

The extraction of zinc from chloride solutions using dibutyl butylphosphonate (DBBP) in Exxsol D100^(*)

F.J. Alguacil^(*), B. Schmidt^(**), R. Mohrmann^(**) and E. Giebel^(***)

Abstract The reaction of zinc chloride with dibutyl butylphosphonate in Exxsol D100 has been studied. The distribution coefficient of zinc is independent of equilibrium pH, thus, suggesting a solvation extraction reaction. Experimental data indicate that this reaction is exothermic ($\Delta H^\circ = -28.4$ kJ/mol). Slope analysis for the system at various DBBP concentrations reveals the formation in the loaded organic phases of species which probable 1:2 (Zn:DBBP) stoichiometries. This was confirmed by results obtained at full DBBP Zn-loading capacity. The stoichiometric factor of water in the extraction reaction is found to be 4, whereas experimental data also indicated that two chloride ions are involved for each metal extracted, resulting in a $ZnCl_2 \cdot 2L \cdot 4H_2O$ stoichiometry (L represents the extractant).

Keywords: Solvent extraction. Zinc. Chloride. Phosphonates.

La extracción de zinc de disoluciones en medio cloruro mediante dibutil butilfosfonato (DBBP) en Exxsol D100

Resumen Se estudia la extracción de zinc, en medio cloruro, con el dibutil butilfosfonato disuelto en Exxsol D100. El coeficiente de distribución del metal es independiente del pH de equilibrio de la fase acuosa, lo que sugiere un mecanismo de extracción por solvatación. Los resultados experimentales indican que la reacción es exotérmica ($\Delta H^\circ = -28,4$ kJ/mol). Mediante análisis de la pendiente obtenida cuando se emplean distintas concentraciones de DBBP en la extracción de zinc se deduce la formación de una especie con estequiometría 1:2 (Zn:DBBP) en la fase orgánica. Este hecho se confirma con los resultados obtenidos cuando se satura completamente la fase orgánica. En esta fase, el factor estequiométrico para el agua es 4, mientras que para el ion cloruro es 2, por lo que la especie extraída tiene una estequiometría final representada por $ZnCl_2 \cdot 2L \cdot 4H_2O$ (L representa al agente de extracción).

Palabras clave: Extracción con disolventes. Zinc. Cloruro. Fosfonatos.

1. INTRODUCTION

In recent years the recovery of metals from aqueous chloride solutions has attracted much attention and the development of solvent extraction technology has increased the possibility of metal beneficiation by hydrometallurgical processes. This technology is in widespread use for the recovery and purification

of copper from acidic, mainly sulphate, leach solutions with hydroxyoximes (1).

The recovery of zinc(II) from chloride solutions using solvent extraction technology is also of particular interest and various extractants had been investigated (Table I).

The aim of the present work was to study the reaction of zinc, with DBBP diluted in Exxsol D100, from aqueous chloride solutions in order to identify the stoichiometry of extracted species and to contribute to the understanding of the chemistry of such systems and their possibilities in the recovery of zinc from various chloride solutions, e. g. waste streams from hot galvanizing or zinc electroplating processes.

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TABLE I.— Solvent extraction systems for zinc extraction from chloride systems

TABLE I.— *Sistemas de extracción con disolventes empleados en la extracción de zinc de disoluciones en medio cloruro*

| Extractant type | Reagent | Reference |
|-----------------|------------------|-----------|
| Acid | Kelex 100 | 2 |
| | Carboxylic acids | 3 |
| | DEHPA | 4, 5 |
| | CYANEX 302 | 6, 7 |
| Basic | Secondary amines | 8 |
| | Aliquat 336 | 9 |
| Neutral | TBP | 10 |
| | DPPP | 11 |
| | Acorga ZNX50 | 12 |

2. EXPERIMENTAL METHOD

The extractant DBBP was obtained from Albright and Wilson Inc., and was used without further purification. Exxsol D100, using as diluent of the organic phase, was obtained from Exxon Chem. Iberia, its characteristics are: boiling range 234-264°C, flash point 99°C, aromatics content 0.9, density (15°C) 0.816 g/cm³. All other chemicals were of AR grade.

Experiments were carried out by the next procedure. Measured amounts of the aqueous and organic phases were placed in separatory funnels provided with mechanical shaking (600 min⁻¹) and thermostatted at the required temperature. Agitation was applied for 15 min as previous experiments showed that this time was sufficient to achieve equilibrium. All experiments were conducted at an O/A phase ratio of 1 and the organic solutions were of 50 % v/v DBBP in Exxsol D100 unless otherwise noted. After settling, the zinc content in the equilibrated aqueous solutions was analysed by AAS. Metal in the organic phase was calculated by mass balance.

3. RESULTS AND DISCUSSION

The distribution coefficient D is defined as the ratio of total metal concentration in the organic phase to the total metal concentration in the aqueous phase.

3.1. Influence of the pH on the extraction of zinc

Two series of experiments were performed to examine the effect of pH on zinc extraction. In the

first series of experiments, the aqueous feed, with various pH values adjusted with HCl, contained 1.0 g/L of zinc. The results are given in figure 1. In the other case, the aqueous solutions contained 1.0 g/L of zinc and 7 mol/L of Cl⁻, adding as CaCl₂. Figure 1 also shows the effect of pH on metal extraction. In both cases, temperature was of 20 °C.

The extraction of zinc is independent of aqueous pH, being this result similar to that obtained with phosphonates but not when using TBP (11 and 13).

3.2. Influence of chloride ion on zinc extraction

From results shown above it is clear that the presence of CaCl₂ in the aqueous feed greatly improves the extraction of zinc by DBBP. To obtain further information on this behaviour, experiments were conducted with aqueous solutions of 1.0 g/L zinc and various contents of chloride ion, added as CaCl₂. Results were presented in table II. It can be seen that the increase of the anion concentration in the aqueous feed increases the extraction of zinc.

3.3. Influence of temperature

The study of the influence of this variable on zinc extraction by DBBP was carried out using aqueous feed of 1.0 g/L zinc and 7 mol/L Cl⁻ (added as CaCl₂). Temperature was varied in the range 10-50 °C. Results obtained are presented in figure 2, plotting log D_{Zn} versus 1000/T, it can be seen that

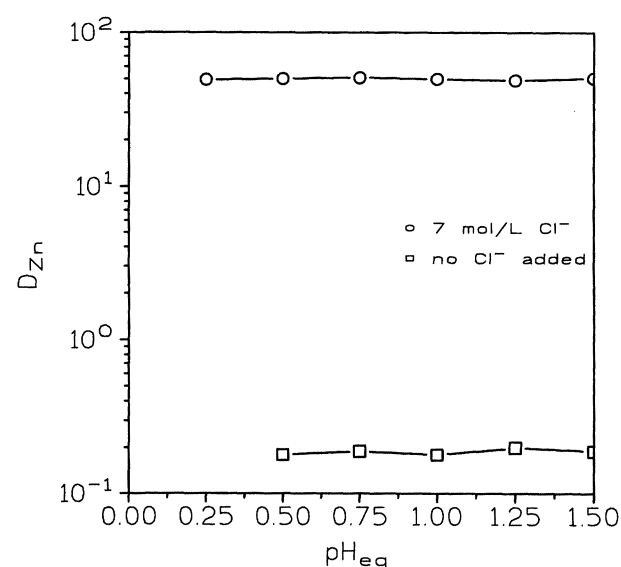


FIG. 1.— Influence of pH on the extraction of zinc by DBBP.

FIG. 1.— *Influencia del pH en la extracción de zinc mediante DBBP.*

TABLE II.— The effect of Cl⁻ on zinc extraction by DBBP

TABLA II.— El efecto de la presencia de Cl⁻ sobre la extracción de zinc mediante DBBP

| Chloride concentration, mol/L | D _{Zn} |
|-------------------------------|-----------------|
| 1.5 | 1.99 |
| 3.5 | 7.94 |
| 7.0 | 49.4 |

pH_{eq}: 0.5.

Temperature: 20 °C.

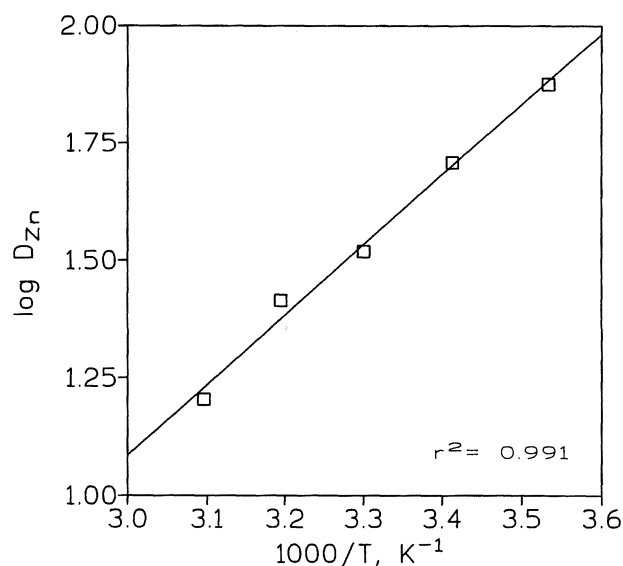


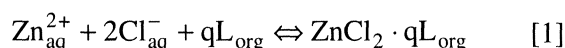
FIG. 2.— Arrhenius plot for zinc extraction by DBBP.

FIG. 2.— Representación de Arrhenius para la extracción de zinc mediante DBBP

the increase of temperature decreases zinc extraction, although phase separation is good even at lower temperatures. From this figure is obtained that ΔH° is -28.4 kJ/mol, the reaction is exothermic.

3.4. Extraction mechanism

DBBP is a solvating extractant (14) and considering the results obtained above, e.g. the extraction is independent of aqueous pH and the positive influence of chloride ion on zinc extraction, the extraction reaction can be generalized as:



where L represents the extractant molecule and aq and org the respective aqueous and organic phases. On the other hand, and considering the solvating

characteristics of DBBP it can be assumed that water molecules also enter the metal-DBBP extracted species.

The equilibrium constant for the above reaction can be expressed, in terms of activities, as:

$$k_{\text{ext}} = \frac{[\text{ZnCl}_2 \cdot q\text{L}]_{\text{org}}}{[\text{Zn}^{2+}]_{\text{aq}} [\text{Cl}^{-}]_{\text{aq}}^2 [\text{L}]_{\text{org}}^q} \quad [2]$$

and for zinc speciation in the aqueous solution:

$$[\text{Zn}]_{\text{T}} = [\text{Zn}^{2+}] + [\text{ZnCl}^{+}] + [\text{ZnCl}_2] + [\text{ZnCl}_3^{-}] + [\text{ZnCl}_4^{2-}] \quad [3]$$

The formation constant for the above complexes is defined as:

$$\beta_n = \frac{[\text{ZnCl}_n^{2-n}]}{[\text{Zn}^{2+}][\text{Cl}^{-}]^n} \quad [4]$$

where n varies from 1 to 4.

By substituting, eq. [3] becomes:

$$[\text{Zn}]_{\text{T}} = [\text{Zn}^{2+}] (1 + \sum \beta_n [\text{Cl}^{-}]^n) \quad [5]$$

The substitution of eq. [5] into eq. [2] and considering the definition of D_{Zn} gives:

$$k_{\text{ext}} [\text{Cl}^{-}]^2 (1 + \sum \beta_n [\text{Cl}^{-}]^n) = \frac{D_{\text{Zn}}}{[\text{L}]_{\text{org}}^q} \quad [6]$$

Results of extraction experiments at 20 °C are presented in table III. In all the cases the total chloride ion concentration in the aqueous solution was maintained at 7 mol/L, and considering that the amounts of zinc and chloride extracted are much smaller than the amounts of water and Cl⁻, the activities of both water and chloride ion can thus be considered as constant.

Equation (6) can be rewritten as:

TABLE III.— The influence of DBBP on zinc extraction

TABLA III.— La influencia de la concentración de DBBP sobre la extracción de zinc

| DBBP, % v/v | D _{Zn} |
|-------------|-----------------|
| 1 | 0.002 |
| 2.5 | 0.013 |
| 5 | 0.046 |
| 7.5 | 0.11 |
| 10 | 0.19 |

Aqueous phase: 1.0 g/L Zn in 7 mol/L Cl⁻.
pH_{eq}: 0.5 ± 0.02.

$$\log D_{Zn} = \log K_{ext} + q \log [L] \quad [7]$$

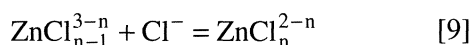
where K_{ext} is an effective extraction constant defined as:

$$K_{ext} = k_{ext} [Cl^-]^2 (1 + \sum \beta_n [Cl^-]^n) \quad [8]$$

A plot of $\log D_{Zn}$ versus $\log [DBBP]_{org}$ will give a straight line of slope q . The equilibrium zinc concentration in the equilibrated organic solutions is much smaller than the initial extractant concentration, thus, it can be assumed that the equilibrium DBBP concentration in the organic phase is equal to the initial reagent concentration and at lower extractant concentrations the activities can be considered equal to the concentrations. By plotting $\log D_{Zn}$ against $\log [DBBP]_{org}$, as shown in figure 3, a straight line of slope 2 is obtained, thus the coefficient q of eq. [1] can be considered 2 and the value of $\log K_{ext}$ being 0.19.

The possibility of extractant dimers formation at higher DBBP concentrations should result in a slope different than 2 either if the extraction constant remained unaltered or changed with the formation of dimers. On the other hand, it was found that the viscosity of the loaded DBBP organic phases increases with the loading of zinc into the organic solutions.

The formation of zinc chlorocomplexes can be written as:



where the overall constant, K_n , is defined as:

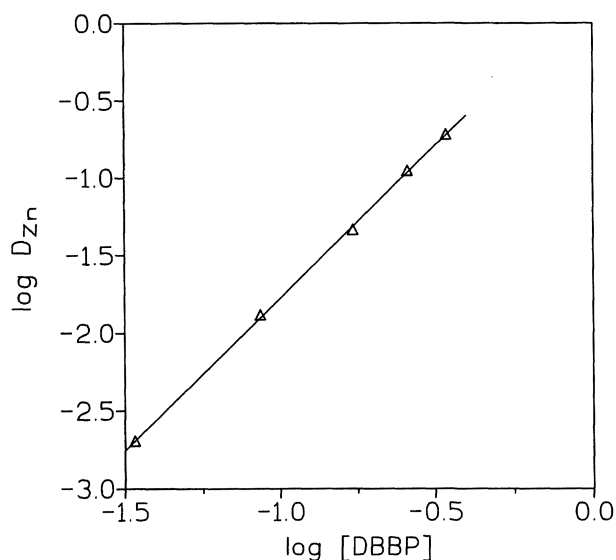


FIG. 3.— Variation of zinc extraction with initial DBBP concentration. Temperature 20 °C.

FIG. 3.— Variación de la extracción de zinc con la concentración de DBBP. Temperatura 20 °C.

$$K_n = \frac{[ZnCl_n^{2-n}]}{[ZnCl_{n-1}^{3-n}][Cl^-]} \quad [10]$$

where n changes from 1 to 4. The reported values of the respective constants (K_1 through K_4) varied. In any case, $ZnCl_2$ should not be the predominant species in the solution at certain chloride concentrations. On the other hand, the 1:2 (Zn:Cl⁻) is the major species that DBBP can extract. It is a fact that independent of which species of zinc is extracted, at chloride ion activities constant, the slope analysis can be carried out because the kinetics of eq. [9] are fast and, thus, there is a redistribution of the zinc species in favour of the 1:2 species.

A number of experiments was carried out to saturate the organic solution with zinc. The initial concentration of DBBP in the organic solution was 50 % v/v, while the zinc concentration in the initial aqueous solution varied from 0.5 to 180 g/L. In all the cases the total Cl⁻ concentration was maintained constant at 7 mol/L by addition of CaCl₂. The results are shown in table IV, from which molar ratios concentrations of DBBP to zinc in the organic phase were calculated and plotted against the zinc equilibrium concentration in the raffinate (Fig.4).

The molar ratio DBBP/[Zn] in the organic solution decreases to near 2 when the metal concentration in the aqueous feed increases to near

TABLE IV.— Zinc extraction by DBBP at various metal initial concentrations

TABLA IV.— Extracción de zinc mediante DBBP a distintas concentraciones iniciales del metal

| Zinc initial, g/L | Zinc aqueous phase, g/L | Zinc organic phase, g/L |
|-------------------|-------------------------|-------------------------|
| 0.5 | 0.01 | 0.49 |
| 1.0 | 0.02 | 0.98 |
| 2.5 | 0.05 | 2.45 |
| 5.0 | 0.1 | 4.90 |
| 10.0 | 0.42 | 9.58 |
| 20.0 | 3.81 | 16.19 |
| 50.0 | 19.0 | 31.0 |
| 75.0 | 35.1 | 39.9 |
| 100.0 | 52.9 | 47.1 |
| 120.0 | 67.8 | 52.2 |
| 135.0 | 79.3 | 55.7 |
| 150.0 | 91.1 | 58.9 |
| 160.0 | 99.7 | 60.3 |
| 170.0 | 109.5 | 60.5 |
| 180.0 | 119.6 | 60.4 |

Temperature: 20 °C.
pH_{eq}: 0.5 ± 0.02

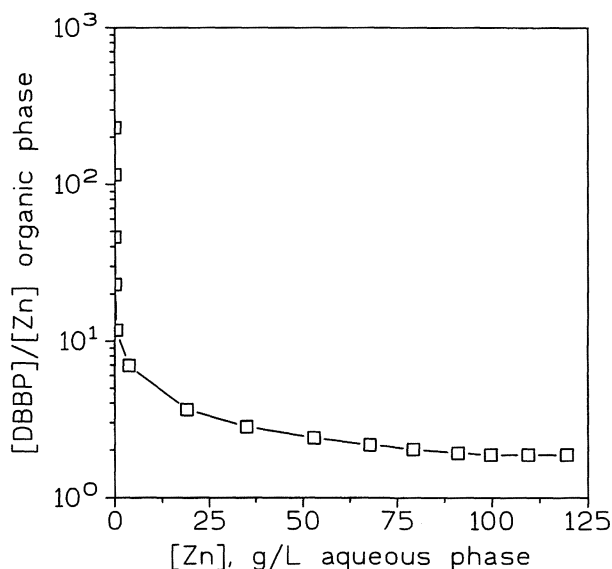


FIG. 4.— Influence of zinc concentration in the aqueous feed on the molar ratio [DBBP]/[Zn] in the organic phase.

FIG. 4.— Influencia de la concentración de zinc en la fase acuosa en la relación molar [DBBP]/[Zn] en la fase orgánica.

100 g/L. Further increases of zinc concentration in the aqueous solution do not decrease this ratio, because DBBP has reached its maximum loading capacity.

The corresponding zinc equilibrium loading isotherm is shown in figure 5. The isotherm can be mathematically described by the equation:

$$[\text{Zn}]_{\text{org}} = \frac{73.09 [\text{Zn}]_{\text{aq}}}{24.96 + [\text{Zn}]_{\text{aq}}} \quad [11]$$

where $[\text{Zn}]_{\text{org}}$ and $[\text{Zn}]_{\text{aq}}$ represented the corresponding zinc concentrations at equilibrium in the respective organic and aqueous phases.

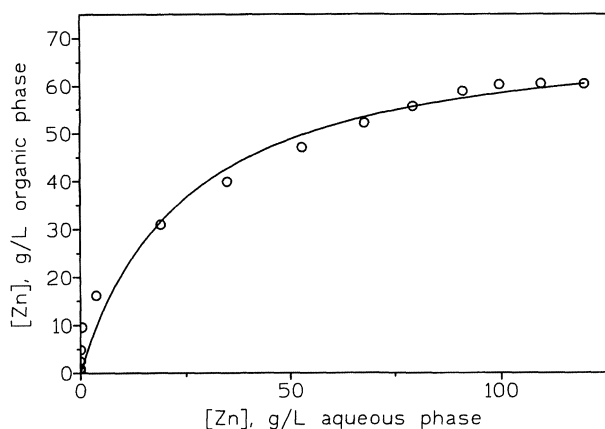


FIG. 5.— Zinc loading equilibrium isotherm. Temperature: 20 °C.

FIG. 5.— Isotherma de extracción de zinc. Temperatura: 20 °C.

The stoichiometric factor of chloride ion in this system was estimated by varying the chloride ion concentration from 1 to 3.5 mol/L by CaCl_2 addition. As preliminary IR studies had shown, the possibility of finding water associated with the extracted species can not be neglected, thus a water stoichiometric factor was also estimated considering that the activity of water varies with the chloride ion concentration.

The activity coefficient of chloride ion was obtained from reported data (15 y 16), whereas the activity of water was determined accordingly with the literature (17 y 18). The results are given in table V.

Plots of $\log D_{\text{Zn}}$ versus $(2 \log a_{\text{Cl}^-} + b \log a_{\text{H}_2\text{O}})$ were made using different b values. With $b = 4$, the plot can be represented by a straight line with slope near to 1, as shown in figure 6. Thus, the stoichiometry of the extracted species can be represented by $\text{ZnCl}_2 \cdot 2\text{L} \cdot 4\text{H}_2\text{O}$. It is estimated that the hydration number of zinc chloride is 10-15 (19), during the extraction of zinc by DBBP (20), a number of water molecules in the primary coordination layer of zinc chloride are replaced by DBBP molecules, remaining only 4 water molecules coordinated with zinc.

4. CONCLUSIONS

The extraction of zinc from chloride solutions using DBBP dissolved in Exxsol D100 has been studied. The extraction is independent of aqueous pH but dependent on the presence of chloride ions in the aqueous media, a solvation reaction is suggested. This reaction is exothermic ($\Delta H^\circ = -28.4$ kJ/mol). Slope analysis indicated that the stoichiometric factor between Zn and the extractant is 1:2 (Zn:DBBP), this has been confirmed at maximum zinc load of the DBBP organic solution. The equilibrium loading isotherm has been obtained at 20 °C. The experimental data indicate that the stoichiometric factor for chloride and water in the

TABLE V.— Activities of chloride ion and water at different chloride ion concentrations

TABLA V.— Actividades de los iones cloruro y agua a varias concentraciones de ion cloruro

| Cl^- , mol/L | a_{Cl^-} | $a_{\text{H}_2\text{O}}$ |
|-----------------------|-------------------|--------------------------|
| 1.0 | 0.604 | 0.989 |
| 1.5 | 0.875 | 0.977 |
| 2.0 | 1.146 | 0.929 |
| 2.5 | 1.422 | 0.910 |
| 3.0 | 1.707 | 0.885 |
| 3.5 | 2.000 | 0.857 |

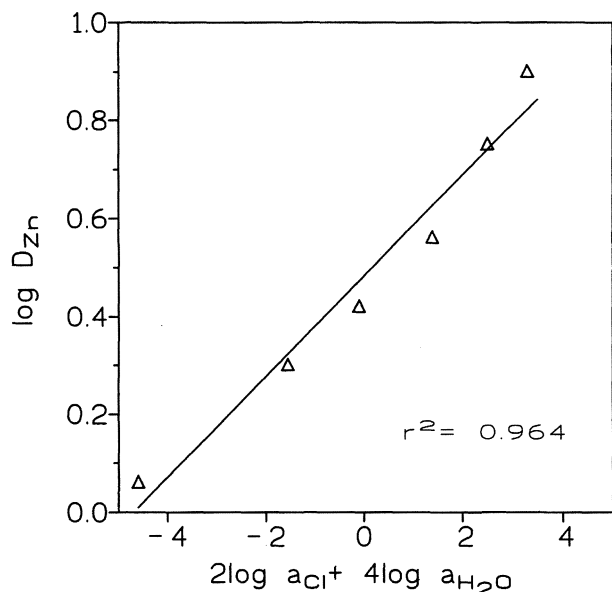


FIG. 6.— Plot of $\log D_{Zn}$ vs $2 \log a_{Cl^-} + 4 \log a_{H_2O}$.

FIG. 6.— Representación de $\log D_{Zn}$ frente a $2 \log a_{Cl^-} + 4 \log a_{H_2O}$.

organic phase are 2 and 4, respectively; thus, the final stoichiometry of the extracted species can be represented by $ZnCl_2 \cdot 2L \cdot 4H_2O$, being L the extractant.

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