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Extraction equilibrium of manganese(II) from sulfate solutions by di(2-ethylhexyl)phosphoric acid dissolved in kerosene

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A B S T R A C T

The distribution ratios of manganese(II) extracted from an aqueous sulfate medium by di(2-ethylhexyl)phosphoric acid (D2EHPA) dissolved in kerosene were studied at 25 °C. The extraction equilibria are influenced by the total extractant concentration in the organic phase, equilibrium pH values and total sulfate concentration in the aqueous phase. The distribution data have been analyzed both graphically and numerically. The results show that the species extracted into the organic phase have compositions of $\overline{\mathrm{MnR_2(HR)_2}}$ and $\overline{\mathrm{MnR_2(HR)_3}}$. The stability constants of $MnSO_4$ and HSO_4^- in the sulfate solutions were also estimated from the extraction data.

1. Introduction

Di(2-ethylhexyl)phosphoric acid (abbreviated as D2EHPA in the text and HR in the equation) is an organophosphorus acid extractant and has been widely used in hydrometallurgical processes for the separation and purification of a variety of metal ions, due to its chemical stability, extremely low solubility in aqueous acidic solutions, and high selectivity for metal ions (Biswas *et al.*, 2005; Haghshenas *et al.*, 2009; Huang and Huang, 1987, 1988; Huang and Juang, 1986; Huang and Tsai, 1989, 1990; Nathsarma and Devi, 2006; Ritcey and Ashbrook, 1984; Sekine and Hasegawa, 1977; Zhang and Cheng, 2007).

In recent years, the extraction equilibrium of the extraction of manganese(II) with D2EHPA has been characterized by many investigators. Islam and Biswas (1981) explored the extraction of Mn^{2+} from sulfate–acetate medium with D2EHPA in benzene and demonstrated the formation of $Mn(HR_2)_2$. Biswas *et al.* (2000) studied the distribution of manganese between an aqueous chloride solution and a solution of D2EHPA in kerosene and proposed that the $MnR_2(HR)_2$ compound was formed in the organic phase. In a chloride/kerosene medium, the extraction of manganese with D2EHPA was investigated by Biswas *et al.* (1997) using a single drop technique, and the extracted species was determined to be $Mn(HR_2)_2HR$, located in the organic phase. In the above researchers' studies, the stability constants of the complexes were ignored and the effect of the ionic strength on the extraction was not fully investigated. In short, the mechanism of the manganese extraction system had not yet been fully understood.

Although the extraction of manganese(II) with D2EHPA has already been explored, the uncertainties regarding the species composition are not the same and have not been reported in detail in the above literature. However, a number of equilibrium studies for the metal/D2EHPA/diluent system had been proposed in the literature and indicated that more than one complex exist simultaneously in the organic phase (Huang and Tsai, 1989, 1990; Mansur *et al.*, 2002; Nagaosa and Binghua, 1997). Therefore, further experimental studies are necessary in order to determine the composition of the various extracted manganese species and the stoichiometry of the metal–organic complexes in the organic phase consisting of D2EHPA and kerosene. In addition, the distribution coefficients and extraction constants of the metal–organic complexes should be determined. To get a complete understanding of the system, the extraction of manganese was studied first by graphic and slope analysis techniques, which assume no complex formation in the aqueous phase. Then, by numerical analysis of the experimental data, values for stability constants of the $MnSO_4$ and HSO_4^- complexes in the aqueous sulfate solutions were obtained.

2. Experimental

2.1. Reagents and solutions

D2EHPA used in this work is the product of Daihachi Chemical Ind. Co., Ltd., Osaka, Japan. A purity of 95% was found by potentiometric titration with NaOH in ethanolic medium. D2EHPA

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was further precipitated as a copper complex from toluene and acetone solutions and then dissolved in toluene and a 4 kmol/m^3 sulfuric acid solution, following the procedure of McDowell *et al.* (1976). The purity of D2EHPA was more than 99.5%. Kerosene (density = 786 kg/m^3, boiling range = 200–250 °C) was used as a diluent (supplied by Chinese Petroleum Co., Taiwan). The mixture was then washed twice with 1/5 volume of 98% H_2SO_4 to remove aromatics and then washed with distilled water until neutral (Sato, 1965). The other inorganic chemicals were analytical reagent grade supplied by Shimakyu's Pure Chemical Ind., Ltd., Osaka, Japan. The stock solutions for the extraction process were prepared by dissolving the manganese sulfate ($MnSO_4 \cdot H_2O$) in distilled water. Working solutions of manganese were always prepared by sampling the appropriate volumes of the stock solution and diluting with distilled water.

2.2. Procedure

Twenty milliliters of the organic solution and an equal volume of aqueous solution were mixed in glass flasks with ground glass stoppers and shaken by a mechanical shaker for at least 30 min at 25.0 ± 0.2 °C until equilibrium was attained. Preliminary experiments had shown the reaction time needed to reach equilibrium was less than 15 min. The organic solutions contained a 0.0100–0.200 kmol/m^3 solution of monomeric form D2EHPA dissolved in kerosene.The concentration of manganese ion in the initial aqueous solutions ranged from 4.04×10^{-5} to 4.66×10^{-3} kmol/m^3. The two phases separated after they had been allowed to settle for over 6 h at 25.0 ± 0.2 °C.

After phase disengagement, the equilibrium hydrogen ion concentration was measured by a pH meter. The concentration of manganese was measured with a GBC SenseAA atomic absorption spectrophotometer (AAS) at a wavelength of 280.1 nm, coupled with background correction. Manganese in the organic phase was stripped with 2 kmol/m^3 nitric acid and the metal concentration in the acidic solutions was analyzed by AAS. The process has been shown to be quantitative and the mass balance for the metal was always fulfilled in the extraction–stripping procedure to within ±2%.

3. Results and discussion

3.1. Extraction equilibrium of manganese

Metal complexes of D2EHPA tend to form very large polymeric species in a fully loaded organic phase. These polymers are strongly depolymerized in the presence of free D2EHPA molecules and ethylene glycol (Kolarik and Grimm, 1974). Thus, it is necessary to assume that manganese is extracted as an *m*-merized complex into the slightly loaded organic phase. The extraction of manganese(II) with D2EHPA can be represented by the following general reaction

$$m\,\mathrm{Mn}^{2+} + \left\{\frac{m(p+q)}{2}\right\}\overline{\mathrm{H_2R_2}} \rightleftharpoons \overline{(\mathrm{MnR}_p(\mathrm{HR})_q)_m} + m\,p\,H^{+} \tag{1}$$

where

$$K_{mpq} = \frac{\left[\overline{(\mathrm{MnR}_p(\mathrm{HR})_q)_m}\right][\mathrm{H}^+]^{mp}}{[\mathrm{Mn}^{2+}]^m\left[\overline{\mathrm{H_2R_2}}\right]^{m(p+q)/2}} \tag{2}$$

is the stoichiometric equilibrium constant for sulfate solutions with kerosene as the diluent, and the bar indicates the species in the organic phase.

The distribution ratio of manganese is defined as:

$$D_{\mathrm{Mn}} = \frac{\left[\overline{\mathrm{Mn(II)}}\right]}{[\mathrm{Mn(II)}]} \tag{3}$$

Substituting Eq. (2) into Eq. (3), we obtain

$$\begin{aligned} D_{\mathrm{Mn}} &= \frac{m\left[\overline{(\mathrm{MnR}_p(\mathrm{HR})_q)_m}\right]}{[\mathrm{Mn}^{2+}]} \\ &= m\,K_{mpq}\left[\mathrm{Mn}^{2+}\right]^{m-1}\left[\overline{\mathrm{H_2R_2}}\right]^{m(p+q)/2}\left[\mathrm{H}^+\right]^{-mp} \end{aligned} \tag{4}$$

At constant concentrations of D2EHPA and a low distribution ratio, $\left[\mathrm{Mn}^{2+}\right]^{m-1}\left[\overline{\mathrm{H_2R_2}}\right]^{m(p+q)/2}$ will be approximately constant. Thus, a plot of log D_{Mn} *versus* pH will give a straight line with a slope of *mp*. The experimental results are shown in Fig. 1. The straight lines have slopes of 2, *i.e.*, *mp* = 2. Thus, Eq. (4) can be simplified to

$$\left[\overline{\mathrm{Mn(II)}}\right]\left[\mathrm{H}^+\right]^2 = m\ \ K_{mpq}\left[\mathrm{Mn}^{2+}\right]^m\left[\overline{\mathrm{H_2R_2}}\right]^{m(p+q)/2} \tag{5}$$

At constant concentrations of D2EHPA, the degree of aggregation of the Mn–D2EHPA complex in the organic phase, *m*, is obtained from the plot of $\log\left[\overline{\mathrm{Mn(II)}}\right]\left[\mathrm{H}^+\right]^2$ *versus* $\log\left[\mathrm{Mn}^{2+}\right]$. As shown in Fig. 2, the straight lines have unit slopes. Therefore, the extracted species is monomeric, *i.e.*, *m* = 1. And then, *p* = 2. Thus, Eqs. (2) and (4) can be simplified to

$$K_{2q} = \frac{\left[\overline{(\mathrm{MnR_2(HR)}_q)}\right]\left[\mathrm{H}^+\right]^2}{[\mathrm{Mn}^{2+}]\left[\overline{\mathrm{H_2R_2}}\right]^{(2+q)/2}} \tag{6}$$

and

$$D_{\mathrm{Mn}} = K_{2q}\left[\overline{\mathrm{H_2R_2}}\right]^{(2+q)/2}\left[\mathrm{H}^+\right]^{-2} \tag{7}$$

Rearranging Eq. (7), it follows that

$$\log D_{\mathrm{Mn}} - 2\mathrm{pH} = \log K_{2q} + \left\{\frac{(2+q)}{2}\right\}\log\left[\overline{\mathrm{H_2R_2}}\right] \tag{8}$$

First, it could be assumed that only species of the type $\overline{\mathrm{MnR_2(HR)}_q}$ are formed. Thus, a plot of $\log(D_{\mathrm{Mn}}\left[\mathrm{H}^+\right]^2)$ *versus* $\log\left[\overline{\mathrm{H_2R_2}}\right]$ would give a straight line with an intercept equal to K_{2q} and a slope equal to (2 + *q*)/2.

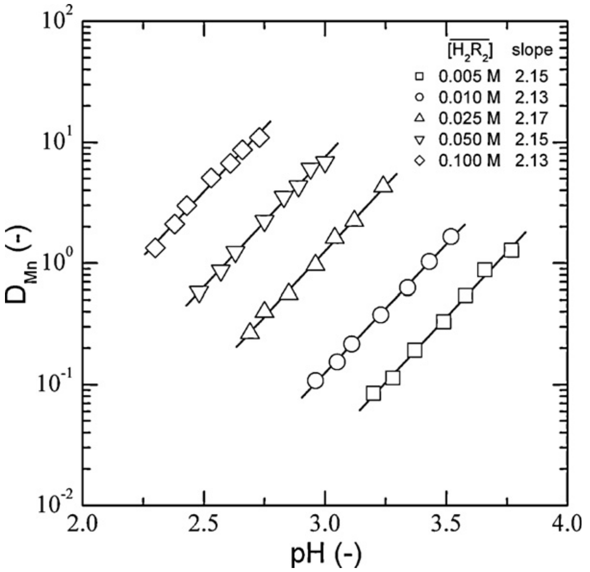

Fig. 1. Plots of log D_{Mn} *versus* pH at equilibrium for various D2EHPA concentrations in kerosene at 25 °C. $[\mathrm{Mn}^{2+}]_t = [\mathrm{SO}_4^{2-}]_t = 4.04 \times 10^{-5}$ to 4.66×10^{-3} kmol/m^3. (□) $\left[\overline{\mathrm{H_2R_2}}\right] = 0.005$ kmol/m^3, slope = 2.15; (○) $\left[\overline{\mathrm{H_2R_2}}\right] = 0.010$ kmol/m^3, slope = 2.13; (▽) $\left[\overline{\mathrm{H_2R_2}}\right] = 0.025$ kmol/m^3, slope = 2.17; (△) $\left[\overline{\mathrm{H_2R_2}}\right] = 0.050$ kmol/m^3, slope = 2.15; (◇) $\left[\overline{\mathrm{H_2R_2}}\right] = 0.100$ kmol/m^3, slope = 2.13.