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# Extraction Equilibrium 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

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## Abstract

The title system has been studied elaborately. 3% (v/v) octan-1-ol is added as de-emulsifier. Equilibration time is < 2 min. Distribution ratio ($D$) at constant $pH_{(eq)}$ and [$H_2A_2$] is independent of $[Ni(II)]_{(aq)}$. The pH dependency is always found to be 2; whilst the extractant dependence is found to vary from 1 (at lower concentration region, lcr) to 3 (at high concentration region, hcr). Moreover, the distribution ratio is found to be inversely proportional to (1+6.92 [$SO_4^{2-}$]) and [$Ac^-$]. Based on these results, the extraction equilibrium reactions have been proposed at various parametric conditions. The extraction process is endothermic ($\Delta H$ = 54.66 kJ/mol). The $K_{ex}$ values at 303 K are evaluated to be $10^{-11.086}$ and $10^{-11.56}$ at lcr and hcr of extractant, respectively. The maximum loading capacity is 21.28 g Ni(II) per 100 g extractant indicating the formation of NiAcA at maximum loading. The stripping ability of various inorganic acids towards loaded nickel, as well as, the possibilities of separation of Ni(II) from its binary mixtures with other ions of 3d-block elements have also been investigated.

*Keywords*: Extraction equilibrium; Ni(II) extraction; Cyanex 272; Sulphate-acetato medium; Kerosene-octanol.

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## 1. Introduction

Nickel is a very important commercial metal having diversified applications as alloy constituent, catalyst and in electroplating, battery and electronic industries. World production of nickel has been increased recently due to recycling of various nickel containing wastes. The particular attention given to recycling of nickel is due to the lack of profitable nickel mine and to the fact that as it is very toxic to environment, nickel containing waste exerts problem in its disposal. Consequently, ~40% (87,000 ton) nickel is extracted by the recycling process annually. On the other hand, 0.14 billion ton of nickel is available in identified deposits as sulphide. Now-a-days, nickel is extracted either

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from its ores or wastes by the hydrometallurgical route, mostly involving (a) leaching of ore or waste, (b) purification of leach solution either by solvent extraction or cementation and (c) hydrogen reduction of the purified solution. Leaching can be done either by the ammonia solution or by an acid solution. In acid leaching, sulphuric acid is preferred due to non-corrosiveness of sulphate ion. In acid leach solution most metal ions existing in the ore or waste come into solution. Therefore, in order to isolate nickel from other metallic ions, the principle of solvent extraction is applied.

Among the studies with Cyanex 272 for Ni(II), all studies [1-38] have been carried out to separate Ni(II) from other metal ions, mainly from Co(II). It is notable that cobalt has no natural deposit as its mine; and all nickel deposits contain invariably small proportion of cobalt. Consequently, the Co(II)/Ni(II) separation is a big challenge to hydrometallurgists.

As there is no report on the thorough mechanistic study on the extraction of Ni(II) from sulphate-acetato medium (acetate being used as buffer) by Cyanex 272 dissolved in kerosene containing 3% (v/v) octan-1-ol (de-emulsifier), the mechanism of Ni(II) distribution in the said two phases has been evaluated at various experimental conditions. Stripping abilities of various acid solutions for the extracted nickel have also been studied. Finally, the possibilities of mutual separation of Ni(II) from other 3d-block metal ions in their binary mixtures have been examined.

## 2. Experimental

### 2.1. *Reagents*

Cyanex 272 was donated by Cytec Canada Inc. Kerosene was obtained from the local market and distilled to collect the fraction distilling over 200-260$^{o}$C. It was colorless and mostly aliphatic in nature. Hexahydrated nickel sulphate (Fluka, > 99%) was used as a source of Ni(II). All other chemicals were of reagent grade and used as received.

### 2.2. *Analytical*

The concentration of Ni(II) in the aqueous phase was determined by the bromine-dimethylglyoxime method [39] at 445 nm using WPA S104 spectrophotometer and occasionally by the atomic absorption spectrophotometric method using a Shimadzu AA-6800 Spectrophotometer, particularly, when its concentration was low. The stock solution of Ni(II) was prepared by dissolving 22.39 g $NiSO_4.6H_2O$ in water to make 1 L solution and standardized by EDTA-titration. The solution was found to contain 4.99 g/L Ni(II). The acidity of the aqueous solutions was measured by a Mettler-Toledo 320 pH meter.

### 2.3. *Extraction procedure*

The extraction was done as per procedure given in our earlier work [40]. Equal aliquots (20 mL) of aqueous and organic phases were taken in a 125 mL reagent bottle and agitated for predetermined time (2 min) at 303 K in a thermostatic water bath. After mechanical agitation, the phases were allowed to settle, disengaged and the aqueous phase was analyzed for its Ni(II) content and equilibrium pH. The concentration of Ni(II) in the organic phase was calculated from the difference of its initial and equilibrium concentrations. The value of the distribution ratio (*D*) was calculated as the ratio of concentration of Ni(II) in the organic phase to that existing in the aqueous phase at equilibrium.

### 2.4. *Loading procedure*

Loadings of Ni(II) in 0.025 and 0.05 M Cyanex 272 solutions were carried out by vigorous contact of these solutions (100 mL) separately and repeatedly with fresh aqueous solutions (containing 1.95 g/L Ni(II), 0.034 M $SO_4^{2-}$ and 0.25 M acetate at initial pH of 6.85) of same volume until the organic phases were saturated with Ni(II). After each contact, phases were disengaged and aqueous phases were analyzed for their Ni(II) contents. The amount of Ni(II) transferred into the organic phase for each contact was calculated from the difference of its initial and equilibrium concentrations and then the cumulative concentration of Ni(II) in the organic phase (cumulative $[Ni]_{(o)}$, g/L) after each stage of contact was determined.

### 2.5. *Stripping procedure*

The loaded organic phases obtained above were diluted separately with kerosene so that the resultant solutions contained 1 g/L Ni(II) as complex and practically no free extractant. These solutions were used to study stripping by 0.1 and 0.01 M $H_2SO_4$, HCl, $HNO_3$ and $HClO_4$ solutions. In stripping, 10 mL of Ni(II)-loaded organic phase was equilibrated with an equal aliquot of each of the above acid solution for 5 min at 303 K. After equilibration, phases were settled, separated and the aqueous phase was analyzed for Ni(II) content. In stage-wise stripping, the organic phase was recycled with equal aliquot of fresh aqueous phase.

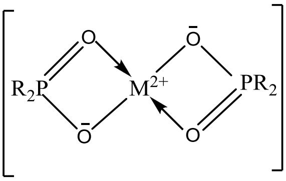
### 2.6. *Procedure for Ni(II)-extraction equilibrium data treatment*

Cyanex 272 is a commercial extractant containing 84% bis-(2,4,4-trimethylpentyl=R)phosphinic acid (BTMPPA, $R_2POOH$), 5% $RPO(OH)_2$ and 11% $R_3PO$. It can be purified to contain about 99% BTMPPA by the microemulsion formation method [41]. Even though, Cyanex 272 without further purification has been used in this investigation. BTMPPA and $RPO(OH)_2$ are both acidic chelating extractants but $R_3PO$ is an ion pair solvating agent. Therefore, all the components of Cyanex 272 have the extracting power. Moreover, equimolar mixture of $RPO(OH)_2$ and $R_3PO$ may behave as BTMPPA ($R_2POOH$) as illustrated below:

$$M(H_2O)_6^{2+} + 2\ R_2PO(OH)_{(o)} \rightleftharpoons [M(R_2POO)_2]_{(o)} + 2\ H^+ + 6H_2O \qquad (1)$$

$$M(H_2O)_6^{2+} + RPO(OH)_{2\,(o)} + R_3PO_{(o)} \rightleftharpoons [M(H_2O)RPOO_2R_3PO]_{(o)} + 2\,H^+ + 5H_2O \qquad (2)$$

with the respective structures of the extracted species being:



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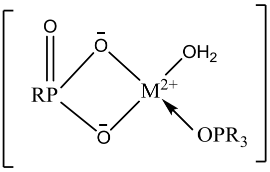

In aqueous solution $Ni^{2+}$ may be complexed with coexsisting $OH^-$, $HSO_4^-$ or $CH_3COO^-$ ($L^-$). Consequently, if $Ni^{2+}$ exists in the aqueous phase as $NiL_n^{(2-n)+}$ (L being the coexisting anion of unit charge) and BTMPPA is considered as dimeric ($H_2A_2$) in nonpolar solvents like kerosene [42-45] then the extraction equilibrium reaction may be depicted as:

$$Ni\,L_n^{(2-n)+} + x\,[H_2A_2]_{(o)} \rightleftharpoons [Ni\,L_{n-z}\,A_{(2-n+z)}\,\frac{2x-2+n-z}{2}\,H_2A_2]_{(o)} + zL^- + (2-n+z)\,H^+ \qquad (3)$$

where, subscript (o) represents organic species. The equilibrium constant ($K_{ex}$) at a constant temperature of the reaction represented by Eq. (3) can be expressed as:

$$\log D = \log K_{ex} + (2-n+z)\,pH + x\log [H_2A_2]_{(o)} - z\log [L^-] \qquad (4)$$

where, $D$ represents distribution ratio i.e. the ratio of $[Ni^{2+}]$ in the organic phase to that in the aqueous phase at equilibrium. Equation (4) represents the basic equation for a chelate forming solvent extraction system involving a metal ion by an acidic extractant. It is mentionable here that all concentrations and pH terms in Eq. (4) refer to the equilibrium values. Consequently, Eq. (4) represents that the value of log $D$ should be independent of initial or equilibrium metal ion concentration at a constant equilibrium pH, equilibrium extractant concentration and coexisting anion concentration in the aqueous phase. The corrected log $D$ i.e. log ${}^{C}D$ values have been calculated using the following mass balance relation:

$$\log {}^{C}D = \log D + x\,(pH_{(ini)} - pH_{(eq)}) + y\,[\log [H_2A_2]_{(o,ini)} - \log ([H_2A_2]_{(o,ini)} - y[Ni(II)]_{(o,eq)})] \qquad (5)$$

where, x = pH dependence = 2 and y = extractant dependence = 1 (as will be seen later) and all concentration terms are in M. Moreover, as equilibrium constant of a reaction is related to temperature by Vant Hoff equation, log $D$ will also depend on temperature.

## 3. Results and Discussions

### *Extraction equilibrium*

Some preliminary experiments were carried out to examine the pH range at which Ni(II) could be extracted. During these measurements, it was observed that stable emulsions were formed in the Ni(II)-$SO_4^{2-}$-$Ac^-$($Na^+$, $H^+$)-Cyanex 272-kerosene system at the extractable pH range of ~6 to 7.5. As the emulsion formation hindered analysis of phases during investigation, its formation was eliminated by adding 3% (v/v) octan-1-ol into the organic phase. The effects of following parameters on the distribution ratio (*D*) of Ni(II) have been found out:

The variations of the aqueous phase [Ni(II)] as well as of log ($[Ni(II)]_{(o)}$/[Ni(II)]) with the extraction time have been found out for (1 g/L Ni(II)-0.034 M $SO_4^{2-}$-0.25 M $Ac^-$-7.0 $pH_{(ini)}$) - (0.025 M $H_2A_2$-3% (v/v) octan-1-ol-kerosene) system at 303 K and O/A = 1, whence phase agitation speed is kept at 300 strokes/min. The aqueous phase [Ni(II)] is decreased up to phase contact time of 1.75 min, whilst log ($[Ni(II)]_{(o)}$/[Ni(II)]) is increased up to 1.75 min. It has been reported [1,7] that equilibration time for Co(II) and Ni(II) extraction from sulphate medium by Cyanex 272 dissolved in Xylene is 2-3 min; whilst Gandhi et al. [9] and Tiat [10] have reported the equilibration time of 5 min for Ni(II)-$SO_4^{2-}$-Cyanex 272-toluene system and of 10 min for Ni(II)-$SO_4^{2-}$-Cyanex 272-toluene system, respectively. Therefore, the system under consideration appears as more labile than the reported ones. In the subsequent experiments, equilibration time of 2 min has been allowed to ensure equilibration at different experimental parameters.

The effect of [Ni(II)] on distribution ratio has been examined for (0.2 - 2.0 g/L Ni(II)-0.034 M $SO_4^{2-}$- 0.25 M $Ac^-$ -7.4 $pH_{(ini)}$) - (0.025 M $H_2A_2$ - 3% (v/v) octan-1-ol - kerosene) system at 303 K and O/A = 1. The estimated log *D* values are found to be decreased with increasing the initial [Ni(II)] of the aqueous phase which is apparently in contrary to the general principle of the solvent extraction technique (*cf.* Eq. 4). On the other hand, the log $^{C}D$ values at constant equilibrium pH of 6.95 and equilibrium extractant concentration of 0.025 M remain unchanged (log $^{C}D$ = 1.30±0.05) with variation of initial or equilibrium [Ni(II)] in the aqueous phase. It is therefore concluded that Ni(II) behaves ideally in the investigated system and the aqueous or organic phase Ni(II) speciation is not changed as well with the variation of [Ni(II)] in the system provided equilibrium pH and extractant concentration remain unchanged.

The variations of *D* with the variation of extractant concentration have been found out at initial pH values of 5.98, 6.30 and 7.08. Although initial pH is kept constant for a particular set of data, it is observed that the equilibrium pH values together with the extractant concentrations are varied considerably for mass transfer. So the corrected *log D* values at a chosen constant equilibrium pH value (log $^{C}D_{\text{const. pH}}$) has been calculated by the first two terms of the left hand side of Eq. (5). Moreover, log $[H_2A_2]_{(o,eq)}$ values have been calculated by the last logarithmic term of Eq. (5). Fig. 1 represents the log *D* vs. log ($[H_2A_2]_{(o,ini)}$, M) and the log $^{C}D_{\text{const. pH}}$ vs. log ($[H_2A_2]_{(o,eq)}$, M) plots. The first type plot does not represent the typical plot (not at constant equilibrium pH) as should be used in solvent extraction equilibrium studies. However, the slope of the plots at least at the lower concentration regions of Cyanex 272 is one. At the higher concentration region, it remains constant for the system of initial pH 7 but is decreased considerably for systems of $pH_{(ini)}$ = 6.30 and 5.90. The second type of plots do not yield straight lines, but curves are obtained with limiting slopes of +1 and +3 at lcr and hcr of equilibrium extractant concentrations, respectively. It is concluded from this result that 1 mole of Cyanex 272 is added up with 1 g ion of Ni(II) to form the extractable species ($NiA_2$), whence there is a scarcity of extractant in the system; and with the availability of the surplus extractant in the system, solvation of $NiA_2$ takes place to form the extractable species like $NiA_2$. $H_2A_2$ and $NiA_2.2H_2A_2$. For the first solvated species to form, the extractant dependence should be 2 and for the formation of the second solvated species, it should be 3.

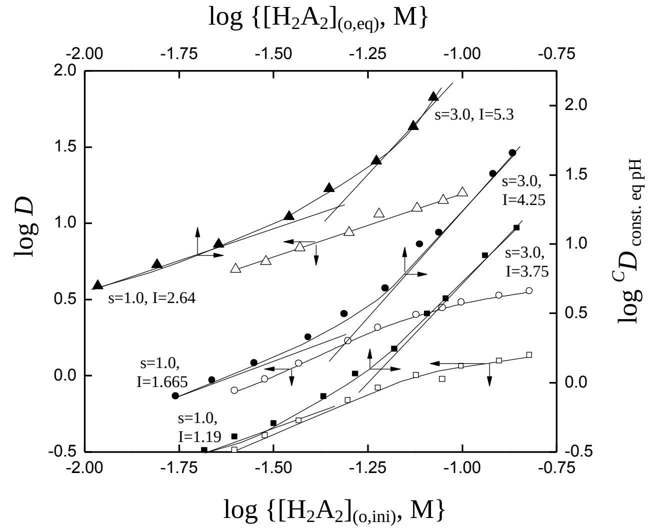

Fig. 1. Effect of extractant concentration on the distribution ratio of Ni(II) being extracted by Cyanex 272. $[Ni(II)]_{(ini)}$ = 1.00 g/L, $[Ac^-]$ = 0.25 M, $[SO_4^{2-}]$ = 0.017 M, de-emulsifier = 3% (v/v) octan-1-ol, Equilibration time = 2 min, Temperature = 303 K, O/A = 1; (△), $pH_{(ini)}$ = 7.08; (▲), $pH_{(eq)}$ chosen constant = 6.55; (○), $pH_{(ini)}$ = 6.30; (●), $pH_{(eq)}$ chosen constant = 6.10; (□), $pH_{(ini)}$ = 5.90; (■), $pH_{(eq)}$ chosen constant = 5.90.

The experimental data have been collected for studying the variation of equilibrium pH on $D$ at constant $[H_2A_2]_{(o,ini)}$ of 0.025, 0.05 and 0.10 M. As the equilibrium $[H_2A_2]_{(o,eq)}$ will differ from its initial concentration due to various extents of extractions at various pH values, the log $^{C}D$ values at a chosen constant $[H_2A_2]_{(o,eq)}$ have been calculated by Eq. (5) after excluding its pH containing term. Fig. 2 shows the log $D$ vs. $pH_{(eq)}$ and log $^{C}D$ vs. $pH_{(eq)}$ plots. In both cases, straight lines are obtained for all three constant Cyanex 272 concentration systems. It is found that the log $D$ vs. $pH_{(eq)}$ plots have slopes within 1.8 to 1.9; whereas, the more acceptable type of plots (log $^{C}D$ vs. $pH_{(eq)}$) have slopes of 2.00, 2.11 and 2.50 for constant $[H_2A_2]_{(o,eq)}$ chosen systems of 0.025, 0.05 and 0.10 M, respectively. The slope of the line at 0.10 M Cyanex 272 system (2.5) is considerably higher than the expected value of 2. It is possibly due to errors encountered during data correction period for the non-constancy of the extractant dependency (1-3). It is however, concluded that 2 g ion of $H^+$ is eliminated from the extractant during its reaction with 1 g ion of Ni (II).

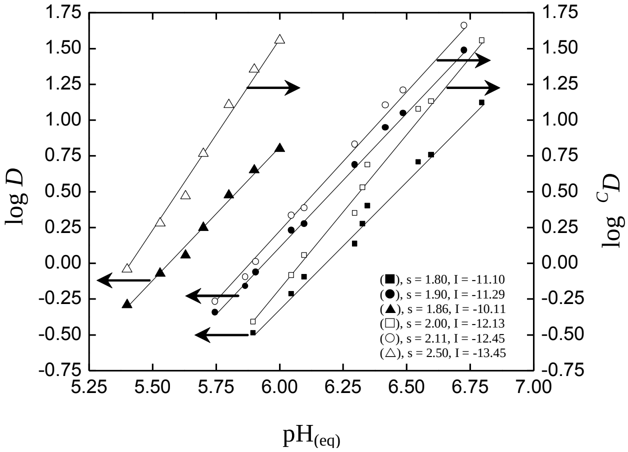

Fig. 2. Effect of equilibrium pH on the extraction of Ni(II) by Cyanex 272 in kerosene. $[Ni(II)]_{(ini)}$ = 1.0 g/L, $[Ac^-]$ = 0.25 M, $[SO_4^{2-}]$ = 0.017 M, de-emulsifier = 3% (v/v) octan-1-ol, Equilibration time = 2 min, Temperature = 303 K, O/A = 1; (■), $[H_2A_2]_{(o,ini)}$ = 0.025 M; (□), constant $[H_2A_2]_{(o,eq)}$ chosen = 0.025 M, y = 1; (●), $[H_2A_2]_{(o,ini)}$ = 0.05 M; (○), constant $[H_2A_2]_{(o,eq)}$ chosen = 0.05 M, y = 1; (▲), $[H_2A_2]_{(o,ini)}$ = 0.10 M; (△), constant $[H_2A_2]_{(o,eq)}$ chosen = 0.10 M, y = 3.

The effect of co-existing sulfate ion concentration of the aqueous phase on $D$ has been examined at constant pH$_{(eq)}$ (chosen) of 6.08 (pH$_{(ini)}$= 6.75 ± 0.05) and constant $[H_2A_2]_{(o,eq)}$ (chosen) of 0.025 M (= $[H_2A_2]_{(o,ini)}$); while the sulfate ion concentration is varied within 0.017 M and 1.50 M. The experimental log $D$ values have been converted to log $^{C}D$ values at constant equilibrium pH of 6.08 and constant equilibrium free extractant concentration of 0.025 M as cited before. The log $D$ vs. log $[SO_4^{2-}]$ plot in Fig. 3 informs about the independency of the distribution ratio of Ni(II) on sulfate ion concentration. On the contrary, the log $^{C}D$ vs. log $[SO_4^{2-}]$ plot (Fig. 3) is not a straight line. A curve is obtained showing a little and huge effect at lcr and hcr of sulfate ion, respectively. In this Figure, the curve is theoretical representing: log $^{C}D$ = 0.075 - log (1 + 6.92 $[SO_4^{2-}]$); and the dotted horizontal line is the asymptote at lcr of $SO_4^{2-}$: log $^{C}D$ = 0.075 and the dotted inclined line is the asymptote at hcr of $SO_4^{2-}$: log $^{C}D$ = - 0.075 - log $K_{SO_4^{2-}}$ - log $[SO_4^{2-}]$; so that at the point of intersection of two asymptotes -log $K_{SO_4^{2-}}$ - log $[SO_4^{2-}]$ = 0 giving $K_{SO_4^{2-}}$ = 6.92.

The log $D$ and log $^{C}D$ values in the [1 g/L Ni(II) - 0.017 M $SO_4^{=}$ - (0.1-2.0 M) $Ac^-$ - (6.65 ± 0.05) pH$_{(ini)}$ (constant pH$_{eq}$ chosen = 6.05)] – [0.025 M $[H_2A_2]_{(o,ini)}$ (= constant $[H_2A_2]_{(o,eq)}$) - 3% (v/v) octan-1-ol - kerosene] systems have been estimated. It is found that the log $D$ vs. log $[Ac^-]$ plot is almost a horizontal line with slope equaling to -0.08 (intercept = -0.062); whilst the log $^{C}D$ vs. log $[Ac^-]$ plot is a straight line with slope equaling to -0.91 (intercept = -0.65). It is therefore, concluded that the distribution ratio in the investigated system is inversely proportional to acetate ion concentration at a constant equilibrium pH and extractant concentration.

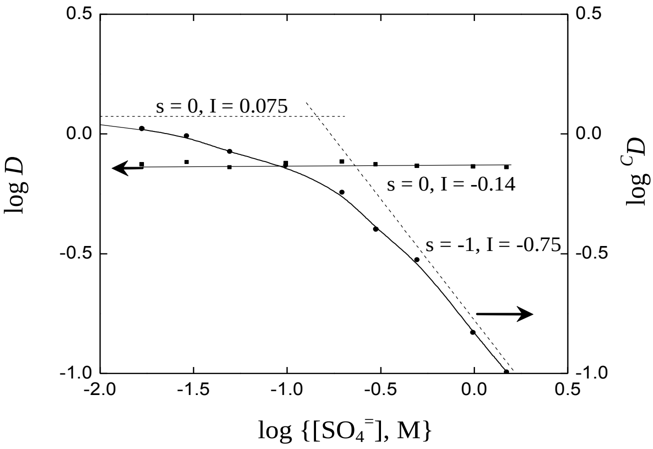

Fig. 3. Effect of co-existing sulphate ion concentration on the extraction of Ni(II) by Cyanex 272 in kerosene. $[Ni(II)]_{(ini)}$ = 1.0 g/L, $pH_{(ini)}$ = 6.75 ± 0.05; constant $pH_{(eq)}$ chosen = 6.08, $[H_2A_2]_{(o,ini)}$n= 0.025 M = constant $[H_2A_2]_{(o,eq)}$ chosen, $[Ac^-]$ = 0.25 M, de-emulsifier = 3% (v/v) octan-1-ol, equilibration time = 2 min, Temperature = 303 K, O/A = 1. For log $^{C}D$ vs. log $[SO_4^{2-}]$ plot, the points are experimental, whilst the curve is theoretical represented by: log $^{C}D = 0.075 - \log(1 + K_{SO_4^{2-}}[SO_4^{2-}])$; where $K_{SO_4^{2-}}$ is a proportionality constant whose value has been evaluated to be 6.92 $dm^3$/mol by the Curve-Fitting method.

The effect of temperature on the distribution ratio has been determined by the Vant Hoff equation for a single set of experimental parameters: 1 g/L Ni(II)-0.017 M $SO_4^{2-}$ - 0.25 M $Ac^-$-6.6 $pH_{(ini)}$ ($pH_{eq}$ chosen = 6.34) - 0.25 M $H_2A_{2\,(o,ini)}$ (= $H_2A_{2\,(o,\,eq)}$) - 3% (v/v) octan-1-ol – kerosene. The log $^{C}D$ vs. (1/T), $K^{-1}$ plot is a straight line with slope of -2857 giving $\Delta H$ value of 54.66 kJ/mol and hence the process is endothermic. The higher $\Delta H$ value indicates that the extraction occurs via chelation and the extraction process is very much sensitive to temperature.

With almost similar stability constants of $NiHSO_4^+$ and $NiSO_4$ with those of $MnHSO_4^+$ and $MnSO_4$, respectively, the aqueous solution of $Ni^{2+}$ at pH > 4 contains some $NiSO_4$ but not $NiHSO_4^+$ (like in the case of Mn(II) solution [47]). Moreover, $NiAc^+$ species also exists in the aqueous solution. Considering pH and extractant dependences of 2 and 1 (at lcr of extractant), the extraction equilibrium reaction should be as follows:

$$Ni^{2+} + H_2A_{2\,(o)} \rightleftharpoons NiA_{2\,(o)} + 2\,H^+ \tag{6}$$

At hcr of sulphate ion, the equilibrium reaction would be as:

$$NiSO_4 + H_2A_{2\,(o)} \rightleftharpoons NiA_{2\,(o)} + 2\,H^+ + SO_4^= \tag{7}$$

and at hcr of acetate ion, the equilibrium reaction would be as:

$$NiAc^+ + H_2A_{2\,(o)} \rightleftharpoons NiA_{2\,(o)} + Ac^- + 2\,H^+ \tag{8}$$

But at hcr of extractant, the disolvated species will be formed as:

$$Ni^{2+} + 3\ H_2A_{2\ (o)} \rightleftharpoons NiA_2.2H_2A_{2\ (o)} + 2\ H^+ \tag{9}$$

Based on related foregoing results and discussion, the following equations are valid for Ni(II) extraction by Cyanex 272:

$$\log {}^{C}D = \log K_{ex} + 2\ pH_{(eq)} + \log [H_2A_2]_{(o,eq)} - \log (1 + 6.92\ [SO_4^{=}]) - \log [Ac^-] \\ = \log K_{ex} + \log f(R) \tag{10}$$

valid at $[H_2A_2]_{(o,eq)} \geq 0.05$ M; and

$$\log {}^{C}D = \log K_{ex} + 2.5\ pH_{(eq)} + 3 \log [H_2A_2]_{(o,eq)} - \log (1 + 6.92\ [SO_4^{=}]) \\ - \log [Ac^-] = \log K_{ex} + \log f(R) \tag{11}$$

valid at $[H_2A_2]_{(o,eq)} \geq 0.10$ M.

The values of $K_{ex}$ have been estimated from the intercepts of various plots and tabulated (Table 1). The average log $K_{ex}$ value is -11.086 with standard deviation of 0.041 for systems having $[H_2A_2]_{(o,eq)} \leq 0.05$ M. This value is -11.56 with standard deviation of 0.04 for systems having $[H_2A_2]_{(o,eq)} \geq 0.10$ M.

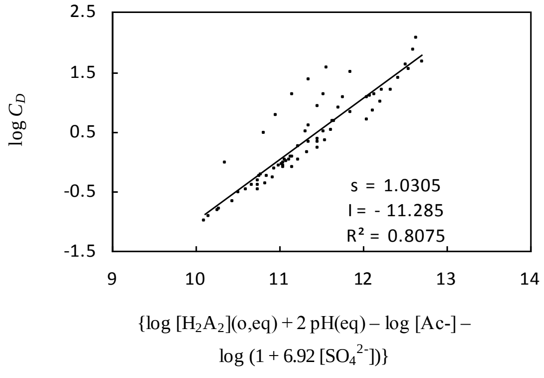

Fig. 4. Plot for the estimation of extraction equilibrium constant ($K_{ex}$) of Ni(II) being extracted by Cyanex 272 at 303 K.

The value of log $K_{ex}$ has also been evaluated graphically. The values of (log $[H_2A_2]_{(o,eq)}$ + 2 $pH_{(eq)}$ - log $[Ac^-]$ - log (1 + 6.92 $[SO_4^{2-}]$) at different parameters have been calculated for all data obtained in equilibrium studies at 303K. The log ${}^{C}D$ vs. (log $[H_2A_2]_{(o,eq)}$ + 2 $pH_{(eq)}$ - log $[Ac^-]$ - log (1 + 6.92 $[SO_4^{2-}]$) plot is given in Fig. 4.

It is found that the points are considerably scattered due to the change in extractant dependency on its concentration variation. The Least Squares slope of 1.0305 (should be 1.0) with intercept of -11.285 and correlation coefficient of only 0.8075 are obtained. The intercept (-11.285) apparently indicates the log $K_{ex}$ value, which is between the values obtained at lcr and hcr of extractant.

Table 1. Evaluation of the extraction equilibrium constant ($K_{ex}$) at 303 K.

| Type of plot log $^{C}D$ vs. | $[H_2A_2]_{(o,eq)}$, M | $pH_{(eq)}$ | $[Ac^-]$, M | $[SO_4^{2-}]$, M | Intercept, I | log $K_{ex}$ | Av. log $K_{ex}$ | Standard deviation | Remarks |
|---|---|---|---|---|---|---|---|---|---|
| i) $[H_2A_2]_{(o)}$ region ≤ 0.05 M, where extractant dependence is *1:* | | | | | | | | | |
| log ($[H_2A_2]_{(o,eq)}$, M) | - | 5.90 | 0.250 | 0.017 | 1.190 | -11.164 | -11.163<br>(-11.086)* | 0.208<br>(0.041)* | Extractant dependence = 1 and pH dependence = 2 |
| | | 6.10 | | | 1.665 | -11.089 | | | |
| | | 6.55 | | | 2.640 | -11.014 | | | |
| $pH_{(eq)}$ | 0.050 | - | 0.250 | 0.017 | -12.450 | -11.703 | | | |
| | 0.025 | | | | -12.130 | -11.082 | | | |
| log ($[Ac^-]$, M) | 0.025 | 6.05 | - | 0.017 | -0.650 | -11.100 | | | |
| log ($[SO_4^{2-}]$, M) | 0.025 | 6.08 | 0.250 | - | 0.075 (lcr) | -11.085 | | | |
| | | | | | -0.750 (hcr) | -11.070 | | | |
| ii) $[H_2A_2]_{(o)}$ region ≥ 0.10 M, where extractant dependence is *3:* | | | | | | | | | |
| log ($[H_2A_2]_{(o,eq)}$, M) | - | 5.90 | 0.250 | 0.017 | 3.750 | -11.554 | -11.560 | 0.045 | Extractant dependence = 3 and pH dependence = 2.5 |
| | | 6.10 | | | 4.250 | -11.554 | | | |
| | | 6.55 | | | 5.300 | -11.629 | | | |
| $pH_{(eq)}$ | 0.10 | - | 0.250 | 0.017 | -13.95 | -11.503 | | | |

* Values in parenthèses are obtained after excluding the abnormal value of -11.703, obtained possibly due to error in intercept measurement on choosing extractant dependence as 1.

### 3.2. *Loading of cyanex 272 solution with Ni(II)*

The loadings of 0.025 and 0.05 M Cyanex 272 solutions with Ni(II) has been performed accordingly and the experimental results together with the experimental conditions are presented in Fig. 5. It is found that the organic phase is saturated with Ni(II) after 7th and 8th contacts for 0.025 and 0.05 M Cyanex 272 systems, respectively. At saturation level, the Ni(II)-concentrations in 0.025 and 0.05 M Cyanex 272 solutions are 3.033 and 6.1714 g/L, respectively. A simple calculation shows that 1 L 0.025 M Cyanex 272 solution contains as much as 0.05167 g ion/L Ni(II) and 1 L 0.05 M Cyanex 272 solution contains as much as 0.1051 g ion/L Ni(II). These results indicate the presence of $Ni_2A_2$ or $NiA^+$ type complex, which can only be possible when acetate ion takes part in the formation of extractable species as follows:

$$NiA_{2\,(o)} + Ni^{2+} + 2\,Ac^- \rightleftharpoons 2\,NiAcA_{(o)} \qquad (12)$$

The loading capacity, defined as the maximum amount of metal ion in gram extracted per 100 g of pure extractant, is a very important factor for an extractant's commercial applicability. High loading capacity is desirable for a particular extractant-metal ion system. Moreover, the species extracted at high loading may be easily converted to pure (usually solid) complexes for its structure determination by chemical and instrumental analyses. In this case, the loading capacity is calculated to be 21.28 g Ni(II)/100 g Cyanex 272. This is considerably a high loading capacity compared to 13.47 g Cu [44], 9.52 g Mn(II) [45], 9.6 g Fe(III) [47] and 11.5 g Zn(II) [48] per 100 g Cyanex 272.

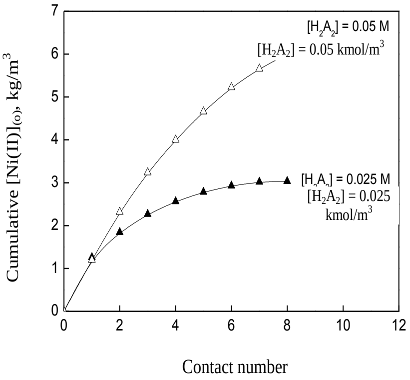

Fig. 5. Loading of Cyanex 272 by Ni(II). $[Ni(II)]_{(ini)}$ =1.95 g/L, $pH_{(ini)}$= 6.85, de-emulsifier = 3%(v/v) octan-1-ol, $[Ac^-]$ = 0.25 M, $[SO_4^{2-}]$ = 0.034 M, equilibration time in each stage = 2 min, temperature = 303 K, phase ratio = 1:1, organic phase being recycled.

### *Stripping*

The stripping of the Ni(II) complex extracted at high loading has been investigated with 0.001, 0.01 and 0.10 M HCl, $HNO_3$, $HClO_4$ and $H_2SO_4$ at organic to aqueous phase ratio (O/A) of 1 at 303 K. All acids appear as good stripping agent (Table 2). Table 2 also illustrates the stripping results with 0.1 and 1.0 M $H_2SO_4$ solutions at higher O/A ratio. With 0.1 M $H_2SO_4$ at O/A of 5 and 10, stripped solutions contain 4.1 g/L and 6.5 g/L Ni(II) in the 1st stage of stripping. On the other hand, with 1 M $H_2SO_4$ at O/A = 100, stripped solution obtained in the 1st stage may contain as much as 55 g/L Ni(II). So stage-wise stripping is also feasible in order to obtain highly concentrated solution of Ni(II) in the aqueous phase on using high O/A ratio in stripping and to regenerate the extractant for further use in extraction.

### *Separation of Ni(II) from other ions in binary mixture*

Table 3 shows the extraction percentages of Ni(II) and the commonly occurring ions of 3d-block elements in binary mixtures at various $pH_{(eq)}$ values of 0 - 7 with an interval of 0.5. At $pH_{(eq)}$ = 4.5, Ni(II) is not extracted at all, but Sc(III), Ti(IV), V(IV), Fe(III) and Zn(II) are completely extracted. So Ni(II) in mixture with either Sc(III), Ti(IV), V(IV), Fe(III) and Zn(II) can be separated easily by single stage extraction at $pH_{(eq)}$ 4.5; whence the second components will be completely extracted into the organic phase leaving whole amount of Ni(II) in the aqueous phase.

Table 2. Stripping of Ni(II)-cyanex 272 complex by various acid solutions. $[Ni(II)]_{(o,ini)}$ = 1 g/L, temp. = 303 K, shaking speed = 300 strokes/min, equilibration time = 3 min.

| Acid | Acid concentration, M | O/A | *Stage No. | % Ni(II) stripped |
|---|---|---|---|---|
| HCl | 0.100 | 1 | 1 | ~100.0 |
| | 0.010 | 1 | 1 | 97.0 |
| | 0.001 | 1 | 1 | 82.0 |
| $HNO_3$ | 0.100 | 1 | 1 | 99.0 |
| | 0.010 | 1 | 1 | 96.0 |
| | 0.001 | 1 | 1 | 80.0 |
| $HClO_4$ | 0.100 | 1 | 1 | ~100.0 |
| | 0.010 | 1 | 1 | 98.0 |
| | 0.001 | 1 | 1 | 84.0 |
| $H_2SO_4$ | 0.100 | 1 | 1 | ~100.0 |
| | 0.010 | 1 | 1 | 98.5 |
| | 0.001 | 1 | 1 | 88.0 |
| | 0.100 | 5 | 1 | 82.0 |
| | | | 2 | ~100.0(c) |
| | 0.100 | 10 | 1 | 65.0 |
| | | | 2 | 91.0 (c) |
| | | | 3 | 99.4 (c) |
| | 1.000 | 100 | 1 | 55.0 |
| | | | 2 | 78.0 (c) |
| | | | 3 | 94.0 (c) |
| | | | 4 | 99.0 (c) |

* Organic phase being recycled in stage-wise stripping studies at the specified O/A ratio.
(c) represents cumulative data.

Table 3. Separation of Ni(II) from its binary mixture with ions of 3d-block elements. [metal ion] = 1 g/L, $[SO_4^{2-}]$ = 0.10 M above $pH_{(eq)}$ of 1.5 (at $pH_{(eq)} < 1.5$ $[SO_4^{=}] = [H_2SO_4]$, [Cyanex 272] =0.10 M in kerose containing 3 % (v/v) octan-1-ol, O/A = 1, equilibration time allowed = 10 min, temp. = 303 K.

| $pH_{(eq)}$ (± 0.05) | Ni(II) | Extraction percentage of | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Sc(III) | Ti(IV) | V(IV) | V(V) | Cr(III) | Mn(II) | Fe(III) | Co(II) | Cu(II) | Zn(II) |
| 0.0 | NE[f] | 54.0 | 6.0 | 2.8 | 21.0 | NE | NE | NE | NE | NE | NE |
| 0.5 | NE | 86.0 | 70.0 | 4.7 | 16.5 | NE | NE | NE | NE | NE | NE |
| 1.0 | NE | 98.0 | 96.0 | 8.8 | 11.8 | NE | NE | 1.0 | NE | NE | 1.1 |
| 1.5 | NE | 99.5 | 99.7 | 34.0 | 8.0 | NE | NE | 8.5 | NE | NE | 9.0 |
| 2.0 | NE | CE* | CE | 55.0 | 6.0 | NE | NE | 40.0 | NE | 0.2 | 48.0 |
| 2.5 | NE | CE | CE | 72.0 | 4.0 | NE | 0.4 | 85.5 | NE | 1.0 | 88.5 |
| 3.0 | NE | CE | CE | 85.0 | 3.0 | NE | 4.8 | 97.8 | 0.5 | 7.5 | 98.5 |
| 3.5 | NE | CE | CE | 97.0 | 1.0 | NE | 40.0 | 99.5 | 2.0 | 45.0 | CE |
| 4.0 | NE | CE | CE | 99.0 | NE | NE | 85.5 | CE | 7.8 | 92.0 | CE |
| 4.5 | NE | CE | CE | CE | NE | NE | 96.5 | CE | 15.5 | 97.5 | CE |
| 5.0 | 1.5±0.3 | CE | CE | CE | NE | NE | 99.6 | CE | 36.5 | 99.4 | CE |
| 5.5 | 4.2±0.5 | CE | CE | CE | NE | NE | CE | CE | 83.5 | CE | CE |
| 6.0 | 12.0±0.5 | CE | CE | CE | NE | NE | CE | CE | 95.0 | CE | CE |
| 6.5 | 70.0±1.2 | CE | CE | CE | NE | NE | CE | CE | 99.0 | CE | CE |
| 7.0 | 90.0±1.2 | CE | CE | CE | NE | NE | CE | CE | CE | CE | CE |

[f] not extracted; *completely extracted.

Vanadium (V) can be separated by extracting (2-3 stages) nickel (II) at $pH_{(eq)}$ of 7.0; since V(V) is extractable at high acidities and not extractable above $pH_{(eq)}$ of 4.0. Ni(II)-Cu(II) separation is feasible at $pH_{(eq)}$ of 5.0 with 99.4 % Cu(II) extraction accompanied by only 1.5% Ni(II) extraction; and so a clear-cut separation will need more than one stage extraction. Similar is the case with Ni(II)-Mn(II) mixture. As Cr(III) is not extracted within allowed time of phase contact, Ni(II)-Cr(III) separation can be made effective by extracting Ni(II) at $pH_{(eq)} > 7$. A clear-cut separation of Ni(II) from Co(II) is not possible in single stage; but extraction at $pH_{(eq)}$ of 5.5 results in 4.2 % Ni(II) extraction with 83.5% Co(II) extraction.

## 4. Conclusion

The following conclusions have been drawn:

- i) Nickel(II) can be extracted from sulfate-acetato medium by cyanex 272-octan-1-ol in kerosene system in the pH range 5-7.
- ii) The pH dependence is 2 and the extractant dependence is 1 at lcr or 3 at hcr. The distribution ratio is found to be inversely proportional to terms $(1 + 6.92\,[SO_4^{2-}])$ and $[Ac^-]$ in the aqueous phase.
- iii) Extraction mechanism depends on the availability of extractant in the system. The extraction reaction: $NiAc^+ + 3\,H_2A_{2\,(o)} \rightleftharpoons [NiA_2.2H_2A_2]_{(o)} + 2\,H^+ + Ac^-$ shifts to $NiAc^+ + H_2A_{2\,(o)} \rightleftharpoons [NiA_2]_{(o)} + 2\,H^+ + Ac^-$ and finally to $NiAc^+ + 0.5\,H_2A_{2\,(o)} \rightleftharpoons [NiAcA]_{(o)} + H^+$ with the the decrease in equilibrium free extractant concentration in the system.
- iv) The equilibrium constant, $K_{ex}$ has been evaluated to be $10^{-11.56}$ and $10^{-11.086}$ at hcr and lcr of extractant, respectively, at 303 K.
- v) The $\Delta H$ value of the extraction reaction is 54.66 kJ/mol showing the process is endothermic.
- vi) The loading capacity of Ni(II) is 21.28 g Ni(II) per 100 g extractant indicating that the extracted species of the highest loading in the organic phase is [NiAcA].
- vii) The extracted nickel complex can be stripped by inorganic acids and the highly concentrated Ni(II) aqueous solution can be obtained by using high O/A ratio in stripping. Stage-wise stripping is also feasible.
- viii) Mutual separation of Ni(II) from other metal ions of 3d – block elements are possible by cyanex 272 just by prior adjustment of aqueous pH of mixed metal ion solutions.

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