

SOLVENT EXTRACTION STUDIES OF INDIUM

IV. Primene JM-T Extraction in Presence of Malonic Acid

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ABSTRACT

Solvent extraction of indium from malonic acid medium by Primene JM-T has been studied. The extraction has been studied as a function of pH and concentrations of malonic acid and sodium malonate. The nature of the acid-amine complex has been established by chemical analysis and by the application of the method of Hogfeldt and Fredlund. The equilibrium constant for the reaction has also been calculated. The nature of the indium complexes getting extracted has also been discussed.

INTRODUCTION

WORK on long chain amines has generally been confined to strong mineral acids and the extraction of metals from weak acids has received less attention.¹ Several acids form complexes with metals which are extracted by amines. With this in view, the solvent extraction of indium from different organic acids² has been taken up for study. The extraction of indium from malonic acid medium by Primene JM-T is reported here.

EXPERIMENTAL

Indium was obtained as In¹¹⁴ from Isotope Division, B.A.R.C. A mixture of aliphatic primary amines Primene JM-T (Rohm and Haas Co.) was purified by distilling twice *in vacuo* and the middle fraction was used in the present studies. Solutions (usually 1% v/v) of the amine prepared in carbon tetrachloride (B.D.H., AnalaR) were standardised by titration with perchloric acid (E. Merck, G.R.) in glacial acetic acid (B.D.H., AnalaR).

Malonic acid (Riedel-De Haen Ag Seelze, Hannover) was standardised by titration with standard sodium hydroxide. Sodium malonate was prepared by neutralising malonic acid and sodium hydroxide potentiometrically.

Calculated amounts of indium, malonic acid, sodium malonate and water were added to make up to 15 ml. This was equilibrated with 15 ml of the organic phase in a mechanical shaker at $30 \pm 1^\circ \text{C}$ for about eight hours. The two phases were allowed to stand for sufficient time to effect complete phase-separation. The aqueous phase was generally turbid when the concentration of malonic acid exceeded 0.01 M. The mixture, in such a case, was centrifuged till the phases were clear. Studies of the aqueous phase with and without centrifugation indicated the apparent third phase formation to be due to the presence of amine salt in the aqueous phase.

The pH of the aqueous phase was measured. Malonic acid in the aqueous phase was determined by titration with sodium hydroxide using phenolphthalein as indicator. The amine and the malonic acid associated with the amine in the aqueous phase were estimated by the addition of a known excess of sodium hydroxide. The amine liberated by the alkali was extracted with carbon tetrachloride. Both the unreacted alkali in the aqueous phase and the amine in the organic phase were estimated by titration. Sodium hydroxide was titrated against standard acid. The amine was estimated by titration with perchloric acid in glacial acetic acid. Perchloric acid was standardised against potassium hydrogen phthalate in glacial acetic acid using methyl violet as indicator.

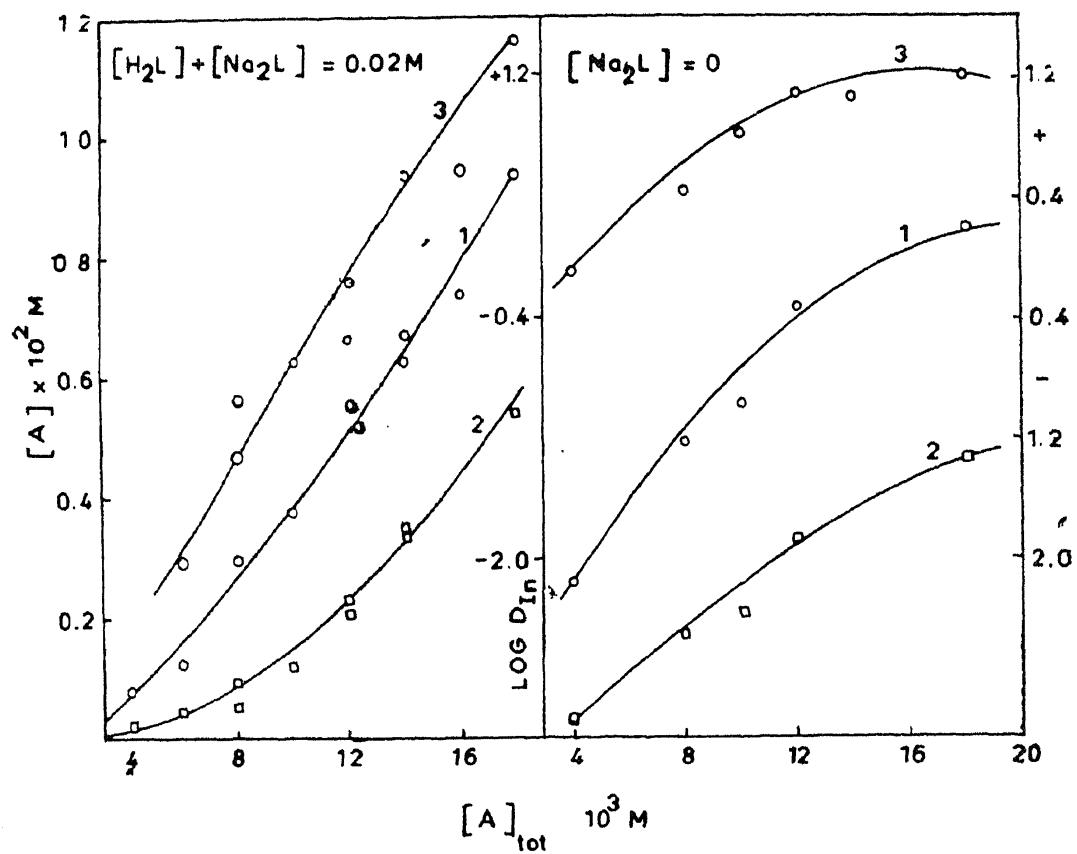
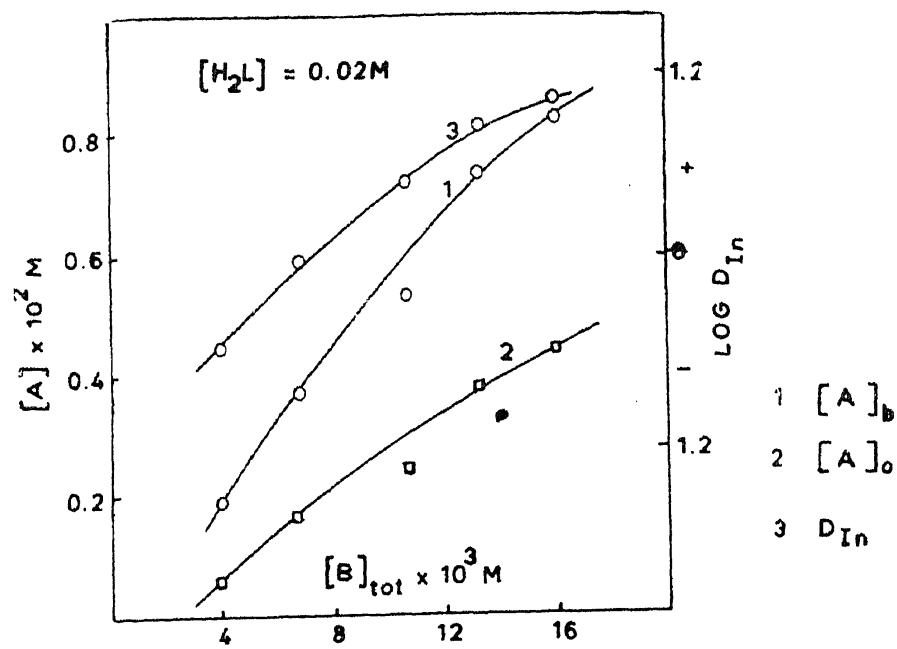
The organic phase was stripped with a solution of 0.2 M sodium perchlorate and about 0.3 M perchloric acid. Indium in the aqueous phase was estimated using a G.M. Counter (M/s. Electronics Corporation of India Ltd.). Malonic acid in the organic phase was estimated by equilibrating an aliquot with standard sodium hydroxide and estimating the excess alkali. The amine in the organic phase was estimated by non-aqueous titrations.

Corrections for blank were made for the titre values. The material balance for amine as well as malonic acid was better than ± 5 per cent. The extraction of malonic acid in pure diluent was negligible.

RESULTS AND DISCUSSION

The composition of the organic phase changes with that of the aqueous phase in the case of extraction with organic acids. It is, therefore, not possible to keep the composition of one of them constant while varying the other as is generally done with extraction from strong mineral acids. Hence the extraction of malonic acid has been investigated in detail and the data have been analysed to determine the nature of the extracted species and the equilibrium constant of the reaction.

FIG. 1



EXTRACTION OF MALONIC ACID AND INDIUM

EXTRACTION OF MALONIC ACID

The extraction of malonic acid was studied at different pH, keeping the concentrations of malonic acid and sodium malonate constant at 0.02 M. Experiments were also carried out in the absence of malonate at different concentrations of the acid as well as amine. The two phases were analysed as described earlier. The results are given in Table I and Fig. 1.

It can be seen from the table that part of the amine goes into the aqueous phase. Analysis of the malonic acid bound with the amine indicates a composition of amine to acid as 2:1. The composition of the acid-amine complex in the organic phase can be assumed to be the same. This was confirmed by the application of the method of Hogfeldt and Fredlund³ assuming polymerisation to be negligible at such low concentrations.

The number of malonic acid molecules extracted per amine is given by⁵

$$Z = \frac{[\text{Malonic acid}]_{\text{bound}}}{[\text{Amine}]_{\text{tot}}} = \frac{[A]_b}{[B]_{\text{tot}}} \quad (1)$$

where [A] and [B] represent the concentrations of malonic acid and amine respectively.

The complexity sum, S, in the case of mononuclear complexes, is defined as⁵

$$S = \sum K_i [a]^i \quad (2)$$

and can be obtained from

$$\log (S + 1) = \int_{a=0}^{\infty} Z d \log [a]. \quad (3)$$

The concentration of free malonic acid, [a], was calculated from

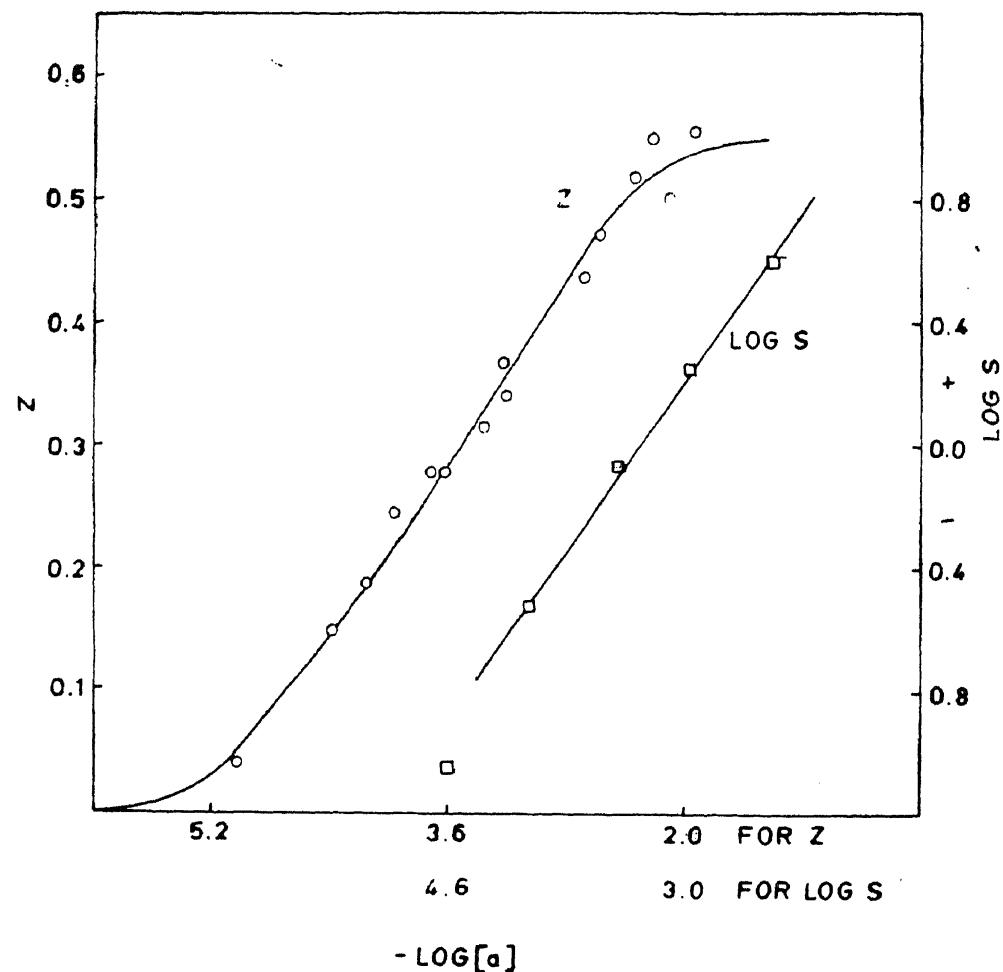
$$[a] = [\text{H}_2\text{L}]_{\text{free}} = \frac{m}{1 + \frac{K_1}{[\text{H}^+]} + \frac{K_1 K_2}{[\text{H}^+]^2}} \quad (4)$$

where K_1 and K_2 are the stepwise dissociation constants of malonic acid⁴, equal to $10^{-2.85}$ and $10^{-5.70}$ respectively and m is the total concentration of malonic acid and sodium malonate.

The plot (Fig. 2) of Z vs. $\log a$ was obtained from the experimental values. The function, S, was calculated by a graphical integration of this plot. The

plot (Fig. 2) of $\log S$ vs. $\log a$ resulted in a straight line with a slope of about 0.65 indicating the presence of a complex of the type B_2A .

FIG. 2



PLOT OF Z AND LOG S VS. LOG [a]

The equilibrium constant for the formation of the complex can be written as

$$K = \frac{[B_2A]}{[B]^2 [A]} = \frac{[A]_b}{[b]^2 [a]} \quad (5)$$

TABLE I

Extraction of malonic acid and indium by Primene JM-T [Amine] = 0.02 M

$[A]_{tot} \times 10^2 \text{ M}$	$[Na_2L]_{tot} \times 10^2 \text{ M}$	pH	$-\log[a]$	$[A]_{aq}$	$[B]_{aq} \times 10^2 \text{ M}$	$[A]_{b, aq}$	$[A]_c$	$[A]_b \text{ tot}$	Z	$\log K$	$-\log[C]$	$\log D_{In}$
0.40	1.60	5.90	5.19	0.273	0.199	0.109	0.128	0.237	0.119	..	1.86	-1.55
0.40	1.60	5.79	5.01	0.311	0.121	0.065	0.018	0.083	0.042	5.4	1.98	-0.96
0.80	1.20	5.32	4.38	0.562	0.404	0.192	0.095	0.287	0.144	5.6	2.29	-1.32
0.80	1.20	5.28	4.32	0.571	0.287	0.135	0.046	0.181	0.091	5.2	2.31	-0.94
1.00	1.00	5.13	4.17	0.660	0.507	0.255	0.120	0.375	0.188	5.5	2.46	-0.71
1.20	0.80	4.62	3.63	0.734	0.652	0.320	0.228	0.548	0.274	5.5	2.94	-0.54
1.20	0.80	4.74	3.58	0.738	0.434	0.218	0.200	0.418	0.209	..	2.65	-0.15
1.40	0.60	4.30	3.36	0.726	6.542	0.268	0.354	0.622	0.311	5.4	3.31	0.56
1.60	0.40	4.12	3.23	0.789	0.886	0.449	0.290	0.739	0.370	5.6	3.54	0.52
1.80	0.20	3.32	2.58	0.843	0.784	0.376	0.542	0.918	0.459	..	4.51	1.46

where $[b]$ represents the concentration of free amine. The function

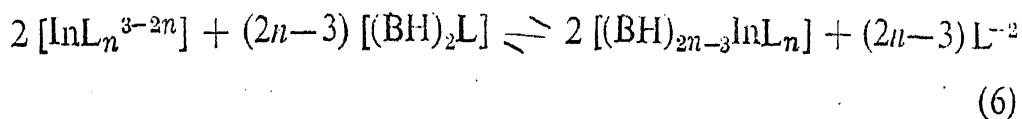
$$\log \left\{ \frac{[A]_b}{[b]^2 [a]} \right\}$$

was plotted (Fig. 3) as a function of $\log [b]^2 [a]$. Although the data showed some scatter, the plot did not indicate any systematic variation as would be the case if higher polymers were present. Hence the amine-acid complex is predominantly B_2A with the equilibrium constant as $10^{5.5}$.

EXTRACTION OF INDIUM

Extraction of indium was also studied under different experimental conditions described earlier. The results are given in Table I.

Indium may be present predominantly as the malonate complex in the pH range of these studies. The mechanism for the extraction of indium can be written in a general form as

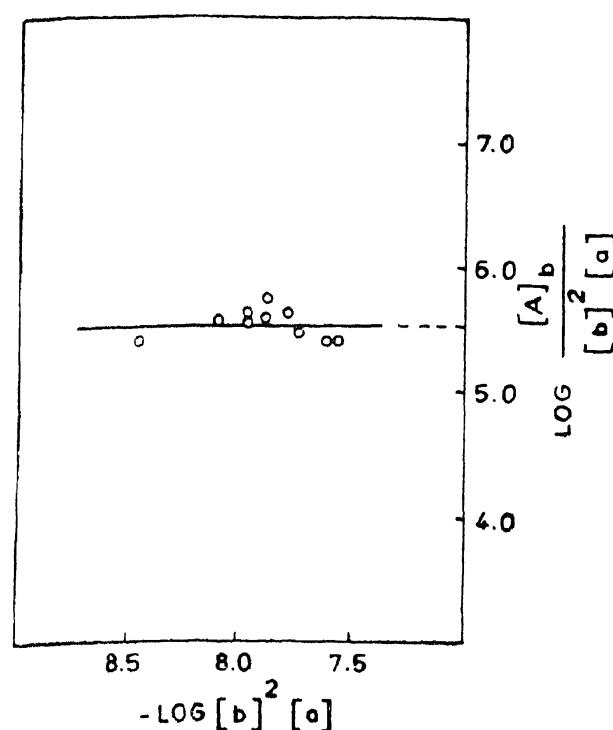


where L^{-2} represents the malonate ion and the equilibrium constant is given by

$$K_{In} = D_{In}^2 \left\{ \frac{[L]}{[(BH)_2 L]} \right\}^{2n-3} \quad (7)$$

where D_{In} represents the distribution ratio of indium. Hence a plot of $\log D_{In}$ vs. $\log [(BH)_2 L] [L]^{-1}$ should give a straight line with a slope of 0.5 if the predominant species were $[InL_2^{-1}]$ or 1.5 for $[InL_3^{-3}]$. The existence of $[In(HL)_n]$ cannot also be neglected.

FIG. 3



PLOT OF $\log \frac{[A]_b}{[b]^2 [a]}$ vs. $\log [b]^2 [a]$

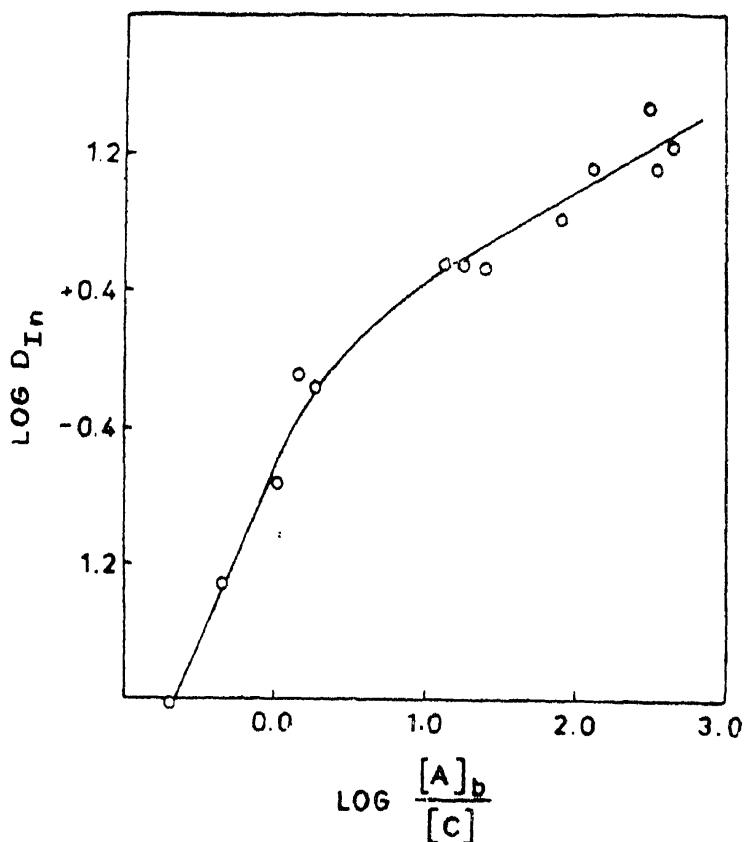
The distribution ratio for indium was obtained at different pH. The concentration of free malonate ion was calculated from

$$[L^{-2}] = [C] = \frac{K_1 K_2 m}{[H]^2 \left\{ 1 + \frac{K_1}{[H^+]} + \frac{K_1 K_2}{[H^+]^2} \right\}} \quad (8)$$

A plot of $\log D_{In}$ vs. $\log [A]_b [C]^{-1}$ resulted in a curve (Fig. 4) with the slope varying from about 1.5 to 0.5 indicating the extraction of a number

of species, viz., $[(BH) InL_2]$, $[(BH)_3InL_3]$ and $[(BH) In (HL)_4]$. In view of the presence of different species, no further evaluation of the data could be carried out.

FIG. 4

PLOT OF $\log D_{In}$ vs. $\log \frac{[A]_b}{[c]}$

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