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Kinetic and Thermodynamic Separation of Cu(II) and Fe(III) by Liquid-Liquid Extraction with a β-Hydroxy-oxime in Toluene

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ABSTRACT

A quantitative study of the thermodynamic and kinetic separation of Cu(II) and Fe(III) by liquid-liquid extraction with toluene solutions of the oxime 2-hydroxy-5-t-octyl(acetophenone oxime) has been conducted. On the basis of the stoichiometry, equilibrium constants, rate laws and rate constants of the extraction reactions of Cu(II) and Fe(III) an equation has been derived which describes how the separation of Cu from Fe varies with the chemical composition of the system, the hydrodynamics of the extracting apparatus and the contact time between the aqueous and the organic phases. Our results show that separations which are not feasible thermodynamically are possible when the contact time between the two phases is kept much shorter than that required to reach equilibrium.

INTRODUCTION

Liquid-liquid extraction has been widely used since long ago as a very effective separation technique of metal species (1).

Nevertheless, nearly all the separations whose chemistry has been thoroughly elucidated are based only on the different thermodynamic stabilities of the chemical species which the extractable metals can form with the various reagents present in the aqueous and organic phases.

In the present paper an analysis of the possibility of performing a separation between two metals by liquid-liquid extraction by taking advantage of the different extraction rates is reported. Separations which are not thermodynamically feasible are shown here to be possible, provided the chemical composition of the system and the hydrodynamics of the extraction apparatus are properly chosen.

The separation of Cu(II) from Fe(III) by liquid-liquid extraction using as the extracting phase a β-hydroxy-oxime (2-hydroxy-5-t-octyl(acetophenone oxime)) dissolved in toluene is described from both the thermodynamic and the kinetic point of view.

EXPERIMENTAL

Materials

The β-hydroxy-oxime used throughout this work was 2-hydroxy-5-t-octyl(acetophenone oxime), HOx, (mol. wt. = 263.4) kindly supplied by Dr. M. Cox of Hatfield Polytechnic, Herts, United Kingdom. The purity of the products and the analytical procedures used have been described previously (2). All the aqueous solutions used in this work had a constant chloride concentration, $[Cl^-] = 2$ M.

All experiments were performed at a constant temperature (25 ± 1°C).

Kinetic Measurements

The kinetic measurements have been described in reference (2).

Equilibrium Distribution of Cu(II) and Fe(III)

The distribution ratios K_d, defined as the ratio between the organic phase metal concentration and the aqueous phase metal concentration were determined by shaking equal volumes of each phase for several hours and then analyzing the metal concentrations in both the resulting aqueous and organic phases.

Aggregation

The aggregation data of HOx in toluene were taken from reference (3). In toluene HOx undergoes only a monomer-dimer equilibrium according to the equation $2\ \overline{HOx} \rightleftharpoons \overline{(HOx)}_2$, $\beta_2 = 8.9\ M^{-1}$, where the bar indicates organic species and β_2 the dimerization constant. It then follows:

$$[\overline{HOx}]_{total} = [\overline{HOx}]_m + 2\ \beta_2\ [\overline{HOx}]_m^2 \ .$$

In the following sections $[\overline{HOx}]_m$ will always represent the toluene monomer concentration of HOx.

RESULTS AND DISCUSSION

Stoichiometry and Equilibrium Constants of the Extraction Reactions

By analyzing the slope values of the logarithmic plots $\log K_d$ vs $\log [\overline{HOx}]_m$, at constant $[H^+]$, and $\log K_d$ vs $\log [H^+]$, at constant $[\overline{HOx}]_m$ the stoichiometric coefficients as well as the conditional equilibrium constants of the extraction reactions can be evaluated. These plots are shown in Figure 1 for Cu(II) and in Figure 2 for Fe(III).

In the case of the $[\overline{HOx}]_m$ dependencies, Figures 1a and 2a, both the oxime and proton concentrations were in large excess with respect to those of the extracted metals. Therefore the equilibrium and initial concentrations of $[\overline{HOx}]_m$ and $[H^+]$ have been considered as equal. In the case of the $[H^+]$ dependencies, Figures 1b and 2b, the aqueous equilibrium hydrogen ion con-

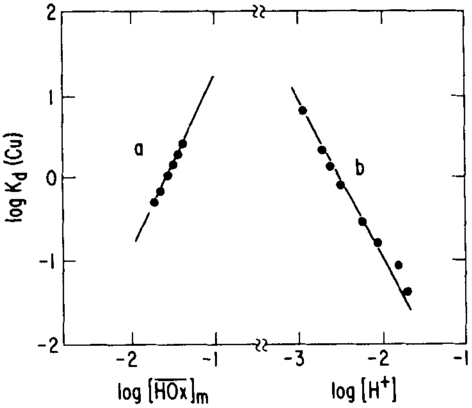

FIGURE 1.

Logarithmic plot of:

a) K_d(Cu) vs $[\overline{HOx}]_m$ (M), at [Cu(II)] = $3.06 \cdot 10^{-4}$ M, $[H^+]$ = $2 \cdot 10^{-2}$ M, $[Cl^-]$ = 2 M; the slope of the straight line is +2.1.

b) K_d(Cu) vs $[H^+]$ (M), at [Cu(II)] = $3.06 \cdot 10^{-4}$ M, $[\overline{HOx}]_m$ = $4.6 \cdot 10^{-3}$ M, $[Cl^-]$ = 2 M; the slope of the straight line is -1.9.

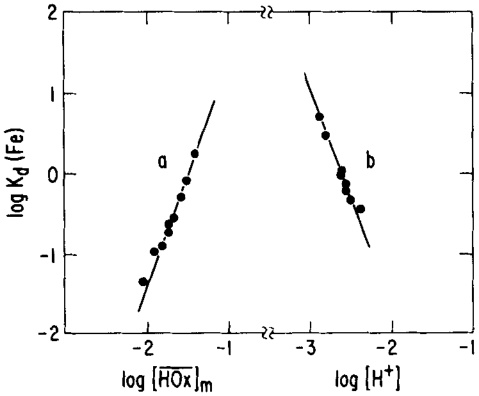

FIGURE 2.

Logarithmic plot of:

a) K_d(Fe) vs $[\overline{HOx}]_m$ (M), at [Fe(III)] = $3.06 \cdot 10^{-4}$ M, $[H^+]$ = $2.7 \cdot 10^{-3}$ M, $[Cl^-]$ = 2 M; the slope of the straight line is +2.8.

b) K_d(Fe) vs $[H^+]$ (M), at [Fe(III)] $3.06 \cdot 10^{-4}$ M, $[\overline{HOx}]_m$ = $3.10 \cdot 10^{-2}$ M, $[Cl^-]$ = 2 M; the slope of the straight line is -2.8.

centrations have been corrected by considering that two hydrogen ions are released into the aqueous phase for each Cu^{2+} ion entering the organic phase and that three hydrogen ions are released into the aqueous phase for each Fe^{3+} entering the organic phase.

The data shown in Figures 1 and 2 fall on straight lines having slopes of +2.1 ($[\overline{HOx})_m$ dependency) and -1.9 ($[H^+]$ dependency) for copper(II) and of +2.8 ($[\overline{HOx}]_m$ dependency) and -2.8 ($[H^+]$ dependency), for iron(III), indicating that the stoichiometries of the extraction reactions are the following:

$$Cu^{2+} + 2\ \overline{HOx} \rightleftharpoons \overline{CuOx_2} + 2\ H^+ \qquad (1)$$

$$Fe^{+3} + 3\ \overline{HOx} \rightleftharpoons \overline{FeOx_3} + 3\ H^+ \qquad (2)$$

The bar indicates organic phase species. The data of Figures 1 and 2 also allow one to evaluate the values of the conditional equilibrium constants of reactions (1) and (2), K_{eq} (Cu) = 0.55 and K_{eq} (Fe) = $5.5 \cdot 10^{-4}$.

Rate Laws and Rate Constants of the Extraction Reactions

The kinetics of the extraction reactions have been previously reported (2). The forward extraction reaction rates have been shown to be well represented by the laws:

$$-\frac{d\,[Cu]}{dt} = a_i\ k_{1Cu}\ [Cu^{2+}]\ [\overline{HOx}]_m\ [H^+]^{-1} \qquad (3)$$

$$-\frac{d\,[Fe]}{dt} = a_i\ k'_{Fe}\ [Fe^{+3}]\ [\overline{HOx}]_m\ [H^+]^{-1} + k''_{Fe}\ [Fe^{+3}]\ [\overline{HOx}]_m \qquad (4)$$

where a_i = specific interfacial area, i.e., the ratio between the interfacial area available for the extraction and the volume of either the aqueous (V_A) or organic phase (V_0). Equal values of V_A and V_0 are considered throughout this work.

By applying the principle of microscopic reversibility to reactions (1) and (2), whose conditional equilibrium constants are known, it follows

$$-\frac{d\,[Cu]}{dt} = a_i\,(k^*_{1Cu}\,[Cu^{2+}] - k^*_{-1Cu}\,[\overline{CuOx_2}]) \qquad (5)$$

$$-\frac{d\,[Fe]}{dt} = a_i\,(k^*_{1Fe}\,[Fe^{+3}] - k^*_{-1Fe}\,[\overline{FeOx_3}]) \qquad (6)$$

Since both $[\overline{HOx}]_m$ and $[H^+]$ are much larger than $[Cu^{2+}]$ and $[Fe^{+3}]$, k^*'s represent pseudo first order rate constants, i.e.

$$k^*_{1Cu} = 2.83\cdot10^{-4}(cm\cdot s^{-1})[\overline{HOx}]_m[H^+]^{-1} \qquad (7)$$

$$k^*_{-1Cu} = 5.15\cdot10^{-4}(cm\cdot s^{-1})[\overline{HOx}]_m^{-1}[H^+] \qquad (8)$$

$$k^*_{1Fe} = 1.94\cdot10^{-5}(cm\cdot s^{-1})[\overline{HOx}]_m[H^+]^{-1} + 9.23\cdot10^{-4}(cm\cdot s^{-1}\ M^{-1})\ [\overline{HOx}]_m \qquad (9)$$

$$k^*_{-1Fe} = 3.5\cdot10^{-2}(cm\cdot s^{-1})\ [\overline{HOx}]_m^{-2}[H^+]^2 + 1.68(cm\cdot s^{-1}\ M^{-1})[\overline{HOx}]_m^{-2}[H^+]^3 \qquad (10)$$

Thermodynamic and Kinetic Separation Parameters

In order to express the extent of separation which can be achieved by liquid-liquid extraction as a function of time it is convenient to introduce a separation parameter, S_t, defined as the concentration ratio of the two metals in the organic phase after a given time divided by the initial concentration ratio of the two metals in the aqueous phase, i.e.

$$S_t = \frac{[\overline{Cu}]_t}{[\overline{Fe}]_t} \Bigg/ \frac{[Cu]_{in}}{[Fe]_{in}} \qquad (11)$$

$[\overline{Cu}]_t$ and $[\overline{Fe}]_t$ are the organic concentrations of Cu and Fe after a contact time between the two phases equal to t, and $[Cu]_{in}$ and $[Fe]_{in}$ are the initial concentrations of the two metals in the aqueous phase. The thermodynamic separation parameter will then be expressed by

$$S_\infty = \frac{\overline{[\mathrm{Cu}]}_\infty}{\overline{[\mathrm{Fe}]}_\infty} \Bigg/ \frac{[\mathrm{Cu}]_{in}}{[\mathrm{Fe}]_{in}} = \qquad (12)$$

$$\frac{K_{eq}(\mathrm{Cu})\cdot K_{eq}^{-1}(\mathrm{Fe})[\mathrm{H}^+]^3 + K_{eq}(\mathrm{Cu})\cdot\overline{[\mathrm{HOx}]}_m^3}{\overline{[\mathrm{HOx}]}_m\,[\mathrm{H}^+]^2 + K_{eq}(\mathrm{Cu})\overline{[\mathrm{HOx}]}_m^3}$$

At very low acidities $S_\infty \sim 1$ and no separation of Cu from Fe is possible at equilibrium. On the other hand, at very high acidities S_∞ becomes extremely large since reaction (2) is displaced to the left more than reaction (1). pH values <1 are however impracticable because of the very low extraction of Cu. Further, equation (12) clearly indicates that at a given acidity S_∞ decreases by increasing $\overline{[\mathrm{HOx}]}_m$. The curves a, b, c, d, and e shown in Figure 3, which describe how the thermodynamic separation factor varies with the acidity of the aqueous solution, have been calculated through equation (12) at different total oxime concentrations, $\overline{[\mathrm{HOx}]}_{total}$.

For times $\neq \infty$ an equation which describes the kinetic separation factor as function of the chemical parameters ($\overline{[\mathrm{HOx}]}_m$, $[\mathrm{H}^+]$), the hydrodynamic of the system (a_i) and time (t), can be easily derived by integrating equations (5) and (6). It follows then

$$S_t = \frac{1 - \dfrac{k^*_{-1Cu} + k^*_{1Cu}\exp\left[-(k^*_{1Cu} + k^*_{-1Cu})\,a_i t\right]}{k^*_{1Cu} + k^*_{-1Cu}}}{1 - \dfrac{k^*_{-1Fe} + k^*_{1Fe}\exp\left[-(k^*_{1Fe} + k^*_{-1Fe})\,a_i t\right]}{k^*_{1Fe} + k^*_{-1Fe}}} \qquad (13)$$

The concentration dependence of the k^*'s is reported in equations (7) through (10). When t is very close to zero it follows from equations (13), (7), (8), (9) and (10) that

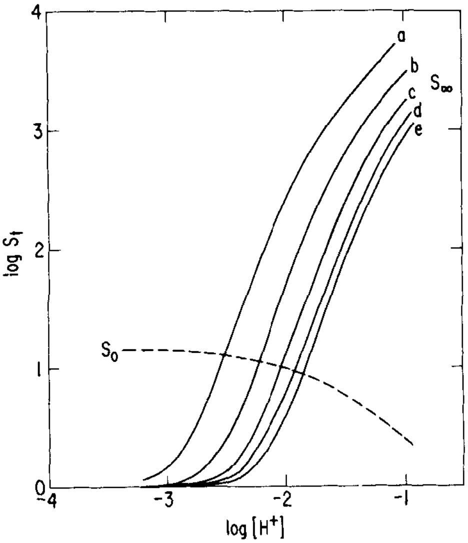

FIGURE 3.

Logarithmic plot of the separation parameter between Cu and Fe, S, vs aqueous phase acidity, $[H^+]$. The S_∞ curves represent equilibrium (thermodynamic) separation parameters calculated through equation (12) for organic phases where the total oxime concentration in toluene is the following $2 \cdot 10^{-2}$ M(a), $5 \cdot 10^{-2}$ M(b), $1 \cdot 10^{-1}$ M(c), $1.5 \cdot 10^{-1}$ M(d), $2 \cdot 10^{-1}$ M(e). The aqueous phase composition is $[Cl^-] = 2$ M, $[H^+]$ variable. The dashed line represents the kinetic separation parameter at time zero, S_0, evaluated through equation (14). The Cu and Fe concentrations are assumed as negligible in comparison to those of $\overline{HOx}$ and H^+.

$$S_0 = \frac{2.83 \cdot 10^{-4}}{1.94 \cdot 10^{-5} + 9.23 \cdot 10^{-4}\,[H^+]} \tag{14}$$

The separation parameter obtained after very short contact times, S_0, is therefore independent of both the specific interfacial area and the extractant concentration. The dashed line of Figure 3 shows how S_0 varies with $[H^+]$. The point of intersection of S_0 with the curves S_∞ represents the "kinetic critical acidity", KCA. For acidities below the KAC $S_0 > S_\infty$ and kinetic separations are superior to those obtained at equilibrium. For acidities > KCA it is always the case that $S_\infty > S_0$ and improved separations using kinetic factors are impossible. For acidities equal to the KCA the separation is obviously time independent.

For contact times t, $0 < t < \infty$, equation (13) can be used to evaluate the kinetic separation parameter. The curves shown in Figure 4 have been evaluated through equation (13) at the constant total oxime concentration $[\overline{HOx}]_{total} = 0.1$ M and for different values of the $a_i \times t$ variable. All curves intersect at the KCA. For acidities below the KCA, where kinetic separations are possible, equation (13) allows one to evaluate the contact time between the two phases which is required to obtain a given separation, provided both the chemical composition of the system ($[\overline{HOx}]_m$, $[H^+]$) and the specific interfacial area a_i (which depends on the geometry of the extractor, the degree of mixing of the phases, viscosity, density, interfacial tension, etc.) are specified. If for example $[\overline{HOx}]_{total} = 0.1$ M, $[H^+] = 3 \cdot 10^{-3}$ M (pH = 2.5) and $a_i = 5$ cm^{-1} after about 2 minutes it is $S_t > \sim 5$ and copper is practically completely separated from iron. After about 5 minutes $S_t \sim 2.5$ and appreciable amounts of iron start to be coextracted.

Although the separation parameters described in equations (12) and (13) have been derived under the limiting assumption of negligible metal concentrations, they show which key parameters need to be controlled in order to perform kinetic separations by liquid-liquid extraction. Further they also clearly indicate the primary importance of knowing in a detailed way the rate laws and the constants which control the liquid-liquid extraction kinetics to perform separations of metals which on the basis of thermodynamic predictions alone would be considered impossible.

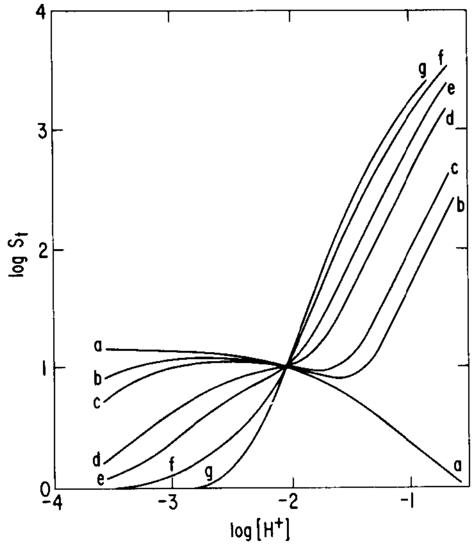

FIGURE 4.

Logarithmic plot of the kinetic separation parameter, S_t, vs aqueous phase acidity, $[H^+]$. The S_t curves have been calculated through equations (13), (7), (8), (9) and (10) at $[\overline{HOx}]_{total}$ = 0.1 M in toluene, aqueous phase $[Cl^-]$ = 2 M, and at the following values of the a_i x t parameter: 0(a), 25(b), 50(c), 250(d), 500(e), f(1500), g(∞) $[s \cdot cm^{-1}]$.

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