SHORT PAPER

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Solvent extraction of zinc from acidic calcium chloride solutions by Cyanex 923[†]

Susana Martínez and Francisco José Alguacil*

Centro Nacional de Investigaciones Metalúrgicas (CSIC), Avda. Gregorio del Amo 8, Ciudad Universitaria, 28040 Madrid, Spain.

The reaction of zinc chloride with Cyanex 923 (phosphine oxide) in Solvesso 100 has been studied from acidic calcium chloride solutions. The distribution coeffient of zinc is independent of equilibrium pH, thus, suggesting a solvation extraction mechanism. Experimental data indicate that the reaction is exothermic ($\Delta H° = –55.2$ kJmol^{-1}). Slope analysis for the system at various Cyanex 923 concentrations reveals the formation in the loaded organic phases of species which probable 1:2 (Zn : Cyanex 923) stoichiometries. The stoichiometric factor of water in the extraction reaction was found to be 0, 1 or 2, whereas experimental data indicated that two chloride ions are involved for each metal extracted.

Solvent extraction had attracted a considerable interest and activity with a number of potential applications within product routes of zinc. On the other hand, this technique had been proposed for zinc recovery from solid and liquid effluents. In general terms, one can say that the organophosphoric acid D2EHPA is by far the most useful and widespread extractant for zinc from complex solutions,[1–3] but other reagents had also been studied and data were published elsewhere; these extractants included: Kelex 100,[4] carboxylic acids,[5] Cyanex 302,[6,7] secondary amines,[8] Aliquat 336,[9] TBP,[10] DPPP,[11] DBBP,[12] and Acorga ZNX 50.[13] There are no data available in the literature about the use of Cyanex 923 (a commercially available phosphine oxide) in this field of interest; thus, the present investigation deals with the study of zinc extraction from calcium chloride solutions using this reagent. Cyanex 923 (CYTEC Ind.) was used as received, its composition and characteristics had been published elsewhere.[14] Solvesso 100 (Exxon Chem. Iberia) with >99% aromatics was used to dilute the extractant. All other chemicals were of AR grade. Extractions were carried out by mechanical agitation (700 rpm^{-1}) in separatory funnels, thermostatted at the required temperature and for 10 min (time necessary to achieve metal extraction equilibrium) of the appropiate volumes of the corresponding aqueous and organic solutions. After phases settling, the zinc content in the equilibrated aqueous solutions was analysed by AAS, metal in the organic phase was calculated by mass balance.

The distribution of zinc between the organic and aqueous phases was obtained as the ratio of the total metal concentration in the equilibrated phases:

$$D_{\mathrm{Zn}} = \frac{[\mathrm{Zn}]_{\mathrm{org}}}{[\mathrm{Zn}]_{\mathrm{org}}} \tag{1}$$

Experiments carried out to study the influence of various chloride concentrations (added as calcium chloride) and pH (adjusted by using nitric acid) on zinc extraction show that the increase of the chloride salt concentration in the aqueous solution increases zinc extraction (i.e. log $D_{\mathrm{Zn}}= –0.60$ at 1 M total chloride concentration, log $D_{\mathrm{Zn}}= 0.47$ at 3.5 M total chloride concentration), furthermore zinc extraction is independent of the equilibrium pH (i.e. log $D_{\mathrm{Zn}}= –0.60$ at 1 M total chloride concentration and $\mathrm{pH}_{\mathrm{eq}}$ range 0.25–1.5, log $D_{\mathrm{Zn}}= 0.47$ at 3.5 M total chloride concentration and $\mathrm{pH}_{\mathrm{eq}}$ range 0.25–1.5) and this suggests that zinc extraction by Cyanex 923 is governed by a solvation mechanism.

According to this suggestion and experimental data obtained from the present work, the extraction reaction can be written as:

$$\mathrm{Zn}^{2+}_{\mathrm{aq}} + 2\mathrm{Cl}^{-}_{\mathrm{aq}} + nL_{\mathrm{org}} \leftrightarrow \mathrm{ZnCl}_2 \bullet nL_{\mathrm{org}} \tag{2}$$

where L represents the extractant and aq. and org. the aqueous and organic phases, respectively.

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

$$k_{\mathrm{est}} = \frac{[\mathrm{ZnCl}_2 \bullet nL]_{\mathrm{org}}}{[\mathrm{Zn}^{2+}]_{\mathrm{aq}}[\mathrm{Cl}^{-}]^{2}{}_{\mathrm{aq}}[L]^{n}{}_{\mathrm{org}}} \tag{3}$$

and for zinc specification in the aqueous phase:

$$[\mathrm{Zn}]_{\mathrm{T}}=[\mathrm{Zn}^{2}]+[\mathrm{ZnCl}^{+}]+[\mathrm{ZnCl}_2]+[\mathrm{ZnCl}^{-}{}_{3}]+[\mathrm{ZnCl}^{2-}{}_{4}] \tag{4}$$

and:

$$B_m = \frac{[\mathrm{ZnCl}^{2-m}_{m}]}{[\mathrm{Zn}^{2+}]_{\mathrm{aq}}[\mathrm{Cl}^{-}]^{m}} \qquad m = 1 \text{ to } 4 \tag{5}$$

Then:

$$[\mathrm{Zn}]_r=[\mathrm{Zn}^{2+}](1+\Sigma\beta_m[\mathrm{Cl}^{-}]^{m}) \tag{6}$$

and also taking into account the definition of zinc distribution coefficient:

$$k_{ext}[\mathrm{Cl}^{-}]^{2}(1+\Sigma\beta_m[\mathrm{Cl}^{-}]^{m}) = \frac{D_{\mathrm{zn}}}{[L]^{n}_{\mathrm{org}}} \tag{7}$$

In all the experimental work, the concentration of chloride ions was maintained at values (*e.g.* typically 1.5 mol L^{-1}) in which the amounts of zinc and chloride extracted are smaller than the amounts of water and chloride ion; then activities of both water and chloride ion can thus be considered as constant.

The last equation can be re-written as:

$$\log D_{\mathrm{Zn}}=\log K_{\mathrm{ext}}+n\log[L]_{\mathrm{org}} \tag{8}$$

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

$$K_{\mathrm{est}}=k_{\mathrm{ext}}[\mathrm{Cl}^{-}]^{2}(1+\Sigma\beta_m[\mathrm{Cl}^{-}]^{m}) \tag{9}$$

A plot of log D_{Zn} versus log $[L]_{\mathrm{org}}$ will give a straight line of slope n. 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 Cyanex 923 concentration in the organic phase is equal to the initial reagent concentration. By plotting log D_{Zn} against log $[\text{Cyanex 923}]_{\mathrm{org}}$, as shown in Fig. 1, a straight line of slope 2 is obtained and thus, the coefficient n for the extractant is 2. The value of log K_{ext} was estimated as 2.9.

The stoichiometric factor of chloride ion in this system was estimated by varying the chloride ion concentration from 1 to

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* To receive any correspondence. E-mail: fjalgua@cenim.csic.es

[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

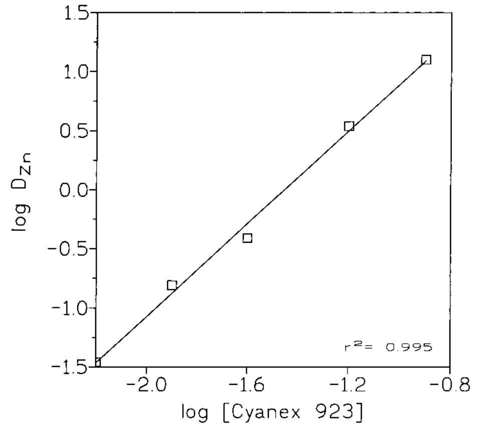

Fig. 1 Variation of zinc extraction with Cyanex 923 concentration. Aqueous phase: 0.015 mol l^{-1} zinc in 1.5 mol l^{-1} chloride ion. Organic phase: Cyanex 923 in Solvesso 100. O:A phase ratio: 1:1. Temperature: 20°C. Equilibrium pH: 0.75±0.02.

3.5 mol l^{-1} by $CaCl_2$ addition, plots of log D_{Zn} versus log $[Cl^-]$ shows straight lines of slope 2 as suggested by the extraction reaction shown above.

The extraction of metals by solvation reagent can be accompanied by the extraction of water associated with the metal, thus a water stoichiometric factor was also estimated considering that the activity of water varies with the chloride ion concentration. The activity coefficients of chloride ions were obtained from reported data,[15,16] whereas the activity of water was determined accordingly with the literature.[17,18]

Plots of log D_{Zn} versus (2 log a_{Cl} + P log a_{H2O}) were made using different P values. With $P = 0$, 1 or 2, the plot can be represented by straight lines with slopes closest to 1 (Fig. 2). As it is expected with organophosphorous derivates, water is eliminated from the organic phase and this is the cause of the low water stoichiometric factor found in the present investigation. It should also be noted that higher deviation of the lineality has been found when greater p coefficients were used in the calculations. Thus, the stoichiometry of the extracted species can be represented by $ZnCl_2{\cdot}2L{\cdot}pH_2O$ (p=0, 1 or 2). The stoichiometry with p=2 fulfills the octahedral coordination requirements for zinc.

The influence of temperature on zinc extraction by Cyanex 923 was studied using an organic solution of 0.13 mol l^{-1} Cyanex 923 in Solvesso 100 and aqueous solution of 0.015 mol l^{-1} zinc in 1.5 mol l^{-1} chloride ion at pH_{eq} 0.75±0.03 using a volume phase ratio of 1:1 (organic: aqueous). Results indicated that there is a decrease in zinc extraction as the temperature is increased; the value of $\Delta H°$ (change of enthalpy) is –55.2 kJ mol^{-1}, the extraction reaction being exothermic.

An equilibrium loading isotherm was obtained using the continuous organic : aqueous phases variation procedure. The organic phase was of 0.025 mol l^{-1} Cyanex 923 in Solvesso 100 whereas the aqueous solution contained 0.015 mol L^{-1} zinc in 1.5 mol l^{-1} chloride ion. The corresponding curve is shown in Fig. 3, the isotherm can be mathematically described by the equation:

$$[Zn]_{org} = \frac{0.014[Zn]_{aq}}{6.2\times10^{-4}+[Zn]_{aq}} \qquad (10)$$

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

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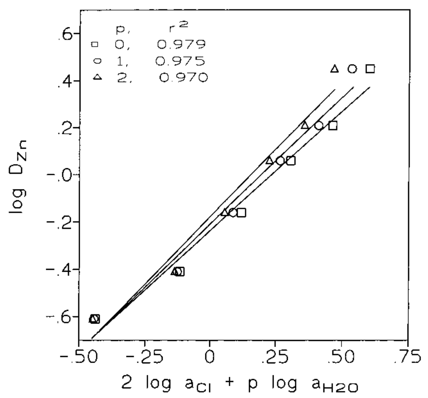

Fig. 2 Plot of log D_{Zn} *vs* $2\log a_{Cl}+p\log a_{H_2O}$ Aqueous phase: 0.015 mol l^{-1} zinc in 1 to 3.5 M chloride ion concentration range. Organic phase: 0.025 mol l^{-1} Cyanex 923 in Solvesso 100. Other experimental conditions as in Fig. 1.

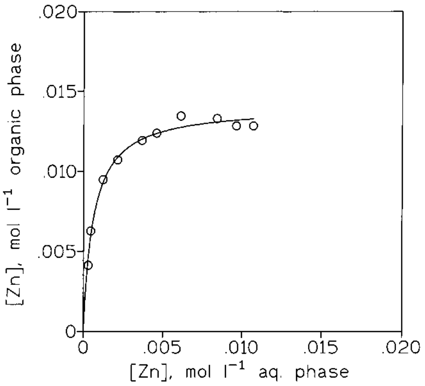

Fig. 3 Zinc loading equilibrium isotherm. Temperature 20°C. Equilibrium pH: 0.75 ± 0.02.

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