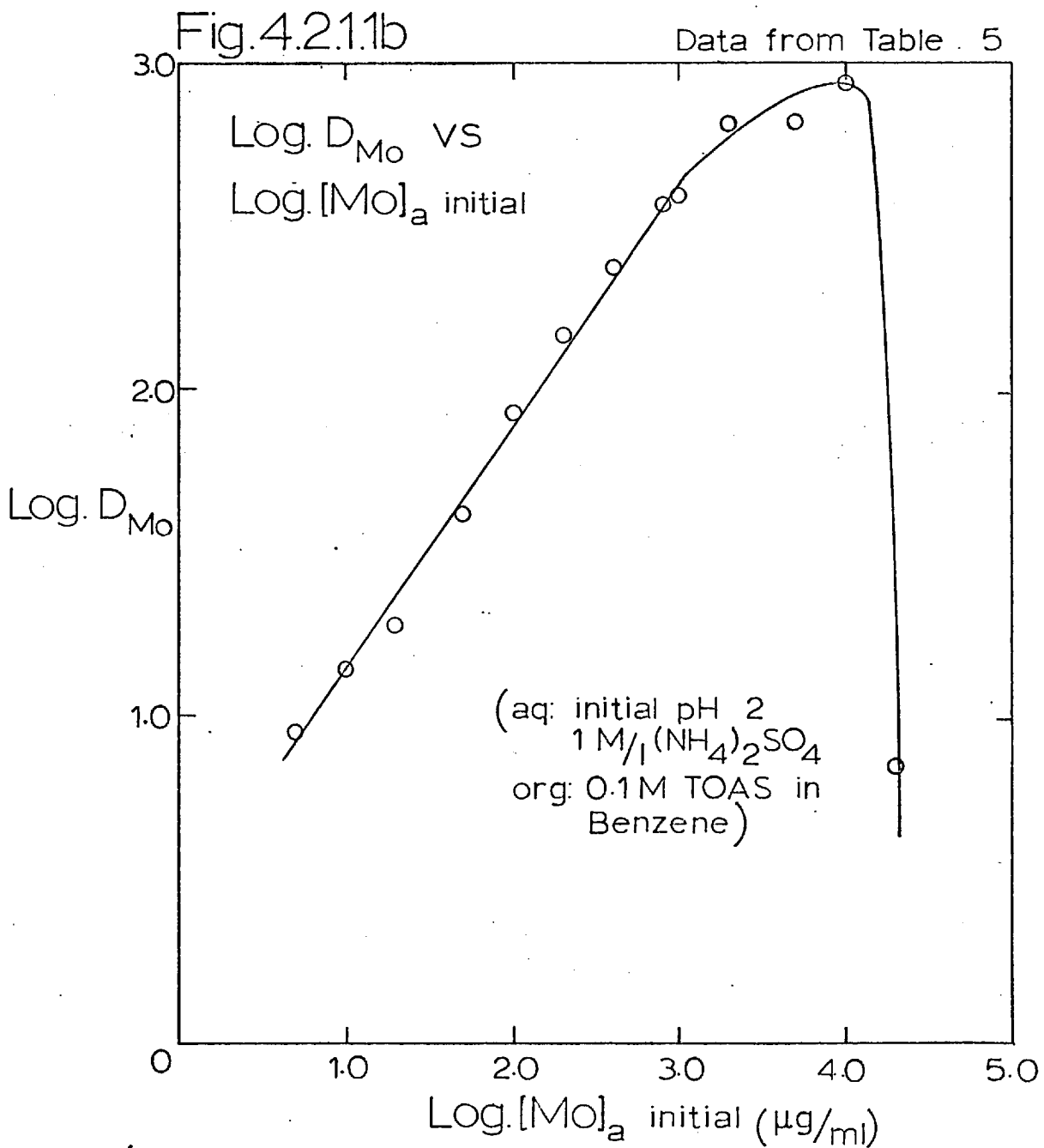


Fig. 4.2.1.2

Data from Table 6

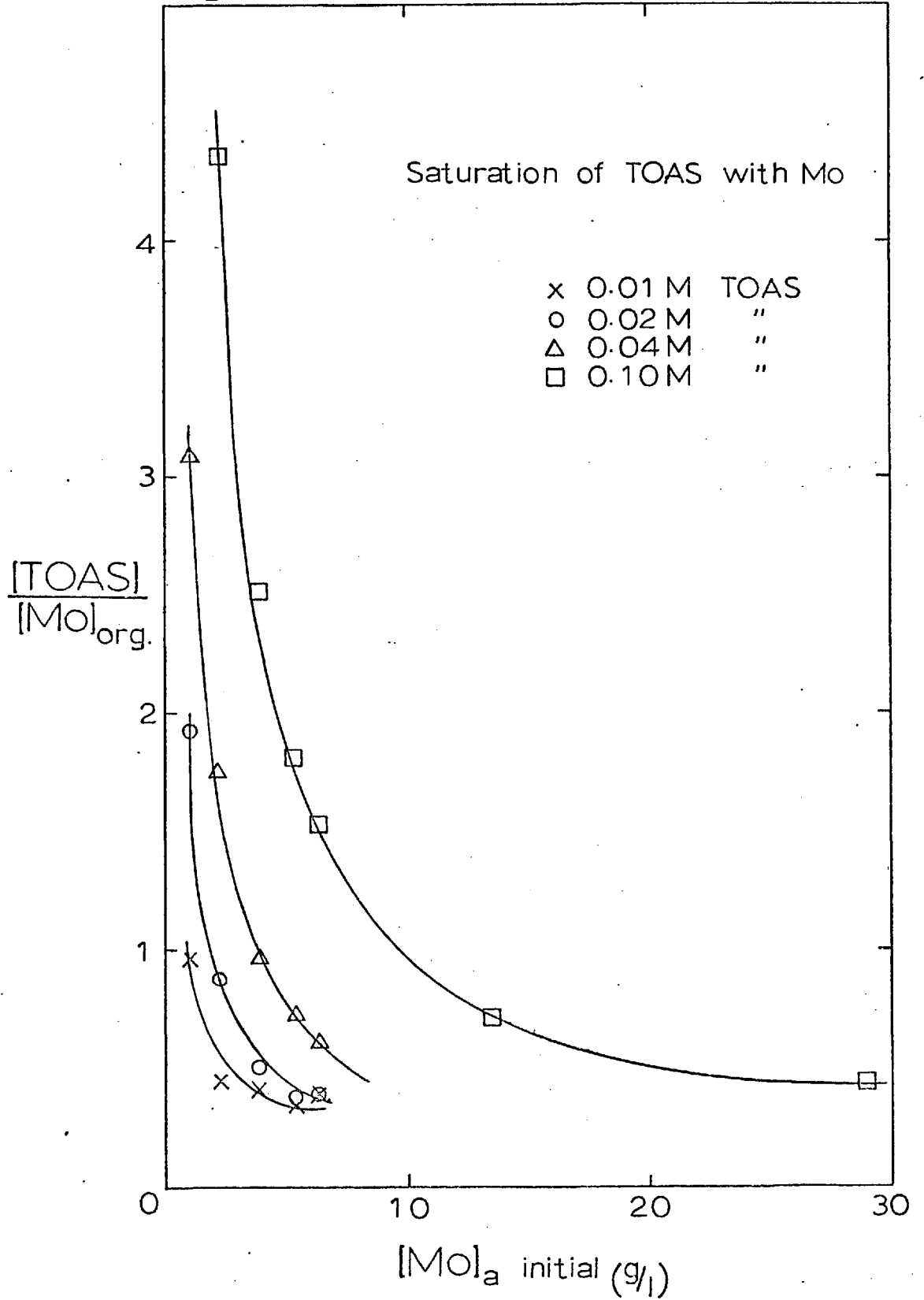


Fig. 4.2.1.3

Data from Table 7

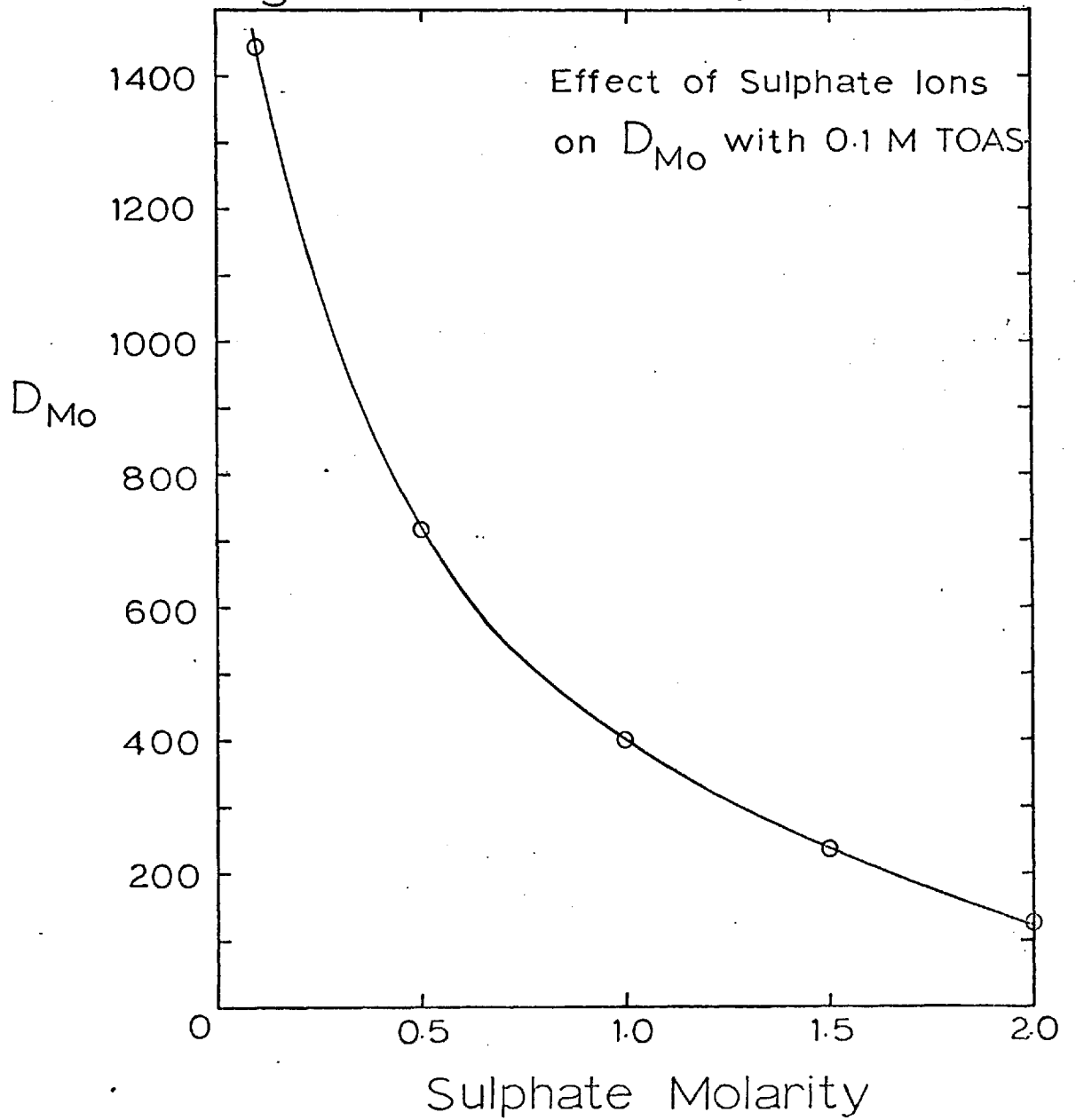


Fig. 4.2.1.4

Data from Table 8

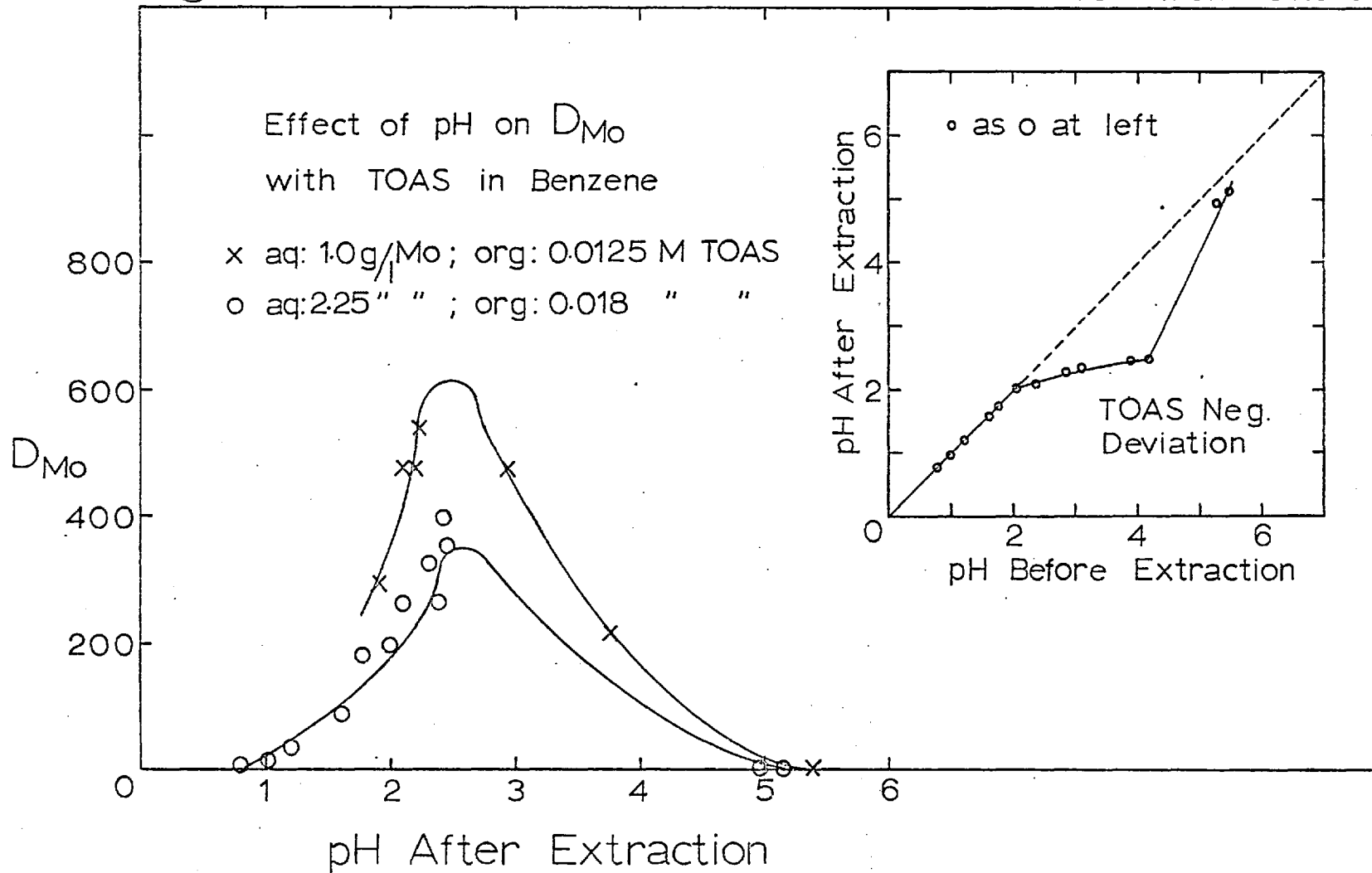


Fig.4.2.21

Data from Table 9

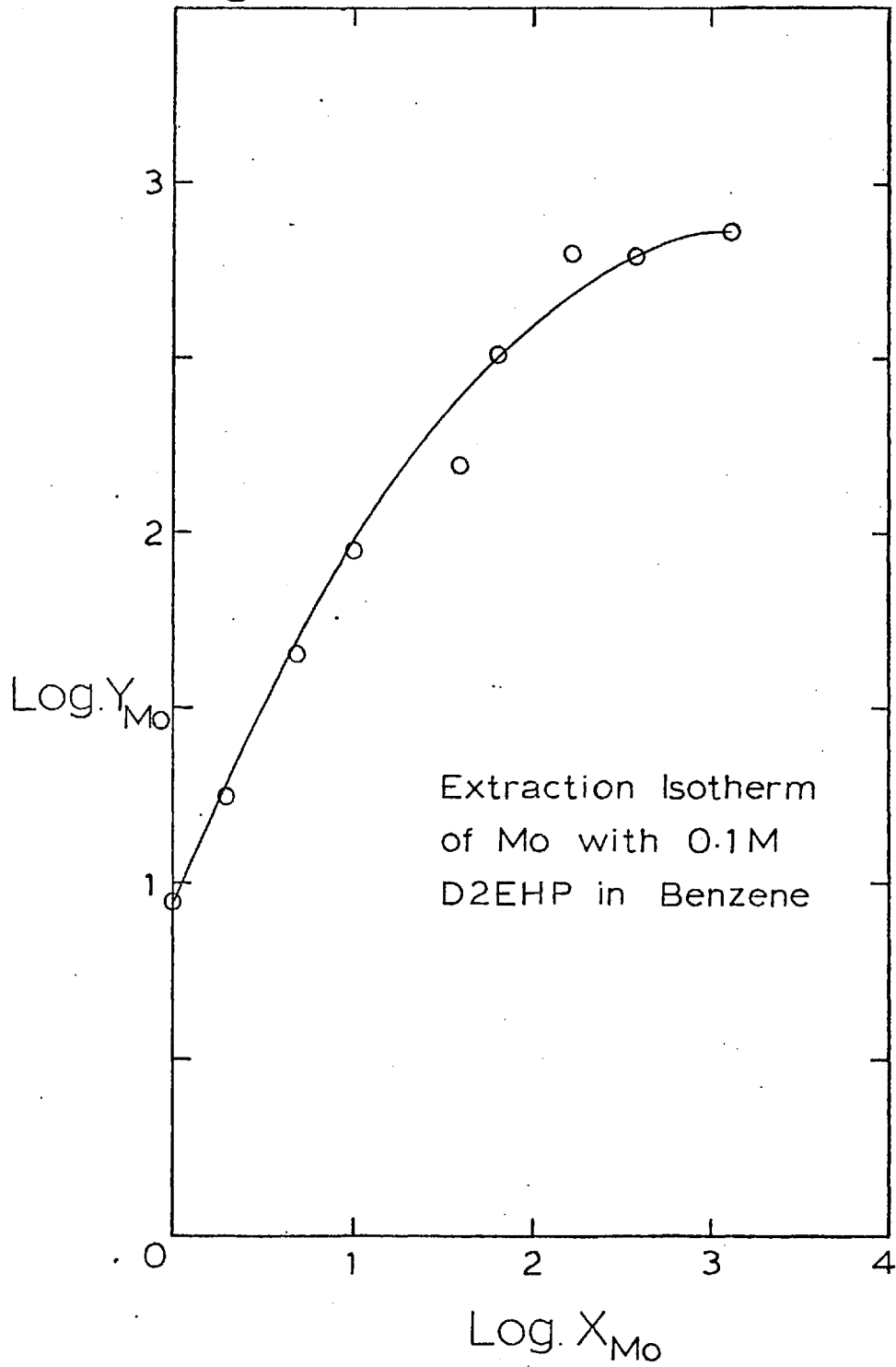
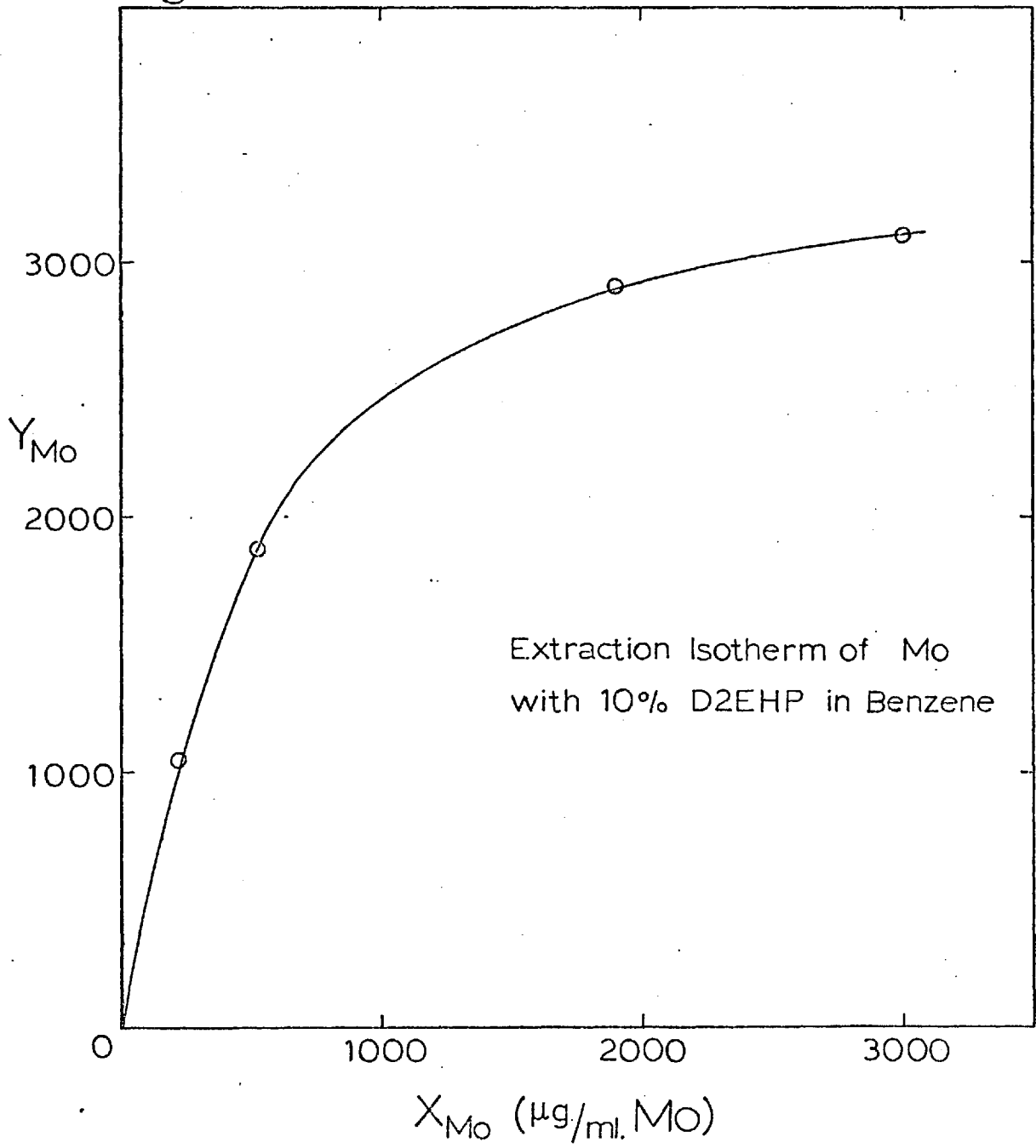


Fig. 4.2.2.2

Data from Table 10





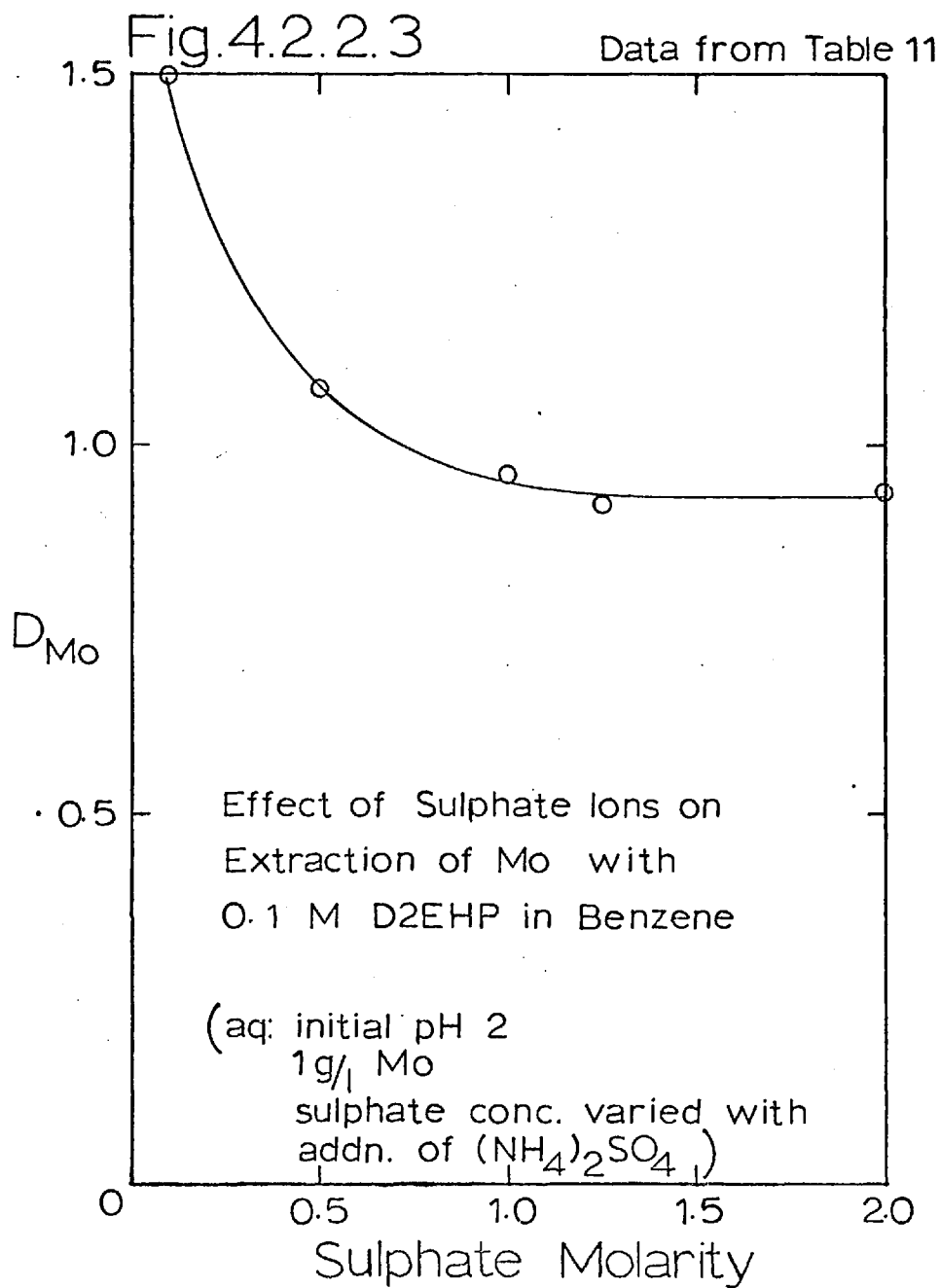
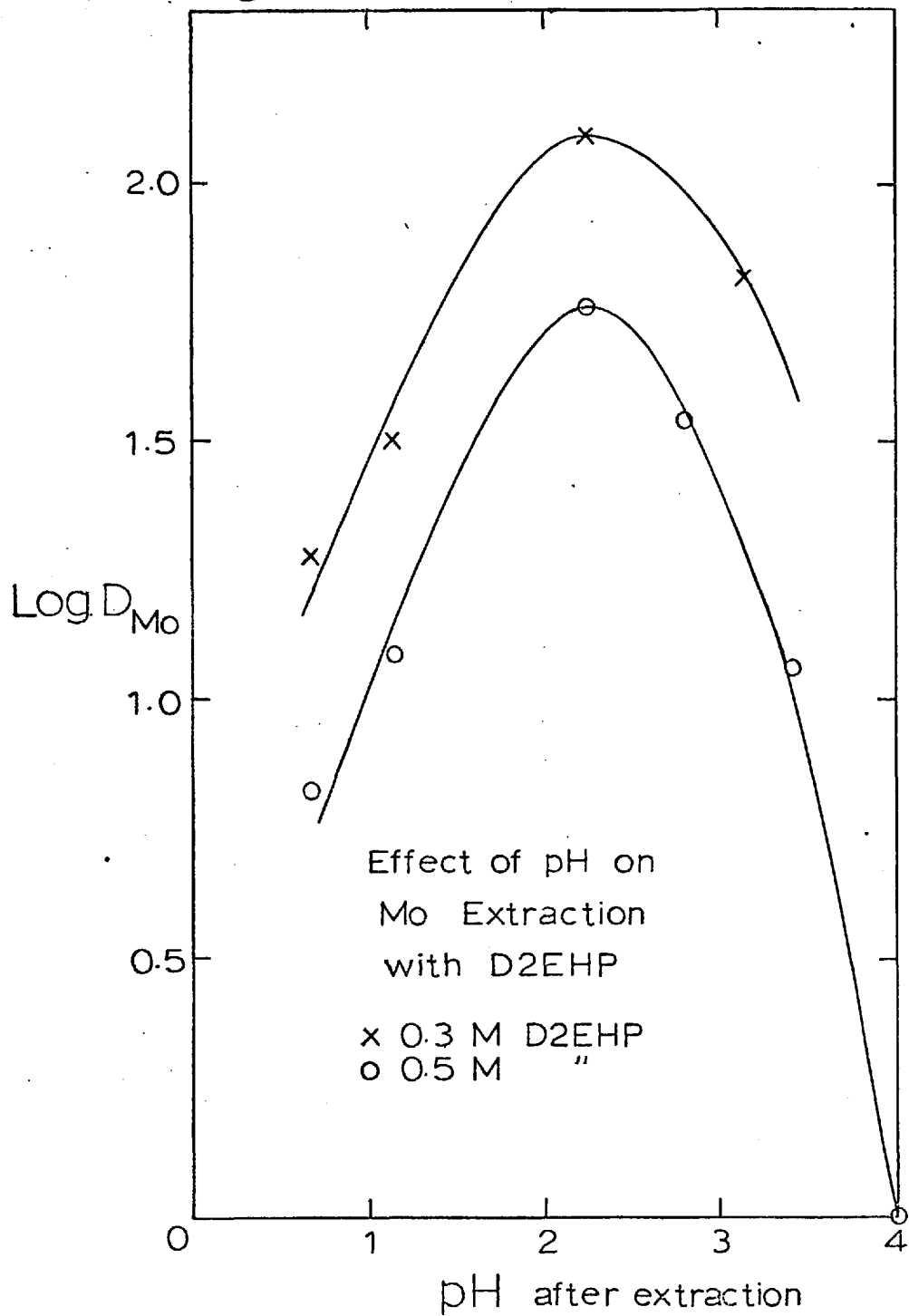


Fig. 4.2.2.4

Data from Table 12



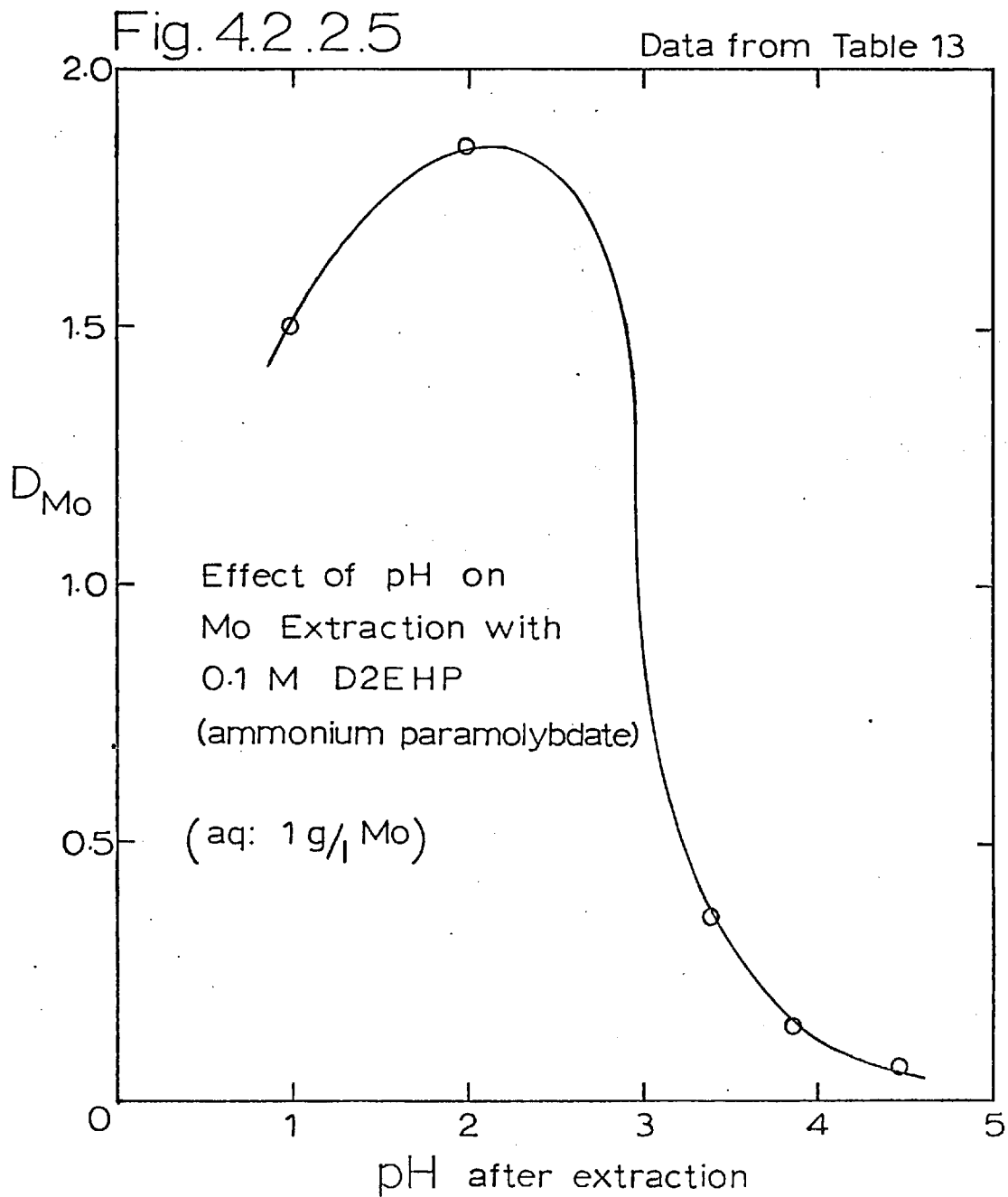


Fig. 4.2.2.6

Data from Table 14

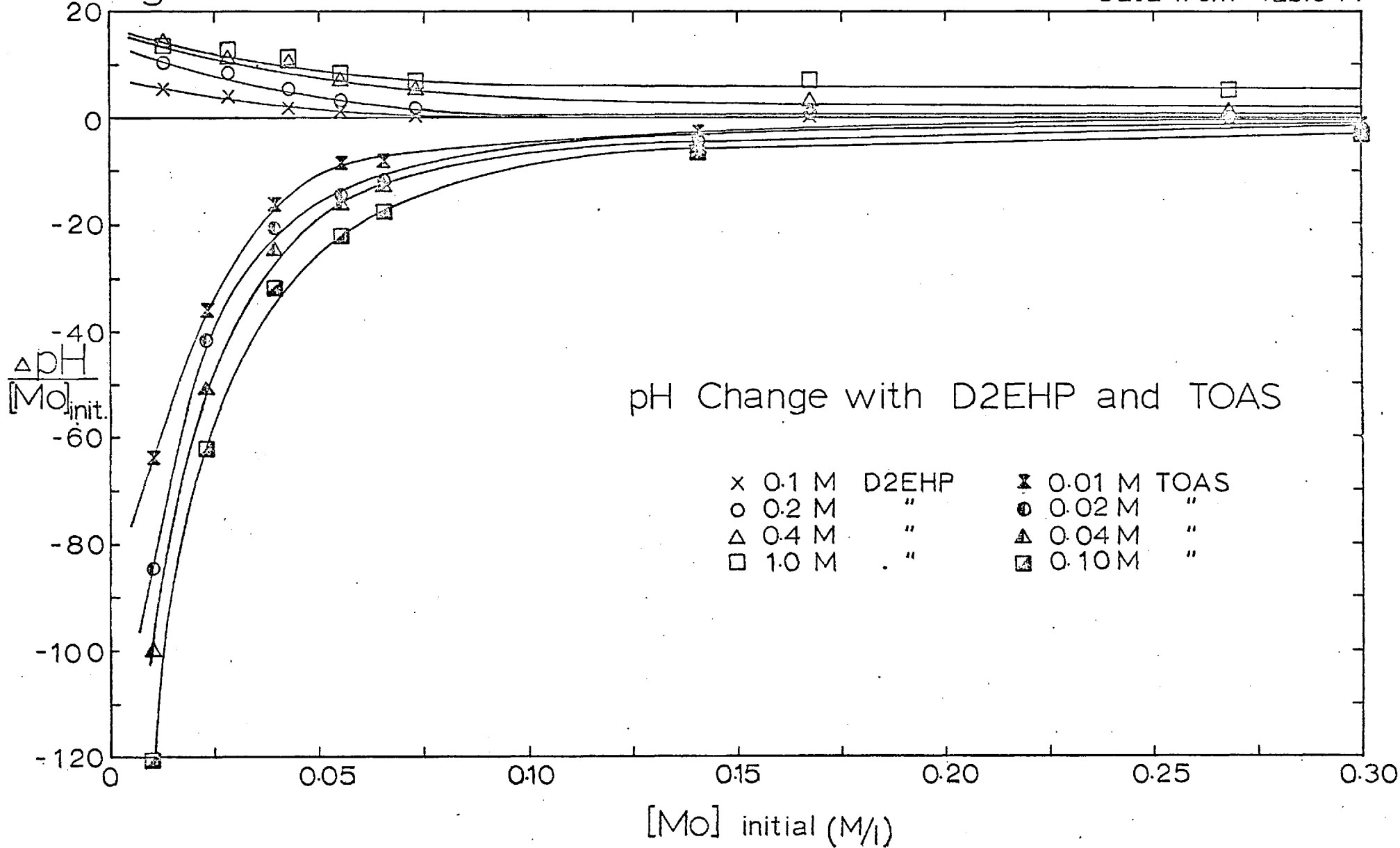


Fig. 4.2.2.7

Data from Table 15

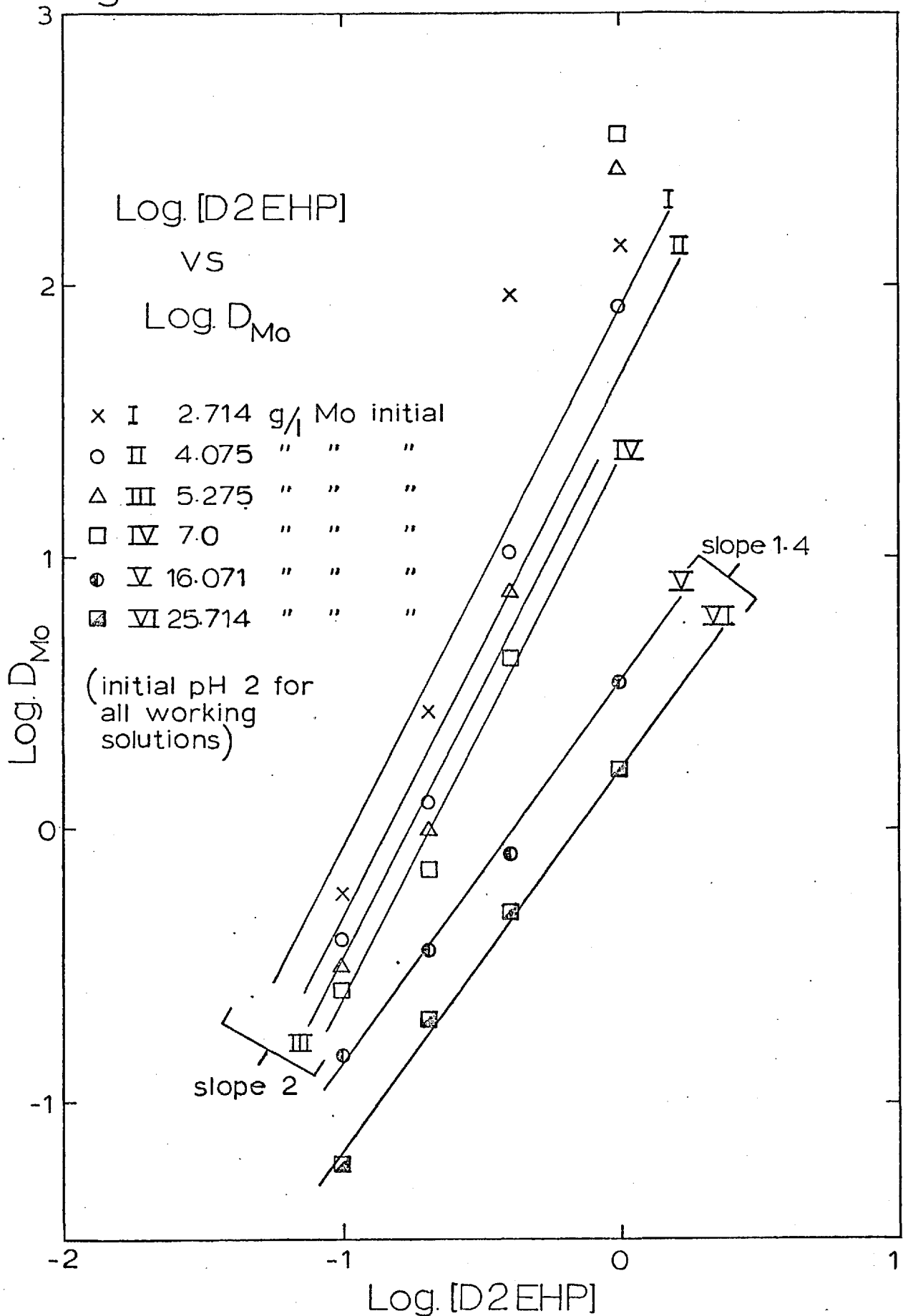


Fig. 4.2.2.8

Data from Table 16

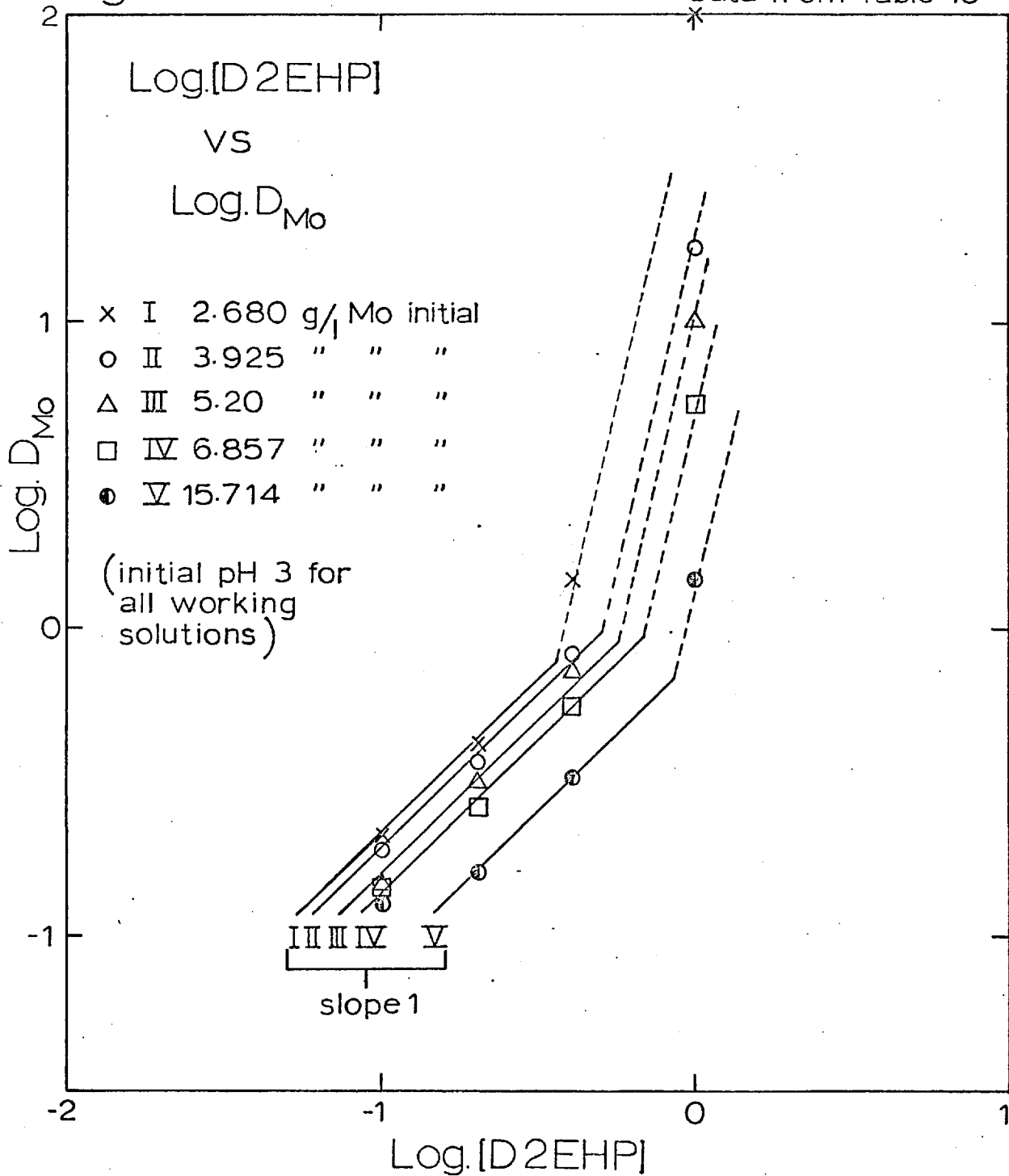


Fig. 4.2.2.9

Data from Table 17

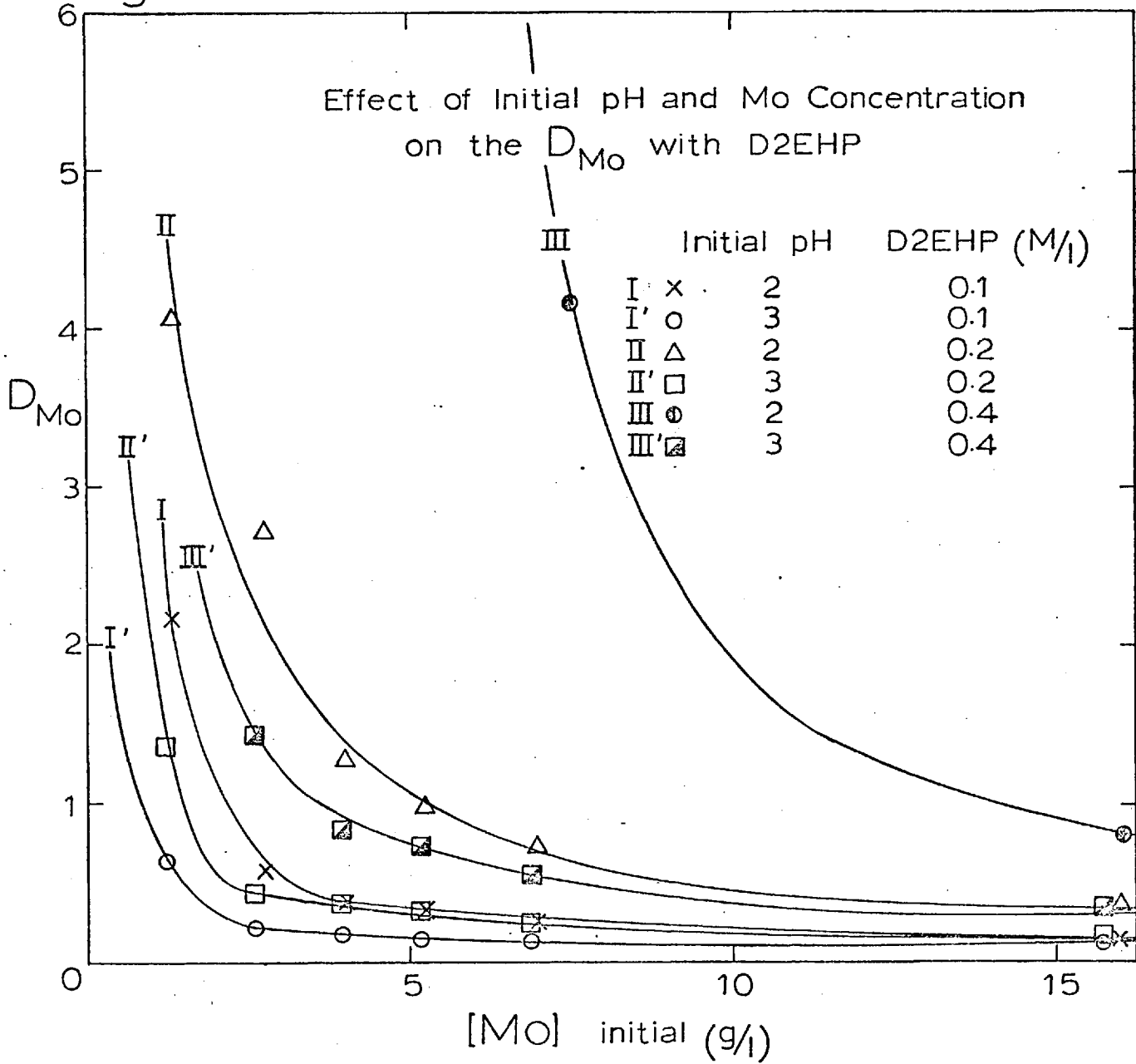


Fig. 4.2.2.10

Data from Table 18

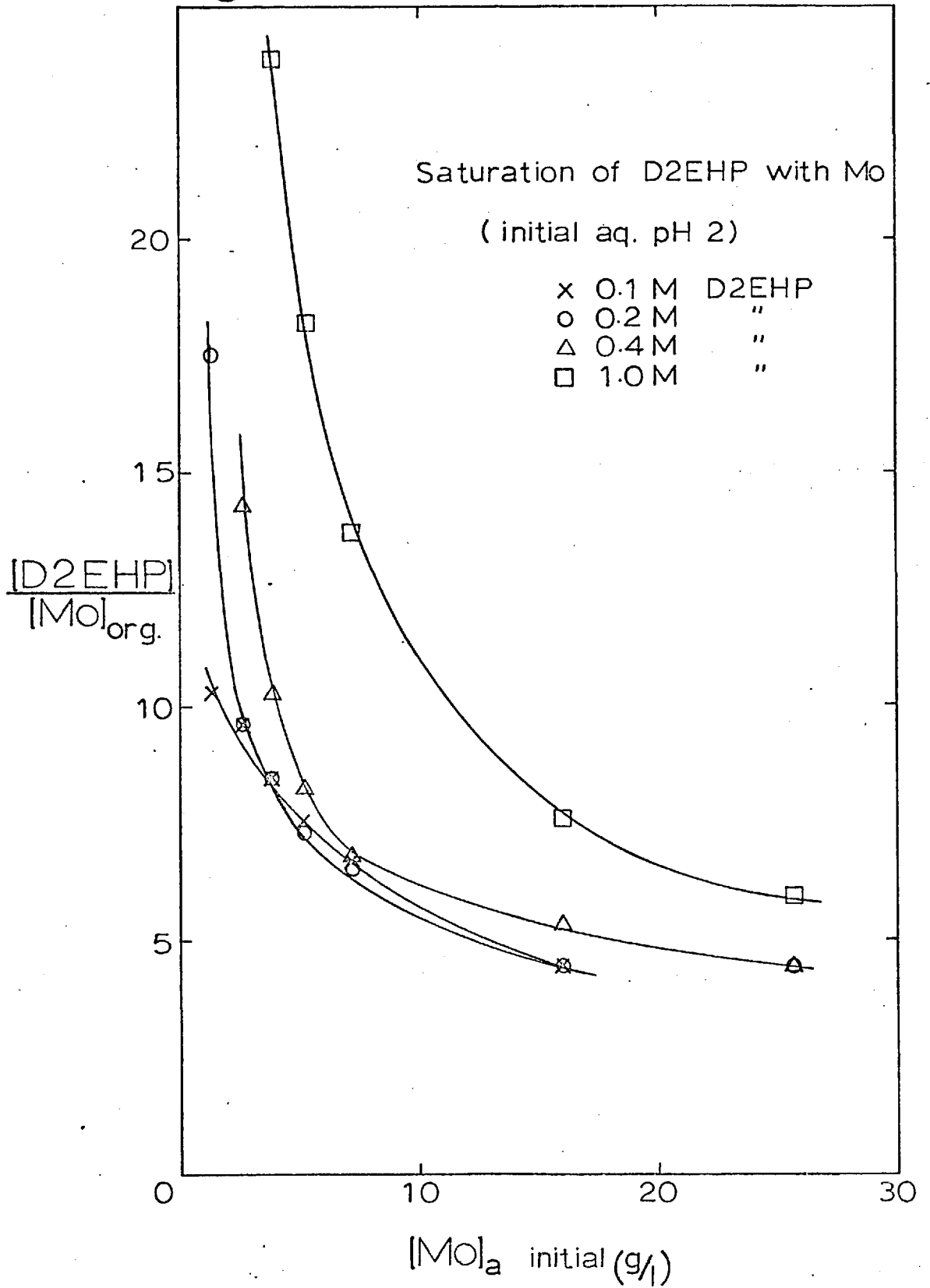




Fig.4.2.2.11

Data from Table 19

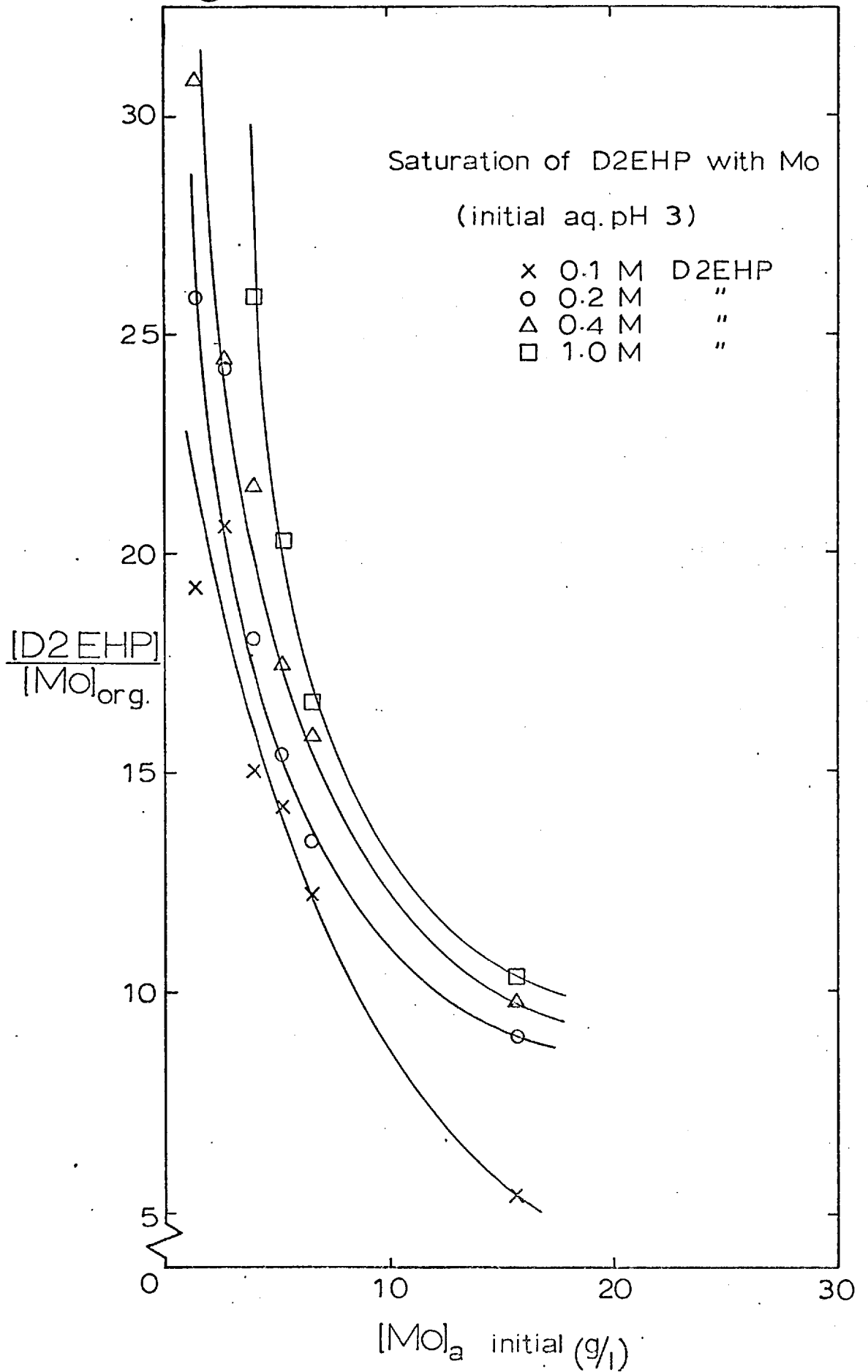
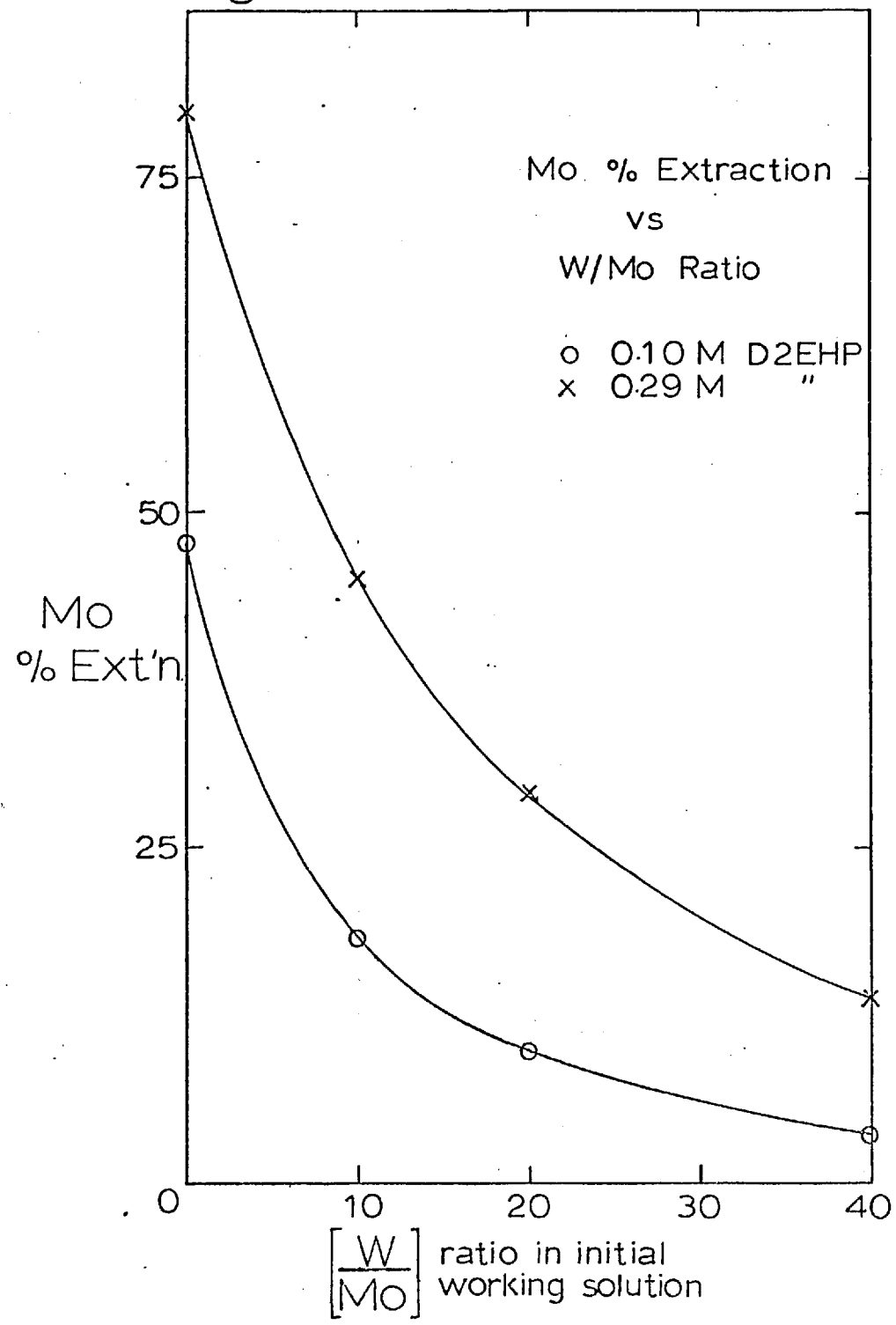


Fig. 4.31

Data from Table 20



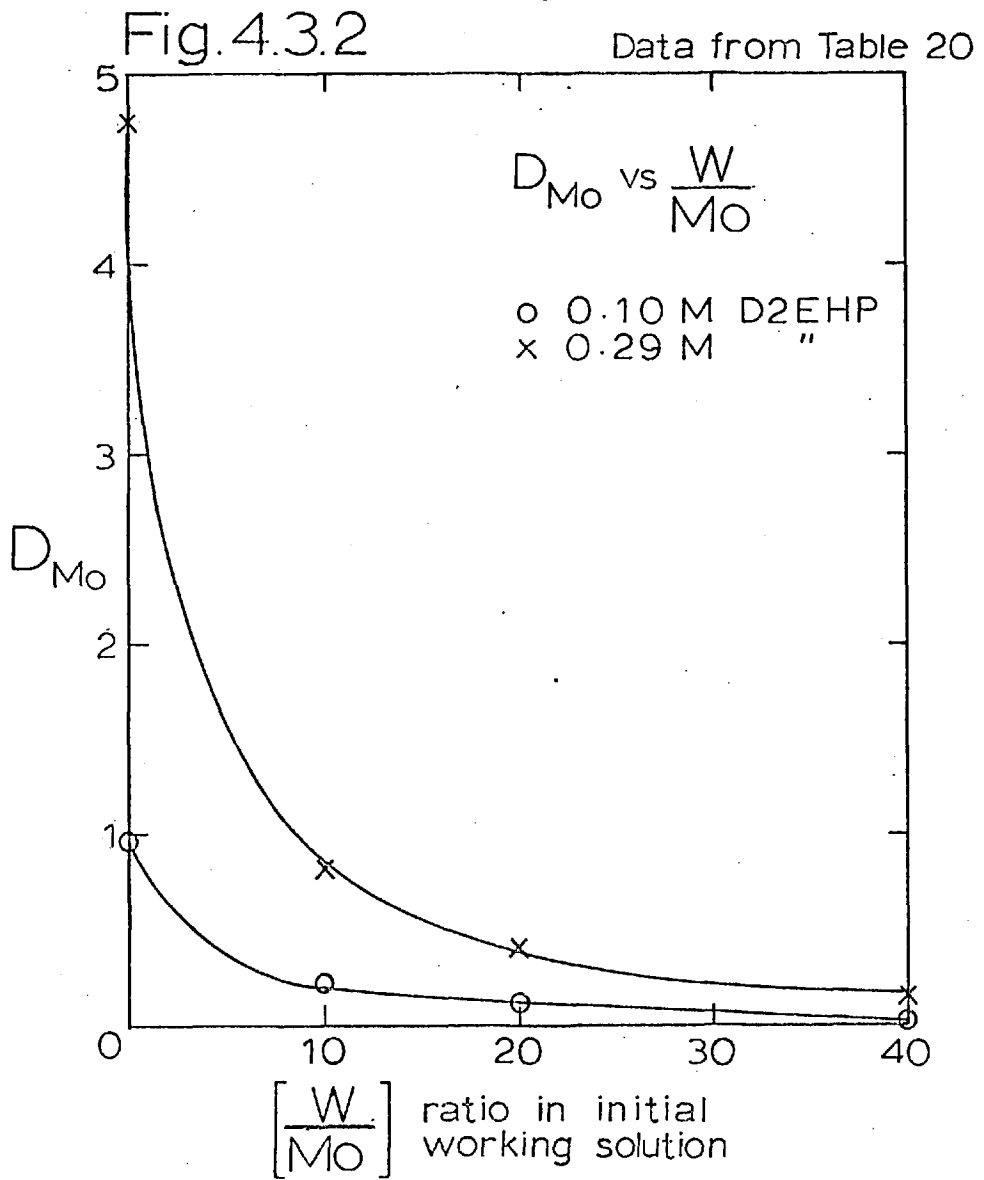


Fig.4.3.3

Data from Table 21

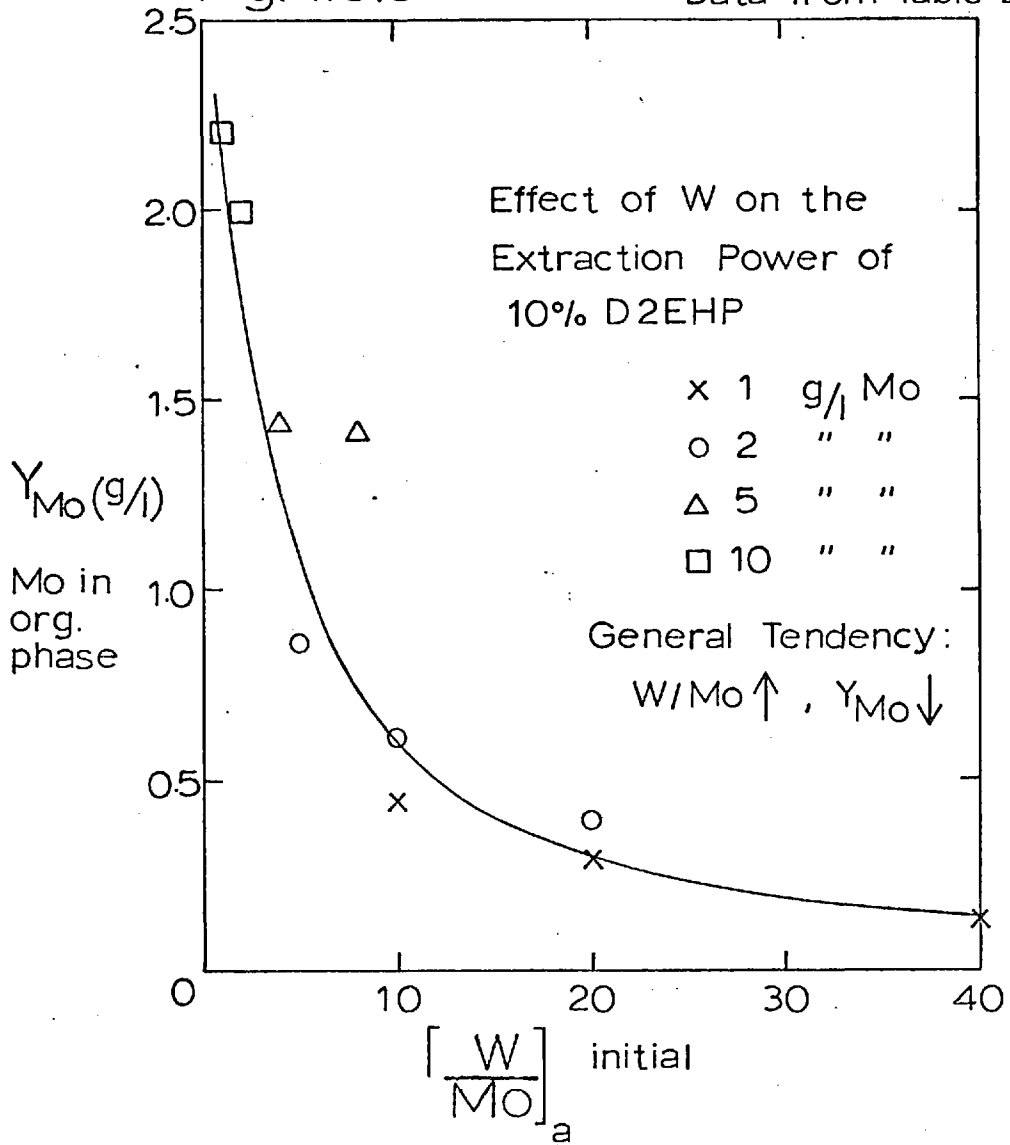
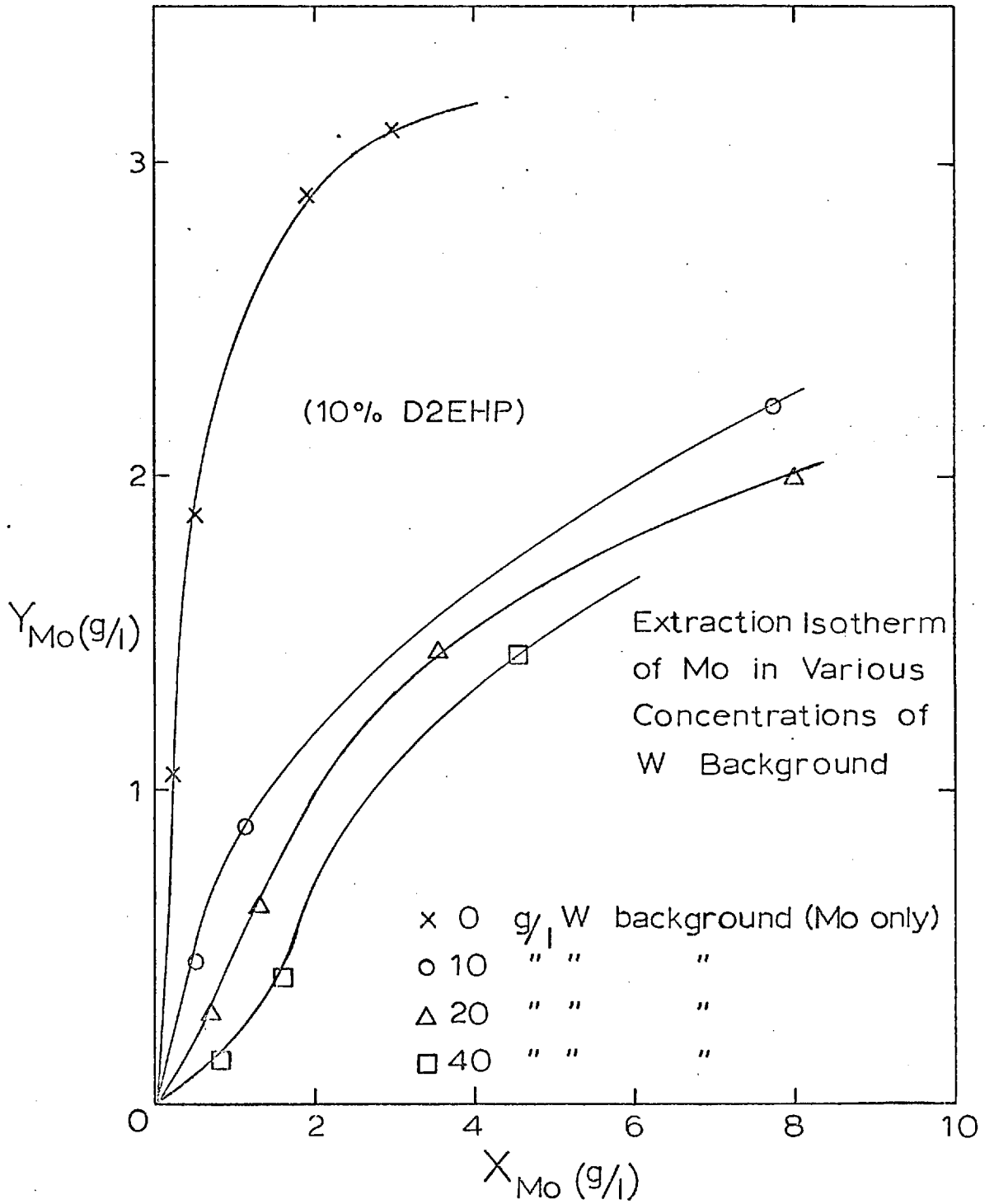


Fig.4.3.4

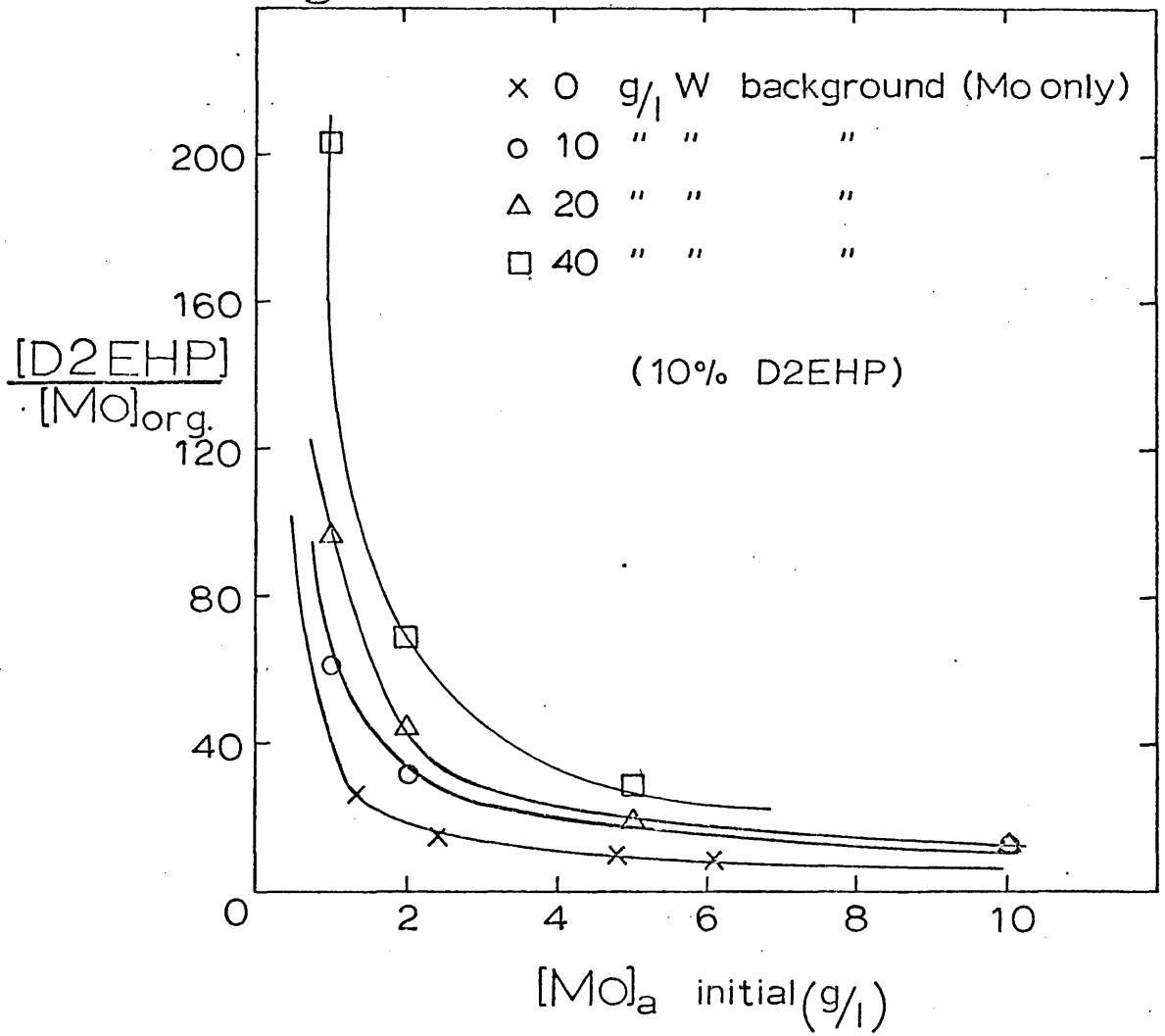
Data from Table 21



### Effect of W Presence on [D2EHP] / [Mo]<sub>org.</sub>

Fig. 4.3.5

Data from Table 21



### Effect of W Presence on $D_{Mo}$ with 10% D2EHP

Fig. 4.3.6

Data from Table 22

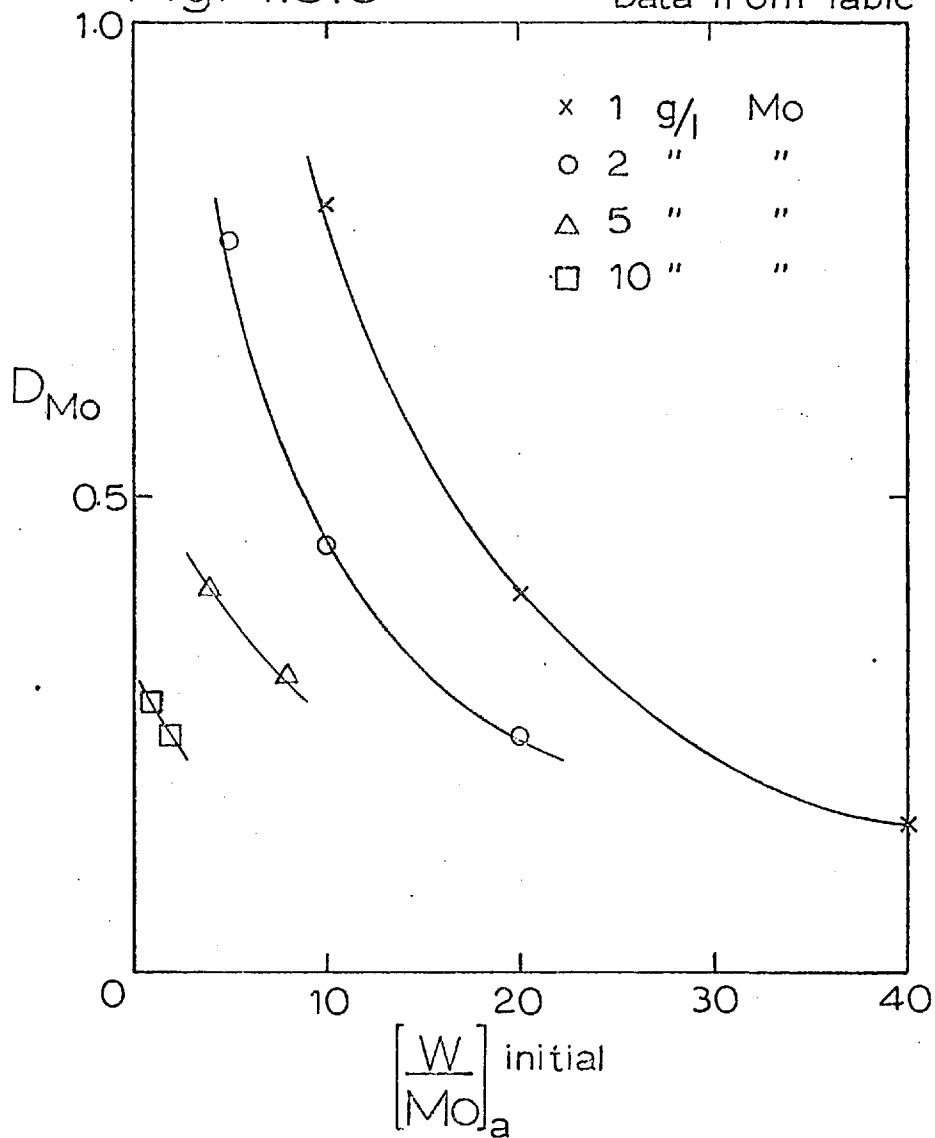


Fig. 4.3.7

Data from Table 23

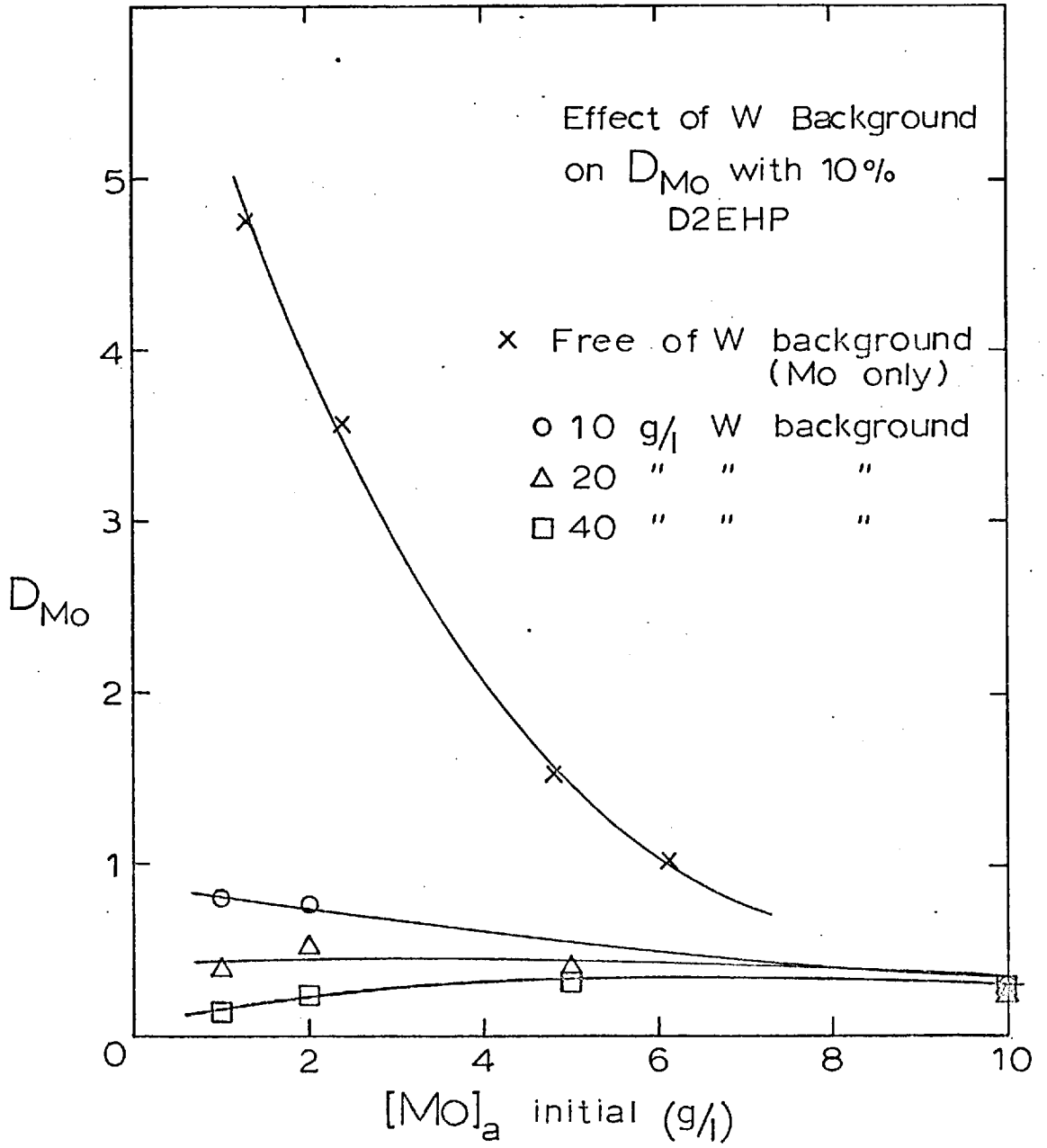




Fig. 4.3.8

Data from Table 24

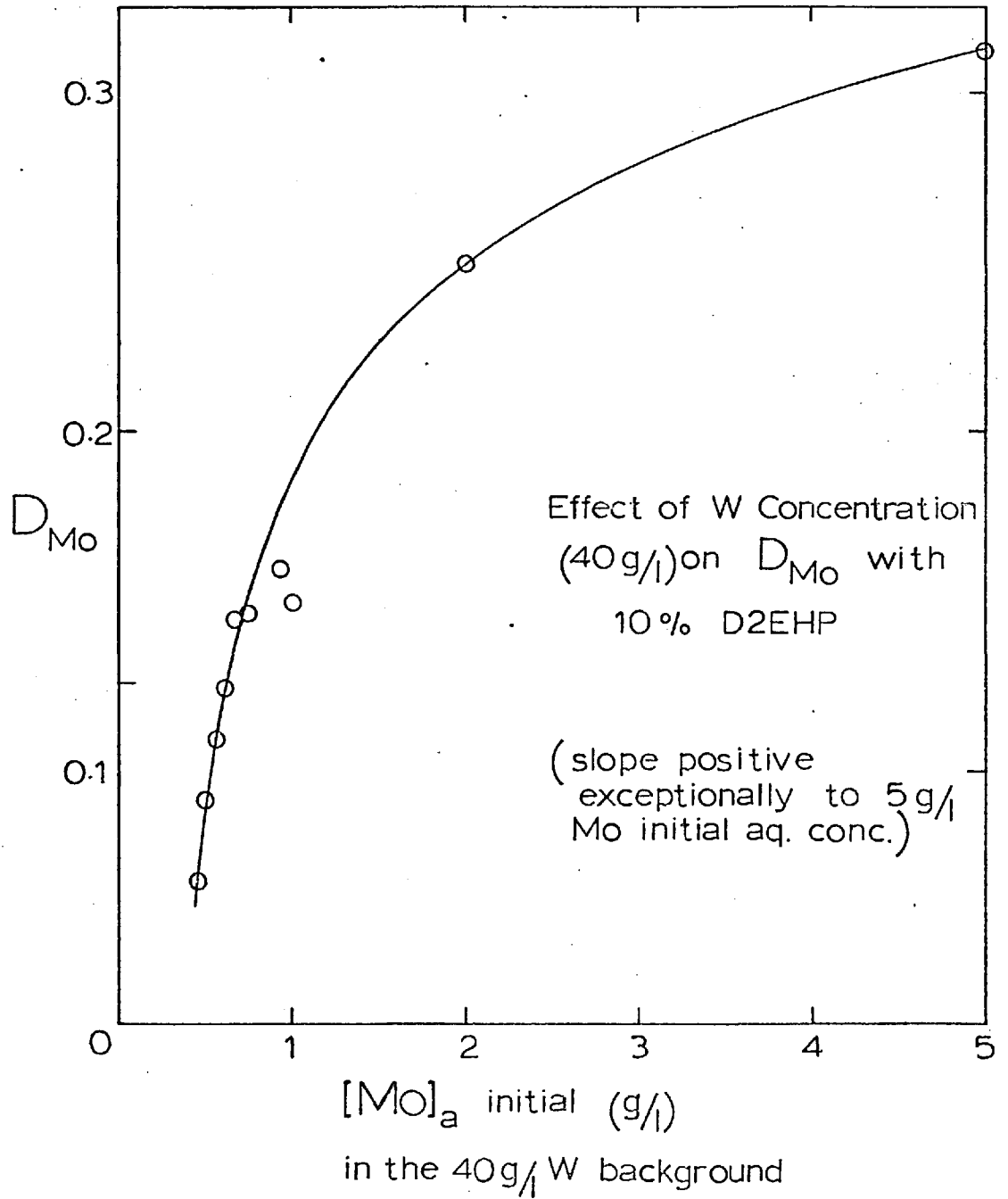


Fig. 4.3.9

Data from Table 25

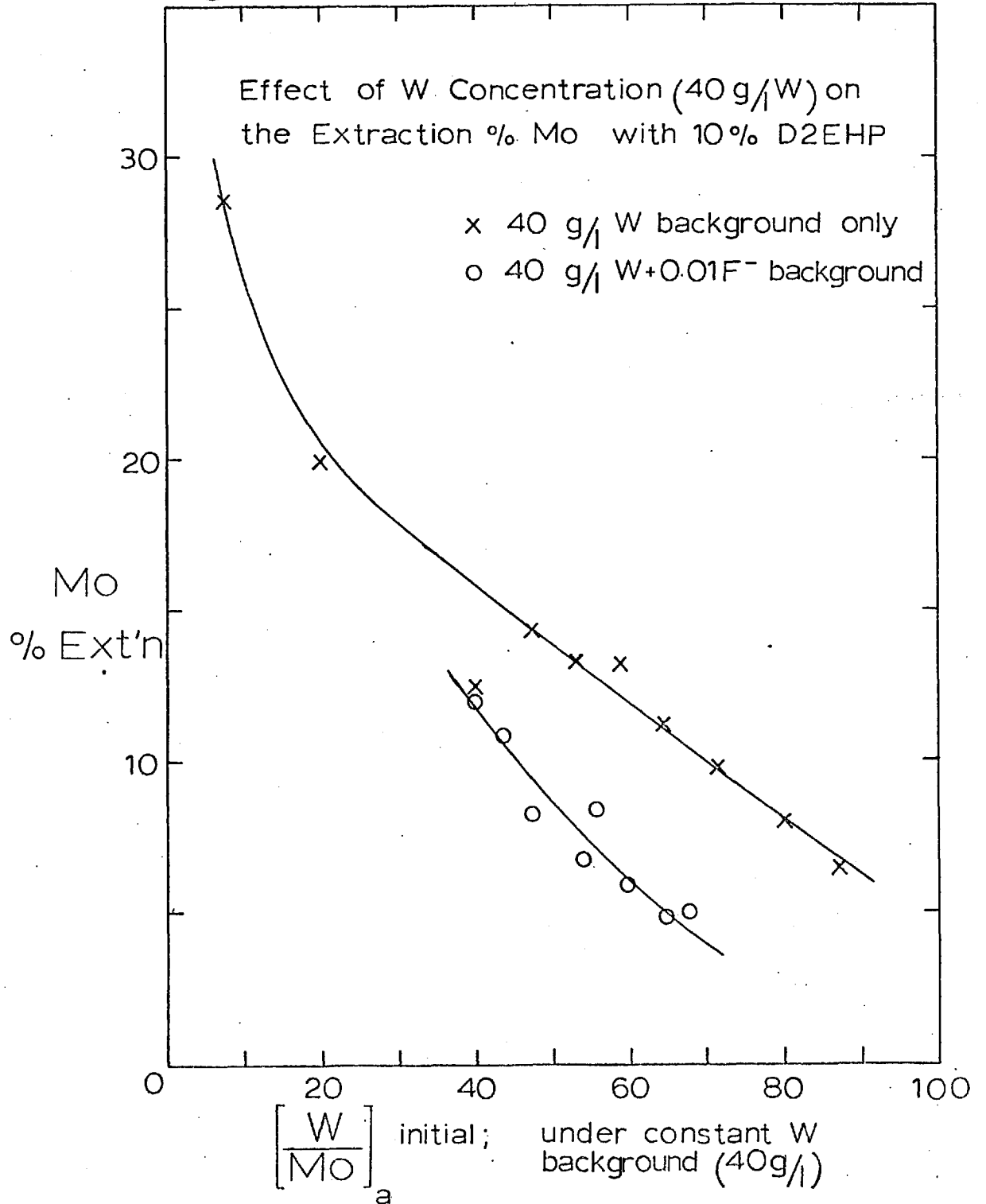


Fig. 4.3.10

Data from Tables 26 & 27

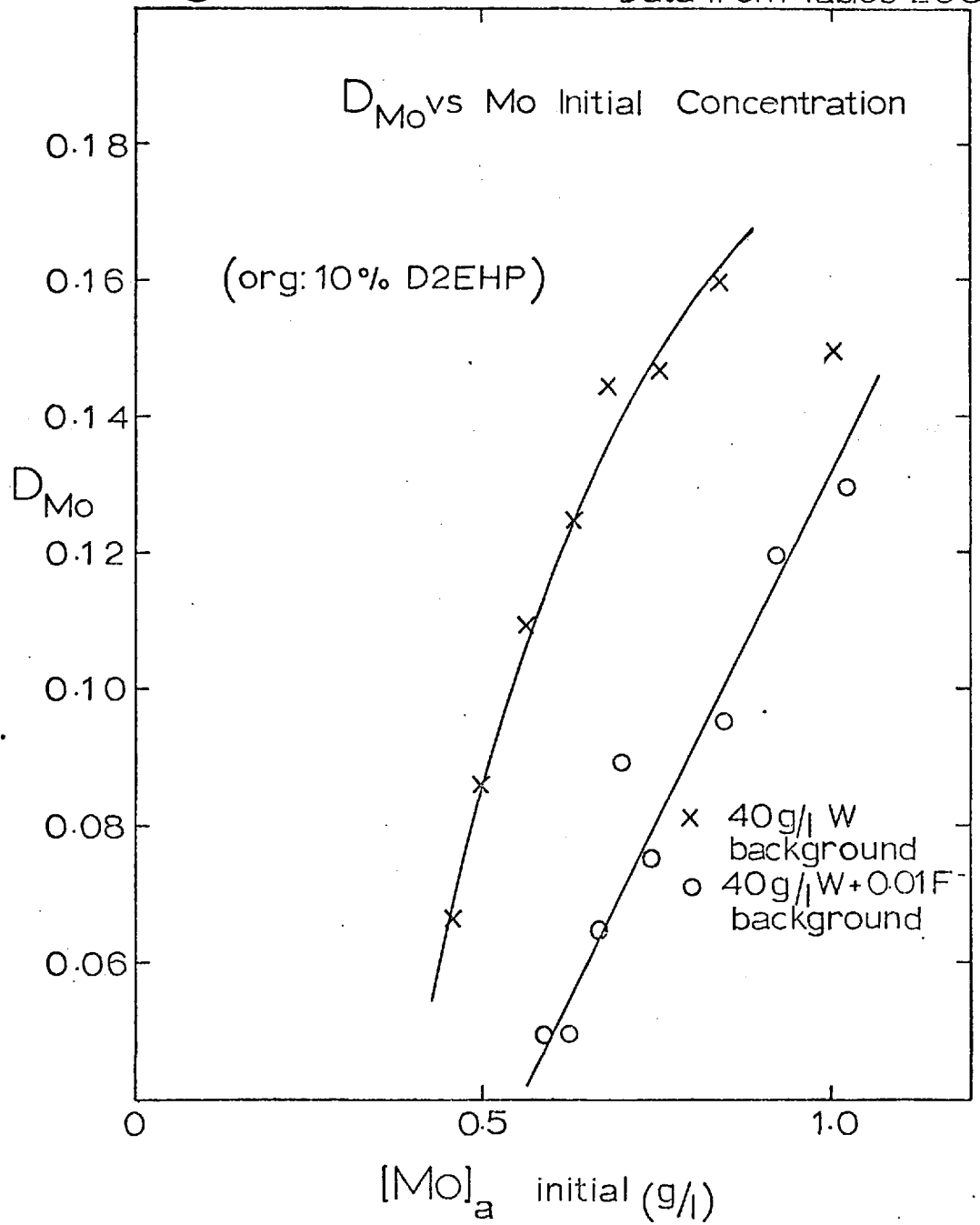
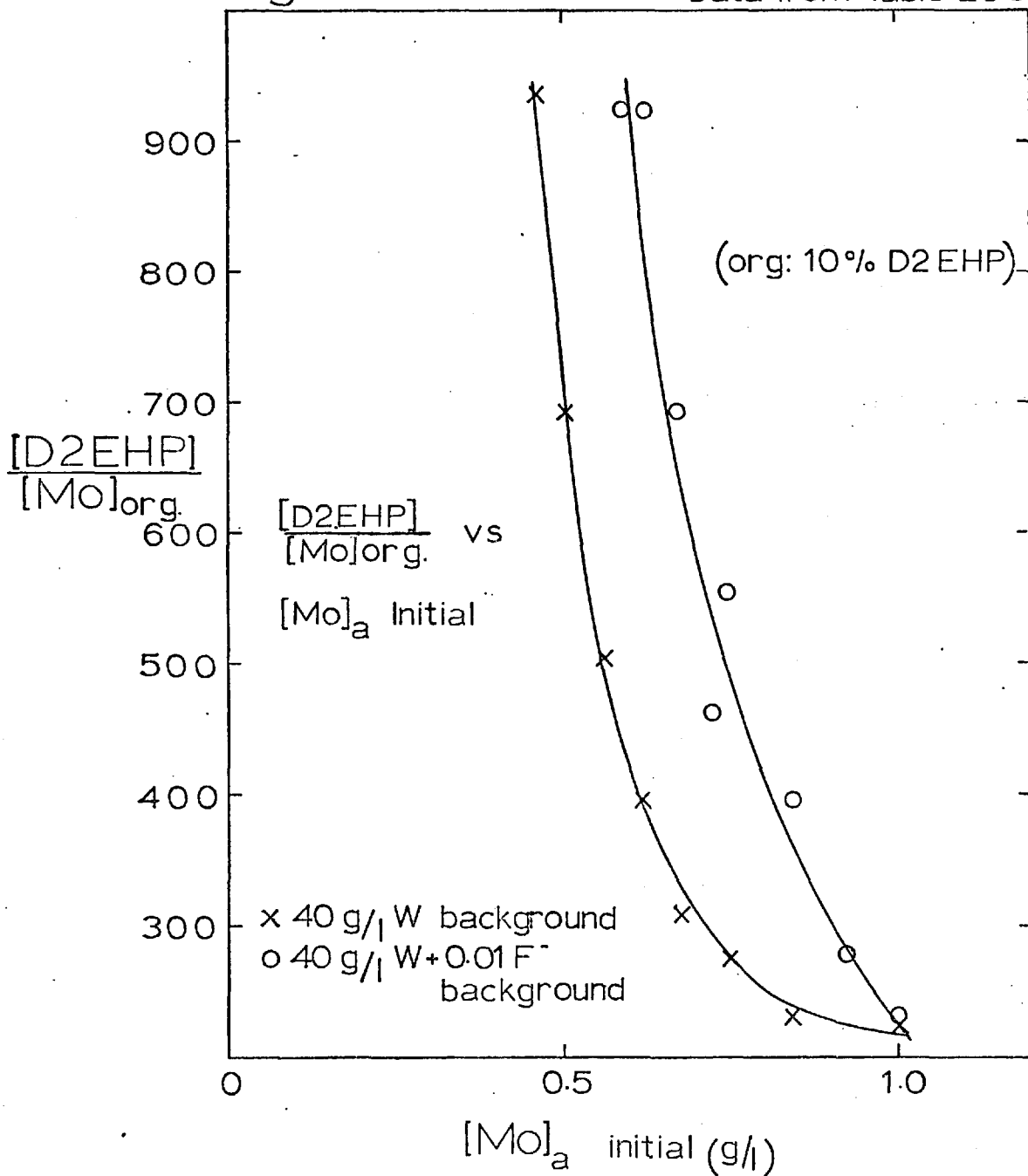


Fig. 4.3.11

Data from Table 26 & 27



## 5. Discussion of Results

### 5.1. TOAS System

A typical isotherm for the extraction of tungsten by 0.01M TOAS in benzene from aqueous sulphuric acid is shown in Fig. 4.1.1.1 (page 63 ). Extraction isotherms obtained using other conditions are generally similar to the one shown.

The linearity and zero slope of these curves at higher aqueous tungsten levels show that the organic phase is saturated with respect to tungsten. The extremely steep slope of these curves at the lower tungsten levels shows that the TOAS has an extremely strong extraction power for tungsten.

A typical isotherm for the extraction of molybdenum by 0.1M TOAS in benzene from aqueous sulphuric acid is shown in Fig. 4.2.1.1a(p 66 ). The shape of the isotherms is very different from those of tungsten. The S-shape of the molybdenum is due to the polymerization of molybdenum in the organic phase. In the region of lower molybdenum concentration ( $\mu\text{g/ml}$ ), the slope of the isotherm is close to 1. This is due to the fact that the molybdenum is not polymerized in dilute solutions.

It is certain that tungsten and molybdenum exist in alkaline aqueous solutions as  $\text{WO}_4^{2-}$  and  $\text{MoO}_4^{2-}$ , which have the tetrahedral configuration. When solutions of molybdates and tungstate are made weakly acidic, however, polymeric anions are formed (50). In spite of the fact that much work has been done to determine the species present in the solutions of tungstic and molybdic acid, no general agreement has been reached.

In very dilute solutions molybdic acid is not polymerized; the start of polymerization is controlled by the two factors, concentration and pH.

Yatsimirskii and Alekseeva (48) showed that the acid is not polymerized in a  $10^{-4}$ M solution, or in solutions of pH above 6.5. In the pH range 1 - 4 polymerization was found to begin to occur when the concentration of molybdic acid was about  $10^{-3}$ M. At the lower values of pH the complex species were homonuclear.

The poly-acids of molybdenum and tungsten are of two types

- (a) the iso-poly acids which contain only molybdenum or tungsten together with oxygen and hydrogen, and
- (b) the hetero-poly acids which contain one or two atoms of another element in addition to the molybdenum or tungsten, oxygen and hydrogen.

All of the polyanions contain octahedral groups, so that their formation from  $\text{MoO}_2^{2-}$  or  $\text{WO}_4^{2-}$  requires an increase in coordination number.

It is not clear why only certain metal oxo-ions can polymerize, or why for those metals which can, only certain species, for example  $\text{Mo}_7\text{O}_{24}^{6-}$  and  $\text{HW}_6\text{O}_{21}^{5-}$  predominant under a given set of conditions (50). The experimental results show that the distribution coefficient for molybdenum ( $D_{\text{Mo}}$ ) is lower than that for tungsten ( $D_{\text{W}}$ ) with the same strength of TOAS but is much higher than that for molybdenum when D2EHP is used.

$D_{\text{W}}$  and  $D_{\text{Mo}}$  from sulphate solutions at pH 2 - 3 were found to be proportional to the concentration of amine in the organic phase.

Fig. 4.1.1.2 (p 64) shows the dependence of the  $D_{\text{W}}$  on total amine concentration, at constant initial pH and constant initial concentration of tungsten. On such a plot, since the TOAS extracts almost all of the tungsten from the aqueous phase into 0.1M amine solution it is difficult to measure the activity of tungsten remaining in the aqueous phase. The very low concentration of tungsten remaining in the aqueous phase when 0.01 and 0.1M TOAS was used caused very high values of  $D_{\text{W}}$ , and

this is the reason why the line in Fig. 4.1.1.2 (p. 64 ) is curved and why the pH changed after extraction. With  $10^{-3}$  and  $10^{-4}$ M TOAS solutions, the loading numbers (equivalents of amine per mole of tungsten in the saturated organic phase) are around 0.4. The  $10^{-2}$ M and  $10^{-1}$ M solutions of TOAS were not saturated with tungsten, and so deviated from the straight line in Fig. 4.1.1.2 (p. 64 ).

The experimental results show that the loading number of tungsten with TOAS (Fig. 4.1.1.3 (p. 65 )) is lower than that of molybdenum (Fig. 4.2.1.2.(p. 68 )). This means that the chemical affinity between tungsten and TOAS is stronger than that of molybdenum and TOAS.

However the separation of tungsten and molybdenum using TOAS was impossible because when molybdenum and tungsten were present together in solution both were extracted together. Molybdenum was totally coextracted when tungsten was totally extracted.

From a practical industrial point of view, the extraction of tungsten or molybdenum with a long chain aliphatic tertiary amine sulphate is rapid and easy. No problems have been found.

## 5.2. D2EHP System

Molybdenum, like uranium, can exist in acidic solutions as both anion and cation species in equilibrium, so that either cationic types of organic extractants (e.g. TOAS) or anionic types of extractants (e.g. D2EHP) may be used for recovering the metal from the aqueous phase. Tungsten, however, does not exhibit this property of forming cations as far as its recovery by solvent extraction is concerned.

The solvent extraction process can take advantage of this difference and it is possible to separate molybdenum from tungsten when both are present in acidic solutions, by extracting the molybdenum with D2EHP.

D2EHP shows little or no extraction power for tungsten from acidic sulphate solutions (Table 4. (p.107)). This confirms that tungsten never exists in a cationic form in the acidic sulphate solutions. The negatively charged tungsten species are particularly easy to extract solutions with TOAS as was shown above.

At low concentrations of hydrogen ions in the aqueous phase, D2EHP behaves as a typical cation - exchange extracting agent, and the complexes extracted are usually co-ordinatively solvated metal salts with general formula  $M^{2+}(R_2PO_4)_2 \cdot q HR_2PO_4$ , where  $q$  is the number of D2EHP molecules solvating the metal cation, and where  $HR_2PO_4$  is the acid D2EHP.

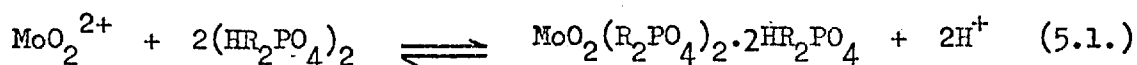
It has been demonstrated that the experimental data can be explained in a satisfactory manner by considering that the molybdenum is extracted by D2EHP predominantly in the form  $MoO_2^{2+}$ , the complex present in the organic phase being mainly  $MoO_2(R_2PO_4)_2 \cdot 2HR_2PO_4$  anhydrides (30).

Fig. 4.2.2.10.(p.80 ) shows that saturation of D2EHP with molybdenum



occurred with 4 molecules of D2EHP per atom of molybdenum, which is in good agreement with formula of the complex  $\text{MoO}_2 \cdot (\text{R}_2\text{PO}_4)_2 \cdot 2\text{HR}_2\text{PO}_4$ . The dimerisation of D2EHP molecules in the organic phase has been established by a number of authors.(49).

The fundamental reaction taking place between D2EHP and  $\text{MoO}_2^{2+}$  can be described by equation (5.1).



for which the equilibrium constant is (in terms of concentration rather than activity)

$$\begin{aligned} K_1 &= \frac{[\text{MoO}_2(\text{R}_2\text{PO}_4)_2 \cdot 2\text{HR}_2\text{PO}_4] [\text{H}^+]^2}{[\text{MoO}_2^{2+}] [(\text{HR}_2\text{PO}_4)_2]^2} \\ &= \frac{[\text{Mo}]_{\text{org.}} [\text{H}^+]^2}{[\text{Mo}]_{\text{aq.}} [(\text{HR}_2\text{PO}_4)_2]^2} \\ &= D_{\text{Mo}} \cdot \frac{[\text{H}^+]^2}{[(\text{HR}_2\text{PO}_4)_2]^2} \end{aligned}$$

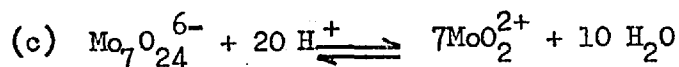
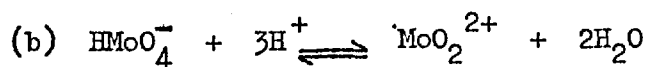
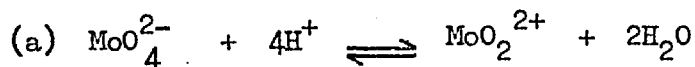
$$\text{and } \log D_{\text{Mo}} = \log K_1 + 2 \log [(\text{HR}_2\text{PO}_4)_2] + 2\text{pH}$$

Fig. 4.2.2.4 (p. 74) and Fig. 4.2.2.5 (p. 75) show the effect of pH on the  $D_{\text{Mo}}$ . They show that the cation  $\text{MoO}_2^{2+}$  can be extracted to a maximum extent between pH 2 and 3, and  $\text{MoO}_2^{2+}$  can exist at least to pH 4 - 5 although undoubtedly at a very low concentration.

According to equation (5.1), the pH of the aqueous phase after extraction of  $\text{MoO}_2^{2+}$  should have decreased because two hydrogen ions ( $2\text{H}^+$ ) are released per molybdenum extracted. Practical results showed, however, that the pH

after extraction with D2EHP had always increased. These results can be explained as follows.

As molybdenum co-exists in anion and cation forms we can explain possible anion  $\rightleftharpoons$  cation equilibrium:



To convert anionic molybdenum to the cationic form, the system consumes considerable quantity of hydrogen ions. Equations (a) and (b), where the molybdenum exists in a monomeric state (at low concentration), show that conversion of an anion to a cation so as to replace a cation extracted, and so re-establish equilibrium, consumes more hydrogen ions than are released by the extraction process, equation (5.1).

As it is well known that molybdenum is polymerized in weakly acidic solutions, it is better to take equation (c) as representing the cation  $\rightleftharpoons$  anion equilibrium equation.

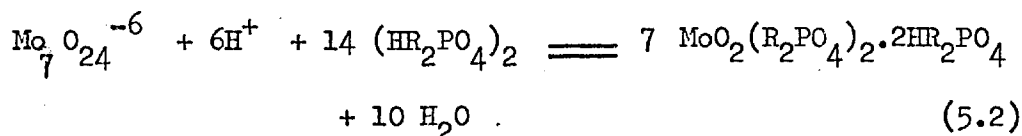
Thus consumption of hydrogen ions to produce  $\text{MoO}_2^{2+}$  is always much larger than the amount of hydrogen ions released according to equation (5.1). This is assumed to be the reason for the increase of pH after extraction with D2EHP (pH positive deviation).

pH negative deviation can obviously be explained in an analogous way, because TOAS extracts anions only and the equilibrium should move to the left hand side of equations (a), (b) and (c), where large numbers of hydrogen ions are released to lower the pH of the system. Fig. 4.2.2.6 (p 76 )

shows this effect.

Cationic molybdenum distribution coefficients were much lower than those of anionic molybdenum. The extraction isotherms of Fig. 4.2.1.1.a (p. 66) and 4.2.2.1. (p.71) may be compared. The latter shows that the extraction isotherm is linear to the saturation point, which means that the cation does not polymerize.

The over-all extraction equation with D2EHP can therefore be described as follows.



for which the equilibrium constant is

$$K_2 = \frac{a_{[\text{MoO}_2(\text{R}_2\text{PO}_4)_2 \cdot 2\text{HR}_2\text{PO}_4]}^7 \cdot a_{\text{H}_2\text{O}}^{10}}{a_{\text{Mo}_7\text{O}_{24}^{-6}} \cdot a_{\text{H}^+}^6 \cdot a_{[\text{HR}_2\text{PO}_4]_2}^{14}}$$

(ionic charges of species are ignored in activity and concentration expressions)

$$= \frac{c_{\text{Mo, org}}^7}{c_{\text{Mo, aq}}} \cdot \frac{a_{\text{H}_2\text{O}}^{10} \cdot \gamma_{\text{Mo, org}}^7}{a_{\text{H}^+}^6 \cdot [\text{HR}_2\text{PO}_4]_2^{14} \cdot \gamma_{\text{org}}^{14} \cdot \gamma_{\text{Mo, aq}}}$$

If we assume that D2EHP in the organic phase is in large excess and at constant concentration, the pH is constant, and the activity of H<sub>2</sub>O and activity coefficients of molybdenum in both organic (γ<sub>Mo, org.</sub>) and aqueous (γ<sub>Mo, aq</sub>) phases are constants

$$K_3 = \frac{c_{\text{Mo, org}}^7}{c_{\text{Mo, aq}}}$$

$$c_{\text{Mo, org}} = K_4 \cdot c_{\text{Mo, aq}}^{1/7} \quad (5.3)$$

$$D_{\text{Mo}} = \frac{C_{\text{Mo,org}}}{C_{\text{Mo,aq}}} = K_4 \cdot \frac{C_{\text{Mo,aq}}^{1/7}}{C_{\text{Mo,aq}}} = K_4 \cdot C_{\text{Mo,aq}}^{-6/7} \quad (5.4)$$

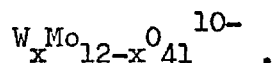
$D_{\text{Mo}}$  is the distribution coefficient of the molybdenum being extracted by D2EHP. Equation (5.3) indicates that the concentration of molybdenum in the organic phase does not depend very much on its concentration in the aqueous phase, and this must be the good reason why the distribution coefficients with D2EHP are so low compared with those of TOAS extractions. These are good agreement with the results obtained.

Equation (5.4) indicates that the distribution coefficient increases in proportion to the decrease in concentration of molybdenum in the aqueous phase and is independent of the molybdenum concentration in organic phase; the smaller  $C_{\text{Mo,aq}}$ , the larger the  $D_{\text{Mo}}$  value, which is in good agreement with the results obtained.

5.3. Separation of Tungsten and Molybdenum with D2EHP

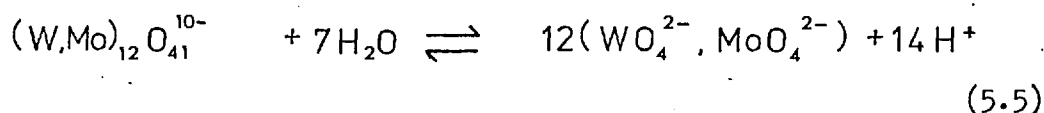
When molybdenum and tungsten were present together in solution, and molybdenum was extracted by D2EHP, the molybdenum distribution coefficient decreased significantly as the tungsten concentration was increased.

When the concentration of tungsten is much larger than that of molybdenum ( $C_W \gg C_{Mo}$ ) and if it is assumed that in weakly acidic medium the predominant tungsten polyanion is  $W_{12}O_{41}^{10-}$ , the corresponding tungsten - molybdenum polyanion can be expressed



The concentration of molybdenum which is not bound with tungsten (free molybdenum), is determined by the dissociation equilibrium of the hetero-polyanions and the ratio of the concentrations of tungsten and molybdenum.

Since



where  $K_5 = \frac{a_{(WO_4, MoO_4)}^{12} \cdot a_{H^+}^{14}}{a_{(W, Mo)_{12} O_{41}} \cdot a_{H_2O}^7}$

when  $a_{H^+}$  and  $a_{H_2O}$  are constants

$$a_{(WO_4, MoO_4)} = K_6 a_{(W, Mo)_{12} O_{41}}^{1/12} \quad (5.6)$$

and since

$$a_{MoO_4} \approx \frac{C_{Mo}}{C_{Mo} + C_W} \cdot a_{(WO_4, MoO_4)}$$

therefore

$$a_{MoO_4} \approx \frac{C_{Mo}}{C_{Mo} + C_W} \cdot K_6 \cdot a_{(W, Mo)_{12} O_{41}}^{1/12} \quad (5.7)$$

If the concentration of tungsten in the solution is much higher than that of molybdenum, i.e.  $C_W \gg C_{Mo}$

$$a_{(W,Mo)_{12}O_{41}} \approx a_{W_{12}O_{41}}$$

and

$$\frac{C_{Mo}}{C_{Mo} + C_W} \approx \frac{C_{Mo}}{C_W}$$

and

$$a_{MoO_4} \approx K_6 \cdot \frac{C_{Mo}}{C_W} \cdot a_{W_{12}O_{41}}^{1/2} \quad (5.8)$$

In acidic solutions tungsten is almost completely in the form of polymeric ions and

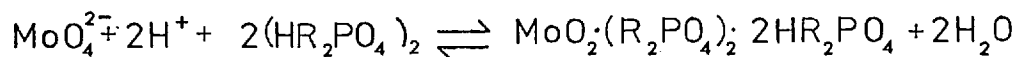
$$a_{W_{12}O_{41}} \approx \frac{1}{12} C_W \cdot \gamma_{\pm} \quad (5.9)$$

taking activity coefficient of ions  $W_{12}O_{41}^{10-}$  as constant

from (5.8) and (5.9) we get

$$a_{MoO_4} = K_7 \cdot C_{Mo} \cdot C_W^{-11/12} \quad (5.10)$$

Assuming that the molybdenum is not polymerized when in dilute solutions and is present in the form of  $MoO_4^{2-}$ , the extraction of molybdenum with D2EHP can be given as following:



where

$$K_8 = \frac{a_{MoO_2 \cdot (R_2PO_4)_2} \cdot 2HR_2PO_4 \cdot a_{H_2O}^2}{a_{MoO_4} \cdot a_{H^+}^2 \cdot a_{(HR_2PO_4)_2}^2}$$

or

$$K_8 = \frac{C_{Mo,org.}}{a_{MoO_4}} \cdot \frac{a_{H_2O}^2 \cdot \gamma_{Mo,org.}}{a_{H^+}^2 \cdot [HR_2PO_4]^2 \cdot \gamma_{org.}^2}$$

when the activities of water and hydrogen ions and the concentration and activity coefficient of the organic phase are constant,

then

$$C_{Mo,org.} = K_9 a_{MoO_4}$$

or substituting the value  $a_{MoO_4}$  from equation (5.10)

we get  $C_{\text{Mo,org.}} = K_{10} \cdot C_{\text{Mo}} \cdot C_{\text{W}}^{-11/12}$  (5.11)

and  $D_{\text{Mo}} = K_{10} \cdot C_{\text{W}}^{-11/12}$  (5.12)

Equation (5.11) and (5.12) indicate that the concentration of molybdenum in the organic phase is proportional to the concentration of molybdenum in the aqueous phase and it decreases in proportion to the increase of tungsten concentration to the power of  $11/12$ .

The distribution coefficient of molybdenum in the presence of tungsten is inversally proportional to the concentration of tungsten in the solution to the power of  $11/12$  and it does not depend upon the molybdenum concentration in the aqueous phase.

Both of these deductions are in good agreement with the results obtained experimentally.

## 6. Conclusions

The following conclusions may be drawn from the experimental results.

- (1) TOAS in benzene has been shown to be a remarkably effective extractant for tungsten or molybdenum from acidic sulphate liquors.
- (2) Tungsten distribution coefficients were higher than those of molybdenum with the same strength of TOAS.
- (3) When the aqueous solution contained tungsten and molybdenum together, and was extracted by TOAS, molybdenum was totally coextracted when tungsten was totally extracted. Tungsten and molybdenum separation, therefore, depends on the preliminary extraction of molybdenum.
- (4) D2EHP showed little or no extraction power for tungsten from sulphate solutions. This confirms that tungsten does not exist in a cationic state in the solution.
- (5) The extraction maximum for molybdenum with D2EHP or TOAS was in the pH range 2 - 3.
- (6) Molybdenum distribution coefficients with TOAS were higher than those with D2EHP under the same extraction conditions. This is due to the fact that in the acid aqueous phase, the anionic state of molybdenum is much more predominant than the cationic state of molybdenum.



- (7) The saturation of D2EHP with molybdenum was in good agreement with a formula for the complex,  $\text{MoO}_2(\text{R}_2\text{PO}_4)_2 \cdot 2\text{HR}_2\text{PO}_4$ , corresponding to 4 molecules of D2EHP per atom of molybdenum.
- (8) When molybdenum is extracted with TOAS or D2EHP, the pH of the initial working solutions should be 2 for D2EHP and 3 for TOAS, because D2EHP deviates positively and TOAS negatively, so that the pH after extraction will reach that corresponding to maximum extraction.
- (9) Stripping of molybdenum from D2EHP must take place in an ammonium carbonate medium, since direct stripping of the D2EHP with ammonia solution forms a stable emulsion.
- (10) The molybdenum distribution coefficient with D2EHP was significantly decreased when the tungsten was introduced into the solution.
- (11) Separation of molybdenum from tungsten by D2EHP seems to be applicable to solutions where the  $W/M_0$  ratio is not too great. In that case molybdenum is comparatively easily separated from tungsten.
- (12) For solutions with greater tungsten concentrations and small amounts of molybdenum it was not possible to extract all of the molybdenum in a simple extraction system. An infinite number of theoretical stages is necessary.
- (13) Addition of fluorine ( $\text{F}^-$ ) into a molybdenum - tungsten solution as a depolymerization agent did not give any improvement of the molybdenum distribution coefficient.

7. Appendix (Tables of Data)

Table 1. Extraction isotherm of tungsten with 0.01M TOAS in benzene  
(Initial working solution pH 2.5)

Xw (g/l)	Yw (g/l)	Dw
0	3.677	-
0.23	4.36	18.957
0.606	4.36	7.195
1.066	4.45	4.174
5.58	4.42	0.792
15.54	4.46	0.287
35.62	4.38	0.123

Table 2. Extraction of W (5 g/l) with various strength of TOAS  
(Data for log TOAS v log Dw)

pH		TOAS	log	Xw	Yw	Dw	log Dw	% Mass
Before	After	(M/l)	TOAS	(g/l)	(g/l)			balance
2.47	1.56	0.1	-1	0.0003	5.1160	17053	4.2317	102.32
2.47	2.20	0.01	-2	0.6064	4.3598	7.1896	0.8567	99.32
2.47	2.49	0.001	-3	4.5167	0.4645	0.1028	-0.9887	99.62
2.47	2.49	0.0001	-4	4.9070	0.0540	0.0110	-1.9587	99.22

Table 3. Saturation of TOAS with W

(All working solutions pH 2.5 initial)

Initial working solns. (W g/l)	0.01M TOAS		0.02M TOAS		0.04M TOAS		0.08M TOAS	
	<u>(TOAS)</u>		<u>(TOAS)</u>		<u>(TOAS)</u>		<u>(TOAS)</u>	
	(W) <sub>o</sub> (M/l)	(W) <sub>o</sub>	(W) <sub>o</sub> (M/l)	(W) <sub>o</sub>	(W) <sub>o</sub> (M/l)	(W) <sub>o</sub>	(W) <sub>o</sub> (M/l)	(W) <sub>o</sub>
10	0.024	0.417	0.0515	0.3988	0.0573	0.698	0.0559	1.4311
20	0.024	0.417	0.04999	0.4001	0.1063	0.3763	0.1114	0.7181
40	0.0238	0.42	0.04939	0.4049	0.1044	0.3881	0.2151	0.3719

Table 4. Extraction of W with 10% D2EHP in benzene

Initial working soln.		X <sub>w</sub>	Y <sub>w</sub>	D <sub>w</sub>	% Mass balance
W (g/l)	pH <sub>equil.</sub>	(g/l)	(g/l)		
10	2.46	10.26	0.029	0.0026	102.88
20	2.34	20.128	0.045	0.0022	100.87
40	2.34	41.430	0.037	0.0009	103.67

Table 5. Extraction Isotherm of Mo with 0.1M TOAS in benzene

Initial working soln. Mo ( $\mu\text{g}/\text{ml}$ )	$\log(\text{Mo})_a$	$X_{\text{Mo}}$ $\mu\text{g}/\text{ml}$	$\log X_{\text{Mo}}$	$Y_{\text{Mo}}$ $\mu\text{g}/\text{ml}$	$\log Y_{\text{Mo}}$	$D_{\text{Mo}}$	$\log D_{\text{Mo}}$
5	0.6990	0.5	-0.301	4.5	0.65	9	0.95
10	1	0.67	-0.174	9.33	1.14	13.9	1.14
20	1.3010	1	0	19	1.28	19	1.28
50	1.6990	1.17	0.07	48.83	1.69	41.7	1.62
100	2	1.17	0.07	98.83	1.99	84.5	1.93
200	2.3010	1.34	0.13	198.66	2.30	148.3	2.17
400	2.6021	1.67	0.22	398.33	2.60	238.5	2.38
800	2.9031	2.16	0.33	797.84	2.90	369.4	2.57
1000	3	2.5	0.39	975.5	2.99	399	2.60
2000	3.3010	3	0.48	1997	3.29	665	2.82
5000	3.6990	7.6	0.88	4992.4	3.69	656.9	2.82
10,000	4	11.6	1.06	9988.4	3.99	861.1	2.94
20,000	4.3010	2500	3.39	17500	4.24	7	0.85

Table 6

Saturation of TOAS with Mo

(All working solution pH 3 initial)

Initial	0.01M TOAS		0.02M TOAS		0.04M TOAS		0.01M TOAS	
Working	-----		-----		-----		-----	
Solutions	(Mo)org.	(TOAS)	(Mo)org.	(TOAS)	(Mo)org.	(TOAS)	(Mo)org.	(TOAS)
(Mo g/l)	(M/l)	(Mo) org.	(M/l)	(Mo) org.	(M/l)	(Mo) org.	(M/l)	(Mo)org.
1	0.0104	0.96	0.0104	1.923	0.01042	3.839	0.01042	9.597
2.2	0.0224	0.446	0.0228	0.877	0.0229	1.747	0.0229	4.367
3.8	0.0249	0.402	0.0395	0.506	0.04145	0.965	0.0396	2.52
5.294	0.0291	0.34	0.0541	0.370	0.0551	0.726	0.0551	1.815
6.28	0.0262	0.382	0.0514	0.389	0.0654	0.611	0.0654	0.529
13.5					0.0843	9.474	0.1407	0.711
29							0.2287	0.437

Table 7 The effect of sulphate ions on the extraction of Mo with 0.1 M TOAS in benzene.

Aqueous Initial				X <sub>Mo</sub> (µg/ml)	Y <sub>Mo</sub> (µg/ml)	D <sub>Mo</sub>
Mo (g/l)	SO <sub>4</sub> (M/l)	pH before after				
1	0.1	2.00	1.60	0.69	999.31	1448.28
1	0.5	2.02	1.78	1.39	998.61	718.42
1	1.0	2.07	1.87	2.50	997.50	399
1	1.5	2.02	1.87	4.17	995.83	238.81
1	2.0	2.00	1.86	7.78	992.22	127.53

Table 8. pH effect on the extraction of Mo with TOAS

a) Aqueous 1 g Mo/l , organic 0.0125 M TOAS

pH		X <sub>Mo</sub> ( $\mu\text{g}/\text{ml}$ )	Y <sub>Mo</sub> ( $\mu\text{g}/\text{ml}$ )	D <sub>Mo</sub>
Before	After			
2.09	1.92	3.35	996.65	297.51
2.46	2.10	2.1	997.9	475.19
2.0	2.20	2.1	997.9	475.19
3.57	2.23	1.85	998.15	539.54
5.39	2.92	2.1	997.9	475.19
9.12	3.74	4.54	995.46	219.26
10.40	5.38	667	333	0.50

b) Aqueous 2.25 g Mo/l , organic 0.018 M TOAS

pH		X <sub>Mo</sub> ( $\mu\text{g}/\text{ml}$ )	Y <sub>Mo</sub> ( $\mu\text{g}/\text{ml}$ )	D <sub>Mo</sub>
Before	After			
0.8	0.8	275	1975	7.18
1.0	1.0	165	2160	13.09
1.2	1.2	70	2330	33.29
1.6	1.6	26	2299	88.42
1.76	1.76	18	2482	180
2.0	2.0	12.5	2487.5	199
2.36	2.10	9.5	2490.5	262.2
2.87	2.30	7.5	2442.5	325.7
3.08	2.38	9	2391	265.67
3.88	2.42	6	2394	399
4.10	2.45	7	2493	356.1
5.24	4.94	410	1790	4.37
5.42	5.14	900	1400	1.56

Table 9

Extraction isotherm of Mo with 0.1 M D2EHP in benzene

Aqueous: pH 2 initial

1 M/l  $(\text{NH}_4)_2\text{SO}_4$  background

Mo conc. 10 - 2000  $\mu\text{g}/\text{ml}$

---

X Mo ( $\mu\text{g}/\text{ml}$ )	log X <sub>Mo</sub>	Y <sub>Mo</sub> ( $\mu\text{g}/\text{ml}$ )	log Y <sub>Mo</sub>
1	0	9	0.95
2	0.30	18	1.25
5	0.69	45	1.65
10	1	90	1.95
40	1.60	160	2.20
63	1.80	337	2.52
163	2.21	637	2.80
384	2.58	616	2.79
1275	3.11	725	2.86

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Table 10. Extn. Isotherm of Mo with 10% D2EHP in benzene

Mo initial $\mu\text{g/ml}$	pH <sub>equil.</sub>	X <sub>Mo</sub> $\mu\text{g/ml}$	Y <sub>Mo</sub> $\mu\text{g/ml}$	D <sub>Mo</sub>
1310	2.12	220	1048	4.76
2400	2.62	525	1875	3.57
4800	2.45	1900	2900	1.53
6100	2.38	3000	3100	1.03

Table 11. The effect of sulphate ions on the extraction of Mo  
with 0.1M D2EHP in benzene

Aqueous initial		pH		X <sub>Mo</sub>	Y <sub>Mo</sub>	D <sub>Mo</sub>
Mo( $\text{g/l}$ )	SO <sub>4</sub> ( $\text{M/l}$ )	Before	After	( $\mu\text{g/ml}$ )	( $\mu\text{g/ml}$ )	
1	0.1	2.0	2.0	400	600	1.5
1	0.5	"	"	470	530	1.1
1	1.0	"	"	510	490	0.96
1	1.5	"	"	520	480	0.92
1	2.0	"	"	515	485	0.94

Table 12

The effect of pH on the extraction of Mo

(Aqueous 1 g/1 Mo)

pH equil.	0.3 M D2EHP	
	$D_{Mo}$	$\log D_{Mo}$
0.68	6.69	0.825
1.14	18.20	1.260
2.24	57.82	1.762
2.80	34.71	1.540
3.40	11.50	1.060
4.02	1	0

(Aqueous 1 g/1 Mo)

pH equil.	0.5 M D2EHP	
	$D_{Mo}$	$\log D_{Mo}$
0.68	19	1.279
1.14	32.33	1.509
2.24	124.0	2.093
3.12	65.7	1.818

Table 13 The effect of pH on Mo extraction with 0.1M D2EHP  
(Ammonium paramolybdate)

<u>pH</u> equil	<u>(Aqueous <math>\lg/1</math> Mo)</u> $D_{Mo}$
1	1.5
2	1.85
3.40	0.357
3.88	0.141
4.46	0.066

Table 14. pH change with D2EHP and TOAS

a) pH change in the extraction of various concentrations of molybdenum with initial pH2 with various concentrations of D2EHP (positive pH change)

WORKING SOLN		0.1M D2EHP			0.2M D2EHP		
$M_o$ (M/l)	pH <sub>init</sub>	pH <sub>eq</sub>	Δ pH	$\frac{\Delta pH}{(M_o)_{init}}$	pH <sub>eq</sub>	Δ pH	$\frac{\Delta pH}{(M_o)_{init}}$
0.0141	2.16	2.24	0.08	5.67	2.31	0.15	10.64
0.0283	2.16	2.28	0.12	4.24	2.40	0.24	8.48
0.0425	2.20	2.30	0.10	2.35	2.44	0.24	5.65
0.0550	2.10	2.18	0.08	1.45	2.29	0.19	3.45
0.0730	2.08	2.14	0.06	0.82	2.24	0.16	2.19
0.1695	2.18	2.23	0.45	0.30	2.37	0.19	1.13
0.2680	2.16	2.18	0.02	0.09	2.25	0.09	0.34

WORKING SOLN		0.4M D2EHP			1M D2EHP		
$M_o$ (M/l)	pH <sub>init</sub>	pH <sub>eq</sub>	Δ pH	$\frac{\Delta pH}{(M_o)_{init}}$	pH <sub>eq</sub>	Δ pH	$\frac{\Delta pH}{(M_o)_{init}}$
0.0141	2.16	2.36	0.20	14.18	2.35	0.19	13.48
0.0283	2.16	2.48	0.32	11.31	2.52	0.36	12.72
0.0425	2.20	2.66	0.46	10.82	2.68	0.48	11.29
0.0550	2.10	2.50	0.40	7.27	2.56	0.46	8.76
0.0730	2.08	2.46	0.38	5.21	2.60	0.52	7.12
0.1695	2.18	2.76	0.58	3.46	3.39	1.21	7.22
0.2680	2.16	2.53	0.37	1.38	3.56	1.40	5.22

b) pH change in the extraction of various concentrations of molybdenum with initial pH3 with various concentrations of TOAS (negative pH change)

WORKING SOLN <sub>init</sub>		0.01M TOAS			0.02M TOAS		
Mo (M/l)	pH <sub>init</sub>	pH <sub>eq</sub>	ΔpH	$\frac{\Delta pH}{(Mo)_{init}}$	pH <sub>eq</sub>	ΔpH	$\frac{\Delta pH}{(Mo)_{init}}$
0.0104	3.00	2.34	-0.66	-63.46	2.12	-0.88	-84.62
0.0229	3.18	2.36	-0.82	-35.81	2.24	-0.94	-41.05
0.0396	3.04	2.41	-0.63	-15.91	2.24	-0.80	-20.20
0.0552	3.02	2.48	-0.54	-8.24	2.22	-0.80	-14.49
0.0655	2.98	2.46	-0.52	-7.94	2.23	-0.75	-11.45
0.14017	2.89	2.54	-0.35	-2.49	2.34	-0.55	-3.91
0.3023	3.06	2.77	-0.29	-0.96	2.57	-0.49	-1.62

WORKING SOLN <sub>init</sub>		0.04M TOAS			0.1M TOAS		
Mo (M/l)	pH <sub>init</sub>	pH <sub>eq</sub>	ΔpH	$\frac{\Delta pH}{(Mo)_{init}}$	pH <sub>eq</sub>	ΔpH	$\frac{\Delta pH}{(Mo)_{init}}$
0.0104	3.00	1.96	-1.04	-100	1.24	-1.26	-121.15
0.0229	3.18	2.02	-1.16	-50.66	1.76	-1.42	-62
0.0396	3.04	2.06	-0.98	-24.75	1.77	-1.27	-32
0.0552	3.02	2.14	-0.88	-15.94	1.80	-1.22	-22.1
0.0655	2.98	2.16	-0.82	-12.12	1.81	-1.17	-17.8
0.1407	2.89	2.12	-0.77	-5.49	2.02	-0.89	-6.18
0.3023	3.06	2.31	-0.75	-2.48	1.98	-1.08	-3.57

Table 15.  $\log D_{2EHP}$  v  $\log D_{Mo}$

(All working solutions initial pH2)

$\log (D_{2EHP})$	$\log D_{Mo}$					
	Mo 2.714g/l	Mo 4.075g/l	Mo 5.295g/l	Mo 7 g/l	Mo 16.071g/l	Mo 25.714g/l
-1.0	-0.2366	-0.4089	-0.4949	-0.5850	-0.8239	-1.2218
-0.6990	0.4346	0.1072	0	-0.1427	-0.4437	-0.6990
-0.3979	(1.9685)	1.0212	0.8759	0.6201	-0.0969	-0.3010
0	2.1492	1.9232	2.4378	2.5611	0.5441	0.2227

Table 16.  $\log D_{2EHP}$  v  $\log D_{Mo}$

(All working solutions initial pH3)

$\log (D_{2EHP})$	$\log D_{Mo}$				
	Mo 2.680 g/l	Mo 3.925	Mo 5.2 g/l	Mo 6.857g/l	Mo 15.714 g/l
-1.0	-0.6778	0.7212	-0.8239	-0.8386	(-0.8928)
-0.6990	-0.3768	-0.4318	-0.4949	-0.5850	-0.7959
-0.3979	0.1523	-0.0809	-0.1367	-0.2596	-0.4815
0	(2.0492)	1.238	1.009	0.7324	0.1614

Table 17 The effects of initial pH and concentrations of molybdenum on the  $D_{Mo}$  with D2EHP.

WORKING SOLUTION (initial)		$D_{Mo}$		
Mo ( $g/l$ )	pH	0.1M D2EHP	0.2M D2EHP	0.4M D2EHP
1.357	2.16	2.16	4.07	-
2.714	2.16	0.58	2.72	93
4.075	2.20	0.39	1.28	10.49
5.275	2.10	0.32	1	7.21
7.000	2.08	0.26	0.72	4.17
16.071	2.18	0.15	0.36	0.80
1.286	2.92	0.64	1.37	31.97
2.680	3.23	0.21	0.42	1.42
3.925	3.10	0.19	0.37	0.83
5.200	3.06	0.15	0.32	0.73
6.875	3.00	0.145	0.26	0.55
15.714	2.85	0.128	0.16	0.33

Table 18. Saturation of D2EHP with Mo  
 (All working solutions pH 2 initial)

Initial working solutions (Mo g/l)	0.1M D2EHP		0.2M D2EHP	
	(Mo) <sub>org</sub>	$\frac{(D2EHP)}{(Mo)_{org}}$	(Mo) <sub>org</sub>	$\frac{(D2EHP)}{(Mo)_{org}}$
	(M/l)	(M/l)	(M/l)	(M/l)
1.357	0.0097	10.31	0.0114	17.54
2.714	0.0104	9.62	0.0207	9.66
4.075	0.0119	8.40	0.0239	8.37
5.275	0.0133	7.52	0.0274	7.30
7	0.0149	6.71	0.0305	6.56
16.071	0.0223	4.48	0.0447	4.47
25.7.14	0.0149	6.71	0.0447	4.47

Initial working solutions (Mo g/l)	0.4M D2EHP		1M D2EHP	
	(Mo) <sub>org</sub>	$\frac{(D2EHP)}{(Mo)_{org}}$	(Mo) <sub>org</sub>	$\frac{(D2EHP)}{(Mo)_{org}}$
	(M/l)	(M/l)	(M/l)	(M/l)
1.357	0.0115	34.78	0.0118	84.75
2.714	0.0279	14.34	0.0281	35.59
4.075	0.0388	10.31	0.0419	23.87
5.275	0.0483	8.28	0.0548	18.25
7	0.0588	6.80	0.0728	13.74
16.071	0.0745	5.37	0.1303	7.67
25.714	0.0893	4.48	0.1675	5.97



Table 19. Saturation of D2EHP with Mo

(All working solutions pH3 initial)

Initial working solutions (Mo g/l)	0.1M D2EHP		0.2M D2EHP	
	(Mo) <sub>org</sub>	$\frac{(D2EHP)}{(Mo)_{org}}$	(Mo) <sub>org</sub>	$\frac{(D2EHP)}{(Mo)_{org}}$
	(M/l)		(M/l)	
1.286	0.0052	19.23	0.0077	25.84
2.680	0.0049	20.59	0.0083	24.21
3.925	0.0067	15.02	0.0111	18.02
5.2	0.0070	14.21	0.0130	15.38
6.857	0.0082	12.21	0.0149	13.42
15.714	0.0186	5.38	0.0223	8.95

Initial working solutions (Mo g/l)	0.4M D2EHP		1 M D2EHP	
	(Mo) <sub>org</sub>	$\frac{(D2EHP)}{(Mo)_{org}}$	(Mo) <sub>org</sub>	$\frac{(D2EHP)}{(Mo)_{org}}$
	(M/l)		(M/l)	
1.286	0.0130	30.77	0.0131	76.34
2.680	0.0164	24.39	0.0277	36.17
3.925	0.0186	21.51	0.0387	25.85
5.2	0.0229	17.44	0.0494	20.26
6.857	0.0253	15.81	0.0603	16.58
15.714	0.0410	9.768	0.0968	10.33

Table 20. Extraction of molybdenum with D2EHP in the presence of tungsten.

Aqueous Mo  $1g/l$  throughout  
W 0, 10, 20, 40  $g/l$   
organic 0.1, 0.29 M D2EHP

(A) % Extraction of Mo in the presence of W

Working soln. W/Mo	% Extraction of Mo	
	0.1M D2EHP	0.29M D2EHP
0	48.50	80
10	18.40	45
20	9.80	28.6
40	3.60	13.6

(B) Effect of W presence on  $D_{Mo}$

Working soln. W/Mo	$D_{Mo}$	
	0.1M D2EHP	0.29M D2EHP
0	0.924	4.764
10	0.229	0.8182
20	0.123	0.4005
40	0.040	0.1574

Table 21. Extn<sup>of Mo</sup> with 10% D2EHP at various concentrations of tungsten background.

Initial Working Soln.			$X_{\text{Mo}}$	$Y_{\text{Mo}}$	$Y_{\text{Mo}}$	$\frac{(\text{D2EHP})}{(\text{Mo})_{\text{org}}}$
Mo (g/l)	W g/l	pH <sub>equil</sub>	(g/l)	(g/l)	(M/l)	
1.31	0	2.12	0.220	1.048	0.01092	26.56
2.4	0	2.62	0.525	1.875	0.01954	14.84
4.8	0	2.45	1.900	2.900	0.03023	9.59
6.1	0	2.38	3.000	3.100	0.03231	8.98
1	10	1.28	0.550	0.450	0.00469	61.83
2	10	1.80	1.128	0.872	0.00909	31.90
10	10	2.60	7.780	2.220	0.02314	12.53
1	20	1.47	0.714	0.286	0.00298	97.31
2	20	2.44	1.376	0.624	0.00650	44.62
5	20	2.50	3.560	1.440	0.01501	19.32
10	20	2.50	8	2	0.02084	13.92
1	40	2.52	0.864	0.136	0.00142	204.23
2	40	2.48	1.6	0.4	0.00417	69.54
5	40	2.53	4.570	1.430	0.01490	19.46

Table 22. Extraction of W and Mo with 10% D2EHP

Initial Working Soln.				$X_W$	$Y_W$	$X_{Mo}$	$Y_{Mo}$	% Mass Balance of W	$D_W$	$D_{Mo}$	$\beta$ $\left(\frac{D_{Mo}}{D_W}\right)$
Mo (g/l)	W	W/Mo	pH <sub>eq</sub>								
0	10		2.46	10.26	0.027			102.88	0.0026		
1	10	10	1.28	10.23	0.077	0.55	0.45	103.27	0.0075	0.8182	108
2	10	5	1.80	9.799	0.092	1.128	0.872	98.91	0.0094	0.7930	82
10	10	1	4.18	10.082	0.0038	9.624	0.376	100.86	0.0004	0.0391	103
10	10	1	2.60	10.092	0.041	7.780	2.220	101.33	0.0041	0.2853	70.2
0	20		2.34	20.128	0.045			100.87	0.0022		
1	20	20	1.47	20.997	0.0462	0.714	0.286	105.10	0.0022	0.4005	182
2	20	10	2.44	20.196	0.033	1.376	0.624	101.14	0.0016	0.4535	278
5	20	4	5.17	20.459	0.0051	4.900	0.010	102.32	0.0002	0.0204	82
5	20	4	2.50	20.148	0.045	3.560	1.440	100.96	0.0022	0.4045	184
10	20	2	2.50	19.564	0.046	8.000	2.000	98.05	0.0023	0.250	106
0	40		2.34	41.430	0.037			103.67	0.0009		
1	40	40	2.52	40.172	0.0304	0.864	0.136	100.51	0.0007	0.1574	208
2	40	20	2.48	39.350	0.0299	1.6	0.40	98.45	0.0007	0.250	329
5	40	8	2.53	38.564	0.053	4.570	1.430	96.39	0.0013	0.3129	239

Table 23. The effect of W background on the  $D_{Mo}$  with 10% D2EHP

<u>Aqueous initial</u>		
Mo (g/l)	W (g/l)	$D_{Mo}$
1.31	0	4.76
2.4	0	3.57
4.8	0	1.53
6.1	0	1.03
1	10	0.8182
2	10	0.7730
10	10	0.2853
1	20	0.4005
2	20	0.4535
5	20	0.4045
10	20	0.250
1	40	0.1574
2	40	0.250
5	40	0.3129
10	40	0.2853

Table 24. The effect of W concentration (40 g/l) on  $D_{Mo}$  with 10% D2EHP

Aqueous initial		
Mo (g/l)	W (g/l)	$D_{Mo}$
0.460	40	0.068
0.500	40	0.087
0.560	40	0.110
0.62	40	0.125
0.68	40	0.145
0.75	40	0.147
0.84	40	0.160
1.0	40	0.150
2.0	40	0.250
5	40	0.3129

Table 25. The effect of tungsten concentration (40 g/l) on the extraction % of Mo with 10% D2EHP.

Aqueous initial

Mo (g/l)	W (g/l)	W/Mo ratio	% Extraction
0.460	40	86.96	6.52
0.500	40	80	8.00
0.560	40	71.43	9.82
0.620	40	64.52	11.29
0.68	40	58.82	13.24
0.75	40	53.33	13.33
0.84	40	47.62	14.29
1	40	40	12.5
2	40	20	20
5	40	8	28.6

Aqueous initial

Mo (g/l)	W (g/l)	F <sup>-</sup> M/l	W/Mo ratio	% Extn.
0.59	40	0.01	67.8	5.08
0.62	40	0.01	64.5	4.84
0.67	40	0.01	59.7	5.97
0.72	40	0.01	55.6	8.33
0.74	40	0.01	54	6.76
0.84	40	0.01	47.6	8.33
0.92	40	0.01	43.5	10.87
1.02	40	0.01	40	12

Table 26. Successive batchwise extraction of 1 g/1 Mo (40g W/1 background) with 10% D2EHP.

Initial Mo conc. (g/1)	pH		X <sub>Mo</sub> (g/1)	Y <sub>Mo</sub> (g/1)	D <sub>Mo</sub>	% Mass balance	Y <sub>Mo</sub> (Mol/1)	$\frac{(D2EHP)}{(Y_{Mo})}$
	Before	After						
1	2.50	2.50	0.840	0.125	0.15	96.5	0.00130	223
0.84	2.50	2.54	0.750	0.120	0.16	103.57	0.00125	232
0.75	2.54	2.54	0.680	0.100	0.147	104.00	0.00104	278.85
0.68	2.54	2.56	0.620	0.090	0.145	104.41	0.00094	309.17
0.62	2.56	2.60	0.560	0.070	0.125	101.61	0.00073	397.26
0.56	2.56	2.62	0.500	0.055	0.11	99.11	0.00057	508.77
0.50	2.62	2.66	0.460	0.040	0.087	100.00	0.00042	695.44
0.46	2.66	2.70	0.440	0.030	0.068	102.17	0.00031	935.48

Table 27. Successive batchwise extraction of 1 g/1 Mo (40g W/1) and 0.01 MF<sup>-</sup> in working solution) with 10% D2EHP.

Initial Mo conc. (g/1)	pH		X <sub>Mo</sub> (g/1)	Y <sub>Mo</sub> (g/1)	D <sub>Mo</sub>	% Mass balance	Y <sub>Mo</sub> (Mol/1)	$\frac{(D2EHP)}{(Y_{Mo})}$
	Before	After						
1.02	2.70	2.70	0.920	0.120	0.13	101.96	0.001251	231.82
0.92	2.70	2.72	0.840	0.100	0.12	102.17	0.001042	278.31
0.84	2.72	2.74	0.740	0.070	0.095	96.43	0.000730	397.26
0.74	2.74	2.78	0.720	0.050	0.07	104.05	0.000521	556.62
0.72	2.78	2.82	0.670	0.060	0.09	101.39	0.000625	464
0.67	2.82	2.88	0.62	0.040	0.065	98.51	0.000417	695.44
0.62	2.88	2.92	0.59	0.030	0.05	100.00	0.000313	926.52
0.59	2.92	2.96	0.56	0.030	0.05	100.00	0.000313	926.52



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