May, 1986] © *1986 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, *59*, *1567—1569 (1986)* 1567

Studies in the Extraction of Cadmium with Some Sulfur Ligands

Roma LAHIRI and G. N. RAO*
Chemistry Department, Indian Institute of Technology, New Delhi-110016, India

(Received April 1, 1985)

Extraction of cadmium(II) with 2-(2-pyridyl)-2,3-dihydrobenzothiazole, *O,O′*-diethyl hydrogenphosphorodithioate, 1-phenyl-3-methyl-4-thiobenzoyl-5-pyrazolone, *N*-(2-naphthyl)mercaptoacetamide, and 2-(*o*-hydroxyphenyl)-2,3-dihydrobenzothiazole has been studied. Extraction constants (K_{ex}) have been calculated for these systems. These reagents have been compared with some common reagents used for the extraction of cadmium. Separation factors have been calculated for the separation of cadmium from zinc with some of these reagents.

Studies in the extraction of cadmium are somewhat limited. In spite of the fact that extraction of every metal has its own importance cadmium has a special significance owing to its toxicity and increasing concentration in the environment. In view of this a study has been undertaken to find effective reagents for cadmium extraction by investigating the extraction of cadmium with some sulfur ligands and by comparing the extraction data obtained with those for other reagents from the literature. Ligands containing donor sulfur atom have been chosen because cadmium which is a soft acid (in HSAB sense) is expected to form more stable complexes with soft bases.

The ligands chosen for the present study are 2-(2-pyridyl)-2,3-dihydrobenzothiazole(HPBT), *O,O′*-diethyl hydrogenphosphorodithioate(HDEDTP), 1-phenyl-3-methyl-4-thiobenzoyl-5-pyrazolone(HSBMPP), *N*-(2-naphthyl)mercaptoacetamide(HTN), and 2-(*o*-hydroxyphenyl)-2,3-dihydrobenzothiazole(H_2SATP).

Experimental

Apparatus and Reagents. A Pye Unicam SP 191 Atomic Absorption Spectrophotometer was used for measuring the metal concentrations. Measurements of pH was made using an expanded scale pH meter (Electronics Corporation of India Ltd.). A wrist action mechanical shaker was used for shaking.

Cadmium(II) solution was prepared by dissolving Analar grade cadmium acetate in distilled water, adding sufficient amount of acetic acid to prevent hydrolysis. The pH of the aqueous phase was maintained by using mixtures of potassium chloride and hydrochloric acid for pH 1—3, sodium acetate and acetic acid for pH 4—6, acetic acid and ammonia for pH 6—8 and ammonium chloride–ammonia for pH 8—10. A constant ionic strength (0.1) in the aqueous phase was maintained by using potassium nitrate solution. Where extraction was carried out from dilute hydrochloric acid solutions, potassium chloride was used to maintain the ionic strength.

The ligand HSBMPP was prepared by the method[1] reported by Chouhan and Rao. The compounds HPBT[2] and H_2SATP[3] were prepared by condensing 2-aminobenzenethiol (Kochlight) with 2-pyridinecarbaldehyde (Fluka), and salicylaldehyde(BDH), respectively. The other ligands used were HDEDTP (BDH) and HTN (E. Merck). Purity of the ligands was established on the basis of microanalysis and infrared spectra. Analar grade benzene, chloroform, carbon tetrachloride, and 1-butanol were used as solvents. Purification was done where necessary by standard methods.

Extraction Procedure. Ten ml of aqueous layer containing 2 ml of 100 ppm cadmium acetate solution, 5 ml of buffer solution and requisite volume of 1 M[†] potassium nitrate solution (to maintain the ionic strength at 0.1) was equilibrated with 10 ml of organic phase containing the required amount of the ligand in a stoppered bottle. The mixture was shaken in a mechanical shaker for a period sufficient for the attainment of equilibrium at 30±1 °C. The period of shaking was determined from preliminary experiments in all the systems studied. This was 60, 5, 120, 10, and 120 min with HPBT, HTN, HSBMPP, HDEDTP, and H_2SATP, respectively. Benzene was used as the solvent in the case of HSBMPP and H_2SATP while chloroform, carbon tetrachloride, and 1-butanol were used in the case of HTN, HDEDTP, and HPBT, respectively on the basis of preliminary solubility checks. After equilibration the aqueous layer was pipetted out. The concentration of the metal in the aqueous phase and the pH were then measured.

Results and Discussion

The extraction of a metal ion (M^{n+}) with a chelating ligand having a replaceable hydrogen atom (HA) may be represented as,

$$M^{n+}_{aq} + nHA_{org} \rightleftarrows MA_{n\,org} + nH^{+}_{aq}. \qquad (1)$$

The extraction constant (equilibrium constant) of this reaction is:

$$K_{ex} = \frac{[MA_n]_{org}[H^+]^n_{aq}}{[M^{n+}]_{aq}[HA]^n_{org}}. \qquad (2)$$

Making the usual approximations[4] the ratio $[MA_n]_{org}/[M^{n+}]_{aq}$ in Eq. 2 may be considered equal to the distribution coefficient (D) and

$$K_{ex} = D\frac{[H^+]^n_{aq}}{[HA]^n_{org}} \qquad (3)$$

or

$$\log K_{ex} = \log D - n\,\mathrm{pH} - n\log\,[HA]_{org}. \qquad (4)$$

Equation 4 implies that, (i) the slope of the plot

[†] 1 M=1 mol dm^{-3}.

of log D vs. pH at constant reagent concentration in the organic phase gives the number of protons released during complex formation and (ii) the slope of the plot of log D vs. log [HA] at constant pH gives the number of reagent molecules incorporated in the extracted complex.

Plots (Fig. 1) of log D vs. pH at constant ligand (HA) concentration and plots (Fig. 2) of log D vs. log [HA] at constant pH for HPBT, HTN, and HSBMPP gave slopes of ≈2. Thus the extraction of cadmium(II) with these ligands can be represented as occurring predominently according to the following equation:

$$\mathrm{Cd^{2+} + 2HA \rightleftharpoons CdA_2 + 2H^+}$$

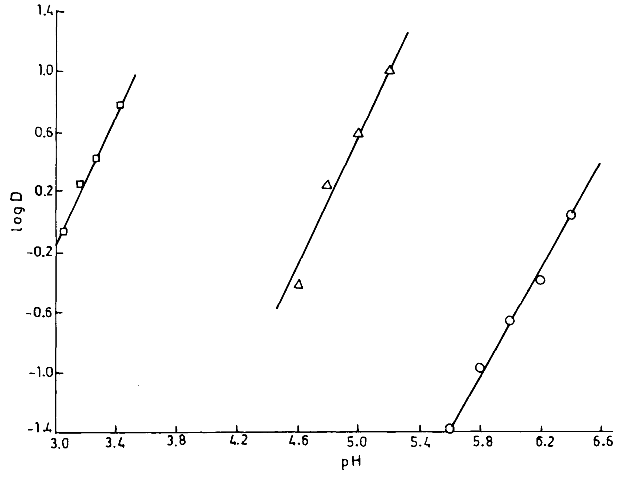

Fig. 1. Effect of pH on the extraction of Cd with HPBT, HTN, and HSBMPP.
○: HPBT (0.001 M), △: HTN (0.0025 M), □: HSBMPP (0.01 M).

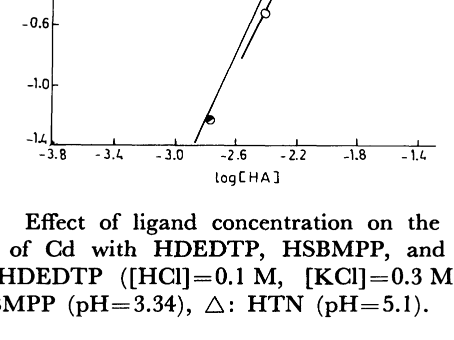

Fig. 2. Effect of ligand concentration on the extraction of Cd with HDEDTP, HSBMPP, and HTN.
○: HDEDTP ([HCl]=0.1 M, [KCl]=0.3 M), ◐: HSBMPP (pH=3.34), △: HTN (pH=5.1).

log K_{ex} values for these systems were calculated by using Eq. 4.

Since the extraction of cadmium(II) with HDEDTP took place from highly acidic solutions (quantitative extraction from 0.01—0.1 M HCl with 0.02 M reagent), a competing reaction in the aqueous phase would be the formation of the chloro complex of cadmium(II). A study of the effect of variation of chloride concentration showed that extraction fell with increase in chloride concentration. The plot (Fig. 2) of log D vs. log[HDEDTP] at constant hydrogen ion and chloride concentration gave a slope of ≈2 indicating the involvement of two moles of HDEDTP in the complex formation. The log K_{ex} value for this system was calculated from Eq. 5[5]

$$\log K_{ex} = \log D - n\log[\mathrm{HA}]_{org} - n\,\mathrm{pH} + \log\{1+\beta_1[\mathrm{X^-}]+\beta_2[\mathrm{X^-}]^2+\cdots\} \qquad (5)$$

Here X^- is the complexing anion (Cl^-) and β_1 is the stability constant of the complex formation reaction.

The formula of the chelate species formed could not be determined in the case of Cd(II)–H_2SATP system as the log D vs. pH or log D vs. log [HA] plots were not regular. A $pH_{1/2}$ value (pH at 50% extraction) of 5.59 was obtained from the plot of percentage extration vs. pH with a 0.01 M solution of the ligand. An approximate K_{ex} value was calculated from this data assuming that the complex species formed here was similar to that in the other systems. Schweitzer et al. also observed irregularities in the extraction of cadmium(II) with salicylaldehyde oxime, acetylacetone, 2-methyl-8-quinolinol etc.[6]

The log K_{ex} values obtained in this study are listed in Table 1. The available K_{ex} values for the extraction of zinc(II) with these reagents are also included in this table.

From this data and other data available in literature[6,7,9,10] it may be concluded that ligands donating through sulfur would be more useful for the extraction of cadmium than their corresponding

Table 1. Extraction Constants for Cadmium(II) and Znic(II)

Reagent	log K_{ex} Cd(II)	log K_{ex} Zn(II)	Solvent
2-(2-Pyridyl)-2,3-dihydrobenzothiazole	−6.8	−9.28[7]	1-Butanol
N-(2-Naphthyl)mercaptoacetamide	−4.27	−8.08[7]	Chloroform
3-Methyl-1-phenyl-4-thiobenzoyl-5-pyrazolone	−2.19	−2.68[8]	Benzene
O,O′-Diethyl hydrogenphosphorodithioate	3.67	—	Carbon tetrachloride
2-(*o*-Hydroxyphenyl)-2,3-dihydrobenzothiazole	−7.18	—	Benzene

Table 2. Separation Factors for Cadmium and Zinc

Reagent	Separation factor
2-(2-Pyridyl)-2,3-dihydrobenzothiazole	300
N-(2-Naphthyl)mercaptoacetamide	6500
3-Methyl-1-phenyl-4-thiobenzoyl-5-pyrazolone	3

oxygen analogues. The ligands HDEDTP, dithizone-(HDTZ),[11] sodium diethyldithiocarbamate (HDEDTC),[12] and HSBMPP appear to be most effective for the extraction of cadmium(II) if the K_{ex} values with these ligands are considered. The higher stability of HDEDTP in highly acidic solutions as compared to HDEDTC makes it a better reagent for analytical purposes.[13] Dithizone in spite of giving a high K_{ex} value is useful only at trace levels since the solubility of HDTZ itself and its chelates is very low in most of the organic solvents. On the other hand, both HDEDTP and its chelates are fairly soluble in organic solvents, and therefore can be useful at trace as well as macro levels. The ligands HPBT, HTN, 1,1,1-trifluoro-4-(2-thienyl)-4-mercaptobut-3-en-2-one,[10] 2-mercaptobenzothiazole,[6] 8-quinolinol,[14] and 5,7-dichloro-8-quinolinol,[6] by virtue of high K_{ex} values will also be useful for the extraction of cadmium. The oxygen donor ligands like *β*-diketones,[6,7,15] *N*-benzoyl-*N*-phenylhydroxylamine[15] etc. do not seem very attractive for the extraction of cadmium(II).

The possibility of utilizing these reagents for separating cadmium from zinc has been investigated by calculating the separation factor S which is the ratio of the distribution coefficients of the elements to be separated.[16] A separation in which not more than 1% of one element is coextracted will be obtained if $S \geq 10^4$ and the product of the distribution coefficients is close to unity. The separation factors for HPBT, HTN, and HSBMPP are given in Table 2.

Considering these separation factors and those for other reagents from literature[6-12,14,15,17] it can be concluded that benzoylacetone,[15] 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone,[8,9] and HTN would be more useful for the separation of cadmium from zinc.

References

1) V. S. Chouhan and G. N. Rao, *Bull. Chem. Soc. Jpn.*, **55**, 301 (1982).

2) L. F. Lindoy, S. E. Livingstone, and T. N. Lockyer, *Aust. J. Chem.*, **18**, 1549 (1965).

3) A. Varadarajulu, Ph. D. Thesis, Indian Institute of Technology, Delhi (1977).

4) Yu. A. Zolotov, "Extraction of Chelate Compounds," Humphrey Science Publishers, INC., Ann Arbor, Michigan (1970), pp. 26—27.

5) E. B. Sandell and H. Onishi, "Photometric Determination of Traces of Metals," Wiley Interscience, New York (1978), p. 898.

6) A. K. Schweitzer and D. R. Randolph, *Anal. Chim. Acta*, **26**, 567 (1962).

7) R. Lahiri, Ph. D. Thesis, Indian Institute of Technology, Delhi (1984).

8) V. S. Chouhan, Ph. D. Thesis, Indian Institute of Technology, Delhi (1978).

9) H. C. Arora and G. N. Rao, *Indian. J. Chem.*, **11**, 488 (1973).

10) T. Honjo, S. Yashima, and T. Kiba, *Bull. Chem. Soc. Jpn.*, **46**, 3772 (1973).

11) Ref. 5, pp. 612—616.

12) Ref. 5, p. 519.

13) T. H. Handley, *Talanta*, **12**, 893 (1965).

14) Ref. 5, p. 428.

15) Ref. 5, Chap. 9B.

16) Ref. 4, pp. 152—154.

17) H. M. N. H. Irving and D. N. Edgington, *J. Inorg. Nucl. Chem.*, **27**, 1359 (1965).