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with an Alkyl Amine**

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Abstract

The results of the extraction behaviour of molybdenum in aqueous sulfuric acid solutions with solutions of an alkyl amine (amberlite LA-2) in kerosene under various pH and in presence of various percentage of 1-octanol has been reported. The concentration of molybdenum employed was high enough to precipitate it partially during extraction as an amine-molybdenum complex. The maximum extraction coefficient was found to lie between pH 1.5-2.5. Presence of 1-octanol increased the extraction coefficient of molybdenum by increasing the solubility of the amine-molybdenum complex in the organic phase without changing the pH at the maximum extraction.

Key words:

pH, effect of,

modifier-concentration, effect of,

solvent extraction of molybdenum,

molybdenum, solvent extraction of,

alkyl amine, solvent extraction of molybdenum with,

effect of pH and modifier-concentration,

## Introduction

Molybdenum is often found in uranium-bearing ores. A part of this molybdenum accompanies uranium during acid or alkaline leaching. Then separation of uranium from molybdenum becomes necessary.

Extraction behaviour of molybdenum is very similar to that of uranium in the amine extraction systems. The presence of molybdenum thus complicates the extraction of uranium with amines.

Molybdenum is strongly extracted by most of the amines and it cannot be removed effectively by the conventional chloride strip solution (1) or controlled pH stripping (2). So the stripping of molybdenum with an alkali solution becomes necessary after the uranium and molybdenum pregnant amine is stripped of its uranium content with a chloride strip. If the molybdenum content of the feed liquor exceeds about 0.03 g of molybdenum per liter, then the organic phase will continue to increase in molybdenum content to its maximum level of tolerance after which a precipitation of complex amine heteropolymolybdate is likely. This tolerance level varies from amine to amine. Usually the tolerance level is higher for the secondary amines and poor for tertiary amines (3) (except trilaurylamine). The tendency for precipitation is influenced by amine-diluent choice, molybdenum concentration, the presence of phosphate and vanadium (V), and the choice of stripping method. The tendency to precipitation is usually more pronounced when the stripping agent is chloride solution than any other stripping agent.

With amberlite LA-2 as the extraction reagent precipitation was found to occur at molybdenum loadings approaching 3 g/liter in unmodified kerosene. But this precipitation did not occur when 2 vol. % tridecanol was added to the solvent. Precipitation with some amine loss occurred in the regeneration step at molybdenum loading of  $\sim$  1.2 g/liter (3).

Arnold et al. (3) have also reported the compatibility of many other amines with molybdenum. In continuous counter current tests with amine S-24 and amberlite LA-1, no precipitation was found to occur with liquors containing the following substance in grams per liter: 0.3 U, 0.3 Mo, 15 Fe (III), 5 Al, 10 PO<sub>4</sub> and 160 SO<sub>4</sub> at pH 1.

Crabtree et al. (4) claimed that molybdyl molybdenum, rather than molybdate molybdenum was primarily responsible for this precipitation. When sodium chlorate is added to the sodium chloride stripping solution it was found that the formation of precipitate was prevented and molybdenum removal during stripping was improved. The tendency of molybdenum to form precipitate can also be reduced with other oxidising agents such as ferric sulphate and hydrogen peroxide. But this method could not resolve the problem as the molybdenum concentration in the recycling organic phase continued to increase progressively with the cycle of operation.

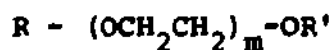
House et al. (5) found that in the extraction of molybdenum with alamine-336 the amine-molybdenum precipitation may be prevented by scrubbing the solvent with a dilute solution of sulfide or sodium hydrogen sulfide prior to the chloride stripping. Drobnick et al. (6) also described a process of extraction of uranium and molybdenum in which the precipitation of molybdenum as amine-molybdenum complex was prevented by nascent hydrogen, hydrogen sulfide, sodium hydrosulfide, sodium thiosulfate, the alkalimetal sulfides and other reducing agents. They found that the interfacial solids do not appear in the amine extractant even when the molybdenum content is very high. Control of the valence state of the molybdenum through the use of reducing agent increases the tolerance level of tertiary amines for molybdenum to a point where the tolerance level is equal to or greater than that of the secondary amines. The molybdenum exists in an equilibrium involving various valence states from molybdenum to the molybdenum cation. Drobnick et al. (6) believed that it requires a

considerable amount of driving force to convert all the molyb-  
dyl ion to a higher oxidation state (a 100 % equilibrium shift)  
as there exists only one such higher oxidation state (molybdate).  
On the other hand a lesser amount of driving force would be re-  
quired to substantially convert molybdyl ion to the lower va-  
lence state as they can move to more than one valence state, when  
a reducing agent is added.

Lewis et al. (1) found that aliquat-336, a quarternary ammonium  
salt, can be employed to reextract the molybdenum from the aque-  
ous sodium carbonate scrub solution of the bleed stream of the  
recycling amine extractant phase at an economically attractive  
cost. This reextraction can effectively be done at about pH 5.

Ableson et al. (7) found that the molybdenum may be stripped from  
uranium barren organic phase - obtained from the uranium strip-  
ping process - with a stripping solution containing a small a-  
mount of sodium carbonate (2-5 % of the alkali requirement) in  
ammonium hydroxide solution at pH 8-8.5. Molybdenum from this  
strip liquor can then be precipitated on acidification with sul-  
furic or hydrochloric acid in the presence of phosphoric acid, to  
a pH 1-1.5. The molybdenum is precipitated as ammonium phospho-  
molybdate. The mother liquor obtained after the precipitation of  
molybdenum can then be used for stripping uranium from the pri-  
mary leach liquor.

Hart (8) claimed that the formation of solid molybdenum-amine  
complex during solvent extraction of molybdenum with amine can  
be minimised by the addition of an ether of the formula.



where  $m = 1$  or  $2$ ,  $R = 4$  to  $6$  carbon alkyl radical, and  $R' = \text{H}$  or  
 $4$  to  $6$  carbon alkyl radical.

Floh et al. (9) studied the extraction behaviour of uranium, molybdenum and vanadium with alamine-336 at various sulfuric acid concentrations. Behaviour of these elements - individually, in binary and in ternary combinations - were studied, in order to determine the optimum condition of their extraction. They found that amongst these three elements, the distribution coefficient of both uranium (VI) and vanadium (V) increases and that of the molybdenum decreases with the increase in concentration of the other two, up to a certain concentration limit. The extraction of these elements from ternary solutions behaves more or less in the same way as they do when extracted from their binary solutions.

Many other workers have also studied the extraction behaviour of molybdenum with amine extractions (10-19).

The present article gives the extraction behaviour of molybdenum in sulfuric acid solution with amberlite LA-2 at comparatively high molybdenum loadings.

### Experimental

Amberlite LA-2 was obtained from SERVA (an agent of Rohm and Haas Co., USA) and used as received. 1-octanol used was procured from Fluka and was of laboratory reagent grade. Sodium molybdate ( $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ ) and other inorganic reagents used were either pure or AnalaR grade.

Sodium molybdate solutions of various concentrations together with 0.1 M amberlite LA-2 solution in kerosene were taken in a separating funnel. The ratio of aqueous to organic phase taken was always of 1:5 v/v. In some experiments the organic phase also contained various percentages of 1-octanol. The separating funnel containing the sample was then immersed in a thermostatic water bath.

and then shaken vigorously for 50 minutes at  $30 \pm 0.1^{\circ}\text{C}$ . The sample was then kept standing in the same water bath at the same temperature till the two phase distinctly separated out from each other. The aqueous phase was then taken out of the funnel and the concentration of Mo in the two phases were measured separately with a PHILIPS PW 1410 X-ray fluorescence spectrometer. The pH of the aqueous phase after extraction of Mo was measured with a glass electrode (Metrohm) with the help of an ORION RESEARCH model 701 A/digital IONALYZER.

Due to the high molybdenum concentration a third phase of amine molybdenum complex appeared during the extraction in most of the samples. This phase was separated out and rejected. In the following section a mention is made about the cases where the third phase did not appear.

## Results and discussion

### Effect of pH

Fig. 1 shows the dependence of the extraction coefficient on the pH of two sets of samples at  $30^{\circ}\text{C}$ . The initial molybdenum concentration of the 1st and the 2nd set of samples were 1 g/liter and 0.25 g/liter respectively. The maximum extraction coefficient was found to lie between pH 1.5-2.5. Good separation of the two phases were possible only when the final pH of the aqueous phase was below 1.2. Above this pH some amount of emulsification of one phase into the other restricted a good separation.



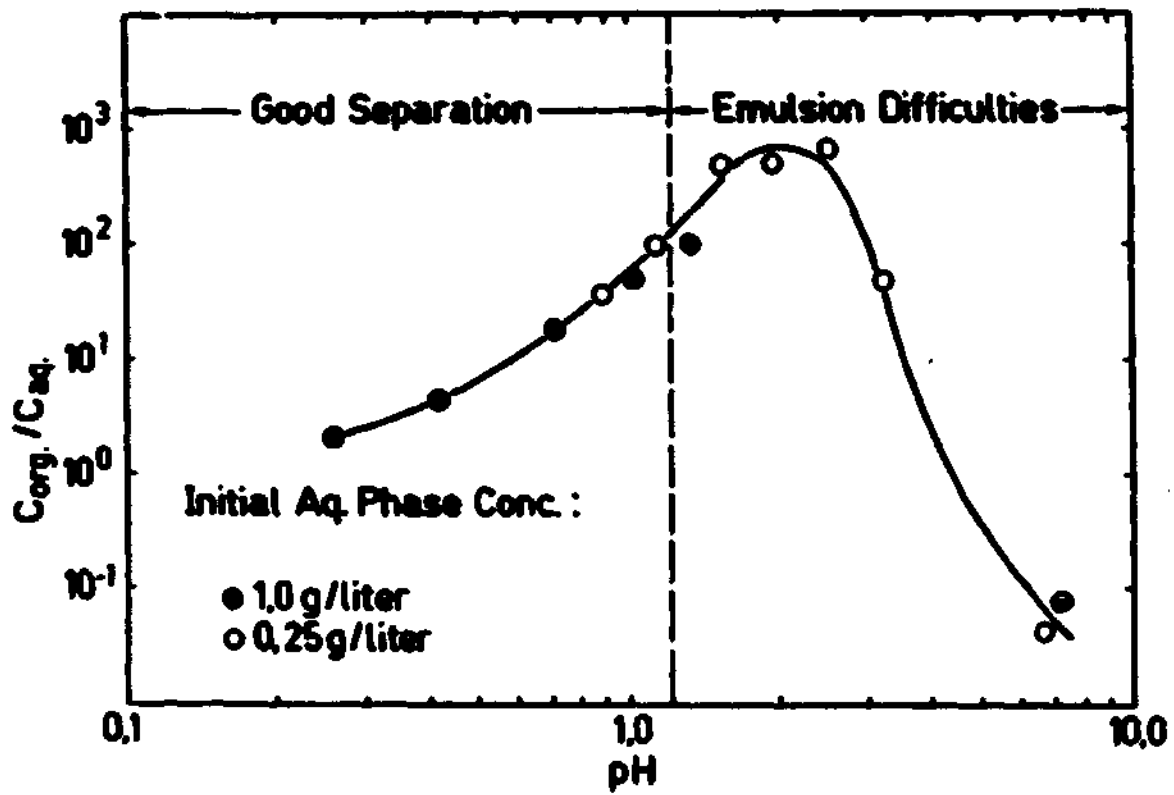
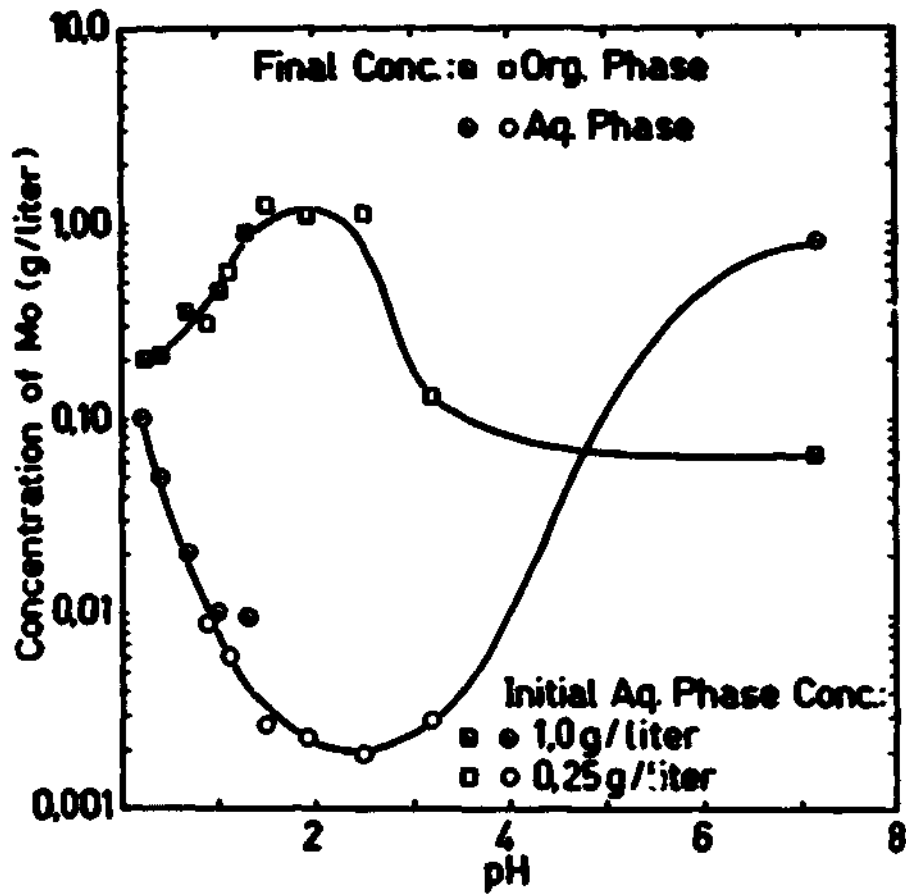


Fig 1 . Effect of pH on the extration coefficient of Mo.



**Fig. 2** Effect of pH on the Mo loading capacity of the org. phase and the conc. of Mo in aq. phase, in presence of org. phase saturated with Mo.

In Fig. 2 the concentration of Mo in aqueous and organic phase were plotted against the pH of the aqueous phase. During the contacting of the two phases a viscous third phase was found to appear with each sample of this experiment. So the curve in Fig. 2 showing the concentration of Mo in the organic phase represents the maximum Mo holding capacity of 0.1 M amberlite LA-2 solution at 30°C. The nature of the curves in Fig. 1 and 2 seems to be independent of the initial concentration of molybdenum in the aqueous phase. At any particular pH, a higher initial molybdenum concentration in the aqueous phase drove a greater amount of molybdenum in the third phase keeping its concentration in the 1st and 2nd phase more or less unchanged. This seems to indicate that in the presence of this third phase the normal organic phase is saturated with the amine-molybdenum complex. The third phase is probably a viscous precipitate of an amine-molybdenum complex (3, 4, 14, 15, 16).

#### Effect of modifier

Fig. 3 shows the dependence of the extraction coefficient on the percentage of 1-octanol in the organic phase. Two sets of samples were used for this experiment. The initial molybdenum concentration of the aqueous phase of both the set was approximately 1 g/liter. The initial sulfuric acid concentration of aqueous phase of one set was 0.2 N and that of the other 0.036 N. The extraction coefficients of both sets were at first found to increase, reaching a maximum at about 1% 1-octanol and then appear to decrease with the increase of the concentration of this alcohol. This was due to the fact that an increase in alcohol concentration in organic phase to more than 1% dissolved the third phase completely transferring most of the molybdenum to the organic phase. For this reason a further increase of 1-octanol concentration could not increase the molybdenum concentration in this phase any further, whereas the concentration in the aqueous phase continued to increase resulting a decrease in the extraction coef-

ficient value. This would appear clear from Fig. 4, where the concentration of molybdenum in the aqueous and organic phase in equilibrium have been plotted against the percentage of 1-octanol present in the organic phase. In this figure one can see that above 1% 1-octanol concentration the 1:5 organic: aqueous ratio of the extraction system concentrated 1 g/liter of molybdenum in the aqueous phase into 5 g/liter in the organic phase.

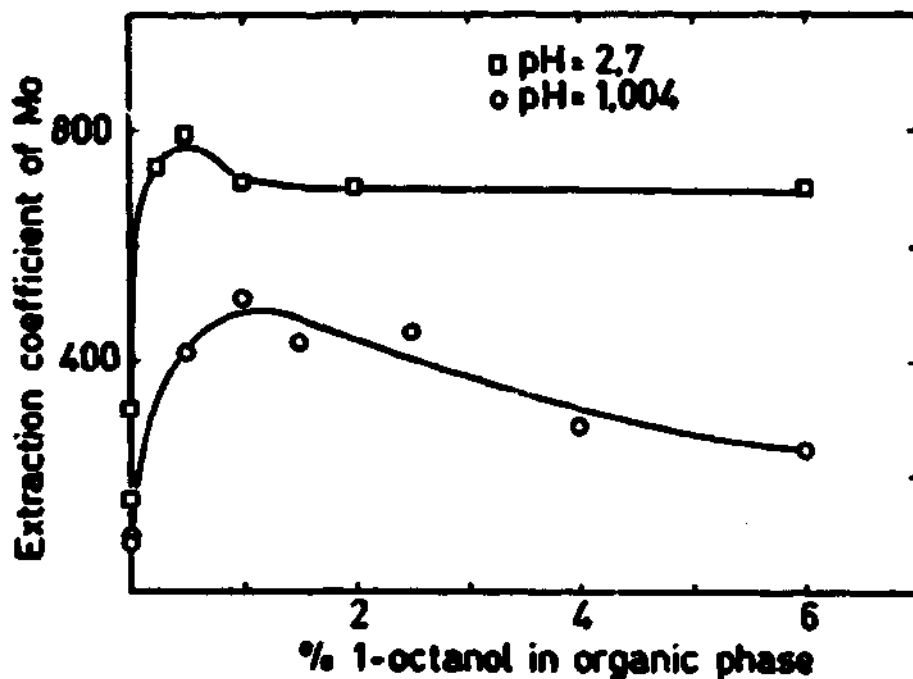
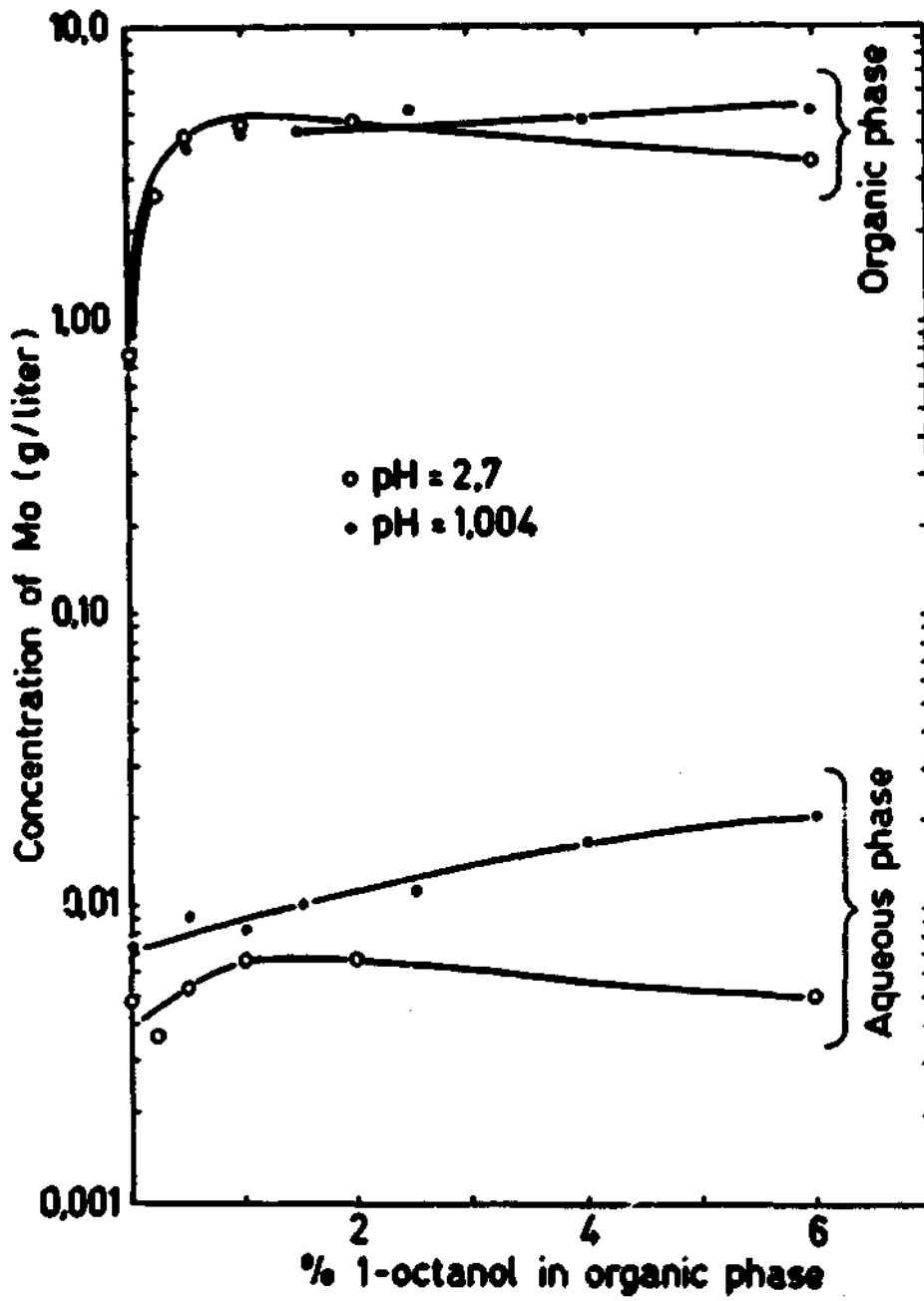


Fig. 3 Effect of 1-octanol on the extraction coefficient of Mo.

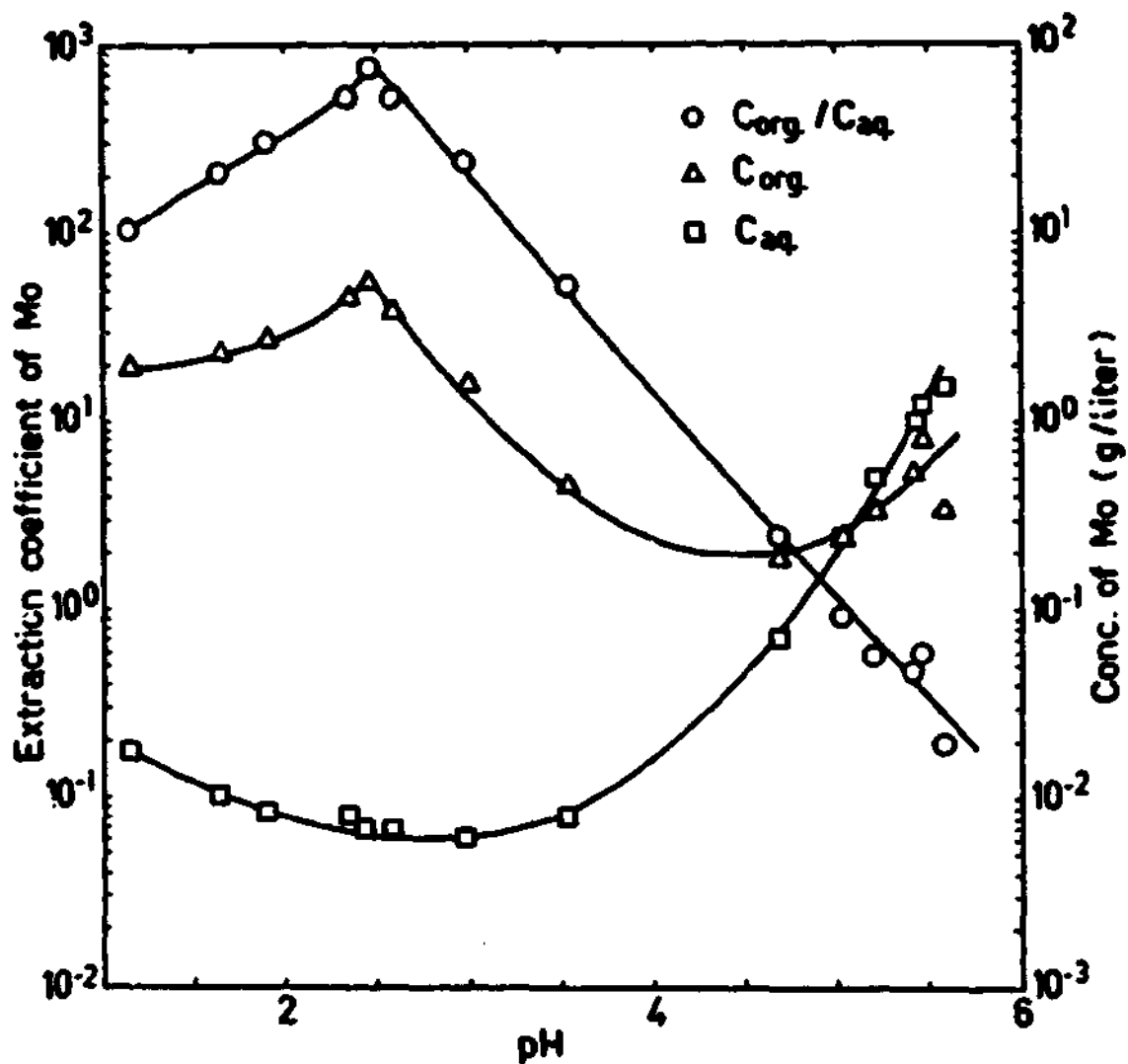


**Fig. 4** Effect of 1-octanol on the conc. of Mo in organic and aqueous phase.

Effect of pH in presence of 1-octanol

Fig. 5 shows the dependence of the extraction behaviour of molybdenum on the pH when the organic phase contains 0.25% of 1-octanol as modifier. In this experiment the initial concentration of molybdenum in aqueous phase was 2 g/liter.

Comparing the curves of Fig. 5 with those of Fig. 1 and 2 it appears that 1-octanol increases the extraction coefficient of molybdenum by increasing the solubility of the amine-molybdenum complex in the organic phase without shifting the position of the peak of the extraction coefficient curve with respect to pH.



**Fig. 5** Effect of pH on the extraction coefficient of Mo and the distribution of Mo between the organic and the aqueous phase when the organic phase contains 0.25% 1-octanol.

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