

Extraction of indium, cadmium and thallium by dinonylnaphthalene sulfonic acid

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ABSTRACT

The extraction of indium, cadmium and thallium by dinonylnaphthalene sulfonic acid (HD) from acid media has been studied. HD extracts the metal ion by an ion exchange mechanism. The nature of the species and the extent of aggregation has been evaluated. The effect of diluents on the extraction has also been studied and the results interpreted on the basis of aggregation of HD. A comparative study with solid ion exchangers has also been made.

1. INTRODUCTION

CARBOXYLIC and sulfonic acids, analogous to cation exchange resins, are useful for the study of metal complexes¹. Higher members of carboxylic and sulfonic acids are good extractants and such systems are also interesting in view of their association in organic solvents. The extraction of indium, cadmium and thallium, being representative elements of the three oxidation states, by dinonylnaphthalene sulfonic acid has been reported here and a comparison has also been made with solid ion exchangers.

2. EXPERIMENTAL

Dinonylnaphthalene sulfonic acid (HD), obtained as a gift from M/s. R. T. Vanderbilt and Co., was used without further purification. A two per cent solution in benzene (B.D.H. AnalaR) served as a stock solution and was estimated by the method of Khopkar and Narayanankutty². This was pre-equilibrated with perchloric acid before use.

Dowex 50W-X8 (Baker analysed) and Amberlite IR-120 (B.D.H.) were used for ion exchange studies. They were converted to acid form and air-dried for several days.

Indium, cadmium and thallium, obtained in the form of In^{114m}, Cd^{115m} and Tl²⁰⁴ from Isotope Division, B.A.R.C., were assayed by β -counting

using liquid G.M. detectors (Electronics Corporation of India Ltd., Hyderabad).

Extraction experiments were carried out by equilibrating 10 ml of the aqueous phase containing the metal and requisite amounts of perchloric acid with an equal volume of HD in benzene. After equilibration, the metal in the organic phase was stripped by extraction with about 2 M hydrochloric acid. The metal ion in both the phases was then estimated by β -counting.

0.25 gm of the resin was equilibrated with 10 ml of the aqueous phase for ion exchange studies. The distribution ratio, D , was calculated from the activity of the metal ion before and after extraction from

$$D = \frac{\text{conc. of metal per gm of resin}}{\text{conc. of metal per ml of solution}} \quad (1)$$

Molecular weight measurements were made on a Perkin-Elmer Hitachi molecular weight apparatus using benzil as the monomeric standard.

3. RESULTS AND DISCUSSION

Extraction studies

Studies were made with indium, cadmium and thallium as representative elements of the three oxidation states. The distribution ratio was studied as a function of the concentration of acid. The activity of perchloric acid was calculated from electrochemical data³ and the results are presented in figure 1. The slopes of 2.6, 1.9, 1.1 obtained for indium, cadmium and thallium respectively were in agreement with expected values. The extraction increases with increased charge on the ion as in the case of strong cation exchangers.

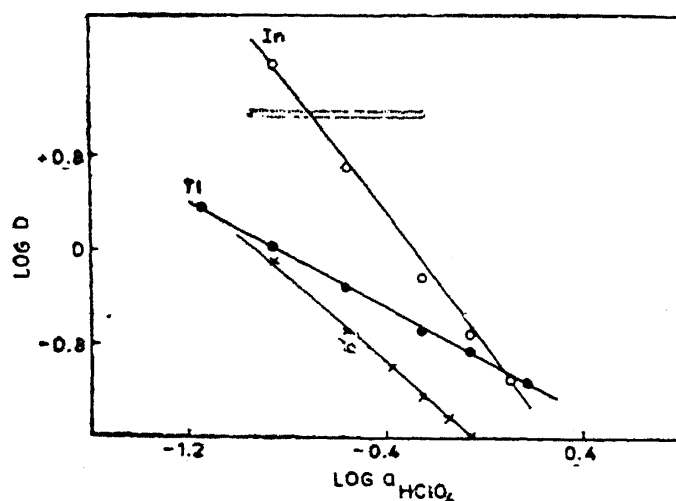
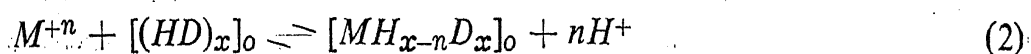


Figure 1. Plot of $\log D$ vs. $\log [a_{\text{HClO}_4}]$.

The dependence of extraction on the concentration of HD was also studied to establish the nature of the extracted species. The plots of $\log D$ vs. $\log [HD]$ in the formality scale, as determined by titration with sodium hydroxide, are shown in figure 2. Contrary to the expected slopes of 3, 2 or 1 on the basis of the monomeric form of HD, a slope of 0.8 was obtained for thallium while the slope was 1.1 in the case of cadmium and indium indicating HD in benzene to be polymeric. Hence the extraction depends on the first power of the concentration of HD. According to Wang and Li⁴ and Kaufman *et al*^{5, 6}, HD is considered as a micelle, the exterior part of which consists of HD radical located such that it can interact with the molecules of the solvent, the cation and the charged sulfonate part of the anion being located in the central region. The aggregation number for HD has been reported by Little and Singletery⁷ as 2.0 in benzene and 2.5 in siloxane dimer. With HD, self association to form an eight membered hydrogen bonded ring imparts lower free energy.

The aggregation of HD was estimated under the present experimental conditions using benzene and chloroform as diluents. The results (table 1) indicated the aggregation number of HD in benzene and chloroform to be 3 and 2 respectively. The decrease in the extent of aggregation in chloroform is due to the hydrogen bonding nature of the solvent. On the basis of the above results, the extraction reactions can be written as



where M represents thallium, cadmium or indium and x is 2 to 3.

Ion exchange studies

Studies were also made under similar conditions to investigate the exchange of these metals with a solid cation exchanger, *viz.*, Dowex 50 W-X8 in hydrogen form. The plots of $\log D$ vs. $\log [a_{HClO_4}]$ resulted in straight lines, the slopes being 1.3, 1.8 and 2.6 for thallium, cadmium and

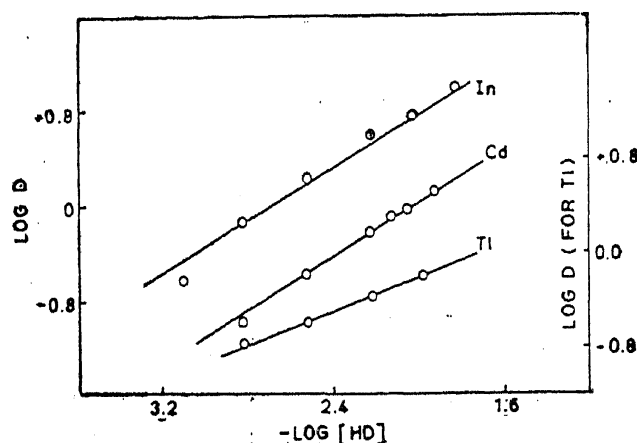


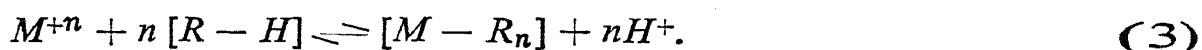
Figure 2. Plot of $\log D$ vs. $\log (HD)$.

Table 1. Aggregation of HD in benzene and chloroform

System	Conc. %	ΔR corrected for zero	Formality $\times 10^3 F$	Exptl. molarity mM	Degree of aggregation
Benzene media					
Benzil	4.0*	47	1.91		
do.	9.5*	106	4.52		
do.	14.6*	161	6.95		
do.	26.7*	295	12.72		
HD	2.0	122	15.0	5.3	Trimer
HD	5.0	314	37.5	13.6	Trimer
Chloroform					
Benzil	11.1*	183	4.83		
do.	14.9*	214	6.48		
do.	22.6*	334	9.83		
HD	2.0	297	15.0	8.9	Dimer
HD	2.0	317	15.0	9.5	Dimer

* Concentration in mg/ml

indium respectively. Results obtained with Amberlite IR-120 also yielded straight lines with slopes of about 1.1, 2.0 and 2.8 respectively for thallium, cadmium and indium. The results can be summarised by the following reaction:



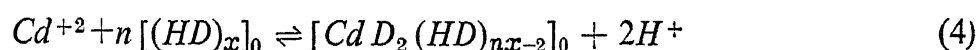
The dependence of extraction on the concentration of the resin was unity in keeping with the highly aggregate nature of the resin. The extent of adsorption was found to be: Tl < Cd < In, which is in the order of increasing charge and decreasing hydrated radii of the metal ions. The slopes of the plots obtained both with the liquid and solid cation exchangers are the same indicating an ion exchange type of reaction.

Effect of diluents

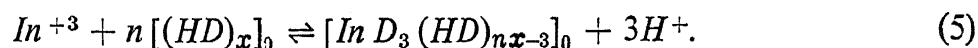
Liquid and solid ion exchangers differ in one respect, *viz.*, the effect of organic diluents on the mechanism of extraction. This effect is not encountered with solid ion exchangers. The effect of diluents on extraction was studied from acid media where the extractant might be assumed to exist

as hydrogen bonded aggregates. The extent of aggregation is also likely to be affected by the solvent polarity. Benzene represents a solvent of low dielectric constant which has been shown to lead to higher aggregation of ion association compounds like HD. With solvents of higher dielectric constants the extent of aggregation decreases and the ionisation of the ligands is favoured. Chloroform and methylisobutylketone (MIBK) are solvents of increasing solvent polarity where an interaction of the diluent with the ion exchanger is to be expected since CHCl_3 is hydrogen bonding and MIBK is a coordinating diluent. Hence the extraction of cadmium and indium was studied from these two media.

The distribution of cadmium and indium was studied from chloroform media as a function of acidity. The plots of $\log D$ vs. $\log [a_{\text{HClO}_4}]$ (figure 3) yielded straight lines with slopes of about 2 and 3 respectively for cadmium and indium in agreement with the earlier results. The ion exchange reactions in the two cases can be written as



and



The extraction was also studied as a function of the concentration of the extractant. The plots of $\log D$ vs. $\log \text{HD}$ (figure 4) were curves, the slopes of the straight line portion being 1.5 for cadmium and 1.2 in the lower portion and 2.3 in the upper portion for indium. These values are higher than those obtained in benzene medium indicating reduced aggregation of HD. Chloroform stabilises the monomer partly by hydrogen bonding and hence the interaction of HD with chloroform can lead to a decrease in the effective concentration resulting in reduced extraction. The

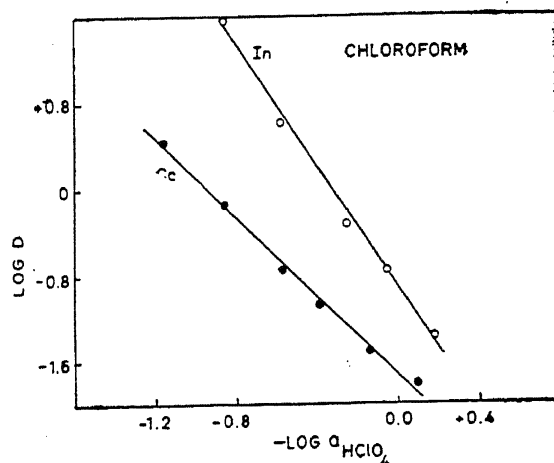


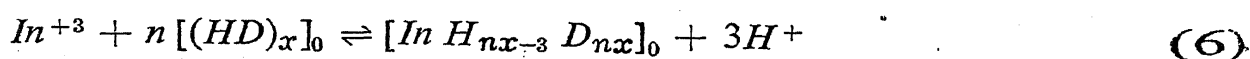
Figure 3. Plot of $\log D$ vs. $\log [a_{\text{HClO}_4}]$

Table 2. Extraction of cadmium and indium by HD in benzene and chloroform

$-\log [a_{\text{HClO}_4}]$	Chloroform		Benzene	
	Cd	In	Cd	In
0.00	-1.70	-0.90	-1.66	-0.80
0.60	-0.60	0.80	-0.58	0.86
1.00	0.10	1.92	0.28	1.80

data for cadmium and indium (table 2) indicate the extent of extraction from these two media to be nearly the same. Hence the effect of the diluent is mainly on the extent of aggregation of HD and this does not influence the extraction considerably.

MIBK having a higher dielectric constant can be expected to interact more with the complex or the extractant owing to the presence of the ketonic oxygen. The extraction of cadmium and indium by HD in MIBK was therefore studied as a function of the activity of perchloric acid and the concentration of HD. No plots could be obtained for cadmium as the extraction was negligible. The extraction was also considerably less in the case of indium and took place only at lower acidities. The increased antisynergistic effect may be due to the interaction of the diluent with HD. The pH of the final solution was also different due to the transfer of hydrogen ions from HD to the aqueous phase. Hence the usual method of plotting $\log D$ vs. $\log HD$ could not be adopted. The reaction between indium and HD can be written as



for which the equilibrium constant is given by

$$K = D [\text{H}]^3 [\text{HD}]_x^{-n} = D [\text{H}]^3 [\text{HD}]^{-n} X^n. \quad (7)$$

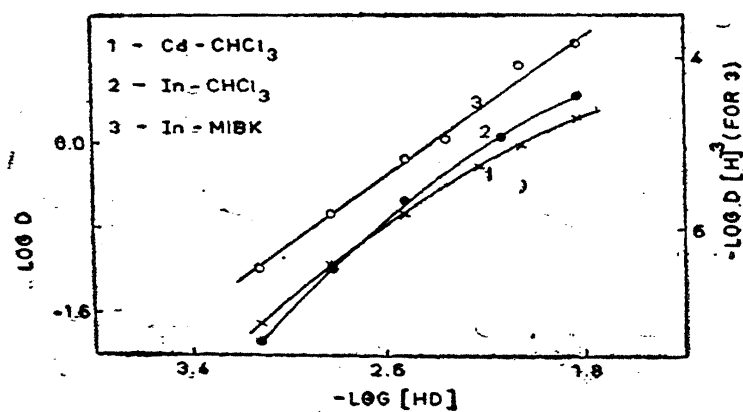


Figure 4. Plot of $\log D$ vs. $\log (HD)$.

Hence a plot of $\log D [H]^3$ vs. $\log [HD]$ was obtained which resulted in a straight line of slope two (figure 4). The increase in the value of n from one for benzene to two in MIBK is due to the variation in the extent of aggregation. The interaction of HD with MIBK reduces the aggregation and also the effective concentration of the extractant resulting in the lowering of the distribution ratio. Such effects are likely to be predominant only in acid media since these interactions may be through the hydrogen ion of HD. It is likely to be absent in salt media and this will form a part of our further work.

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