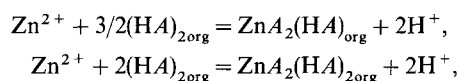


## Comparative Study of the Distribution Equilibria of Zn(II) in Chloride Medium by Organophosphoric, -phosphonic and -phosphinic Acids

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**Summary.** The extraction of Zn(II) from aqueous chloride solutions by di(*n*-octyl)phosphinic acid (*H[DOP]*), mono-2-ethylhexylphosphonic acid 2-ethylhexyl ester (*HEH[EHP]*) and di(2-ethylhexyl)-phosphoric acid (*HDEHP*) dissolved in toluene has been studied at 25 °C. The distribution coefficient of the metal have been determined as a function of the *pH* at different extractant concentrations. The data obtained have been treated graphically and numerically by using the program LETAGROP-DISTR and can be explained assuming the following set of reactions

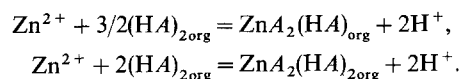


for the extraction of Zn(II) by all the extractants used. The water content in the organic phase was also determined and was related with the predominance of the extracted species.

**Keywords.** Di(*n*-octyl)phosphinic acid; Mono-2-ethylhexylphosphonic acid 2-ethylhexyl ester; Di(2-ethylhexyl)phosphoric acid; Distribution; Zinc.

### Vergleichende Untersuchungen an den Verteilungsgleichgewichten von Zn(II) in Chlorid-Medium mittels Organophosphor-, -phosphon- und -phosphinsäuren

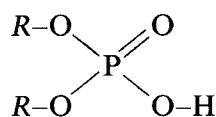
**Zusammenfassung.** Es wurde die Extraktion von Zn(II) aus wäßrigen Chloridlösungen mittels Di(*n*-octyl)phosphinsäure (*H[DOP]*), Mono-2-ethylhexylphosphonsäure-2-ethylhexylester (*HEH[EHP]*) und Di-(2-ethylhexyl)-phosphorsäure (*HDEHP*) in Toluol bei 25 °C untersucht. Die Verteilungskoeffizienten wurden als eine Funktion des *pH* bei verschiedenen Extraktantenkonzentrationen bestimmt. Die erhaltenen Daten wurden graphisch und numerisch mit dem Programm LETAGROP-DISTR ausgewertet und können mit folgenden Reaktionen für alle benutzten Phasensysteme erklärt werden:



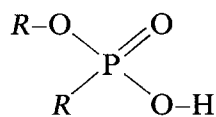
Der Wassergehalt der organischen Phase wurde ebenfalls ermittelt und war mit der Bevorzugung extrahierter Spezies in Verbindung zu setzen.

## Introduction

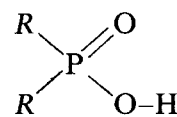
One of the most important groups of extraction reagents used in the field of hydrometallurgy are organophosphorus derivatives. Of these organophosphorus acid compounds are esters of phosphoric, phosphorous and hypophosphorous acids, which gives alkylphosphoric, alkylphosphonic and alkylphosphinic acids, respectively. Their structure is as follows:



Dialkylphosphoric acid



Alkylphosphonic acid alkylester



Dialkylphosphinic acid

Of these, the dialkylphosphoric acid derivatives have been the most studied [1–6], especially di(2-ethylhexyl)phosphoric acid (*HDEHP*).

Nevertheless, the need for increasingly specific reagents, particularly for the separation of cobalt and nickel, have resulted in the appearance of several derivatives belonging to the other two groups [7]. Among these are the mono-2-ethylhexylphosphonic acid 2-ethylhexyl ester (*HEH[EHP]*), which appeared in 1980 and was marketed with the name SME 418 by Shell and PC 88A by Daihachi [8, 9], and di(2,4,4-trimethylpentyl)phosphinic acid, marketed in 1982 by Cyanamid with the name Cyanex 272.

Several studies have been made of metal extraction with various organophosphorus acids, but most of them deal with the separation of Co and Ni [10–13].

In this work a comparative, systematic study has been made of the extraction of Zn(II) with di(*n*-octyl)phosphinic acid (*H[DOP]*), mono-2-ethylhexylphosphonic acid 2-ethylhexyl ester (*HEH[EHP]*) and di(2-ethylhexyl)phosphoric acid in order to determine the composition of the extracted species in the organic phase and their extraction constants.

## Experimental Part

Di(*n*-octyl)phosphinic acid (*H[DOP]*) was synthesized and purified as described in Ref. [14]. Mono-2-ethylhexylphosphonic acid 2-ethylhexyl ester (*HEH[EHP]*) was supplied by Shell with the trade name SME 418. Di(2-ethylhexyl)phosphoric acid (*HDEHP*) was supplied by BDH. The purity of the three acids was determined by potentiometric titration of an acid solution with NaOH 0.1 mol dm<sup>-3</sup> in an 80% ethanol–water mixture. The purities obtained were 96%, 98% and 98.2%, respectively. Toluene from Merck (AR) was used as a solvent without further purification. Zinc chloride and Sodium chloride from Merck (AR) was used.

Stirring was carried out with a rotary mixer from CENCO INSTRUMENT, which was used together with a thermostatically controlled bath to maintain a constant temperature of 25 °C. Centrifugation was performed with a CENCO INSTRUMENT centrifuge. The *pH* was measured with a Methrom AG 9100 Herisau combined electrode connected to a CRISON digital *pH* meter, model Digilab 517. The Zn(II) concentration in the aqueous phase was determined using a Perkin Elmer model 2380 atomic absorption spectrometer. The metal content in the organic phase was measured by atomic absorption after stripping with 1.0 mol dm<sup>-3</sup> hydrochloric acid. The water content of organic solutions was measured by a Karl-Fischer titration using a two-component reagent (Hydranal-solvent and Hydrabak-titrant Riedel de Haën) with an automated Karl-Fischer titrator, Crison Micro KF 2026.

The distribution experiments were carried out at 25 °C, and the distribution coefficient was measured as a function of the concentrations of the various HA organic acids, and *pH*. This was done by shaking 15 ml of organic solution  $S_{\text{org}}$  with 15 ml of aqueous solution  $S_{\text{aq}}$  in 30 ml glass-stoppered test tubes.

The composition of the solution was:

$$S_{\text{org}} = C \text{ mol dm}^{-3} \text{ HA dissolved in toluene.}$$

$$S_{\text{aq}} = B \text{ mol dm}^{-3}, h \text{ mol dm}^{-3} \text{ H}^+, 0.1 \text{ mol dm}^{-3} \text{ Cl}^- (0.1-2B-h) \text{ mol dm}^{-3} \text{ Na}^+.$$

HA refers to the di(*n*-octyl)phosphinic, mono-2-ethylhexylphosphonic acid 2-ethylhexyl ester and di(2-ethylhexyl)phosphoric acids.

After shaking the time necessary for attaining equilibrium, the phases were separated, and *pH* and the zinc concentration were determined in both phases.

Using the quotient of the Zn(II) concentrations in the organic and aqueous phases, the metal's distribution coefficient, *D*, may be determined, where *D* is defined by

$$D = \frac{[\text{Zn(II)}]_{\text{org}}}{[\text{Zn(II)}]_{\text{aq}}} \quad (1)$$

The water content in the organic phase was determined after shaking an organic solution containing different concentration of organophosphorus acid compounds with an aqueous solution containing 0.1 mol dm<sup>-3</sup> of sodium chloride in the presence and in the absence of zinc(II).

## Results

The distribution coefficient *D* has been determined as a function of *pH* and the extractant concentration for the three extractants used. The results are shown in Figs. 1–3. The data were treated in two stages, first graphically, and then numerically.

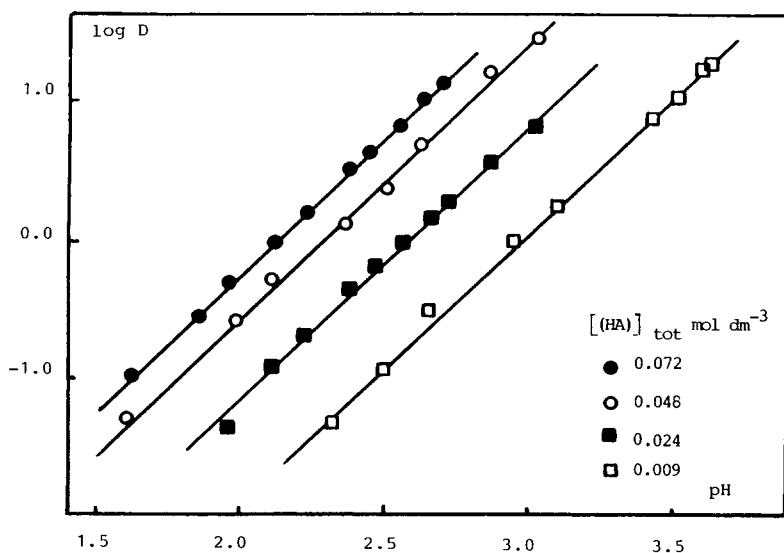


Fig. 1. Variation of the distribution ratio of Zn(II) with the *pH* at several total concentrations of HDEHP; the solid lines have been calculated using the constants given in Table 1

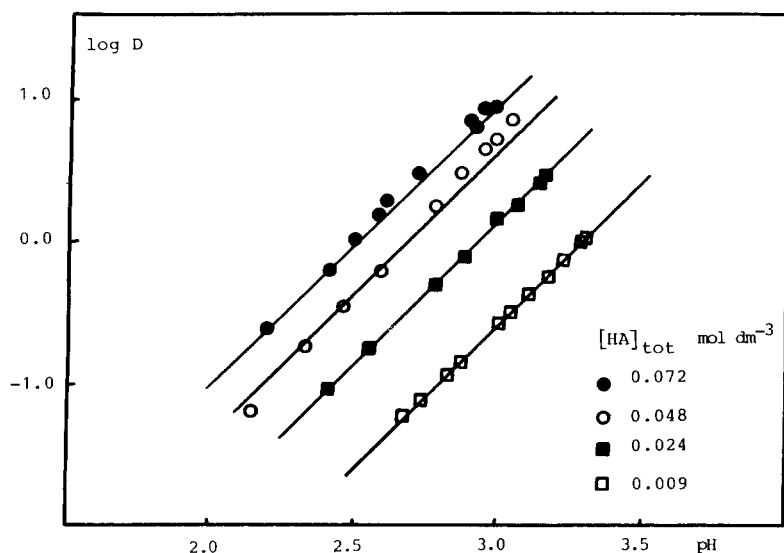
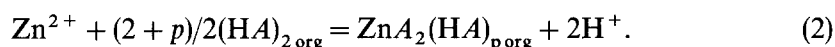


Fig. 2. Variation of the distribution ratio of Zn(II) with the  $pH$  at several total concentrations of HEH[EHP]; the solid lines have been calculated using the constants given in Table 1

Bearing in mind that the dialkylphosphorus acids are found as dimers in toluene solutions [15], the extraction of Zn(II) by liquid cationic exchangers may be written with the general equation



Assuming ideal behaviour in both phases, the extraction constant of the complex may be written as

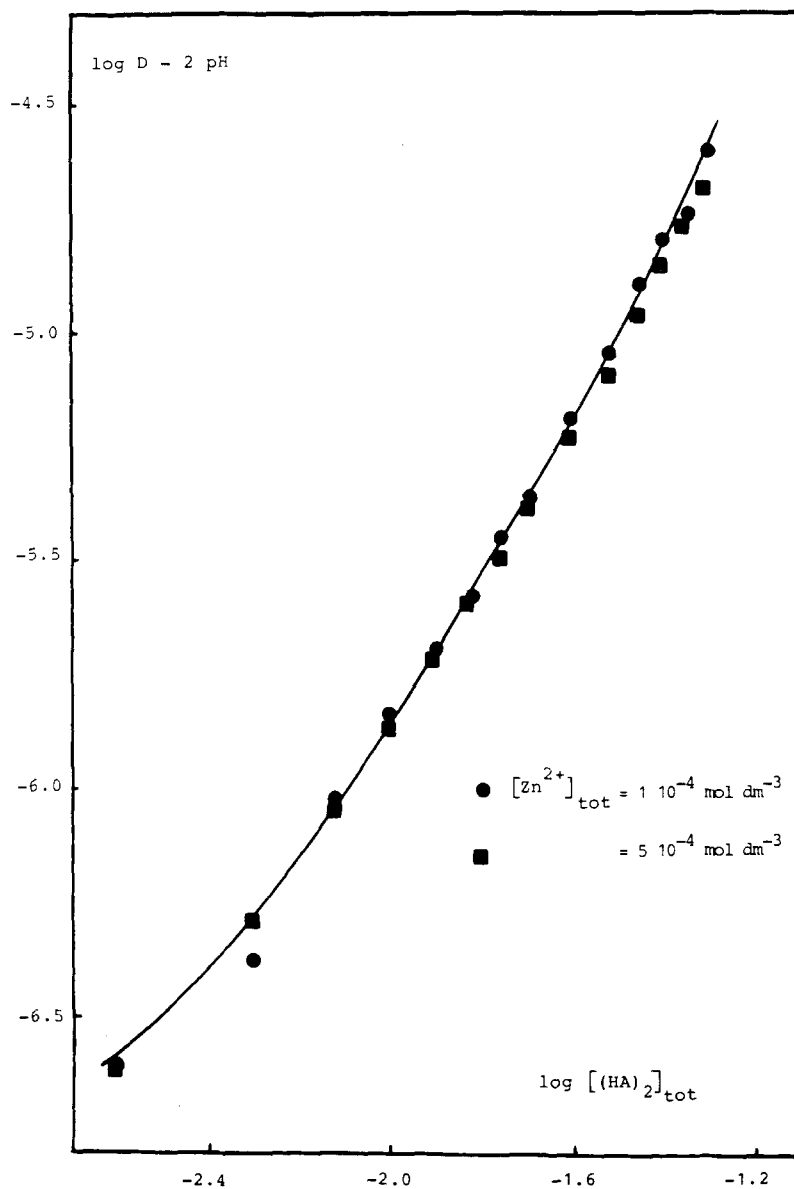
$$K_{2p} = \frac{[\text{ZnA}_2(\text{HA})_p]_{\text{org}} [\text{H}^+]^2}{[\text{Zn}^{2+}] [(\text{HA})_2]_{\text{org}}^{(2+p)/2}} \quad (3)$$

Due to the low metal concentrations and the  $pH$  range used in the experiments, the formation of polynuclear complexes in the organic phase and the formation of hydroxocomplexes of Zn(II) in the aqueous phase may be neglected. Using normalized curves [16,17] the species and their extraction constants were determined, and the results are given in Table 1.

Once the estimated values of the constants were obtained graphically for each extractant the experimental data were treated numerically using the program LETAGROP-DISTR [18] in order to confirm the proposed model and refine the graphical values. In this program the computer searches for the best set of constants which minimizes the sum of square errors defined as

$$U = \sum N_p (\log D_{\text{calc}} - \log D_{\text{exp}})^2,$$

where  $D_{\text{exp}}$  is the distribution coefficient of Zn(II), determined experimentally, and  $D_{\text{calc}}$  is the value calculated by the program using the given set of complexes and their stability constants. The program also calculates the standard deviation  $\sigma(\log D) = (U/N_p)^{1/2}$  where  $N_p$  is the total number of experimental data points. The results are given in Table 1.



**Fig. 3.** Variation of the distribution ratio of Zn(II) with the *pH* at several total concentrations of *H[DOP]*; the solid lines have been calculated using the constants given in Table 1

**Table 1.** Conditional extraction constants of Zn(II) from NaCl  $0.1 \text{ mol dm}^{-3}$  solutions with different organophosphorus derivatives

Extractant	Method of calculation	log $K_{21}$	log $K_{22}$
<i>H[DOP]</i>	Graphical	-2.8	-2.3
	LETAGROP-DISTR	$-2.80 \pm 0.05$	$-2.30_{max} - 2.07$
<i>HEH[EHP]</i>	Graphical	-3.6	-2.5
	LETAGROP-DISTR	$-3.72_{max} - 3.50$	$-2.5 \pm 0.08$
<i>HDEHP</i>	Graphical	-2.9	-1.4
	LETAGROP-DISTR	$-2.80 \pm 0.1$	$-1.43 \pm 0.07$

## Discussion

The extraction of zinc(II) by *HDEHP*, *HEH[EHP]* and *H[DOP]* from chloride media is performed through the formation of two species. Compositions seem to be independent of the type of organophosphorus used. Distribution diagrams of the zinc(II) species in the organic phase with relation to the total metal concentration, *pH* and total HA concentration, as well as percentage extraction curves, were calculated using the program HALTAFALL [19] along with the constants given in this paper. These calculations show that at a *pH* value of 4.4 the percentage of extraction is 100% for all the extractants and the predominance of species  $ZnA_2(HA)_2$  or  $ZnA_2HA$  depends on the type of the reagent and extractant concentrations. Some numerical results are included in Table 2.

It is interesting to note that the extractability of Zn(II) follows the order *HDEHP* > *H[DOP]* > *HEH[EHP]* (Fig. 4) which is not the order of increasing acidity and the values of  $pH_{50}$  are 2.2, 2.45, and 2.60, respectively. This tendency was found by Danesi et al. [20] in the extraction of cobalt and nickel by different organophosphorus acids in toluene.

In order to explain this behaviour not only the acidity constants but also the distribution and dimerization constants should be taken into account. Thus the extractability of zinc follows the order of increasing equilibrium constants between the metal ion and the anion of the reagent and this is proportional to the ratio  $K_2K_D/K_a$  where  $K_a$ ,  $K_2$  and  $K_D$  are the acidity, the dimerization and the distribution constants respectively. The values of  $\log K_2K_D/K_a$  calculated from Ref. [21] are 9.5, 7.6, and 5.7 for *HDEHP*, *H[DOP]*, and *HEH[EHP]*.

Table 2 summarizes the results of the water analyses obtained for the extraction of zinc(II) by organophosphorus acid compounds. The amount of water in organic solutions containing zinc(II) were determined using experimental conditions in

**Table 2.** Water analysis for extractions

Reagent	HA (mol dm <sup>-3</sup> )	Metal	%ZnA <sub>2</sub> HA Species	Water content (mg H <sub>2</sub> O/5 ml org. phase)	Δ*
<i>HDEHP</i>	0.010	–		1.448	
	0.010	Zn(II)	53%	1.323	0.125
	0.100	–		2.387	
	0.100	Zn(II)	25%	1.448	0.286
<i>HEH[EHP]</i>	0.010	–		1.625	
	0.010	Zn(II)	76%	1.512	0.113
	0.100	–		2.059	
	0.100	Zn(II)	50%	1.910	0.149
<i>H[DOP]</i>	0.010	–		1.384	
	0.010	Zn(II)	85%	1.384	0.000
	0.100	–		1.438	
	0.100	Zn(II)	63%	1.328	0.110

\* mg of water displaced to the aqueous phase

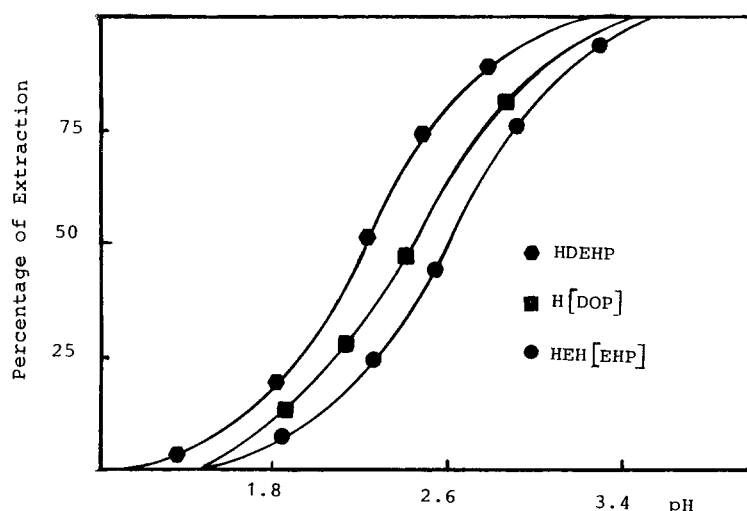


Fig. 4. Percentage of extraction of *HDEHP*, *HEH[EHP]*, and *H[DOP]* as a function of *pH*

which 100% of metal is extracted and only the percentage of different species is varied. As seen in Table 2, the sequence of water solubilization ability of the three extractants follows the order  $HDEHP > HEH[EHP] > H[DOP]$ . As a general trend the water content in organic phase increases when increasing the concentration of organophosphorus compounds and decreases when zinc(II) is extracted into the organic phase.

This diminution of the water content in the organic phase seems to be related with the predominance of different species in the organic phase. For a given extractant the diminution of the water content increases when increasing the extractant concentration due to an increase of the predominance of the  $ZnA_2(HA)_2$  species and the fact that water molecules coordinated to Zn(II) in  $ZnA_2HA$  are progressively replaced by extractant. On the other hand for a given concentration of extractant the diminution of the water content increases when the percentage of the species  $ZnA_2HA$  decreases.

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