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The modelling of $ZnCl_2$ extraction and HCl co-extraction by TBP diluted in ShellSol 2046

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ABSTRACT

Zinc chloride and hydrochloric acid extraction from solutions of high zinc concentration by tri-*n*-butyl phosphate (TBP) diluted in ShellSol 2046 (an aliphatic solvent) has been studied with a combination of experiments and mathematical modelling. Above 0.4 mol/L aqueous zinc chloride, zinc is extracted predominantly as $ZnCl_2$ accompanied by small amounts of an acido–metal complex, most likely to be $HZnCl_3$. The Pitzer and Hildebrand–Scott models are used to estimate the activity coefficient of ions in the aqueous and organic phase respectively. Both the thermodynamic equilibrium constants and Hildebrand–Scott solubility parameters are fitted for the extracted species: $ZnCl_2(H_2O)_3 \cdot 3TBP$ and $HZnCl_3(H_2O)_3 \cdot 3TBP$. The modelling was able to predict both the extraction and stripping processes for aqueous zinc and acid concentration up to 1.6 and 1 mol/L respectively.

1. Introduction

With increased environmental awareness and stricter legislation, there is a greater need for more sustainable treatment of industrial effluents. This is especially true for hot-dip galvanising industries where the major wastewater stream is a spent pickling liquor rich in both $FeCl_2$ and $ZnCl_2$ with a typical ionic strength of 7–13 molal. There is a significant opportunity for zinc recovery from the waste effluent that is otherwise disposed into specialised landfills. For selective zinc recovery from spent pickling liquor, it has been concluded that the best extractants are tri-*n*-butyl phosphate (TBP) and diisotridecylamine (Cierpiszewski et al., 2002; Cook et al., 2011). TBP was chosen in this work as it is more readily available commercially.

TBP as an extractant has been extensively studied and a book series is even dedicated to reviewing these studies (Schulz et al., 1984). However there is still some confusion relating to the extracted species especially from solutions of high zinc and acid concentration. This confusion arises from the variety of extracted species, the solvation numbers reported and also the conditions at which these species are determined.

1.1. Extracted species

Morris and Short (1962) first proposed the reaction equilibria for zinc chloride extraction by TBP (Eqs. (1)–(3)). These authors suggested that below 0.8 mol/L HCl_{aq}, $ZnCl_2$ is extracted (Eq. (1)) while between 0.8 and 2.7 mol/L of acid both $ZnCl_2$ and $HZnCl_3$ are extracted (Eqs. (1) and (2)), and above 2.7 mol/L, H_2ZnCl_4 is extracted (Eq. (3)). The solvation number of the Zn–TBP complex also varies depending on the type of species extracted; two TBP molecules are required for every $ZnCl_2$ or H_2ZnCl_4 extracted while three molecules of the extractant are required for every $HZnCl_3$. However, this study was conducted at low initial zinc concentrations (7.95×10^{-5} mol/L). Therefore, as noted by Cierpiszewski et al. (2002), speciation may vary for solutions with higher zinc concentration.

$$Zn^{2+} + 2Cl^- + 2\overline{TBP} \rightleftharpoons \overline{ZnCl_2 \cdot 2TBP} \tag{1}$$

$$Zn^{2+} + 3Cl^- + H^+ + 3\overline{TBP} \rightleftharpoons \overline{HZnCl_3 \cdot 3TBP} \tag{2}$$

$$Zn^{2+} + 4Cl^- + 2H^+ + 2\overline{TBP} \rightleftharpoons \overline{H_2ZnCl_4 \cdot 2TBP} \tag{3}$$

The extraction of di-solvates ($ZnCl_2 \cdot 2TBP$) was also reported by Forrest et al. (1969). Similar to Morris and Short (1962), benzene was used as diluent but the initial zinc content was higher (0.05 mol/L Zn) and the hydrochloric acid concentration was lower at 0.01 mol/L. However, when Forrest et al. (1969) used kerosene as the diluent, the plot of the zinc distribution ratio against TBP concentration indicated the formation of tri-solvate ($ZnCl_2 \cdot 3TBP$). They concluded that both di- and tri-solvates of the extracted zinc chloride were formed under these conditions, with the latter being predominant (Forrest et al., 1969).

Sato (1972), using kerosene as diluent, also reported the formation of tri-solvates of $ZnCl_2$, with only partial extraction of HCl. These findings were based on experiments conducted across a broader range of zinc concentration (0.005–3.67 mol/L) and 0.01–0.2 mol/L HCl_{aq}. However, Mansur et al. (2008) reported the extraction of di-solvates even though

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Table 1
Comparison of various reported single salt Pitzer parameters for HCl.

Reference	$\beta^{(0)}$	$\beta^{(1)}$	C	Max. $ZnCl_2$ [molal]	Expt. sources
Pitzer and Mayorga (1973)	0.260175	1.6425	−0.08798	1.2	[a]
Kim and Frederick (1988a)	0.08887	2.94869	0.00095	10	[b]
Rard and Miller (1989)	0.228248	1.731375	−0.06553	1.5	[c]
Anstiss and Pitzer (1991) [d]	0.041312	1.80161	0.010082	23	[b]
Herbert and Mönig (1997) [e]	0.14366	2.96848	−0.00253	23	[b,c]

[a] Scatchard and Tefft (1930).
[b] Goldberg (1981).
[c] Rard and Miller (1989).
[d] $\alpha_1 = 1.53469$; $\omega(Zn,3Cl) = -1.77325\times10^{-4}$; $\omega(Zn,4Cl) = 1.30677\times10^{-6}$.
[e] $\beta^{(2)} = -0.2738$; $\alpha_2 = 0.6$.

kerosene was used as the diluent; the feed solution used contained 1.07 mol/L $ZnCl_2$ and 0.25 mol/L HCl.

The extraction of acido–metal species reported by Levin et al. (1972) was different to that of Morris and Short (1962). $HZnCl_3$ was reported to be extracted from a wider range of aqueous acid concentration between 1 and 7 mol/L, while H_2ZnCl_4 extraction occurred above 7 mol/L HCl_{aq}; both the acido–metal species were reported to be extracted as tri-solvates. However, only zinc distribution ratios were reported; both the aqueous and organic phase zinc concentrations and the organic phase acid concentrations were not given.

With zinc chloride capable of forming various chloro complexes, from $ZnCl^+$ to $ZnCl_4^{2-}$, there is speculation as to whether these complexes play a role in the extraction reaction, and if they do, which complex contributes to the extraction of zinc. Various researchers have utilised MEDUSA, a computer program that calculates the formation of such aqueous complexes (Puigdomenech, 2009), to determine that the zinc-chloro complex, $ZnCl_4^{2-}$, is predominant for spent pickling solution (Bartkowska et al., 2002; Cierpiszewski et al., 2002; Mishonov et al., 2004; Niemczewska et al., 2004; Regel et al., 2001; Rice and Smith, 1975; Samaniego et al., 2006). Based on this finding, Samaniego et al. (2006), assumed that zinc is extracted as H_2ZnCl_4, reporting a solvation number of 4 for the extracted species (Eq. (4)). While MEDUSA is certainly useful, the reliability of literature stability constants for zinc chloride speciation and the accuracy of the model used in estimating the activity coefficients of the aqueous phase remains uncertain.

$$Zn^{2+} + 4Cl^- + 2H^+ + 4\overline{TBP} \rightleftharpoons \overline{H_2ZnCl_4 \cdot 4TBP} \tag{4}$$

Using a Lewis cell to study the extraction of zinc chloride by TBP, Niemczewska et al. (2004) suggested that $ZnCl_4^{2-}$ approaches the aqueous-organic interface, but that the $ZnCl_2$ complex is transferred into the organic phase leaving two chloride ions in the aqueous phase (Eq. (5)). In light of the proposed equation, similar equilibrium reactions can be written for other zinc chloride complexes with their respective addition or rejection of chloride ions. This further complicates the zinc extraction mechanism, especially when acido–metal species are added to the extraction system.

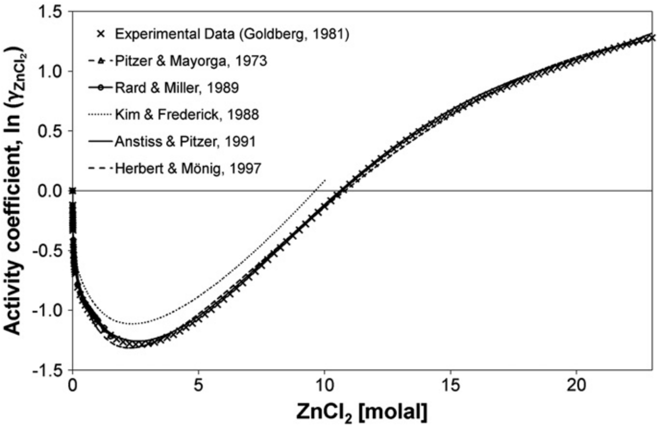

Fig. 1. Comparison of Pitzer single salt parameter for $ZnCl_2$ against experimental data from Goldberg (1981).

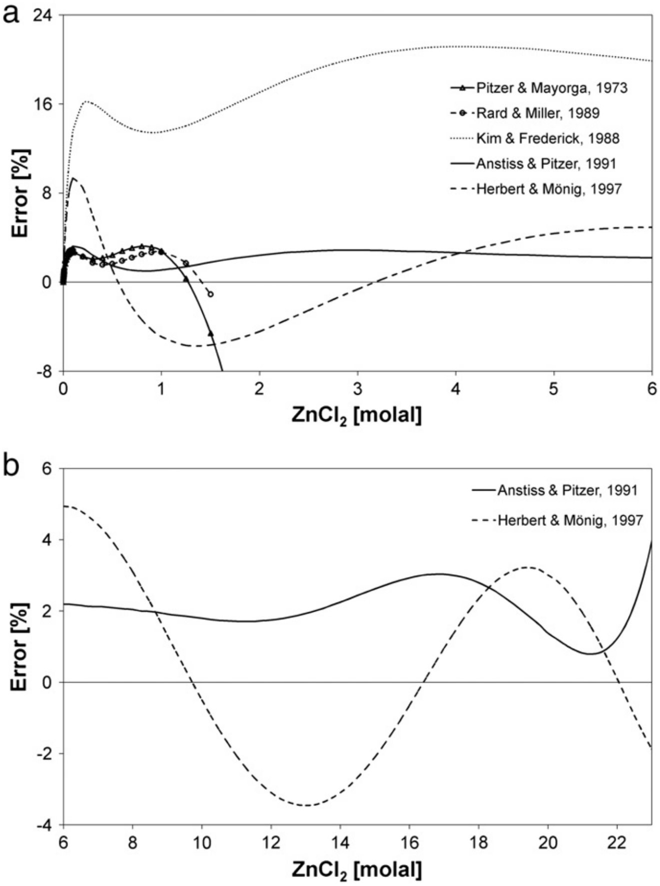

Fig. 2. Comparison of the error generated from the use of different Pitzer single salt parameters for $ZnCl_2$ in fitting the experimental data from Goldberg (1981); a) 0–6 molal $ZnCl_2$; b) 6–23 molal $ZnCl_2$.

$$ZnCl_4^{2-} + 2\overline{TBP} \rightleftharpoons \overline{ZnCl_2 \cdot 2TBP} + 2Cl^- \tag{5}$$

1.2. Chloride ion effect

The effect of acid concentration on zinc extraction has been described earlier when presenting the extraction mechanism proposed by Morris and Short (1962). Experimental results from Morris and Short (1962) showed a maximum zinc distribution ratio at around 2.5 mol/L HCl. Irving and Edgington (1959) and Sato (1972) both also showed similar results. Further increase in the aqueous phase HCl concentration led to a decrease in the zinc distribution ratio due to the competition for hydrochloric acid extraction. However, it is difficult to ascertain whether the increase in distribution ratio is due to the increase of H^+ or Cl^- ions.

In order to independently study the effect of chloride concentration on zinc extraction, Forrest et al. (1969) added calcium chloride to the aqueous phase. They reported a monotonic increase in the zinc distribution ratio with chloride content, with an inflection point at about 5 mol/L Cl^- before a further increase. The monotonic increase was believed to be due to an increase in the extraction of the $ZnCl_2$ complex as a result of the decrease in water activity and increase in chloride concentration (Forrest et al., 1969).