Extraction Kinetics of Ni(II) in the Ni\(^{2+}\)-SO\(_4^{2-}\)-Ac\(^-\) (Na\(^+\), H\(^+\))-Cyanex 272 (H\(_2A_2\))-Kerosene-3% (v/v) Octan-1-ol System Using Single Drop Technique

Ranjit Kumar Biswas*, Aneek Krishna Karmakar, Muhammad Saidur Rahman
Department of Applied Chemistry and Chemical Engineering, Rajshahi University, Rajshahi, Bangladesh
Email: *rkbiswas694@gmail.com
Received January 17, 2013; revised February 16, 2013; accepted February 25, 2013

Copyright © 2013 Ranjit Kumar Biswas et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

ABSTRACT

The kinetics of extraction of Ni(II) in the Ni\(^{2+}\)-SO\(_4^{2-}\)-Ac\(^-\) (Na\(^+\), H\(^+\))-Cyanex 272 (H\(_2A_2\))-kerosene-3% (v/v) octan-1-ol system using the single falling drop technique have been reported. The flux of Ni\(^{2+}\) transfer (F) at 303 K in presence of 3% (v/v) octan-1-ol (de-emulsifier) can be represented as:

\[
F_i \left( \text{kmol/m}^2\text{s} \right) = 10^{-3.7} \left[ \text{Ni}^{2+} \right] \left[ H_2A_2 \right]^{0.5} \left( 1 + 10^{6.35} \left[ H^+ \right] \right)^{-1} \left( 1 + 6.3 \left[ SO_4^{2-} \right] \right)^{-1} \left( 1 + 0.55 \left[ Ac^- \right] \right)^{-1}
\]

Depending on reaction parameters, the activation energy (E\(_a\)) and enthalpy change in activation (\(\Delta H^\ddagger\)) varies within 17 - 58 kJ/mol and 17 - 67 kJ/mol, respectively. Entropy change in activation (\(\Delta S^\ddagger\)) is always negative. Based on the empirical flux equation, E\(_a\) and \(\Delta S^\ddagger\) values, mechanisms of extractions in different parametric conditions are proposed. At low \([SO_4^{2-}]\) and \([Ac^-]\), and pH, the chemical controlled step is: \(Ni^{2+} + A^- \rightarrow NiA^+\); and this reaction occurs via an S\(_N2\) mechanism. But in most parametric conditions, the process is under intermediate control; and at high \([SO_4^{2-}]\) and \([Ac^-]\), and pH, the extraction process is under diffusion control.

Keywords: Kinetics; Cyanex 272; Sulphate; Kerosene; Ni\(^{2+}\); Single Drop Technique

1. Introduction

Cobalt has no natural deposit as its mine; and all nickel deposits contain invariably small proportion of cobalt. In order to obtain purified nickel and to isolate cobalt, it is necessary to separate Co(II) from Ni(II). The Co\(^{2+}\)/Ni\(^{2+}\) separation is a challenge to hydrometallurgists, who extract nickel following 1) leaching of ores, 2) purification of leach solution and 3) either reduction by hydrogen or electrolysis of purified solution. The purification of leach solution by solvent extraction is complicated by the difficult separation of Co\(^{2+}\) from Ni\(^{2+}\).

Previously, organo-phosphorous extractants like D2EHPA [1-10], Cyanex 272 [1-6,11-16], EHEHPA or PC 88A [1-5,17,18], M2EHPA [9], TBP [2,8,9], Cyanex 301 [4,7,11,16,19-21] and Cyanex 302 [4,7,11,14], TOPS 99 [12,22], TIBPS [22], etc. have been used for Ni\(^{2+}\)/Co\(^{2+}\) separation. A few works [2-4,7,17,19] are available on extraction equilibrium of Ni\(^{2+}\) in the Ni\(^{2+}\)-SO\(_4^{2-}\)-Ac\(^-\) (Na\(^+\), H\(^+\))-Cyanex 272-kerosene-3% (v/v) n-octan-1-ol system (where, 3% (v/v) n-octan-1-ol in a de-emulsifier) has been reported from Authors’ Laboratory [23]. The chemical structure of the active component of Cyanex 272 is [11]:

\[
\left( CH_2-C(CH_3)_2-CH_2-CH(CH_3)-CH_2^+ \right)_2 (=O)OH.
\]

It is reported that equilibration time is only 2 min; and

\[
\log \frac{D}{(\text{C})} = 10^{-11.56} + 2pH_{(\text{eq})} + 3\log \left[ H_2A_2 \right]_{(\text{C})} - \log \left[ \text{Ac}^- \right]_{(\text{C})}
\]

(\(\text{C}\) is the concentration of \(Ni^{2+}\) in the aqueous phase)

when, \([H_2A_2]_{(\text{C})} \leq 0.05\) mol/L and

\[
\log \frac{D}{(\text{C})} = 10^{-11.16} + 2pH_{(\text{eq})} + \log \left[ H_2A_2 \right]_{(\text{C})} - \log \left[ \text{Ac}^- \right]_{(\text{C})}
\]

Corresponding author.
when, $[H_2A_2]_{eq} \geq 0.10$ mol/L. These equations have suggested, respectively, the extraction equilibrium reactions as: 

$$Ni^{2+} + H_2A_2 \rightarrow NiA_2 + 2H^+ \quad \text{and} \quad Ni^{2+} + 3H_2A_2 \rightarrow NiA_2 + 2H_2A + 2H^+.$$ 

Although the kinetics of Ni$^{2+}$ extraction by non-phosphorous based extractants [24-28], have been reported, there is no report on the extraction kinetics of Ni$^{2+}$ by organophosphorous extractants except the works of Dresinger and Cooper [29,30] who have used either D2EHPA or EHEHPA as extractant and RDC as the flux measurement technique. As there no report on the extraction kinetics of Ni$^{2+}$ by Cyanex 272, this study has been carried out. In this study, the single drop technique for $F$ (of Ni$^{2+}$-transfer)-measurement has been used.

2. Materials and Methods

2.1. Reagents

Cyanex 272 (Cytec Canada Inc.) was purified by the micro-emulsion formation method [31] to 99% BTMPPA (potentiometric titration), and characterized by its density (0.9152 g/mL at 298 K) and viscosity (120 mN/m at 298 K) [32]. Aliphatic colorless kerosene distilling over 200°C - 260°C was used as diluent. NiSO$_4$·6H$_2$O (Fluka, >99%) was used as a source of Ni$^{2+}$. Other chemicals were of reagent grade and used as received.

2.2. Analytical

The [Ni$^{2+}$] in the aqueous phase was determined by the bromine-dimethylglyoxime method [33] at 445 nm using a WPA S104 Spectrophotometer and occasionally by the AAS method using a Shimadzu AA-6800 Spectrophotometer, especially when its concentration was low. The stock solution of Ni$^{2+}$ was prepared by dissolving 22.39 g NiSO$_4$·6H$_2$O in water to make 1 L solution and standardized by EDTA-titration. The solution was found to contain 4.99 g/L Ni$^{2+}$. The acidity of the aqueous solutions was measured by a Mettler Toledo MP 220 pH meter on calibration by double buffers of pH 4 and 7.

2.3. Procedure with the Single Drop Apparatus

The construction of single drop apparatus is described elsewhere [34]. Its schematic diagram is in Figure 1. A falling drop apparatus was used. In the experiment, the continuum was the organic phase and drops of aqueous solution were allowed to fall through the continuum and collected continuously from the bottom of the column, leaving a pool of ca 2 - 3 drops of aqueous phase to avoid entrainment. For each experiment, the volume of 100 collected drops was estimated by the density-mass method; so that the volume of a single drop could be calculated. In the actual experiments, an uncounted number of aqueous drops (internally circulating and slightly oscillating) of diameter (1.81 ± 0.03) mm were allowed to fall, collected in a previously weighed dry beaker and the volume of the collected aqueous phase (ca 2.5 mL) was determined by the density-mass method. The [Ni$^{2+}$] in the collected mass was then estimated. On knowing the volume of a drop (determined previously), the number of drops in actual experiment could be determined. The cumulative time for 10 separate drops falling one after another was determined to get the average drop fall time, which was mostly dependent of column height and only slightly dependent on the composition of phases.

2.4. Theory of Rate Measurements by Flux ($F$)-Method

At a particular temperature, ($F$) of Ni$^{2+}$ transfer can be represented as [35]:

$$F(\mathrm{kmol/m^2s}) = 3.52A[Ni^{2+}](v/N)^{0.5}(1/t) \times 10^{-6} \quad (1)$$

The quantity, $F$, at a constant temperature is related to the concentration terms as:

$$(F) = (k_f)[Ni^{2+}]^a[H^+]^b[H_2A_2]^c[SO_4^{2-}]^d[Ac^-]^e \quad (2)$$

where, the unit of ($k_f$) depends on the values of $a, b, c, d$ and $e$. Equation (2) can be rewritten as:

$$\log(F) = \log(k_f) + a\log[Ni^{2+}] - b\pH + c\log[H_2A_2] + d\log[SO_4^{2-}] + e\log[Ac^-] \quad (3)$$

Equation (3) states that if pH, [H$_2$A$_2$], [SO$_4^{2-}$] and...
[Ac−] are kept constant at pH, [H2A2], [SO42−] and [Ac−], respectively; and (F)-values are determined for various concentrations of [Ni2+] then the plot of log(F) vs log[Ni2+] will be a straight line with \( s = 1 \) and

\[
I = \log \left( k_f - b \log[H_{2A_2}]_{o} \right) + a \log[SO_4^{2-}] + c \log[Ac^-]
\]

From I-value, \( k_f \) can be calculated after determining the values of \( b, c, d \) and \( e \). Similarly, the values of \( b, c, d \) and \( e \) together with four sets of \( k_f \)-values can be determined from the log(F) vs pH, log(F) vs log[H2A2]o, log(F) vs log[SO42−] and log(F) vs log[Ac−] plots, respectively. The temperature dependence data can be treated by Arrhenius equation and Activated complex theory [36].

3. Results and Discussion

3.1. Characterization of Rate Measurement by Single Drop Experimentation

The plot of \( a_{Ni^{2+}} \) from a drop vs \( t \) (obtained by using different C.H) [37] is a straight line which cuts the time axis at \(-0.5 \ s \) (\( \Delta t = 0.5 \ s \)). This time is designated as end correction term (attributed to time for drop formation and coalescence). In F-calculation, \( \Delta t \) term must be added to \( t \); otherwise, error appears as demonstrated below:

When \( F_f' \) and \( F_f \) are calculated by neglecting and considering \( \Delta t \) value, respectively, then it is seen that log \( F_f' \) is decreased, whilst log \( F_f \) remains unchanged with increasing C.H and at any C.H, \( \log F_f < \log F_f' \) [37]. It is concluded that \( F_f \) will be independent of C.H if \( \Delta t \) is added to \( t \) and any C.H can be used if \( F_f' \) (not \( F_f \)) is calculated.

3.2. Rate Measurements

The log(\( F_f \), kmol/m²·s) vs log([Ni²⁺], kmol/m³) plots are displayed in Figure 2. In all cases, straight lines are obtained with \( s = (1.01 \pm 0.03) \) and \( I \) as typed on the body of figure. The unity \( s \) indicates the rate of forward extraction of Ni²⁺ by Cyanex 272 is directly proportional to initial [Ni²⁺]. In other words, the reaction order \( \omega_{Ni^{2+}} \) is unity (\( i.e., a = 1 \)).

The log(\( F_f \) vs pH(ini) plots are shown in Figure 3 The experimental points for a particular system fall on a curve having higher slope in \( lpHr \) and lower slope in \( hpHr \). The experimental points for a particular set of parameters fall on curve represented by:

\[
\log F_f = \text{constant} - \log \left( 1 + 10^{6.32} \left[ H^+ \right] \right) \  \quad (4)
\]

where, constant = \(-6.382 \) for \( 0.025 \) mol/L [H2A2]o,ini system), \(-6.062 \) for \( 0.10 \) mol/L [H2A2]o,ini system) or.

\[
-5.80 \ (for \ 0.30 \ mol/L [H_2A_2]_{o,ini}) \text{ system) and } 10^{6.32} \text{ is a proportionality constant resulting from non-linear curve fitting. Its unit is L/mol.} \]

I-values of the asymptotic lines are embodied in figure. It is concluded that the rate of Ni²⁺ extraction is independent of [H+] in lpHr; whereas, inversely proportional to [H+] in hpHr. In other words, the reaction order \( \omega_{H^+} \) is \(-1 \) (\( b = 1 \)) and \( 0 \) (\( b = 0 \)) in lpHr and hpHr, respectively.

Figure 4 displays log(\( F_f \) vs \( \log[H_2A_2]_{o,ini} \) plots. For each pH system, the plot is a straight line whose \( s \) and \( I \) are given. The \( s \)-values indicate that the rate of forward extraction is directly proportional to the square root of the extractant concentration (\( i.e., c = 0.5 \)).

The nature and extent of variations of \( F_f \) with \([SO_4^{2-}]\) are displayed in Figure 5. The experimental points for a particular set of parameters fall on a curve represented by:

\[
\log F_f = \text{constant} - \log \left( 1 + 6.30 \left[ SO_4^{2-} \right] \right) \  \quad (5)
\]
Figure 4. Effect of extractant concentration on flux $[\text{Ni}^{2+}]_{\text{ini}} = 1.3405 \text{ g/L}$, $[\text{SO}_4^{2-}] = 0.05 \text{ mol/L}$. (○), $pH_{\text{ini}} = 6.70$, C.H = 0.66 m; (●), $pH_{\text{ini}} = 6.10$, C.H = 0.90 m; (□), $pH_{\text{ini}} = 5.20$, C.H = 1.20 m. Other parameters are as in Figure 2.

Figure 5. Effect of $[\text{SO}_4^{2-}]$ on flux $[\text{Ni}^{2+}] = 1.3405 \text{ g/L}$, $[\text{H}_2\text{A}_2]_{\text{o,ini}} = 0.025 \text{ mol/L}$; (●), $pH_{\text{ini}} = 6.40$, $[\text{H}_2\text{A}_2]_{\text{o,ini}} = 0.30 \text{ mol/L}$. The points are experimental and the solid curves are theoretical representing: $\log F_f = -6.45$ (○) or $-5.95$ (●) $-\log [1 + K_{\text{SO}_4}] [\text{SO}_4^{2-}]$, where $K_{\text{SO}_4}$ is a proportionality constant; whose value in both cases is 6.30 L/mol by the Curve-Fitting method. Other parameters are as in Figure 2.

where, constant = $-6.4$ (for $pH_{\text{ini}} = 6.70$, $[\text{H}_2\text{A}_2]_{\text{o,ini}} = 0.025 \text{ mol/L}$ system) or, $-5.95$ (for $pH_{\text{ini}} = 6.40$, $[\text{H}_2\text{A}_2]_{\text{o,ini}} = 0.30 \text{ mol/L}$ system); and 6.30 is a proportionality constant resulted from non-linear curve-fitting and its unit is considered as L/mol. The intercepts of the asymptotic lines are given in figure. The rate of $\text{Ni}^{2+}$ transfer is therefore inversely proportional to the term $(1 + 0.55 [\text{Ac}^-])$. In other words, $e = 0$ at lcr of [Ac] and $e = -1$ at hcr of [Ac].

The $\log F_f$ vs $1/T$ (Arrhenius) plots for 5-sets of experimental parameters are depicted in Figure 7. From top

Figure 6. Effect of $[\text{Ac}^-]$ on the flux $[\text{Ni}^{2+}] = 1.3405 \text{ g/L}$, $[\text{SO}_4^{2-}] = 0.023 \text{ mol/L}$, $pH_{\text{ini}} = 6.6$. Other parameters are as in Figure 2. The points are experimental and the solid curve is theoretical representing: $\log F_f = -6.50 - \log \left[1 + K_{\text{AC}} [\text{Ac}^-] \right]$, where $K_{\text{AC}}$ is proportionality constant; and its value has been estimated as 0.55 L/mol by the Curve-Fitting method.

Figure 7. Effect of temperature on flux (Arrhenius plots) $[\text{Ni}^{2+}]_{\text{ini}} = 1.3405 \text{ g/L}$. (●), $pH_{\text{ini}} = 6.70$, $[\text{H}_2\text{A}_2]_{\text{o,ini}} = 0.10 \text{ mol/L}$, $[\text{Ac}^-] = 0.25 \text{ mol/L}$, $[\text{SO}_4^{2-}] = 0.05 \text{ mol/L}$, C.H = 0.66 m; (○), $pH_{\text{ini}} = 6.70$, $[\text{H}_2\text{A}_2]_{\text{o,ini}} = 0.10 \text{ mol/L}$, $[\text{Ac}^-] = 0.25 \text{ mol/L}$, $[\text{SO}_4^{2-}] = 0.05 \text{ mol/L}$, C.H = 1.2 m; (□), $pH_{\text{ini}} = 6.70$, $[\text{H}_2\text{A}_2]_{\text{o,ini}} = 0.10 \text{ mol/L}$, $[\text{Ac}^-] = 0.25 \text{ mol/L}$, $[\text{SO}_4^{2-}] = 1.00 \text{ mol/L}$, C.H = 1.2 m; (△), $pH_{\text{ini}} = 6.70$, $[\text{H}_2\text{A}_2]_{\text{o,ini}} = 0.10 \text{ mol/L}$, $[\text{Ac}^-] = 2.00 \text{ mol/L}$, $[\text{SO}_4^{2-}] = 0.023 \text{ mol/L}$, C.H = 1.2 m; (△), $pH_{\text{ini}} = 6.70$, $[\text{H}_2\text{A}_2]_{\text{o,ini}} = 0.10 \text{ mol/L}$, $[\text{Ac}^-] = 2.00 \text{ mol/L}$, $[\text{SO}_4^{2-}] = 1.0 \text{ mol/L}$, C.H = 1.2 m.

Copyright © 2013 SciRes.
to bottom, 1st, 4th and 5th systems yield straight lines and s of these lines give E_a values of 19, 56 and 17 kJ/mol, respectively. On the other hand, for the 2nd and 3rd systems, curves are obtained. From limiting s of the curves, E_a values of 25.5 kJ/mol and 57.5 kJ/mol are obtained at htr and ltr, respectively for the 3rd system; whereas, 27.5 kJ/mol and 62.0 kJ/mol are obtained at htr and ltr respectively, for the 2nd system.

The temperature dependence rate data have also been treated by the Activated Complex Theory to estimate the ΔH^f and ΔS^f. The plots of log (Ff(h/kT)) vs (1/T) are given in Figure 8. Natures of plots are similar to those of Arrhenius plots. The “s”, “f”, ΔH^f and ΔS^f values are embodied in the figure. In calculating ΔS^f values, log f(R)-values are needed which are calculated using the relation:

\[
\log f(R) = \log \left[ \frac{[Ni^{2+}]_{ini}}{[H_2A_2]_{ini}} \right] - \log \left( 1 + 6.3 \times 10^{6.32} \times 10^{-\text{pH}} \right) + 0.5 \log \left[ SO_4^{2-} \right] - \log \left( 1 + 0.55 \left[ Ac^- \right] \right) - \log \left( 1 + 0.55 \left[ Ac^- \right] \right)
\]

The calculated ΔH^f values vary within 17 - 65 kJ/mol; whereas, ΔS^f values are always negative.

### 3.3. Elucidation of the Value of k_f

From “f” of the straight lines or the asymptotic lines in Figures 2-6, the average value of log k_f at 303 K in presence of 3% (v/v) octan-1-ol in the organic phase has been evaluated to be -3.742, with stand. dev. of 0.04. The value of log k_f has also been obtained graphically. As the flux equation can be represented as: log F_f = log k_f + log f(R), the plot of log F_f vs log f(R) should be a straight line with s = 1 and I equaling to the value of log k_f. The plot is given in Figure 9. A good fit Least Squares straight line is obtained with s = 1.0288 (should be 1) and I = -3.6781. The latter value corresponding to log k_f is comparable to that obtained above. Hereafter, k_f = 10^{-3.7} m^2/s/kmol is will be considered in discussion.

### 3.4. Mechanism of Forward Extraction

Based on the results obtained, F in this system at 303 K can be expressed as:

\[
F_f = 10^{-3.7} \left[ \frac{[Ni^{2+}]_{ini}}{[H_2A_2]_{ini}} \right] \left[ SO_4^{2-} \right]^{0.5} \left( 1 + 10^{6.32} \left[ H^+ \right] \right)^{-1} 
\]

Equation (8) is a too much complicated equation. It can be changed to a number of simplified flux equations depending on the concentration regions of H^+, SO_4^{2-} and Ac^-.

1. At hcr of H^+, but ler of SO_4^{2-} and Ac^-:

\[
F_f = 10^{-10.02} \left[ \frac{[Ni^{2+}]_{ini}}{[H_2A_2]_{ini}} \right] \left[ SO_4^{2-} \right]^{0.5} \left( 1 + 0.55 \left[ Ac^- \right] \right)^{-1}
\]

where, 10^{-10.02} = 10^{-3.7} \times 10^{-6.32}; and

2. At ler of H^+ but hcr of SO_4^{2-} and Ac^-:

\[
F_f = 10^{-4.24} \left[ [Ni^{2+}]_{ini} [H_2A_2]_{ini} \right] \left[ SO_4^{2-} \right]^{-1} \left[ Ac^- \right]^{-1}
\]

where, 10^{-4.24} = 10^{-3.7} \times 0.58.

In the present case, as the reaction order wrt extractant is a one-half, the monomeric model of extractant will be applicable [35]. The monomeric model of H_2A_2 is:
where charged ions are involved. If the solvent molecules are tightly attached around Ni^{2+} ions, their entropy is lost i.e. $\Delta S^b$ becomes negative. On the other hand, if the solvent molecules dissociate from the metal ions, their entropy is increased; and so, $\Delta S^b$ becomes positive. Thus for an S_N2 mechanism, where the ligand (A^-) co-ordinates to the metal ion, [$\text{Ni(H}_2\text{O)}$]^{2+} to form the higher co-ordinated activated complex, [$\text{Ni(H}_2\text{O)}$ A]^+, the value of $\Delta S^b$ would be expected to be more negative than the ground state. But for the S_N1 mechanism, where the formation of lower co-ordinated activated complex, [$\text{Ni(H}_2\text{O)}$]_{x}^{2+} takes place, $\Delta S^b$ should be positive. In the present case, $\Delta S^b$ at all experimental parameters are highly negative; and so the rate controlling chemical reaction step represented by Equation (13) occurs via an S_N2 mechanism.

On the other hand, at lcr of H^+ but hcr of SO_4^{2-} and Ac^-, the existing Ni^{2+} species may be considered as [Ni(OH)(SO_4)(Ac^-)]^2-. So Equation (10) takes the form:

$$F_j = 10^{-10.02} K_{1 \text{HA}}^{0.5} P_{\text{tr}} K_{\text{HA}}^{-0.2} \times [\text{Ni}^{2+}] [\text{A}^-] (18)$$

And with the help of $\beta_1$ and $\beta_2$, Equation (18) takes the form:

$$F_j = 10^{-4.24} \beta_1 \beta_2 [\text{Ni}^{2+}] [\text{H}^+]^{-1} [\text{H}_2\text{A}_2]_{0\text{(ini)}}^{0.5} (19)$$

Monomeric model of H_2A_{2(o)} i.e. Equation (11) transforms Equation (19) to

$$F_j = 10^{-4.24} \beta_1 \beta_2 K_{1 \text{HA}}^{0.5} P_{\text{tr}} K_{\text{HA}}^{-0.2} \times [\text{Ni}^{2+}] [\text{A}^-] (20)$$

This equation suggests the rate controlling extraction reaction step given in Equation (15) is also the rate determining chemical reaction step in the latter set of condition. But $E_d$ of 17 kJ/mol obtained at lcr of [H^+] (i.e. high pH: 6.7) and hcr of SO_4^{2-} (1 mol/L) and Ac^- (2 mol/L) suggests that the diffusion of a reactant to the reaction site or the product from the reaction site to the bulk organic phase is slower than the reaction step given in Equation (13).

Thus depending on the extraction condition, the Ni^{2+} extraction in the present system by Cyanex 272 may be either 1) pure chemical controlled (at low pH, [SO_4^{2-}] and [Ac^-]) or 2) pure diffusion controlled (at high pH, [SO_4^{2-}] and [Ac^-]) or 3) mixed (intermediate) controlled. In most of the cases (moderate pH and/or, [SO_4^{2-}] and/or [Ac^-]) at 303 K, the process is mixed controlled which may be chemically controlled at ltr and diffusion controlled at htr.

4. Conclusions

The end effect in the single drop experimentation is 0.50 s and this time is needed to be summed up with drop fall


\[
\log (F) = 10^{-3.7} \left[ \frac{[Ni^{2+}]_{(in)}}{[H_2A]_{(in)}} \right]^{0.5} \left[ 1 + 10^{6.3} [H^+] \right]^{-1} \times \left[ 1 + 6.3 [SO_4^{2-}] \right]^{0.5} \left[ 1 + 0.55 [Ac^-] \right]^{-1}. \\
\]

\( E_a \) and \( \Delta H^\circ \) values depend on experimental conditions and are found to vary within 17 - 58 kJ/mol and 17 - 67 kJ/mol. \( \Delta S^\circ \) value is always negative. At low pH, \([SO_4^{2-}]\) and \([Ac^-]\), the process is under chemical control; whereas, at high pH, \([SO_4^{2-}]\) and \([Ac^-]\), the process is under diffusion control. But in most cases, the process is under intermediate control; which may be chemically controlled at \( ltr \) and diffusion controlled at \( htr \). The rate determining chemical reaction step is identified as the formation of 1:1 complex between \( Ni^{2+} \) and anion \( (A^-) \) of the dimeric extractant. Moreover, negative \( \Delta S^\circ \) value indicates that the chemical rate determining step occurs through an \( S_n2 \) mechanism.

**REFERENCES**


Copyright © 2013 SciRes.


List of Symbols and Abbreviations Used

- $a, b, c, d, e$: Reaction orders w.r.t $[\text{Ni}^{2+}], [\text{H}^+], [\text{H}_2\text{A}_2]_{(o)}$, $[\text{SO}_4^{2-}]$ & $[\text{Ac}^-]$, respectively
- $a_{\text{Ni}^{2+}}$: Amount of $\text{Ni}^{2+}$ transferred, kmol
- $\beta_1$: Stability constant of $\text{NiOH}^+$: $[\text{NiOH}^+] [\text{H}^+]/[\text{Ni}^{2+}]$
- $\beta_2$: Stability constant of $\text{NiOHSO}_4^{2-}$: $[[\text{NiOHSO}_4^{2-}]^2]/[\text{NiOH}^+][\text{SO}_4^{2-}][\text{Ac}^-]$
- $C.\ H$: Column (better to say continuum) height, m
- $\Delta[\text{Ni}^{2+}]$: Concentration change in aqueous drop during travel, mg/L
- $\Delta t$: End correction term, s
- $A^-$: Anion of monomeric BTMPPA
- $\text{Ac}^-$: Acetate ion
- BTMPPA, $\text{H}_2\text{A}_2$: Dimeric bis(2,4,4-trimethylpentyl)phosphinic acid
- $\Delta H^f$: Enthalpy change in activation, kJ/mol
- $\Delta S^v$: Entropy change in activation, kJ/mol K
- $E_a$: Activation energy, kJ/mol
- $F$: $\text{Ni}^{2+}$ Transfer flux, kmol/m$^2$·s
- $f(R)$: Function of reactants
- $h$: Planck’s constant ($6.625 \times 10^{-37}$ kJ·s)
- $hcr$: High concentration region
- $h\text{pHr}$: High pH region
- $htr$: High temperature region
- HA: Monomer of BTMPPA
- $I$: Intercept
- $k$: Boltzman constant ($1.38 \times 10^{-26}$ kJ/K)
- $K_{\text{H}_2\text{A}_2}$: Ionization constant of HA, kmol/m$^3$
- $K_{\text{d}2}$: Dimerization constant of BTMPPA, m$^3$/kmol
- $k_f$: Rate constant in forward extraction, m$^{5/2}$/kmol$^{1/2}$·s
- $lcr$: Low concentration region
- $lpHr$: Low pH region
- $ltr$: Low temperature region
- $N$: Number of collected drop
- $P_{\text{d}2}$: Distribution constant or partition coefficient of HA
- $RDC$: Rotating diffusion cell
- $s$: Slope
- $S_{\text{N}2}$: Substitution nucleophilic bimolecular mechanism
- $S_{\text{N}1}$: Substitution nucleophilic unimolecular mechanism
- $t$: Drop fall time, s
- $T$: Temperature, K
- $v$: Volume of collected drop, cm$^3$
- $wrt$: With respect to
- $E_a$: Activation energy, kJ/mol
- $F$: $\text{Ni}^{2+}$ Transfer flux, kmol/m$^2$·s
- $f(R)$: Function of reactants
- $h$: Planck’s constant ($6.625 \times 10^{-37}$ kJ·s)
- $hcr$: High concentration region
- $h\text{pHr}$: High pH region
- $htr$: High temperature region
- $I$ JNM