

Extraction Kinetics of Ni(II) in the Ni²⁺-SO₄²⁻-Ac⁻ (Na⁺, H⁺)-Cyanex 272 (H₂A₂)-Kerosene-3% (v/v) Octan-1-ol System Using Single Drop Technique

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Received January 17, 2013; revised February 16, 2013; accepted February 25, 2013

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ABSTRACT

The kinetics of extraction of Ni(II) in the Ni²⁺-SO₄²⁻-Ac⁻ (Na⁺, H⁺)-Cyanex 272 (H₂A₂)-kerosene-3% (v/v) octan-1-ol system using the single falling drop technique have been reported. The flux of Ni²⁺ transfer (F) at 303 K in presence of 3% (v/v) octan-1-ol (de-emulsifier) can be represented as:

$$F_f \text{ (kmol/m}^2\text{s)} = 10^{-3.7} [\text{Ni}^{2+}] [\text{H}_2\text{A}_2]_{(o)}^{0.5} (1 + 10^{6.35} [\text{H}^+])^{-1} (1 + 6.3 [\text{SO}_4^{2-}])^{-1} (1 + 0.55 [\text{Ac}^-])^{-1}$$
 . Depending on reaction parameters, the activation energy (E_a) and enthalpy change in activation (ΔH^\ddagger) varies within 17 - 58 kJ/mol and 17 - 67 kJ/mol, respectively. Entropy change in activation (ΔS^\ddagger) is always negative. Based on the empirical flux equation, E_a and ΔS^\ddagger values, mechanisms of extractions in different parametric conditions are proposed. At low $[\text{SO}_4^{2-}]$ and $[\text{Ac}^-]$, and pH, the chemical controlled step is: $\text{Ni}^{2+} + \text{A}^- \rightarrow \text{NiA}^+$; and this reaction occurs via an S_N2 mechanism. But in most parametric conditions, the process is under intermediate control; and at high $[\text{SO}_4^{2-}]$ and $[\text{Ac}^-]$, and pH, the extraction process is under diffusion control.

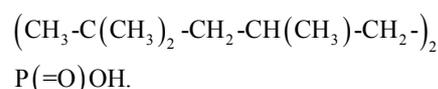
Keywords: Kinetics; Cyanex 272; Sulphate; Kerosene; Ni²⁺; Single Drop Technique

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 Co²⁺/Ni²⁺ 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 Co²⁺ from Ni²⁺.

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 Ni²⁺/Co²⁺ separation. A few works [2-4,7,17,19] are available on extraction equilibrium of Ni²⁺. Recently, the ex-

traction equilibrium of Ni²⁺ in the Ni²⁺-SO₄²⁻-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]:



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

$$\begin{aligned} \log^c D &= 10^{-11.16} + 2\text{pH}_{(\text{eq})} + \log [\text{H}_2\text{A}_2]_{(o,\text{eq})} \\ & - \log (1 + 6.92 [\text{SO}_4^{2-}]) - \log [\text{Ac}^-] \end{aligned}$$

when, $[\text{H}_2\text{A}_2]_{(o,\text{eq})} \leq 0.05$ mol/L and

$$\begin{aligned} \log^c D &= 10^{-11.56} + 2\text{pH}_{(\text{eq})} + 3\log [\text{H}_2\text{A}_2]_{(o,\text{eq})} \\ & - \log (1 + 6.92 [\text{SO}_4^{2-}]) - \log [\text{Ac}^-] \end{aligned}$$

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when, $[H_2A_2]_{(o,eq)} \geq 0.10$ mol/L. These equations have suggested, respectively, the extraction equilibrium reactions as: $Ni^{2+} + H_2A_{2(o)} \rightleftharpoons NiA_{2(o)} + 2H^+$ and



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. $NiSO_4 \cdot 6H_2O$ (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 $NiSO_4 \cdot 6H_2O$ 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

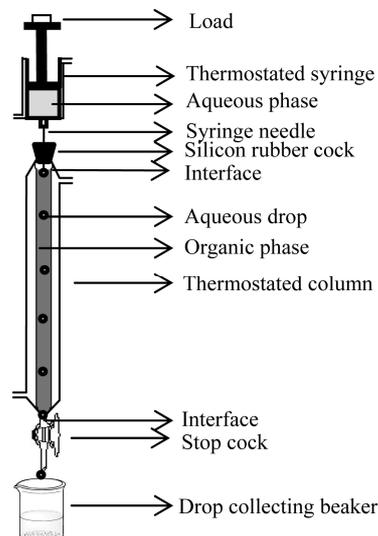


Figure 1. A schematic diagram of a single (falling) drop apparatus. Distance between two interfaces represent C.H. Thermostatic water circulation is aided by water circulating pump.

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]:

$$F \text{ (kmol/m}^2\text{s)} = 3.52\Delta [Ni^{2+}] (v/N)^{1/3} (1/t) \times 10^{-8} \quad (1)$$

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

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

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

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

Equation (3) states that if pH, $[H_2A_2]$, $[SO_4^{2-}]$ and

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

$$I = \log(k_f) - bp\text{H} + c\log[\text{H}_2\text{A}_2]_{(o)} + d\log[\text{SO}_4^{2-}] + e\log[\text{Ac}^-]$$

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 $\log[\text{H}_2\text{A}_2]_{(o)}$, $\log(F)$ vs $\log[\text{SO}_4^{2-}]$ and $\log(F)$ vs $\log[\text{Ac}^-]$ 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 $a_{\text{Ni}^{2+}}$ 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, Δt term must be added to t ; otherwise, error appears as demonstrated below:

When F'_f and F_f are calculated by neglecting and considering Δt 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 will be independent of C.H if Δt is added to t ; and any C.H. can be used if F_f (not F'_f) is calculated.

3.2. Rate Measurements

The $\log(F_f, \text{kmol/m}^2\cdot\text{s})$ vs $\log([\text{Ni}^{2+}], \text{kmol/m}^3)$ 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 that the rate of forward extraction of Ni^{2+} by Cyanex 272 is directly proportional to initial $[\text{Ni}^{2+}]$. In other words, the reaction order wrt $[\text{Ni}^{2+}]_{(ini)}$ is unity (*i.e.*, $a = 1$).

The $\log F_f$ vs $\text{pH}_{(ini)}$ 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:

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

where, constant = -6.382 (for 0.025 mol/L $[\text{H}_2\text{A}_2]_{(o,ini)}$ system), -6.062 (for 0.10 mol/L $[\text{H}_2\text{A}_2]_{(o,ini)}$ system) or,

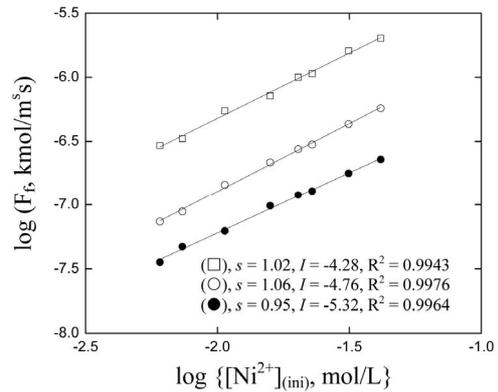


Figure 2. Effect of $[\text{Ni(II)}]_{(ini)}$ on flux $[\text{Ac}^-] = 0.25$ mol/L, $\text{Temp.} = 303$ K, $[\text{SO}_4^{2-}] = 0.042$ mol/L, C.H = 0.66 m. (○), $\text{pH}_{(ini)} = 6.70$, $[\text{H}_2\text{A}_2]_{(o,ini)} = 0.025$ mol/L; (●), $\text{pH}_{(ini)} = 6.00$, $[\text{H}_2\text{A}_2]_{(o,ini)} = 0.025$ mol/L; (□), $\text{pH}_{(ini)} = 6.70$, $[\text{H}_2\text{A}_2]_{(o,ini)} = 0.30$ mol/L.

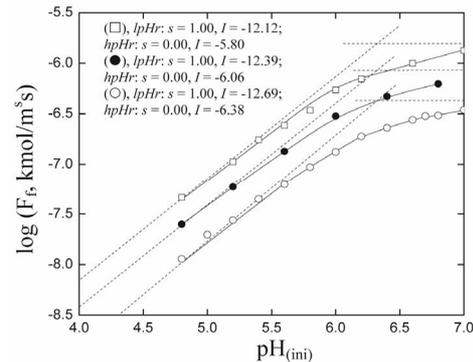


Figure 3. Effect of $\text{pH}_{(ini)}$ on flux. $[\text{Ni}^{2+}]_{(ini)} = 1.3405$ g/L, $[\text{SO}_4^{2-}] = 0.05$ mol/L, C.H = 1.2/0.9/0.66 m. (○), $[\text{H}_2\text{A}_2]_{(o,ini)} = 0.025$ mol/L; (●), $[\text{H}_2\text{A}_2]_{(o,ini)} = 0.10$ mol/L; (□), $[\text{H}_2\text{A}_2]_{(o,ini)} = 0.30$ mol/L. Other parameters are as in **Figure 2**.

-5.80 (for 0.30 mol/L $[\text{H}_2\text{A}_2]_{(o,ini)}$ system) and $10^{6.32}$ 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 Ni^{2+} extraction is independent of $[\text{H}^+]$ in *lpHr*; whereas, inversely proportional to $[\text{H}^+]$ in *hpHr*. In other words, the reaction order wrt $[\text{H}^+]$ is -1 ($b = 1$) and 0 ($b = 0$) in *lpHr* and *hpHr*, respectively.

Figure 4 displays $\log F_f$ vs $\log[\text{H}_2\text{A}_2]_{(o,ini)}$ 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 $[\text{SO}_4^{2-}]$ are displayed in **Figure 5**. The experimental points for a particular set of parameters fall on a curve represented by:

$$\log F_f = \text{constant} - \log(1 + 6.30 [\text{SO}_4^{2-}]) \quad (5)$$

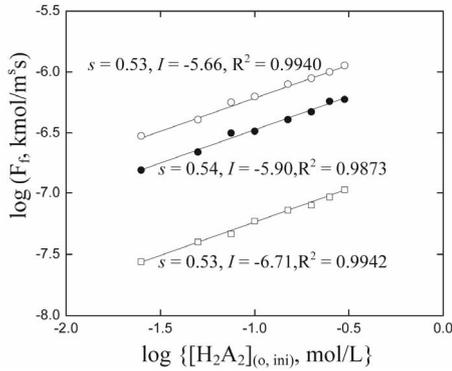


Figure 4. Effect of extractant concentration on flux $[\text{Ni}^{2+}]_{(\text{ini})} = 1.3405 \text{ g/L}$, $[\text{SO}_4^{2-}] = 0.05 \text{ mol/L}$. (O), $\text{pH}_{(\text{ini})} = 6.70$, C.H = 0.66 m; (●), $\text{pH}_{(\text{ini})} = 6.10$, C.H = 0.90 m; (□), $\text{pH}_{(\text{ini})} = 5.20$, C.H = 1.20 m. Other parameters are as in Figure 2.

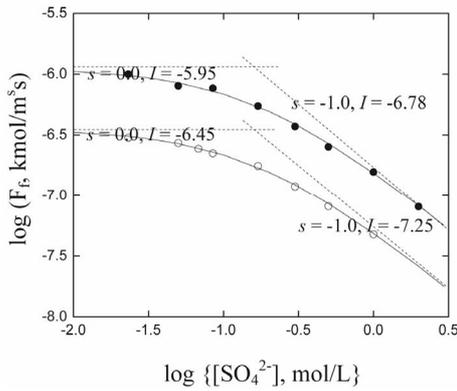


Figure 5. Effect of $[\text{SO}_4^{2-}]$ on flux $[\text{Ni}^{2+}] = 1.3405 \text{ g/L}$. (O), $\text{pH}_{(\text{ini})} = 6.70$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ mol/L}$; (●), $\text{pH}_{(\text{ini})} = 6.40$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.30 \text{ mol/L}$. The points are experimental and the solid curves are theoretical representing: $\log F_f = -6.45$ (O) or -5.95 (●) $-\log\{1 + K_{\text{SO}_4^{2-}}[\text{SO}_4^{2-}]\}$, where $K_{\text{SO}_4^{2-}}$ 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 $\text{pH}_{(\text{ini})} = 6.70$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ mol/L}$ system) or, -5.95 (for $\text{pH}_{(\text{ini})} = 6.40$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.30 \text{ mol/L}$ 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 Ni^{2+} transfer is therefore inversely proportional to the term $(1 + 6.4[\text{SO}_4^{2-}])$. This means that d is 0 at *lcr* of SO_4^{2-} and -1 at *hcr* of SO_4^{2-} .

The $\log(F_f, \text{kmol/m}^2 \text{ s})$ vs $\log[\text{Ac}^-], \text{mol/L}$ plot for $\text{pH}_{(\text{ini})} = 6.60$ and $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.025 \text{ mol/L}$ is represented in Figure 6. Experimental points fall on a curve represented by:

$$\log F_f = -6.50 - \log(1 + 0.55[\text{Ac}^-]) \quad (6)$$

where, 0.55 L/mol is proportionality constant whose value is originated from non-linear regression analysis. I -values of the asymptotic lines are quoted. The rate of Ni^{2+} transfer is therefore inversely proportional to the term $(1 + 0.55[\text{Ac}^-])$. In other words, $e = 0$ at *lcr* of $[\text{Ac}^-]$ and $e = -1$ at *hcr* of $[\text{Ac}^-]$.

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

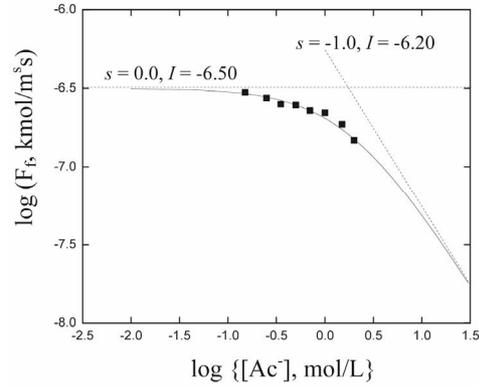


Figure 6. Effect of $[\text{Ac}^-]$ on the flux $[\text{Ni}^{2+}] = 1.3405 \text{ mol/L}$, $[\text{SO}_4^{2-}] = 0.023 \text{ mol/L}$, $\text{pH}_{(\text{ini})} = 6.6$. Other parameters are as in Figure 2. The points are experimental and the solid curve is theoretical representing: $\log F_f = -6.5 - \log\{1 + K_{\text{Ac}^-}[\text{Ac}^-]\}$, where K_{Ac^-} is proportionality constant; and its value has been estimated as 0.55 L/mol by the Curve-Fitting method.

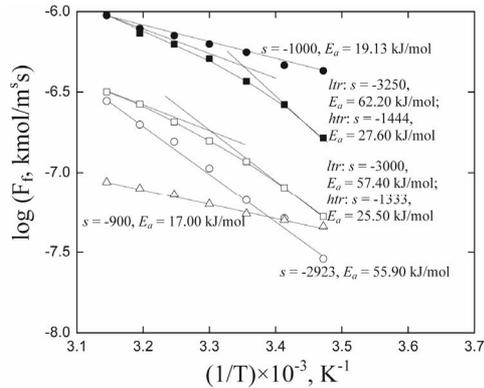


Figure 7. Effect of temperature on flux (Arrhenius plots) $[\text{Ni}^{2+}]_{(\text{ini})} = 1.3405 \text{ g/L}$. (●), $\text{pH}_{(\text{ini})} = 6.70$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.10 \text{ mol/L}$, $[\text{Ac}^-] = 0.25 \text{ mol/L}$, $[\text{SO}_4^{2-}] = 0.05 \text{ mol/L}$, C.H = 0.66 m; (O), $\text{pH}_{(\text{ini})} = 5.20$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.10 \text{ mol/L}$, $[\text{Ac}^-] = 0.25 \text{ mol/L}$, $[\text{SO}_4^{2-}] = 0.05 \text{ mol/L}$, C.H = 1.2 m; (□), $\text{pH}_{(\text{ini})} = 6.70$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.10 \text{ mol/L}$, $[\text{Ac}^-] = 0.25 \text{ mol/L}$, $[\text{SO}_4^{2-}] = 1.00 \text{ mol/L}$, C.H = 1.2 m; (■), $\text{pH}_{(\text{ini})} = 6.60$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.30 \text{ mol/L}$, $[\text{Ac}^-] = 2.00 \text{ mol/L}$, $[\text{SO}_4^{2-}] = 0.023 \text{ mol/L}$, C.H = 1.2 m; (Δ), $\text{pH}_{(\text{ini})} = 6.70$, $[\text{H}_2\text{A}_2]_{(\text{o,ini})} = 0.10 \text{ mol/L}$, $[\text{Ac}^-] = 2.00 \text{ mol/L}$, $[\text{SO}_4^{2-}] = 1.0 \text{ mol/L}$, C.H = 1.2 m.

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^\ddagger and ΔS^\ddagger . The plots of $\log(Fh/kT)$ vs $(1/T)$ are given in **Figure 8**. Natures of plots are similar to those of Arrhenius plots. The “ s ”, “ P ”, ΔH^\ddagger and ΔS^\ddagger values are embodied in the figure. In calculating ΔS^\ddagger values, $\log f(R)$ -values are needed which are calculated using the relation:

$$\log f(R) = \log \left[\text{Ni}^{2+} \right]_{(ini)} - \log \left(1 + 10^{6.32} \times 10^{-\text{pH}} \right) + 0.5 \log \left[\text{H}_2\text{A}_2 \right]_{(o,ini)} - \log \left(1 + 6.3 \left[\text{SO}_4^{2-} \right] \right) - \log \left(1 + 0.55 \left[\text{Ac}^- \right] \right) \quad (7)$$

The calculated ΔH^\ddagger value varies within 17 - 65 kJ/mol; whereas, ΔS^\ddagger values are always negative.

3.3. Elucidation of the Value of k_f

From “ P ” 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

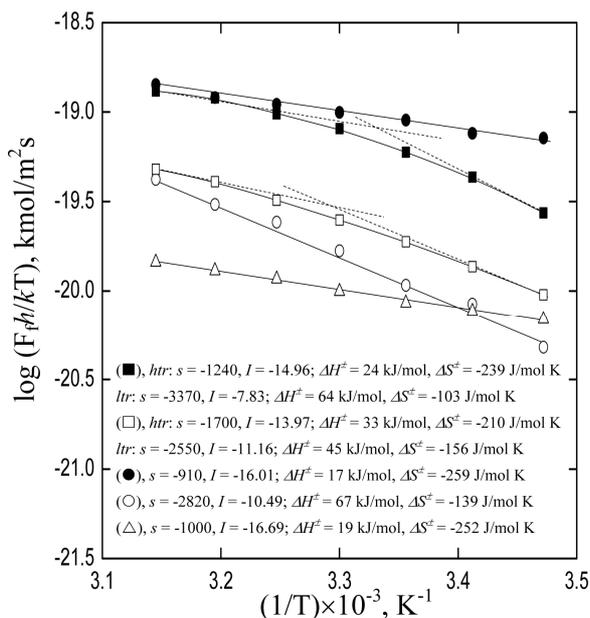


Figure 8. The $\log\{(Fh/kT), \text{kmol/m}^2\text{s}\}$ vs $(1/T)$ plots. Legends are as in **Figure 8**. (●), $\log f(R) = -2.4679$; (○), $\log f(R) = -3.2299$; (□), $\log f(R) = -2.9834$; (■), $\log f(R) = -2.4682$; (△), $\log f(R) = -3.4670$.

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, $k_f = 10^{-3.7} \text{ m}^{5/2}/\text{kmol}^{1/2}\cdot\text{s}$ 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:

$$F_f = 10^{-3.7} \left[\text{Ni}^{2+} \right]_{(ini)} \left[\text{H}_2\text{A}_2 \right]_{(o,ini)}^{0.5} \left(1 + 10^{6.32} \left[\text{H}^+ \right] \right)^{-1} \times \left(1 + 6.3 \left[\text{SO}_4^{2-} \right] \right)^{-1} \left(1 + 0.55 \left[\text{Ac}^- \right] \right)^{-1} \quad (8)$$

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^- . Here, following two extreme cases will be considered for discussion:

1) At hcr of H^+ , but lcr of SO_4^{2-} and Ac^-

$$F_f = 10^{-10.02} \left[\text{Ni}^{2+} \right]_{(ini)} \left[\text{H}_2\text{A}_2 \right]_{(o,ini)}^{0.5} \left[\text{H}^+ \right]^{-1} \quad (9)$$

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

2) At lcr of H^+ but hcr of SO_4^{2-} and Ac^-

$$F_f = 10^{-4.24} \left[\text{Ni}^{2+} \right] \left[\text{H}_2\text{A}_2 \right]_{(o,ini)}^{0.5} \left[\text{SO}_4^{2-} \right]^{-1} \left[\text{Ac}^- \right]^{-1} \quad (10)$$

where, $10^{-4.24} = 10^{-3.7}/6.3 \times 0.55$.

In the present case, as the reaction order *wrt* extractant concentration is a one-half, the monomeric model of extractant will be applicable [35]. The monomeric model of H_2A_2 is:

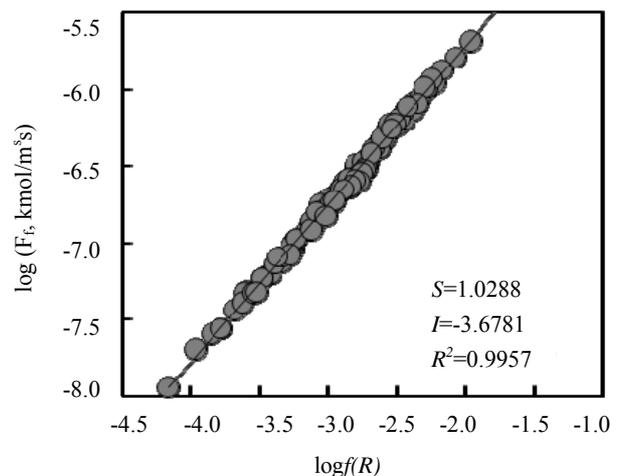


Figure 9. The $\log F_f$ vs $\log f(R)$ plot at 303 K.

$$\begin{aligned}
 [\text{H}_2\text{A}_2]_{(o)} &= \left(K_2^{0.5} [\text{H}_2\text{A}_2]_{(o)} \right)^2 = \left(K_2^{0.5} P_{\text{HA}} [\text{HA}] \right)^2 \\
 &= K_2 P_{\text{HA}}^2 K_{a\text{HA}}^{-2} [\text{A}^-]^2 [\text{H}^+]^2 \quad (11)
 \end{aligned}$$

Combination of Equation (9) with Equation (11) yields the flux equation as:

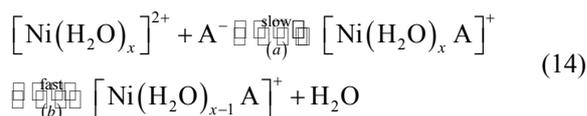
$$F_f = 10^{-10.02} K_2^{0.5} P_{\text{HA}} K_{a\text{HA}}^{-2} [\text{Ni}^{2+}] [\text{A}^-] \quad (12)$$

Equation (12) gives the slow reaction step occurring in the bulk aqueous phase as:



In this experimental parametric condition, Ni^{2+} extraction by Cyanex 272 is therefore chemically controlled and this statement is supported by high E_a (56 kJ/mol) obtained at the investigated *hcr* of H^+ (pH = 5) and *lcr* of SO_4^{2-} (0.05 mol/L) and Ac^- (0.25 mol/L).

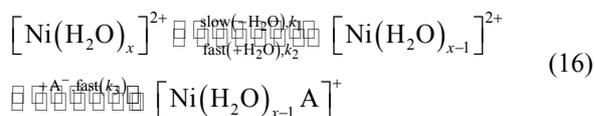
The chemically controlled rate-determining step: $(\text{Ni}^{2+} + \text{A}^- \rightarrow \text{NiA}^+)$ may occur either by an $\text{S}_{\text{N}}1$ or $\text{S}_{\text{N}}2$ mechanism [38]. For $\text{S}_{\text{N}}2$ mechanism, the bimolecular reaction step may be shown as:



with the rate expression :

$$F_f = k_f \left[[\text{Ni}(\text{H}_2\text{O})_x]^{2+} \right] [\text{A}^-] \quad (15)$$

Equation (15) is identical to Equation (12). Consequently in an $\text{S}_{\text{N}}2$ mechanism, the attachment of an additional ligand (A^-) to the restricted co-ordination sphere of Ni^{2+} acts as the rate determining step. The other is the $\text{S}_{\text{N}}1$ mechanism which a unimolecular process as follows:



The steady state approximation results the rate expression for the $\text{S}_{\text{N}}1$ mechanism as:

$$F_f = k_1 k_3 \left[[\text{Ni}(\text{H}_2\text{O})_x]^{2+} \right] [\text{A}^-] / (k_2 + k_3 [\text{A}^-]) \quad (17)$$

and if $k_2 \gg k_3 [\text{A}^-]$, then the Equation (17) takes form of Equation (15); whereby $(k_1 k_3 / k_2)$ will represent k_f .

Thus, it is possible to explain the same rate data by both $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ mechanisms; and as a result, it is difficult to decide whether the reaction proceeds via Equation (14) or (16). But this difficulty may effectively be overcome by the use of the thermodynamic data of the activated state, especially the (ΔS^\ddagger) data for the system.

The solution effect dominates the entropy of activation

where charged ions are involved. If the solvent molecules are tightly attached around Ni^{2+} ions, their entropy is lost *i.e.* ΔS^\ddagger becomes negative. On the other hand, if the solvent molecules dissociate from the metal ions, their entropy is increased; and so, ΔS^\ddagger becomes positive. Thus for an $\text{S}_{\text{N}}2$ mechanism, where the ligand (A^-) co-ordinates to the metal ion, $[\text{Ni}(\text{H}_2\text{O})_x]^{2+}$ to form the higher co-ordinated activated complex, $[\text{Ni}(\text{H}_2\text{O})_x \text{A}]^+$, the value of ΔS^\ddagger would be expected to be more negative than the ground state. But for the $\text{S}_{\text{N}}1$ mechanism, where the formation of lower co-ordinated activated complex, $[\text{Ni}(\text{H}_2\text{O})_{x-1}]^{2+}$ takes place, ΔS^\ddagger should be positive. In the present case, ΔS^\ddagger at all experimental parameters are highly negative; and so the rate controlling chemical reaction step represented by Equation (13) occurs via an $\text{S}_{\text{N}}2$ 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 $[\text{Ni}(\text{OH})(\text{SO}_4)(\text{Ac}^-)]^{2-}$. So Equation (10) takes the form:

$$\begin{aligned}
 F_f &= 10^{-4.24} \left[\text{Ni}(\text{OH})(\text{SO}_4)(\text{Ac}^-) \right]^{2-} \\
 &\cdot [\text{H}_2\text{A}_2]_{(o,\text{ini})}^{0.5} \left[\text{SO}_4^{2-} \right]^{-1} \left[\text{Ac}^- \right]^{-1} \quad (18)
 \end{aligned}$$

And with the help of β_1 and β_2 , Equation (18) takes the form:

$$F_f = 10^{-4.24} \beta_1 \beta_2 \left[\text{Ni}^{2+} \right] \left[\text{H}^+ \right]^{-1} \left[\text{H}_2\text{A}_2 \right]_{(o,\text{ini})}^{0.5} \quad (19)$$

Monomeric model of $\text{H}_2\text{A}_{2(o)}$ *i.e.* Equation (11) transforms Equation (19) to

$$F_f = 10^{-4.24} \beta_1 \beta_2 K_2^{0.5} P_{\text{HA}} K_{a\text{HA}}^{-1} \left[\text{Ni}^{2+} \right] \left[\text{A}^- \right] \quad (20)$$

This equation suggests the rate controlling extraction reaction step given in Equation (13) is also the rate determining chemical reaction step in the latter set of condition. But E_a of 17 kJ/mol obtained at *lcr* of $[\text{H}^+]$ (*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, $[\text{SO}_4^{2-}]$ and $[\text{Ac}^-]$) or 2) pure diffusion controlled (at high pH, $[\text{SO}_4^{2-}]$ and $[\text{Ac}^-]$) or 3) mixed (intermediate) controlled. In most of the cases (moderate pH and/or, $[\text{SO}_4^{2-}]$ and/or $[\text{Ac}^-]$) at 303 K, the process is mixed controlled which may be chemically controlled at *lcr* 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

time to calculate F of independent C.H. At 303 K, the empirical flux equation is:

$$\log(F) = 10^{-3.7} [\text{Ni}^{2+}]_{(\text{ini})} [\text{H}_2\text{A}_2]_{(\text{o,ini})}^{0.5} \left(1 + 10^{6.32} [\text{H}^+]\right)^{-1} \\ \times \left(1 + 6.3 [\text{SO}_4^{2-}]\right)^{-1} \left(1 + 0.55 [\text{Ac}^-]\right)^{-1}.$$

E_a and ΔH^\ddagger values depend on experimental condition and are found to vary within 17 - 58 kJ/mol and 17 - 67 kJ/mol. ΔS^\ddagger value is always negative. At low pH, $[\text{SO}_4^{2-}]$ and $[\text{Ac}^-]$, the process is under chemical control; whereas, at high pH, $[\text{SO}_4^{2-}]$ and $[\text{Ac}^-]$, 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 ΔS^\ddagger value indicates that the chemical rate determining step occurs through an $\text{S}_\text{N}2$ mechanism.

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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 Ni^{2+} transferred, kmol

β_1 : Stability constant of NiOH^+ : $[\text{NiOH}^+][\text{H}^+]/[\text{Ni}^{2+}]$

β_2 : Stability constant of $\text{NiOHSO}_4\text{Ac}^{2-}$:

$[[\text{NiOHSO}_4\text{Ac}^{2-}]/[\text{NiOH}^+][\text{SO}_4^{2-}][\text{Ac}^-]$

C.H: Column (better to say continuum) height, m

$\Delta[\text{Ni}^{2+}]$: Concentration change in aqueous drop during travel, mg/L

Δt : End correction term, s

$[\]$: Sign of concentration

A^- : Anion of monomeric BTMPPA

Ac^- : Acetate ion

BTMPPA, H_2A_2 : Dimeric

bis(2,4,4-trimethylpentyl)phosphinic acid

ΔH^\ddagger : Enthalpy change in activation, kJ/mol

ΔS^\ddagger : Entropy change in activation, kJ/mol K

E_a : Activation energy, kJ/mol

F : Ni^{2+} Transfer flux, $\text{kmol}/\text{m}^2\cdot\text{s}$

$f(R)$: Function of reactants

h : Planck's constant (6.625×10^{-37} kJ·s)

hcr : High concentration region

$hpHr$: High pH region

htr : High temperature region

HA: Monomer of BTMPPA

I : Intercept

k : Boltzman constant (1.38×10^{-26} kJ/K)

$K^{a_{\text{HA}}}$: Ionization constant of HA, kmol/m^3

K_2 : Dimerization constant of BTMPPA, m^3/kmol

k_f : Rate constant in forward extraction, $\text{m}^{5/2}/\text{kmol}^{1/2}\cdot\text{s}$

lcr : Low concentration region

$lpHr$: Low pH region

ltr : Low temperature region

N : Number of collected drop

P_{HA} : Distribution constant or partition coefficient of HA

RDC: Rotating diffusion cell

s : Slope

$\text{S}_{\text{N}2}$: Substitution nucleophilic bimolecular mechanism

$\text{S}_{\text{N}1}$: Substitution nucleophilic unimolecular mechanism

t : Drop fall time, s

T : Temperature, K

v : Volume of collected drop, cm^3

wrt : With respect to

Subscript

f: Forward

(ini): Initial

(int): Interface

(o): Organic