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Extraction of Co(II) from aqueous solution using emulsion liquid membrane

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Abstract

The extraction equilibrium of Co(II) from thiocyanate medium by CYANEX 923 (mixture of straight chain alkylated phosphine oxides) in cyclohexane was studied. The stoichiometry of the extraction reaction was postulated based on slope analysis method and the extraction constant K_{ex} was calculated. The stripping percentage of Co(II) with sulphuric acid from the loaded CYANEX 923 was found to increase with the increase in acid concentration. The extraction of Co(II) from aqueous thiocyanate medium into emulsion liquid membrane using CYANEX 923 extractant was also studied. The influence of different parameters such as stirring speed, surfactant concentration, pH of the extractant phase, carrier concentration, internal phase stripping acid concentration, initial Co(II) concentration as well as temperature on the emulsion stability were investigated. The applicability of the emulsion liquid membrane (ELM) process using CYANEX 923 as extractant and SPAN 80 as surfactant for the removal and the concentration of Co(II) from thiocyanate solution was investigated. The results show that it is possible to recover 95% of cobalt in the inner phase after 10 min of contacting time with a concentration factor of 5.
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Keywords: Emulsion liquid membrane; Co(II); Thiocyanate; CYANEX 923

1. Introduction

CYANEX 923 has gained prominence as extractant during the last decade because of its marked selectivity, hydrolytic stability and easy phase separations [1,2]. Extractive spectrophotometric determination of Co(II) in synthetic and pharmaceutical samples using CYANEX 923 was studied and the results of the proposed method are comparable with atomic absorption spectrometry and were found to be in a good agreement. Cobalt has many industrial applications, where it is used to produce some alloys with iron, nickel, chromium and manganese [3]. The recovery of cobalt from spent catalysts using CYANEX 923 has been studied [4]. As Co(II) was quantitatively extracted, the commercial utility of the extractant is demonstrated by recovery of high purity of Co(II) from spent catalysts. The extraction of mercury(II) from dilute hydrochloric acid solutions has been investigated using CYANEX 923 as extractant [5]. The results demonstrated that Hg(II) is extracted into xylene as $HgCl_2 \cdot 3TRPO$. Extraction

and recovery of cadmium using CYANEX 923 have been carried out by Gupta et al. [6] who assessed the potential use of the extractant for the recovery of pure cadmium from zinc and copper matrices. The extracted cobalt thiocyanate complexes play an important role in the spectrophotometric determination of cobalt [7,8]. Thiocyanate is widely used in a variety of chemical processes such as photofinishing, herbicide production, metal separation, and the coke industry [9]. Because of such wide industrial use, thiocyanate is often released into the environment as an industrial waste [10].

Emulsion liquid membranes (ELM) first invented by Li [11], remove the equilibrium limitations of solvent extraction by combining extraction and stripping in a single operation. The applicability of the emulsion liquid membrane process for removal of cobalt was investigated [12]. The results showed that it is possible to recover 98.83% of cobalt in the inner phase after 2 min of contacting time with concentration factor of 50. Cobalt extraction from simulated industrial leaching liquor by liquid surfactant membranes using CYANEX 302 as carrier was investigated and good results for cobalt–nickel separation by the supported liquid membrane technique was obtained [13]. ELM containing 2-ethylhexyl phosphonic

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acid mono 2-ethylhexyl ester (PC-88A) has been applied to recover Co(II) ions from a dilute sulphate solution containing equal amounts of nickel(II) ions [14]. The results proved that SPAN 80 membranes are hydrolyzed readily in a moderate acidic sulphate solution to form viscous gel and excess carrier [(HR)$_2$] affects the stability of emulsion and thus the separating factor.

In this work, the extraction of Co(II) using CYANEX 923 as extractant using ELM is investigated to select the suitable conditions for the permeation of Co(II) from thiocyanate media by the membrane used. Equilibrium investigations on the extraction of Co(II) from different thiocyanate molarities, pH, Co(II) and extractant concentrations in cyclohexane were first carried out. The stability of the prepared ELM was studied in terms of the degree of extraction of Co(II) at different parameters; the factors affecting the permeation of Co(II) were also studied. The kinetics of Co(II) permeation was investigated and a permeation rate equation is deduced.

2. Experimental

2.1. Materials

Cobalt chloride (CoCl$_2$) analytical reagent grade (AR) was supplied by Fluka while sodium thiocyanate, cyclohexane and sulphuric acid were AR grade and obtained from Merck Company (Germany). CYANEX 923 kindly supplied by Cytec Inc., USA, was used as received.

2.2. Procedure

2.2.1. Liquid–liquid extraction

A stock solution of 0.068 M Co(II) was prepared by dissolving CoCl$_2$ in 0.1 M NaSCN to obtain a solution of cobalt thiocyanate at pH = 5.0 ± 0.1. The concentration of Co(II) in the aqueous thiocyanate solution was spectrophotometrically [15] determined by measuring its maximum absorbance at 515 nm using a Shimadzu double beam recording spectrophotometer model 160 A. The results show that Beer's law is obeyed under the experimental conditions used. The organic phase was 0.25 M CYANEX 923/cyclohexane solution. The extraction procedure was carried out by vigorously shaking equal volumes of the two phases in stoppered glass tubes using a thermostated water bath shaker adjusted at 25 ± 0.1 °C except when studying the effect of temperature. The equilibrium was achieved within 15 min as shown in Fig. 1. The effect of [SCN$^-$] on the extraction process was studied by varying its concentration while fixing the ionic strength at 0.1 M with NaNO$_3$. The metal concentration in the organic phase was determined by the difference in its concentration in the aqueous phase before and after extraction. The distribution ratio (D) was calculated as the ratio of the Co(II) concentration in the organic phase to that in the aqueous phase. The relation between the extraction percent (%E) and the distribution ratio (D) is represented as:
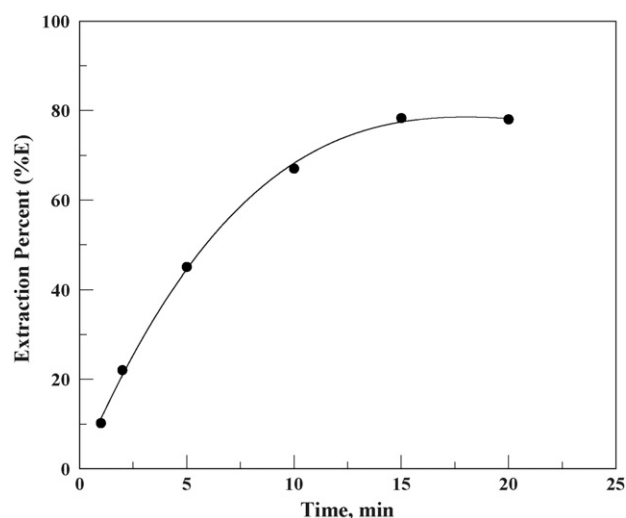
$$\%E = \frac{100 \times D}{D + 1} \tag{1}$$

Fig. 1. Effect of time on the extraction of cobalt by CYANEX 923 in cyclohexane from 0.1 M thiocyanate medium: [Co(II)] = 0.068 M; [CYANEX 923] = 0.25 M; [SCN$^-$] = 0.1 M; T = 25 ± 0.1 °C; pH = 5.0 ± 0.1; O/A ratio = 1.

2.2.2. Emulsion liquid membrane (ELM)

The emulsification was performed with an ultra high speed motor as well as a specially designed turbine plexi glass impeller Cold Stream (Eng.) Ltd., UK. The two phases (organic and internal aqueous) were placed into a beaker. The disperser was introduced and positioned at the interface level; the stirring was maintained at 7000 revolutions per min (as a maximal speed) during 5 min. The W/O emulsion was then poured into the external phase containing the ions to be extracted. The ELM system was stirred with a Cole Parmer (USA) magnetic stirrer of variable speeds ranging from 100 to 400 rpm. All experiments were carried out at a stirring rate of 300 rpm at 25 °C. Samples were taken from the external phase for analysis, and the ion concentration in the internal phase was calculated by mass balance. The aqueous phase pH was adjusted using NaOH and HCl solutions. The stability test was performed in the same manner using distilled water as external phase. The (W/O) emulsion initially containing high concentration of metal ion (4 g/l) in the internal phase was prepared. The metal ion concentration was used as a breakage indicator.

3. Results and discussion

3.1. Equilibrium investigations

The extraction of 0.068 M Co(II) from 0.1 M NaSCN solution was studied at initial pH 5.0 using 0.25 M CYANEX 923 in cyclohexane. The effect of [H$^+$] ((0.054–3.09) × 10^{-7} M), [CYANEX 923] (0.025–0.63 M), [SCN$^-$] (0.01–0.1 M) and metal concentration (0.017–0.14 M) were investigated. The effect of each parameter was separately studied by varying its concentration while fixing the other parameters. The results are shown in Fig. 2 as log–log relations. The extraction of Co(II) linearly increased with the increase in CYANEX 923 concentration with slope equal to 2 suggesting the participation of two CYANEX 923 molecules in the formation of the extracted Co(II)
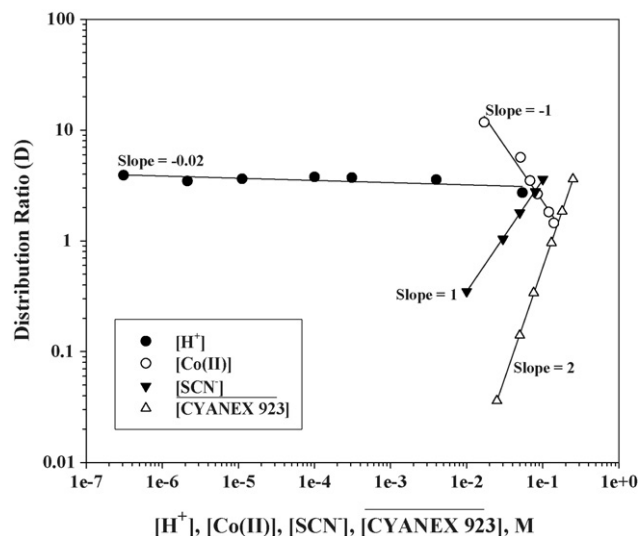
Fig. 2. Effect of [$\overline{\text{CYANEX 923}}$] [H$^+$] [Co(II)] and [SCN$^-$] on the extraction of Co(II) by CYANEX 923 in cyclohexane from 0.1 M thiocyanate medium: $T = 25 \pm 0.1\,^\circ$C; shaking time = 15 min.

Fig. 3. Effect of sulphuric acid concentration on the stripping of Co(II) from CYANEX 923/cyclohexane solution: [Co(II)] = 0.068 M; [CYANEX 923] = 0.25 M; [SCN$^-$] = 0.1 M; $T = 25 \pm 0.1\,^\circ$C; pH = 5.0 $\pm$ 0.1; O/A ratio = 1.

species. The extraction of Co(II) also linearly increased with increasing the NaSCN concentration with slope one indicating the association of one molecule of the thiocyanate ion in the extracted metal species.

The variation in hydrogen ion concentration showed a negligible effect on the extraction of cobalt in the investigated range. The distribution ratio (D) of Co(II) increased with the decrease in the metal concentration with slope -1, which may be related to the insufficient capacity of the used concentration of CYANEX 923 to extract high concentrations of cobalt.

Based on the above results, and considering that [Co(SCN)$^+$] is the predominant cobalt species at low SCN$^-$ concentration [15], the extraction equilibrium of Co(II) with CYANEX 923 (TRPO) in cyclohexane solution can be represented as

$$[\text{Co(SCN)}^+] + \overline{2\text{TRPO}} + \text{SCN}^- \rightleftharpoons \overline{\text{Co(SCN)}_2 \cdot 2\text{TRPO}} \quad (2)$$

The extraction constant K_{ex}, for the above reaction is expressed as

$$K_{\text{ex}} = \frac{[\overline{\text{Co(SCN)}_2 \cdot 2\text{TRPO}}]}{[\text{Co(SCN)}^+]\,[\overline{\text{TRPO}}]^2\,[\text{SCN}^-]} \quad (3)$$

$$K_{\text{ex}} = \frac{D}{[\overline{\text{TRPO}}]^2[\text{SCN}^-]} \quad (4)$$

The extraction constant was calculated at different CYANEX 923 and thiocyanate concentrations and the mean value of K_{ex} was found to be 570 ± 12 M^{-3}.

The effect of H$_2$SO$_4$ concentration on Co(II) stripping from loaded organic solvent consisting of 0.25 M CYANEX 923 in cyclohexane has been investigated and the results are shown in Fig. 3. The results indicate that the percentage of Co stripping from the organic phase increases with increasing H$_2$SO$_4$ concentration from 0.01 to 10 M, where complete stripping was reached at 10 M acid concentration.

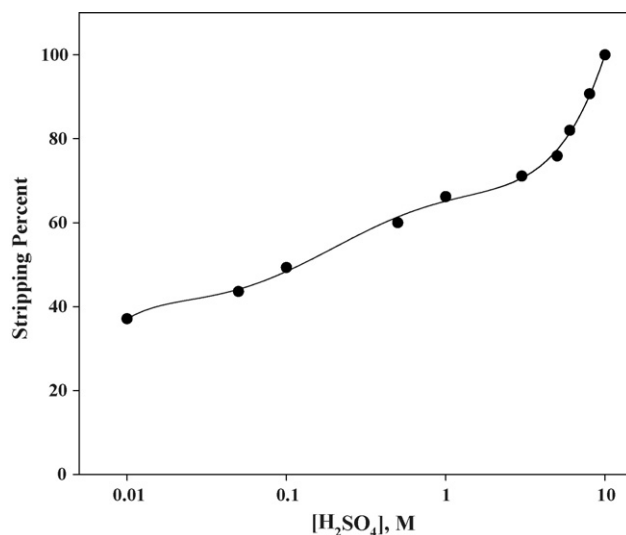### 3.2. The emulsion stability

In the extraction of metal ions emulsion globules, any breakage of the ELM causes a lowering in the extraction efficiency and a loss of both the internal aqueous phase and the extracted species. The stability of the emulsion has been investigated by determining the concentration of the metal ion leaked from the internal phase to the external phase through the emulsion globules.

The percentage of emulsion breakage (%B) was determined using the following equation [16]

$$\%B = \frac{C_{\text{ext}}}{C_{\text{o, int}}} \times 100 \quad (5)$$

where C_{ext} is the concentration of metal ion leaked from the internal phase to the external phase and C_{int} is the total concentration of metal ion in the internal phase.

The different factors governing the emulsion stability were studied. These factors are SPAN 80 concentration, extractant concentration, ratio of the membrane phase volume to the volume of the internal phase, sulphuric acid concentration, rotating speed in the transfer step, emulsification rotating speed, and emulsification time. The results obtained from the different investigations are given in Table 1.

Experiments were performed with 4 g/l Co(II) (0.068 M), 0.1 M NaSCN (while fixing the ionic strength at 0.1 M with NaNO$_3$), 10% CYANEX 923 (0.25 M) in cyclohexane, 4% SPAN 80, 0.5 M sulphuric acid, ratio of the membrane volume/the internal phase = 1, a rotating speed of 300 rpm, 15 min of contact and membrane phase volume: the external phase volume = 0.5 at $25 \pm 0.1\,^\circ$C.

3.2.1. Effect of the emulsification speed on the ELM stability

The results of the effect of the emulsification speed on the stability of the emulsion given in Table 1 shows that the emul-

Table 1
Effect of different parameters on the stability of the liquid emulsion membrane at 25 °C

Investigated parameters		Emulsion breakage percent (%)
Emulsification rotating speed (rpm)	3000	83
	4000	77
	5000	59
	7000	30
	8000	32
Emulsification time (min)	2	57
	5	30
	7	48
	10	52
Stirring speed (rpm)	200	39
	250	42
	300	30
	350	48
	400	65
CYANEX 923 (M)	0.076	60
	0.13	55
	0.25	30
	0.38	43
	0.51	50
H_2SO_4 (M)	0.5	30
	0.7	47
	0.8	49
	1	43
Organic/internal phase	1	30
	2	22
	3	14
	4	10
	6	5
	7	7
SPAN 80 (%)	2	60
	3	50
	4	44
	5	37
	6	30
Membrane/external phase	0.2	17
	0.3	10
	0.4	4
	0.5	3
	0.6	5

sion breakage decreased with the increase of the emulsification speed. An efficient emulsification gives a good dispersion as the internal phase drops into the membrane phase. The fact that these drops become smaller will take much more time to coalesce leading to good stability of the emulsion. In addition, the size of the internal phase droplets is smaller at greater agitation intensity, creating a larger surface area for permeation and hence obtaining a higher fraction of recovery. A speed of 7000 rpm was considered optimal with a breakage of 30%.

3.2.2. Effect of the emulsification time on the ELM stability

The effect of emulsification time on the emulsion stability shows that the lower breakage was obtained for an emulsification time of 5 min, Table 1. For insufficient emulsification time

(<5 min), the breakage was great because the droplets have a large size, which leads to their coalescence. In contrast, for a long emulsification time, the breakage is important because of the high internal shearing leading to a very high number of small droplets which leads to higher stability (as mentioned above).

3.2.3. Effect of stirring speed on the ELM stability

The effect of stirring speed on the stability of the emulsion is shown in Table 1. It is evident from the table that stirring at 300 rpm gives a lower breakage percentage. When the level of agitation decreased (<300 rpm), the size of the emulsion globules increased and the interfacial area available for mass transfer decreased. On the other hand, the break-up of the emulsion was more pronounced and leakage of the internal phase occurred. This can be explained by the increase of the osmotic swelling of the membrane. Increasing the speed of agitation above a critical value (300 rpm) not only affected the stability of the emulsion but also did not increase the extraction efficiency considerably. By increasing the agitation speed, the shear force, which acts on the emulsion globules increased, and this made the globules smaller. The area for mass transfer increased but the membrane ruptured, spilling the internal stripping phase into the outer continuous phase. Hence, the optimum stirring speed was taken as 300 rpm.

3.2.4. Effect CYANEX 923 concentration on the ELM stability

The effect of the concentration of CYANEX 923 as the carrier in the membrane phase is shown in Table 1. Increasing the amount of carrier led to a decrease in the stability of the emulsion. This behavior is due to the interfacial properties of the CYANEX 923 that forms a reversed emulsion O/W, which leads to the rupture of the emulsion. A very high content of carrier in the membrane does not result in a benefit due to the increase in viscosity, which leads to larger globules. On the other hand, the increase in the concentration of the carrier also promotes the permeation swelling, which dilutes the aqueous receiving phase and decreases the efficiency of the process. The best value of the carrier concentration was found to be 0.25 M CYANEX 923.

3.2.5. Effect of the H_2SO_4 concentration in the internal phase on the ELM stability

The results of the effect of the stripping internal phase concentration on emulsion stability show that when the H_2SO_4 concentration increased, the stability of the emulsion decreased, Table 1. This may be due to the reaction between H_2SO_4 and the surfactant that involves a reduction in the properties of the surfactant that consequently led to a destabilization of the emulsion. Concentration of the internal phase which gives the weakest breakage (0.5 M) was chosen in this study.

3.2.6. Effect of the volume ratios on the ELM stability

The volume ratios of the organic phase to the internal phase were varied between 1 and 7. The results given in Table 1 show the effect of variation of this ratio on the stability of the emulsion. It is evident that the increase of volume ratio of the organic phase to the internal phase leads to an increase in the stability of the

emulsion. The results may be explained on the basis that increasing the internal phase volume makes the emulsion unstable and leads to a leakage of the internal phase into the external phase. Hence, in order to obtain a uniform and homogeneous distribution of the internal phase droplets in the membrane space and to avoid the influence of H_2SO_4 on the emulsion stability, the optimum ratio of the organic phase to the internal aqueous phase was taken to be 6 as higher ratio was found to give higher emulsion breakage percent and leading to a decrease in the emulsion stability.

The effect of volume ratio of W/O emulsions to the external phase was studied. Experiments were conducted by taking into account the parameters already optimized and using a volume ratio of the organic phase to the aqueous internal phase of 6. The volume ratio of emulsion to external phase varied between 0.2 and 0.6. Table 1 shows the effect of variation of this ratio on the emulsion stability. It is evident that the increase of volume ratio of the membrane phase to the external phase leads to an increase in the rate constant. The increase of volume ratio of the membrane phase to the external phase from 0.5 led to an increase of the emulsion coagulation. Indeed, with increasing the volume ratio, the swelling phenomenon becomes remarkable, fast, and accompanied by a more significant coalescence of the internal droplets that grow. Therefore, it seems that the optimum volume ratio of emulsion to the external aqueous phase is 0.5.

3.2.7. Effect of the surfactant concentration on the ELM stability

In ELM system, a surfactant added as an emulsifier in the liquid membrane phase affects not only the stability of the liquid membrane but also the swelling of the emulsion and the rate of metal extraction. Table 1 shows the effect of surfactant concentration on the stability of the emulsion. Although the emulsion was expected to be stabilized with increasing surfactant concentration, beyond a critical surfactant concentration, the degree of stability becomes approximately constant due to the saturation of surfactants at the oil–water interface. The optimum SPAN 80 concentration was taken as 6% (v/v).

3.3. Co(II) permeation through the ELM

Based on the results obtained from both the equilibrium studies and the stability of the emulsion membrane, the general conditions used for the permeation of Co(II) by ELM are when the internal phase was prepared from 0.25 M CYANEX 923 and 6% of SPAN 80 in cyclohexane together with 0.5 M H_2SO_4. The external phase prepared from 0.1 M NaSCN contained 4 g/l (0.068 M) Co(II); the volume ratio of membrane phase to the external phase volume = 0.5, the ratio of organic phase to the internal phase = 6, stirring speed 300 rpm, emulsification speed 7000 rpm, emulsification time 5 min and the temperature 25 °C. A simple approach to describe the overall permeation kinetics of Co(II) based on that reported by Teramoto et al. [17] followed a series of experiments on the extraction of Co(II) under the conditions of the rate controlling reaction. In order to get a quantitative measure of the kinetics of Co(II) complexation and permeation, the following simple first order rate
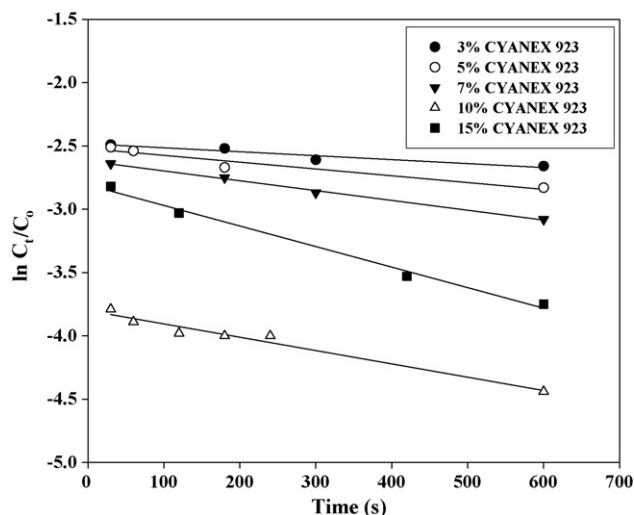

Fig. 4. First order plots for the extraction of Co(II) from thiocyanate medium at different CYANEX 923 concentrations in cyclohexane: [Co(II)] = 0.068 M; [CYANEX 923] = 0.25 M; [SCN$^-$] = 0.1 M; T = 25 ± 0.1 °C; [H$_2$SO$_4$] = 0.5 M; pH = 5.0 ± 0.1; [surfactant] = 6% (v/v); stirring speed = 300 rpm; feed volume:emulsion volume = 2:1.

equation was applied.

$$\frac{C_t}{C_o} = e^{-k_{obs}t} \tag{6}$$

$$\ln\frac{C_t}{C_o} = -k_{obs}t \tag{7}$$

where $[C_t]$ and $[C_o]$ are the molar concentrations of Co(II) remained at time (t) and that initially present in the outer phase solutions, respectively. Fig. 4 represents the first order plots for different concentrations of CYANEX 923 as an example and the values of k_{obs} were calculated from the slopes of the straight lines. The plot of log–log relations between k_{obs} and these different parameters gave linear relations. Plotting log k_{obs} versus the logarithm of the [H$_2$SO$_4$], [Co(II)], [H$^+$] and [SCN$^-$] studied in the same concentration ranges given in Table 1, gives their power dependency Fig. 5. From this figure, it is clear that the rate constant depends on H$_2$SO$_4$ concentration in the internal phase where a slope of 0.97 was obtained and inversely dependent on [Co(II)] concentration with slope = −1. Concerning the ELM composition, the rate constant was found to be independent of the [H$^+$] and [SCN$^-$] while a slope of unity is obtained for extractant and H$_2$SO$_4$ as strippant in the internal phase. From these data, the rate of Co(II) permeation at 25 °C at a ratio of membrane to external phase volume of 0.5 can be represented by the following relation:

$$\frac{d[C]_{per}}{dt} = K[Co(II)]^{-1}[H_2SO_4]^{0.97}[CYANEX\ 923]^{1.04} \tag{8}$$

where $[C]_{per}$ is the molar concentration of the permeated Co(II) and K is a constant.

The investigated system shows that it is possible to recover 95% of cobalt in the inner phase, which is comparable with that obtained by Bourenane et al. [12] who used ELM for 98% removal of traces of Co(II) using HDEHP as extractant from
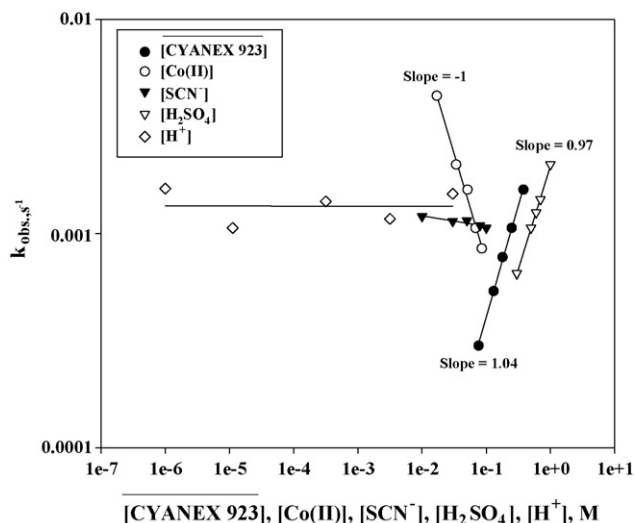
Fig. 5. Effect of [CYANEX 923] [H$^+$] [Co(II)] [SCN$^-$] and [H$_2$SO$_4$] concentrations on the rate constant of Co(II) permeation by CYANEX 923 in cyclohexane from thiocyanate medium though liquid emulsion membrane: [surfactant] = 6% (v/v); stirring speed = 300 rpm; feed volume:emulsion volume = 2:1; T = 25 ± 0.1 °C.

aqueous solution of pH 4. Ribeiro et al. [13] reported that the extraction of Co(II) from a simulated industrial solution by ELM using CYANEX 302 as carrier is pH dependent and no significant metal concentration in the internal phase for a pH value lower than 3. In the present work Co(II) extraction in the internal phase is not affected by pH.

4. Conclusions

- Equilibrium investigations on the extraction of Co(II) by CYANEX 923 (TRPO) in cyclohexane from thiocyanate medium indicate that the stoichiometry of the extracted species is Co(SCN)$_2$·2TRPO.
- The extraction and stripping of Co(II) from thiocyanate solutions by a W/O/W emulsion showed that the stable emulsion is obtained at emulsification speed 7000 rpm, emulsification time 5 min, stirring speed 300 rpm, internal phase concentration (H$_2$SO$_4$) 0.5 M, extractant concentration (CYANEX 923) 10% (v/v), surfactant concentration (SPAN 80) 6% (v/v), volume ratio of the organic phase to the internal phase 6:1 and volume ratio of the membrane phase to the external phase 0.5.
- The proposed system shows that under the above conditions the emulsion breakage decreased, therefore the extraction of Co(II) from thiocyanate medium increased.

- The rate of Co(II) permeation at 25 °C is first order dependent on H$_2$SO$_4$ concentration in the internal phase and inversely dependent on [Co(II)] concentration with slope = −1.

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