

Water adsorption in the organic phase for the D2EHPA–kerosene/water and aqueous Zn^{2+} , Co^{2+} , Ni^{2+} sulphate systems

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Abstract

Water adsorption by bis-2-ethylhexyl phosphoric acid (D2EHPA) during the extraction of zinc, cobalt and nickel using a D2EHPA–kerosene/H₂O mixture is investigated. Based on the experimental results, about 1 mol of water is adsorbed by 2 mol of D2EHPA (which exists in the form of a dimer), irrespective of the pH. Water adsorption decreases with presence of zinc, cobalt and nickel. The stoichiometric coefficients of D2EHPA in water adsorption reactions are determined with and without zinc, cobalt and nickel by applying the slope-analysis method. It is experimentally confirmed that 1.0, 1.8 and 1.2 mol of adsorbed water will be rejected from the organic phase when zinc, cobalt and nickel are extracted, respectively. It is predicted that a similar organic complex is formed by D2EHPA and water during the extraction of different metallic ions.

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1. Introduction

Solvent extraction used in hydrometallurgical processes consists of an aqueous phase containing metallic ions and an organic phase. Water is an important component of these systems. To develop a solvent extraction process, much research must be carried out to ascertain the effects of influential parameters like pH, extractant concentration, metal concentration and tem-

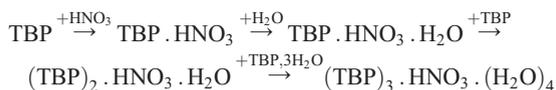
perature. However, compared to the metallic ion, the information on water adsorption is scarce and the effect of water adsorption requires more detailed studies.

The adsorption of water into an organic phase in a solvent extraction process has particular significance in: (a) influencing the mass balance in an engineering design process and (b) formation of organo-metallic complexes. Limited information is given by previous authors on these aspects. Widmer (1970) showed, for example, that under certain conditions, the major complex formed in the organic phase of the HClO₄–H₂O–MIBK system was HClO₄ · 9H₂O · MIBK. It meant that 9 molecules of water were adsorbed by one molecule of MIBK. In

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another study, the complex formation between TBP, nitric acid and H₂O was investigated (Naganawa and Tachimori, 1997). It was reported that the TBP–HNO₃–H₂O system could establish the following complexes:



when $[\text{TBP}]_{\text{total,org}} < 55\%$ (v/v) and $[\text{HNO}_3] < 3$ (mol/L).

Ma et al. (1999) have studied the water structure in water/KDEHPA–D2EHPA/n-heptane micro-emulsion systems by utilizing FT-IR spectroscopy. Whilst Liao et al. (2002) reported that in the TBP–kerosene/H₂SO₄–H₂O system, the two main complexes formed were (TBP)₂ · H₂SO₄ · (H₂O)₃ and TBP · H₂SO₄ · H₂O. Similarly, Zhengshui et al. (1999) have claimed that the composition of the third phase in the TBP–H₂SO₄–Ti (IV)–H₂O system could be one of three complexes: 2TBP · H₂SO₄ · 3H₂O, TBP · H₂SO₄ · H₂O or TBP · TiOSO₄ · 4H₂O when the concentration of sulphuric acid in the aqueous phase is in the range 6.3 to 10.2 mol/L.

This paper deals with water adsorption of the organic phase present in MSO₄/H₂O/D2EHPA–kerosene systems where *M* is a divalent metal ion such as zinc, nickel and cobalt. The number of adsorbed H₂O molecules in each system is estimated by a curve fitting analysis.

2. Experimental procedure

2.1. Materials

The commercial bis-2-ethylhexyl phosphoric acid (D2EHPA) extractant was purchased from Sandong Chemical, Chengdu, China. The Tehran Petrochemical Company supplied kerosene, which was used as a diluent. Aqueous solutions of 5 g/L zinc, cobalt and nickel were prepared by dissolving metal sulfates in distilled water; and NH₄OH and sulfuric acid were used for adjusting the pH of the system. The metal content of the aqueous phase was determined by titration against a standard solution of EDTA.

2.2. Experiments

A batch of experiments was carried out in a flask containing equal volumes (20 ml) of aqueous and organic solutions. The mixture was agitated at a constant temperature with a mechanical shaker for 60 min. Samples were then retained in the flask for a half an hour to allow complete separation of the phases. It was experimentally found that there was no change in the

amount of adsorbed water after 30 min, especially in the acidic pH range. The water content of the organic phases was measured using a Karl–Fischer titration method by Mettler Toledo DL18 titrator.

For estimating the number of moles of water, it is necessary to know the density of water which was measured using a Mettler Toledo DE40 density meter. The water concentration in the organic phase was calculated as:

$$[\text{H}_2\text{O}] = \frac{\text{H}_2\text{O}(\text{ppm}) \times \rho}{M_{\text{H}_2\text{O}} \times 1000} \quad (1)$$

where ρ and $M_{\text{H}_2\text{O}}$ are the density of organic phase and molecular weight of water.

3. Results and discussion

3.1. D2EHPA–kerosene/water system

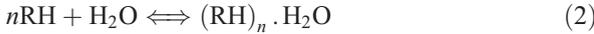
It has been found that the amount of water adsorbed by D2EHPA is significant (Table 1). In the D2EHPA–kerosene/H₂O system at pH 1.5 and ambient temperature, the amount of adsorbed water varies from 109 ppm to 16,000 ppm while the D2EHPA concentration varies from 1 to 80 vol.%. By comparison, the amount of adsorbed water in kerosene alone in the pH range of 1–5 was negligible (approximately 35 ppm). Considering the large volume of this extractant utilized every day in an industrial process, the amount of adsorbed water into the organic phase is indeed large.

As shown in Fig. 1, the variation of pH, at different concentration levels of D2EHPA, does not have a significant effect on the adsorption of water into the organic phase. Therefore it can be assumed that H⁺ is not involved in the water adsorption equilibrium and suggests that water will be adsorbed by D2EHPA through hydrogen bonding, i.e. in the absence of

Table 1
Variation of water adsorption versus the concentration of D2EHPA at 298 K

DEHPA (vol.%)	H ₂ O (ppm)	Density (g/cm ³)
0	35	0.7993
1	109	0.7980
5	406	0.8039
10	882	0.8142
20	2132	0.8327
30	4235	0.8483
40	5931	0.8660
60	10,795	0.9029
80	16,183	0.9390

metallic ion, it is proposed that the adsorption of water into the organic phase can be explained as:



where R is D2EHPA and n is the number of molecules. The equilibrium constant is described by Eq. (3):

$$K = \frac{[(RH)_n \cdot H_2O]}{[RH]_{equ}^n [H_2O]} \times \frac{\gamma[(RH)_n \cdot H_2O]}{\gamma_{[RH]_{equ}}^n \gamma_{[H_2O]}} = \frac{[(RH)_n \cdot H_2O]}{[RH]_{equ}^n [H_2O]} \times Q \quad (3)$$

where Q=activity coefficient term and [RH]_{equ} is defined as the equilibrium concentration of unassociated D2EHPA. Hence

$$\log [(RH)_n \cdot H_2O] = \log \frac{K}{Q} + n \log [RH]_{equ} + \log [H_2O] \quad (4)$$

and substituting for [RH]_{equ} by mass balance gives

$$\log [(RH)_n \cdot H_2O] = \log \frac{K}{Q} + n \log ([RH]_o - n[(RH)_n \cdot H_2O]) + \log [H_2O] \quad (5)$$

Fig. 2 illustrates the plots of log[(RH)_n · H₂O] against f(n)=log([RH]_o - n[(RH)_n · H₂O]). A straight line slope analysis gives the value of n=1.5–2.0, which is the stoichiometric coefficient of extractant in the H₂O/D2EHPA system. A review of previous work (Sainz-

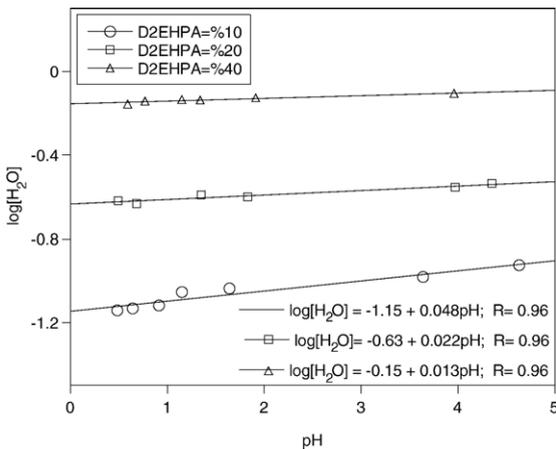


Fig. 1. Variation of log [H₂O] with pH, using D2EHPA as extractant at three concentrations.

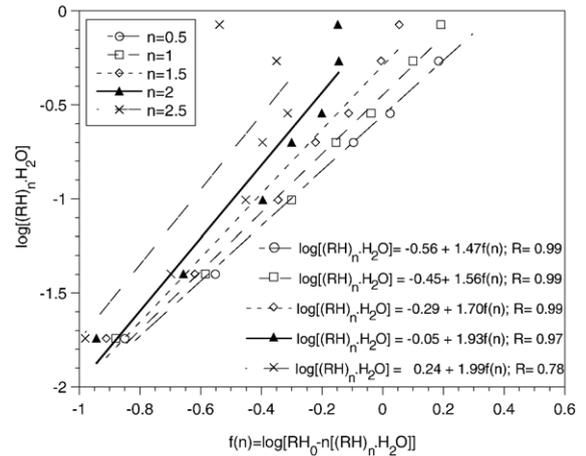


Fig. 2. Variation of log [H₂O] versus log([RH]_o - n[H₂O]), using 20 vol.% D2EHPA as extractant at pH = 1.5.

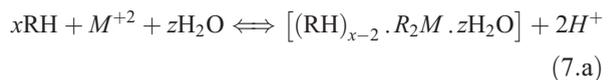
Diaz et al., 1996; Vegilo and Slater, 1996; Mansur et al., 2002) shows that organo-phosphoric acid extractants participate in the metal extraction reaction predominantly in the dimer form. The dimerisation of D2EHPA is due to the formation of hydrogen bonds between the donor oxygen of D2EHPA and the acceptors hydrogen from the P–OH group. The adsorbed water is expected to H-bond to monomeric D2EHPA at both the donor oxygen and P–OH sites. This can, of course, be generalized for other organo-phosphoric acid extractants.

In this work, it has been observed that two molecules of D2EHPA extractant are associated with each molecule of water adsorbed. Hence, the adsorption equation of water can be represented as follows:

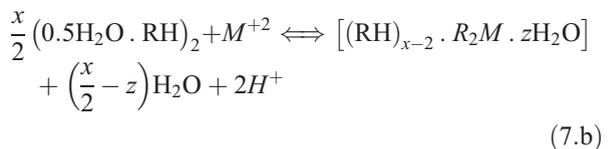


3.2. D2EHPA–kerosene/aqueous metal sulphate system

For simplification, the water adsorption during metal ion extraction by an acidic extractant could be considered as:



If the above equation is considered to be pre-equilibrated with water then:



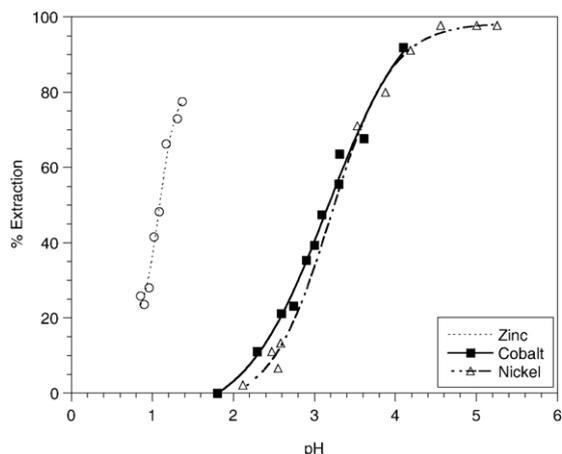


Fig. 3. Extraction of zinc, cobalt and nickel by 20 vol.% D2EHPA at 298 K. (initial concentration 5 g/L).

where R is D2EHPA; x and z are the number of D2EHPA and water molecules respectively; and M^{2+} is a divalent metal including zinc, nickel and cobalt.

Values of x were previously calculated to be 3, 4 and 4 for the aqueous $ZnSO_4$, $NiSO_4$ and $CoSO_4$ /D2EHPA–kerosene systems, respectively (Darvishi et al., 2005a, b). However, these previous investigations were carried out without consideration of water adsorption. The equilibrium concentration of the organic phase should be defined by the general equation (cf Eq. (2)):

$$[RH]_{\text{equ}} = [RH]_o - x[(RH)_{x-2} \cdot R_2M \cdot zH_2O] \quad (8)$$

According to Eqs. (7.a) and (7.b), Eq. (8) can be rewritten as Eq. (9):

$$[RH]_{\text{equ}} = [RH]_o - xz[H_2O] \quad (9)$$

The extraction constant is described by the relation:

$$K = \frac{[(RH)_{x-2} \cdot R_2M \cdot zH_2O][H^+]^2}{[M^{2+}][RH]_{\text{equ}}^x [H_2O]^z} \times \frac{\gamma_{[(RH)_{x-2} \cdot R_2M \cdot zH_2O]} \gamma_{[H^+]^2}}{\gamma_{[M^{2+}]} \gamma_{[RH]_{\text{equ}}}^x \gamma_{[H_2O]}^z} = \frac{[(RH)_{x-2} \cdot R_2M \cdot zH_2O][H^+]^2}{[M^{2+}][RH]_{\text{equ}}^x [H_2O]^z} \times Q \quad (10)$$

The distribution coefficient of M^{2+} may be written as:

$$D = \frac{[(RH)_{x-2} \cdot R_2M \cdot zH_2O]}{[M^{2+}]}$$

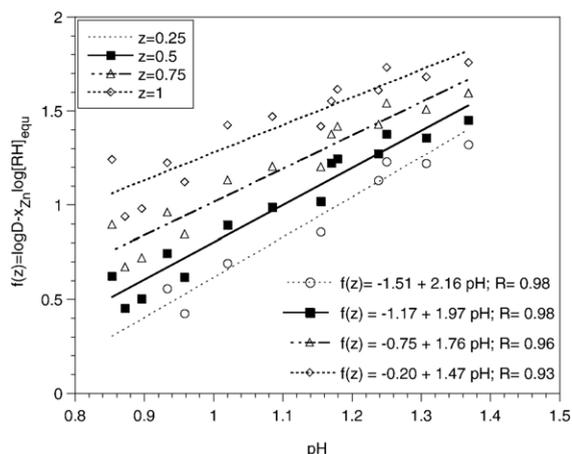


Fig. 4. Variation of $f(z) = \log D - x_{Zn} \log [RH]_{\text{equ}}$ versus pH for zinc. (20 vol.% D2EHPA at 298 K).

Therefore the following expression can be derived:

$$\log D = \log \frac{K}{Q} + 2pH + x \log [RH]_{\text{equ}} + z \log [H_2O] \quad (11)$$

The variation in % extraction of these metals with pH is illustrated in Fig. 3.

The stoichiometric coefficient of H_2O , z , can be calculated by a trial and error method. Plotting $(\log D - x \log [RH]_{\text{equ}})$ against pH at different values of z , gives straight lines with different slopes and intercepts. The correct one for the water adsorption equation is the line with slope 2 because of the stoichiometry of hydrogen ion (H^+) in the extraction Eqs. (7.a) and (7.b).

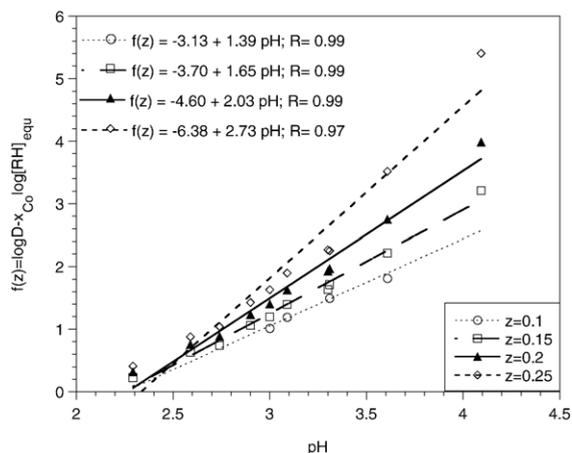


Fig. 5. Variation of $f(z) = \log D - x_{Co} \log [RH]_{\text{equ}}$ versus pH for cobalt. (20 vol.% D2EHPA at 298 K).

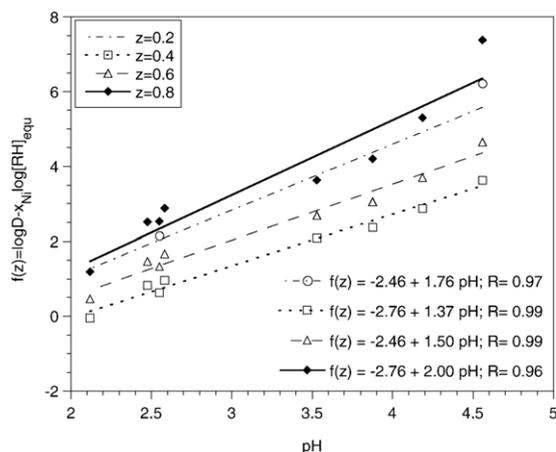
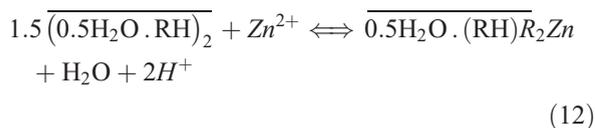


Fig. 6. Variation of $f(z) = \log D - x_{Ni} \log [RH]_{equ}$ versus pH for nickel. (20 vol.% D2EHPA at 298 K).

Fig. 4 shows the plots of $\log D - x_{Zn} \log [RH]_{equ}$ against pH for the Zn^{2+} system. It can be seen that the H_2O stoichiometric coefficient, z , is equal to 0.5 for 3 molecules of D2EHPA. In comparison with the D2EHPA–kerosene/water system, the water content of the organic phase will decrease when the zinc extraction process occurs. Based on the results obtained from slope analysis, the adsorption equation of water during zinc extraction can be represented as follows after pre-equilibration with water:



Eq. (12) shows that the water content of the organic phase will decrease from 1.5 mol to 0.5 mol during zinc extraction.

Similar results have been obtained for the aqueous Co^{2+} and Ni^{2+} systems with different values of H_2O stoichiometric coefficient, z . Figs. 5 and 6 illustrate the plots of $\log D - x \log [RH]_{equ}$ against pH. Results show that with cobalt, very little water (~ 0.2 molecules) participates in the organo-metallic complex; whilst with nickel there is weak association with about 1 molecule of water ($z=0.8$). Therefore, it has been experimentally shown that the amount of the rejected water during zinc, cobalt and nickel extraction is about 1.0, 1.8 and 1.2 molecules respectively. By increasing the extraction percentage of zinc, cobalt or

nickel, the water content of the organic phase decreases. Conversely, in the stripping reaction, water enters into the organic phase which can influence the mass balance of water and concentration of the strip solution.

4. Conclusions

In the large scale industrial solvent extraction process, the amount of water adsorbed by D2EHPA is significant and should be taken into account in mass balance determinations. When D2EHPA concentration varies from 1 to 80 vol.%, the amount of adsorbed water at ambient temperature varies from 109 to 16,000 ppm and is independent of pH. These amounts are less when D2EHPA extracts zinc, cobalt and nickel and forms complexes. By applying the slope analysis method, the stoichiometric amount of D2EHPA per mole of water was found to be about 1.5–2.0 with D2EHPA predominantly present as dimer.

The stoichiometric coefficients of water in the D2EHPA–kerosene/aqueous Zn^{2+} , Co^{2+} and Ni^{2+} systems were found to be 0.5, 0.2 and 0.8, respectively. This means that during zinc, cobalt and nickel extraction, 1, 1.8 and 1.2 mol of water are rejected respectively.

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