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Extraction Equilibria in the Co,Ni(SCN)$_2$–Na,NH$_4$SCN–Aliquat 336, Ethyl Acetate System

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Summary. The extraction behaviour of Co and Ni thiocyanates in combination with methyltrioctylammonium thiocyanate is reported. The Co complexes Co(*A*SCN)$_2$(SCN)$_2$ and HCo(*A*SCN)$_2$(SCN)$_3$ and the Ni species Ni(*A*SCN)(SCN)$_2$ and Ni(*A*SCN)$_4$(SCN)$_2$ were found in the organic phase. The separation factors of Co/Ni are in the range of 10^3–10^4. The extraction of NaSCN, NH$_4$SCN, and H$_2$SO$_4$ into ethyl acetate is described for the first time.

Keywords. Cobalt; Nickel; Extraction; Aliquat 336; Separation factor.

Extraktionsgleichgewichte im System Co,Ni(SCN)$_2$–Na,NH$_4$SCN–Aliquat 336, Ethylacetat

Zusammenfassung. Das Extraktionsverhalten von Kobalt- und Nickelthiocyanat im Zusammenhang mit Methyltrioctylammoniumthiocyanat wird beschrieben. In der organischen Phase wurden die Kobaltkomplexe Co(*A*SCN)$_2$(SCN)$_2$ und HCo(*A*SCN)$_2$(SCN)$_3$ sowie die Nickelkomplexe Ni(*A*SCN)(SNC)$_2$ und Ni(*A*SCN)$_4$(SCN)$_2$ gefunden. Die Co/Ni-Trennfaktoren liegen im Bereich von 10^3 bis 10^4. Zum ersten Mal wird über die Extraktion von NaSCN, NH$_4$SCN und H$_2$SO$_4$ in die Ethylacetat-Phase berichtet.

Introduction

Tertiary amines and quaternary alkylammonium salts are widely used in the extraction of Co and Ni [1–8]. The separation of Co from Ni is easily obtainable due to the relatively high ability of Co to form hydrophobic complexes with inorganic anions in contrast to Ni. In a previous paper we have tried to describe quantitatively the extraction system Co,NiCl$_2$–Aliquat 336–xylene [8]. Because of aggregation of amine in the organic phase and the formation of adducts of amine with other organic phase components it was impossible to characterize correctly all species formed in the organic phase. In the present paper, the system Co,Ni(SCN)$_2$–Aliquat 336, ethyl acetate is described which seemed to be less complicated. Taking into account the fact that ethyl acetate is a more polar solvent than xylene, we expected to find the amine exclusively in monomeric form in the organic phase.

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As a consequence of this fact, the mathematical treatment of the system was expected to be much easier.

Although the system described in this paper has been applied in the membrane extraction of Co and Ni [9], it has never been treated from a mathematical point of view. Apart from Co and Ni, the other reagents like H_2SO_4, NaSCN and NH_4SCN present in the organic and aqueous phases were taken into account. Their extraction into ethyl acetate is described for the first time.

Results and Discussion

Extraction of H_2SO_4, NaSCN, and NH_4SCN

The changes of the distribution coefficients D of the aforementioned reagents with the ionic strength of the aqueous phase are given in Fig. 1. The distribution coefficient of H_2SO_4 decreases with rising ionic strength.

The distribution coefficient of H_2SO_4 may be described by equation (1) where K refers to the extraction constant and γ denotes the activity coefficient of H_2SO_4 in both phases.

$$D = K\gamma_{\text{aq}}/\gamma_{\text{o}} \tag{1}$$

The deviation from *Nernst*'s law, manifested by the change of D with rising ionic strength, results from the change of the ratio $\gamma_{\text{aq}}/\gamma_{\text{o}}$. From the theory of electrolytes

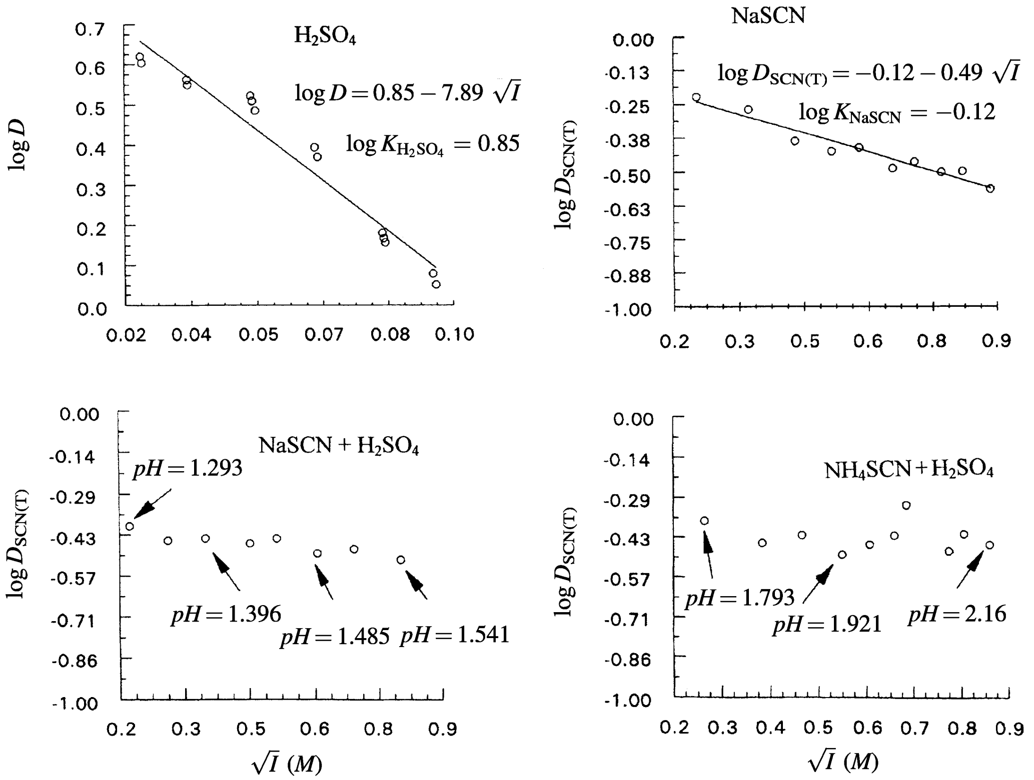

Fig. 1. Variation of the distribution ratio of H_2SO_4, NaSCN, and NH_4SCN with varying ionic strength for ethyl acetate ($T = 23°\text{C}$, $V(\text{o})/V(\text{aq}) = 1$)

it is known that for the majority of electrolytes γ_{aq} strongly decreases in the concentration range of 0–1 M. On the other hand it is difficult to assume any changes of H_2SO_4 in the organic phase with respect to its probable dimerization as the result of the low dielectric constant of ethyl acetate.

In the case of NaSCN, the total distribution coefficients of thiocyanate ions, defined by $D_{SCN(T)} = c_{SCN(O)}/c_{SCN(aq)}$, decrease with the ionic strength. The extraction constants of H_2SO_4 and NaSCN found from the relation $\log D = K + b\sqrt{I}$ obey the order $K_{H_2SO_4} > K_{NaSCN}$ which is understandable if the stronger solvation of the small H^+ ion by ethyl acetate molecules in comparison with the large Na^+ ion is taken into account.

In the case of $NaSCN+H_2SO_4$ and $NH_4SCN+H_2SO_4$, the $D_{SCN(T)}$ values are approximately constant. There are probably two opposite effects: the decrease of γ_{aq} and the increase of HSCN extraction to ethyl acetate with rising SCN^- concentration. The extraction of HSCN is evident if we look at the increasing equilibrium pH values of the aqueous phase.

Extraction of Co

Experimental data concerning the extraction of Co in systems with NaSCN and NH_4SCN in the aqueous phase are presented in Figs. 2 and 3. The extraction is shown in three variants: A: pure ethyl acetate, B: ethyl acetate + Aliquat 336 (with varying concentration), and C: ethyl acetate + Aliquat 336 (with constant concentration).

The extraction of Co from thiocyanate media by Aliquat 336 may be described by the following reaction:

$$m\mathrm{H}^+ + Me^{2+} + nA\mathrm{SCN} + (2+m)\mathrm{SCN}^- \overset{K}{\rightleftharpoons} \mathrm{H_mMe(ASCN)_nSCN_{(2+m)}} \tag{2}$$

Taking into account that the extraction constant relates to the quotient of products and substrates in equilibrium and that the distribution ratio relates to c_o/c_{aq}, we obtain Eq. (3) where $[H^+$, $[A\mathrm{SCN}]$, and $[\mathrm{SCN}^-]$ refer to the equilibrium concentrations of the reagents.

$$D_{cal} = \sum_0^m \sum_0^n K[H^+]^m[\mathrm{ASCN}]^n[\mathrm{SCN}^-]^{m+2} \tag{3}$$

Extraction constants for the different complexes are given in Table 1. They were calculated based on the experimental data visualized in Figs. 2 and 3 using the PSPLOT program (Polysoft Ltd, version 1.01). This program calculates the best compatibility between D_{exp} and D_{cal} using the least squares procedure. At the same time, the program compares the total concentrations of the reagents with the concentrations predicted by the model. From the above reagents, only the concentration of Aliquat 336 is comparable with the metal concentration and may be described by the following equation:

$$[A\mathrm{SCN}_{(o)T}] = [A\mathrm{SCN}] + \sum_0^m \sum_1^n nK[\mathrm{Co}_{(aq)}][\mathrm{ASCN}]^{\mathrm{n}}[\mathrm{SCN}^-]^{\mathrm{m}+2} \tag{4}$$

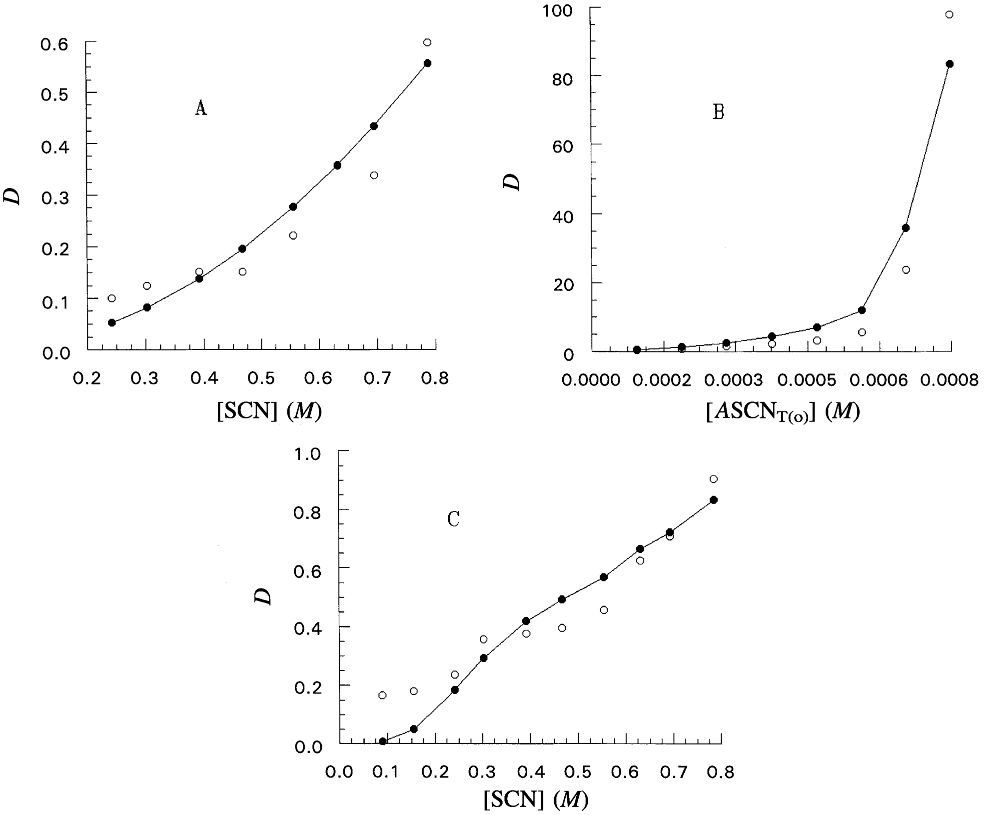

Fig. 2. Change of the distribution ratios of Co in the extraction system $Co(SCN)_2$–NaSCN–Aliquat 336–ethyl acetate; A: pure ethyl acetate, $[H_T^+] = 0.1\,M$, $pH = 1.293$, 1.347, 1.396, 1.427, 1.445, 1.485, 1.517, 1.5406; B: $[ASCN_{(o)T}] = 0.0001–0.001\,M$, $[SCN_T] = 0.5\,M$, $[H_T^+] = 0.1\,M$, $pH = 1.396$; C: $[ASCN_{(o)T}] = 0.0001\,M$, $[SCN_T] = 0.1–1\,M$, $[H_T^+] = 0.1\,M$, $pH = 1.175$, 1.246, 1.293, 1.346, 1.396, 1.427, 1.445, 1.485, 1.517, 1.541; full symbols refer to D_{cal} values, empty symbols to D_{exp}

The chemistry of the extraction of Co by Aliquat 336 is different with respect to ethyl acetate. It results from calculations that int he case of ethyl acetate Co appears in the organic phase in the form of two complexes: $Co(SCN)_2$ and $Co(SCN)_4^{2-}$. Of course it is difficult to imagine the transfer of the negatively charged complex to the organic phase; so probably, instead of $Co(SCN)_4^{2-}$ species, the ionic pairs $(NH_4,Na)_2Co(SCN)_4$ are present in the ethyl acetate phase.

In the case of Aliquat 336, the complexes $Co(ASCN)_2(SCN)_2$ and $HCo(ASCN)_2(SCN)_3$ were found in the organic phase. Taking into account the ion exchange character of the quaternary alkylammonium salt, the probable real structures of these complexes are $[A^+]_2Co(SCN)_4^{2-}]$ and $[A^+]_2Co(SCN)_4^{2-}] \cdot HSCN$. It is known that Co willingly forms hydrophobic complexes with a tetrahedral arrangement of ligands which are easily transferred to the organic phase; and for this reason, the structure $[H^+][A^+]_2[Co(SCN)_5^{3-}]$ is less probable.

The absolute values of the extraction constants of these complexes found for NaSCN and NH_4SCN are somewhat different, probably resulting from the different activity coefficients of Co^{2+} and SCN^- ions in these two electrolytes.

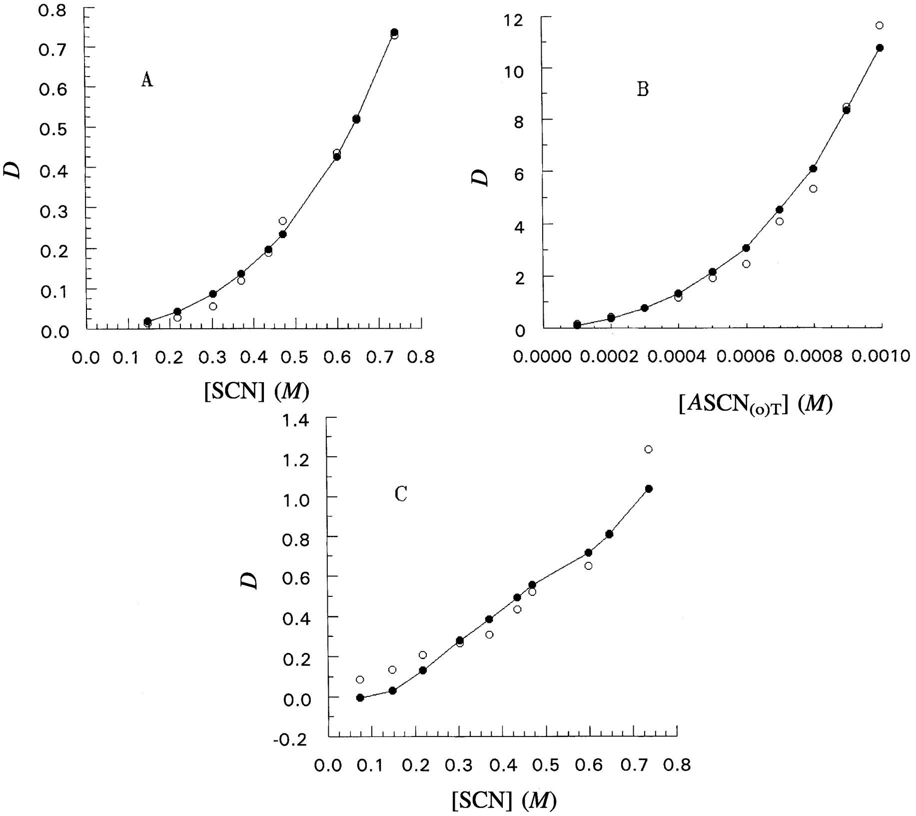

Fig. 3. Change of the distribution ratios of Co in the extraction system $Co(SCN)_2$–NH_4SCN–Aliquat 336–ethyl acetate (A: pure ethyl acetate, $[H^+_T] = 0.1\,M$, $pH = 1.793$, 1.86, 1.917, 1.921, 2.029, 2.00, 2.094, 2.030, 2.160; B: $[ASCN_{(o)T}] = 0.0001$–$0.001\,M$, $[H^+_T] = 0.1\,M$, $[SCN_T] = 0.3\,M$, $pH = 1.859$; C: $[ASCN_{(o)T}] = 0.0001\,M$, $[SCN_T] = 0.1$–$1\,M$, $[H^+_T] = 0.1\,M$, $pH = 1.801$, 1.793, 1.860, 1.917, 1.921, 2.030, 2.004, 2.094, 2.030, 2.162

Extraction of Ni

The distribution ratio of Ni is given in Fig. 4. Based on the values of D, the extraction constants of species appearing in the organic phase were calculated (Table 1). In the organic phase with ethyl acetate as component, only one neutral complex was found ($Ni(SCN)_2$), whereas for the Aliquat 336 system two complexes were recognized ($Ni(ASCN)(SCN)_2$, $Ni(ASCN)_4(SCN)_2$). In the second complex, Ni probably preserve a coordination number of 6 with respect to the SCN^- ions. The probable real structures of the complexes are $[A^+][Ni(SCN)_3^-]$ and $[A^+]_4[Ni(SCN)_6^{4-}]$.

Co/Ni separation efficiency

The separation factors of Co and Ni are given in Fig. 5. They change rapidly with rising Aliquat 336 concentration and range from 10^3 to 10^4. To understand this

Table 1. Extraction constants of $H_mCo,Ni(ASCN)_n(SCN)_{2+m}$ in the system $Co,Ni(SCN)_2$–Na,NH_4SCN–Aliquat 336

Complex $H_mCo(ASCN)_n(SCN)_{2+m}$, defined as m:Co:n:(2+m)	Extraction constant (K)	Organic phase	Aqueous phase
0:Co:0:2	0.71 ± 0.15	E	$NaSCN+H_2SO_4$
0:Co:0:4	0.29 ± 0.15	E	$NaSCN+H_2SO_4$
0:Co:2:2	$(1.45\pm0.35)\times10^9$	E+ASCN	$NaSCN+H_2SO_4$
1:Co:2:3	$(1.6\pm8)\times10^{10}$	E+ASCN	$NaSCN+H_2SO_4$
0:Ni:0:2	0.042 ± 0.01	E	$NaSCN+H_2SO_4$
0:Ni:1:2	135 ± 192	E+ASCN	$NaSCN+H_2SO_4$
0:Ni:4:2	$(1.1\pm8.9)\times10^{10}$	E+ASCN	$NaSCN+H_2SO_4$
0:Co:0:2	0.86 ± 0.08	E	$NH_4SCN+H_2SO_4$
0:Co:0:4	0.87 ± 0.18	E	$NH_4SCN+H_2SO_4$
0:Co:2:2	$2.36\times10^8\pm2\times10^6$	E+ASCN	$NH_4SCN+H_2SO_4$
1:Co:2:3	$2.14\times10^{10}\pm8\times10^9$	E+ASCN	$NH_4SCN+H_2SO_4$

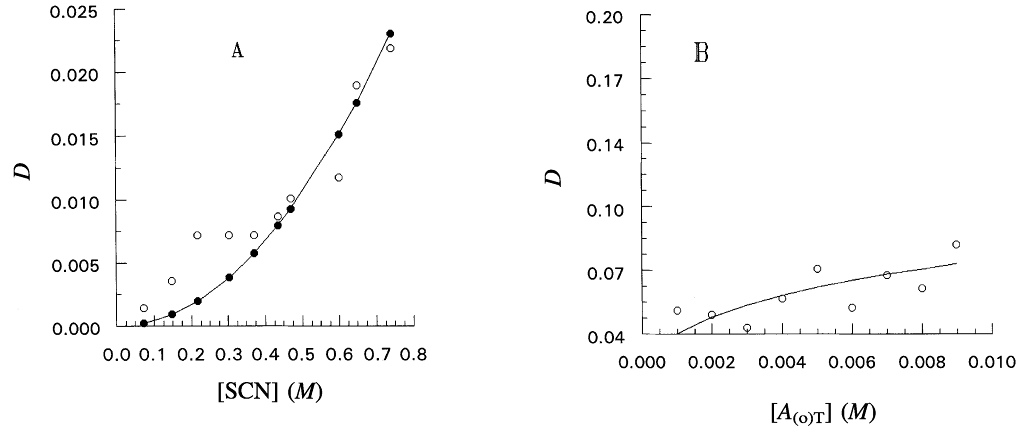

Fig. 4. Change of the distribution ratios of Ni in the extraction system $Ni(SCN)_2$–NaSCN–Aliquat 336–ethyl acetate; A: pure ethyl acetate, $[H^+_T]=0.1\,M$, $pH=1.801$, 1.793, 1.86, 1.917, 1.921, 2.029, 2.000, 2.094, 2.030, 2.162; B: $[ASCN_{(o)T}]=0.001$–$0.01\,M$, $[H_T{}^+]=0.1\,M$, $[SCN_T]=0.5\,M$, $pH=1.921$

trend, we have calculated the molar fractions of Co and Ni species in the organic phase based on the following equation:

$$\alpha = K[H^+]^m[A]^n[SCN^-]^{2+m}\cdot\left(\sum_0^m\sum_1^n[H^+]^m[A]^n[SCN^{m+2}\right)^{-1} \qquad (5)$$

The molar fractions of Co and Ni are given in Fig. 6. It is easy to notice that in the organic phase Co exists predominantly as $Co(ASCN)_2(SCN)_2$. The molar fraction of the protonated species $(HCo(ASCN)_2(SCN)_3$ is much lower, but it increases

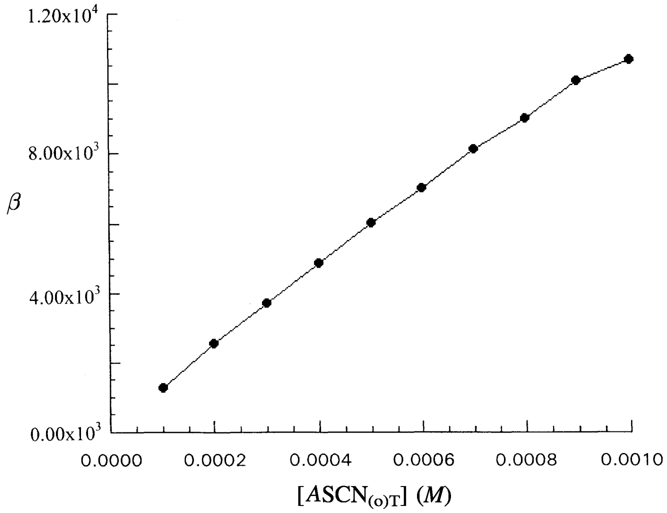

Fig. 5. Change of Co/Ni separation factors β; $[ASCN_{(o)T}] = 0.0001–0.001\,M$, $[SCN_T] = 1\,M$, $pH = 2.00$

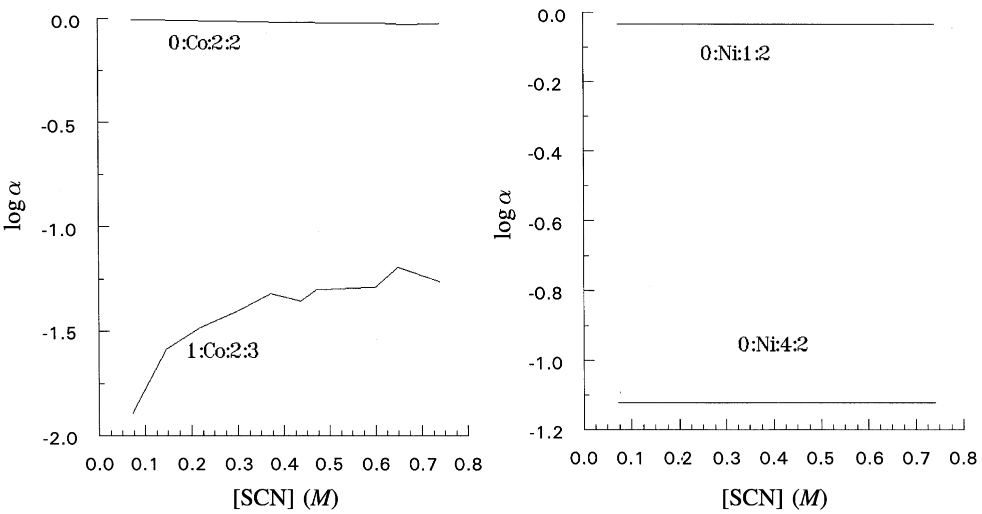

Fig. 6. Molar fractions α of Co and Ni complexes in the organic phase; $[ASCN_{(o)T}] = 0.001\,M$, $[SCN_T] = 0.1–1\,M$, $[H_T^+] = 0.1\,M$, $pH = 1.801$, 1.793, 1.86, 1.917, 1.921, 2.029, 2.000, 2.094, 2.030, 2.162

markedly with rising SCN^- concentration. Nickel forms predominantly $Ni(ASCN)(SCN)_2$ in the organic phase and therefore, when comparing the stoichiometries of the Co and Ni complexes, the separation factor will strongly depend on [ASCN].

From the above results, the following conclusions can be drawn: 1) Ni very unwillingly forms anionic thiocyanate complexes, and 2) the system $Co,Ni(SCN)_2$–Na,NH_4SCN–Aliquat 336, ethyl acetate may be applied for an effective and rapid separation of Co from Ni at an analytical scale.

Experimental

Reagents

The Co, Ni chlorides (Polskie Odczynniki Chemiczne, pure) were dissolved in 0.1–1 *M* solutions of NaSCN or NH_4SCN (Polskie Odczynniki Chemicze, pure). In all experiments described in this paper, the initial concentration of Co in the aqueous phase was 0.0001 *M* and that of Ni 0.01 *M*.

As organic phase a solution of Aliquat 336 (Aldrich, R grade) in ethyl acetate (Polskie Odczynniki Chemiczne, pure) was used. The concentration of Aliquat 336 varied in from 0.0001 *M* to 0.001 *M* for the extraction of Co and from 0.001 *M* to 0.01 *M* for the extraction of Ni.

Distribution experiment

Organic and aqueous phases (equal volumes of 20 ml) were shaken in small glass tubes with glass stoppers. All experiments were carried out at 23°C. After 20 minutes, the phases were left for separation, and 10 ml samples were taken from the aqueous phases for the determination of Co and Ni by atomic flame absorption spectrometry. The concentrations of the elements in the organic phases were determined in the same manner after reextraction with water. The concentration of the hydrogen ions in the aqueous phase was determined potentiometrically, that of the thiocyanate ions in both phases by argentometric titration.

Nomenclature and abbreviations

ASCN	metyltrioctylammonium thiocyanate
E	ethyl acetate
A^+	metyltrioctylammonium cation
c_{aq}	metal concentration in the aqueous phase
$c_{(\mathrm{o})}$	metal concentration in the organic phase
$c_{\mathrm{SCN(aq)}}$	total concentration of thiocyanate ions in the aqueous phase
$c_{\mathrm{SCN(o)}}$	total concentration of thiocyanate ions in the organic phase
I	ionic strength of the aqueous solution
D_{exp}	experimental distribution ratio of metal ions
D_{cal}	calculated distribution ratio of metal ions
$D_{\mathrm{SCN(T)}}$	total distribution ratio of thiocyanate ions
β	Co/Ni separation factor
$\mathrm{H}_m\mathrm{Me}A_n\mathrm{SCN}_{2+m}$	complex of Co/Ni with the ratio H:Me:A:SCN = m:1:n:m+2
K	extraction constant of metal complex to methyltrioctylammonium thiocyanate
$K_{\mathrm{H_2SO_4}}$, K_{NaSCN}	extraction constants of H_2SO_4 and NaSCN to ethyl acetate
$[A\mathrm{SCN}_{(\mathrm{o})\mathrm{T}}]$	total concentration of metyltrioctylammonium in the organic phase
$[\mathrm{H^+}_\mathrm{T}]$	initial concentration of hydrogen ions in the aqueous phase
$[A\mathrm{SCN}]$	equilibrium concentration of metyltrioctylammonium thiocyanate in the organic phase
$[\mathrm{SCN_T}]$	initial concentration of thiocyanate in the aqueous phase
$[\mathrm{SCN^-}]$	equilibrium concentration of thiocyanate in the aqueous phase
$[\mathrm{H^+}]$	equilibrium concentration of hydrogen ions in the aqueous phase

References

[1] Kachanowicz IV (1994) ZH Neorg Khim **39**(2): 347

[2] Saeel MM, Ahmed M, Ali A (1995) J Radioanal Nucl Chem **189**(1): 83

[3] Abdel-Badei MM, Aly MM (1989) Isotopenpraxis **25**(9): 378

[4] Bagreev VV, Kardivarenko LM, Zolotov IA (1988) Zh Neorg Khim **33**(11): 2891
[5] Raieh M, Khalifa SM, El-Dessouky MM (1985) Arab Journal Nuclear Sciences Applications **18**(1): 80
[6] Niinae M, Nakahiro Y, Wakamatsu T (1991) Fuesen Flotation Japan **38**(2): 7
[7] Panesar KS, Singh OV, Tandou SN (1992) J Radioanal Nucl Chem **166**(4): 273
[8] Majdan M, Mierzwa J, Sadowski P (1997) Monatsh Chem **128**: 113
[9] Papantoni M, Djane NK, Ndungo J, Jonnson A, Mathiasson L (1995) Analyst **120**: 1471

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