

On the Separation of Co and Ni from Chloride Media with *Aliquat 336-TBP* and *Aliquat 336-TOPO*

M. Majdan*, J. Mierzwa, and P. Sadowski

Marie Curie Skłodowska University, Faculty of Chemistry, PL-20031 Lublin, Poland

Summary. The extraction behaviour of Co and Ni chlorides with *Aliquat 336-TBP* and *Aliquat 336-TOPO* (*Aliquat 336*: tri-*n*-octylmethylammonium chloride, *TBP*: tri-*n*-butylphosphate, *TOPO*: tri-*n*-octylphosphine oxide) was investigated. The synergistic action of *TOPO* in the extraction of Co and Ni with *Aliquat 336* manifested itself in an increase of the distribution ratio of Co with increasing of *TOPO* concentration at constant *Aliquat 336* concentration without deterioration of the separation factor Co/Ni which still was above 200. Mixed complexes of the general formula $MeCl_{2+m}A_mB_n$ (*Me*: Co or Ni, *A*: *Aliquat 336*, *A*: *TBP* or *TOPO*) with *m* ranging from 2 to 5 and *n* from 1 to 3 were present in the organic phase of both systems. The coexistence of several synergistic Co/Ni species in the equilibrium organic phase is reported for the first time.

Keywords. Cobalt-nickel separation; Extraction; *Aliquat 336*; *TBP*; *TOPO*.

Zur Abtrennung von Co und Ni aus chloridhaltigen Medien mit *Aliquat 336-TBP* und *Aliquat 336-TOPO*

Zusammenfassung. Das Extraktionsverhalten von Kobalt- und Nickelchloriden mit *Aliquat 336-TBP* und *Aliquat 336-TOPO* (*Aliquat 336*: Tri-*n*-octylmethylammoniumchlorid, *TBP*: Tri-*n*-butylphosphat, *TOPO*: Tri-*n*-octylphosphinoxid) wurde untersucht. Die synergistische Wirkung von *TOPO* bei der Extraktion von Co und Ni mit *Aliquat 336* manifestiert sich in einer Erhöhung des Verteilungsverhältnisses von Co mit steigender *TOPO*-Konzentration, ohne daß dadurch der Co/Ni-Trennfaktor verschlechtert wird (> 200). Für beide Systeme konnten in der organischen Phase gemischte Komplexe der allgemeinen Formel $MeCl_{2+m}A_mB_n$ nachgewiesen werden (*Me*: Co oder Ni, *A*: *Aliquat 336*, *B*: *TBP* oder *TOPO*, *m*: 2–5, *n*: 1–3). Zum ersten Mal wird über die Koexistenz verschiedener synergistischer Co/Ni-Spezies in der organischen Phase im Gleichgewicht berichtet.

Introduction

The separation of Co and Ni is still an attractive problem in inorganic chemistry. Among the different extractants used for the separation of these elements, three groups of compounds can be recognized: organophosphorous acids [1], oximes and hydroxyoximes [2, 3], and amines [4–10].

The use of organophosphorous acids has been studied very extensively recently and is important from a practical point of view with respect to the low commercial

price of this type of extractants. However, it is not so attractive with respect to fundamental problems of solvent extraction chemistry as is the case with amines. The latter are very interesting from a theoretical point of view, because many metal complexes exist in the organic phase which result from the tendency of amines to aggregate, especially in nonpolar solvents. A further complication occurs when organic phase modifiers (*TBP* or *TOPO*) are present in the system. The aggregation of the amines decreases, but at the same time the number of the complex species of metal and amine increases. This fact has been quantitatively described for the extraction of lanthanide nitrates with *Aliquat 336-TBP* system [11].

The coexistence of several Co/Ni complexes in the equilibrium organic phase has not yet been reported in the literature. Its quantitative estimation is the aim of this investigation.

Results and Discussion

Basic equations

Extraction of Co or Ni with tri-*n*-octylmethylammonium chloride can be described by Eq. (1), where $K_{1,m,n}$ refers to the extraction constant of the species

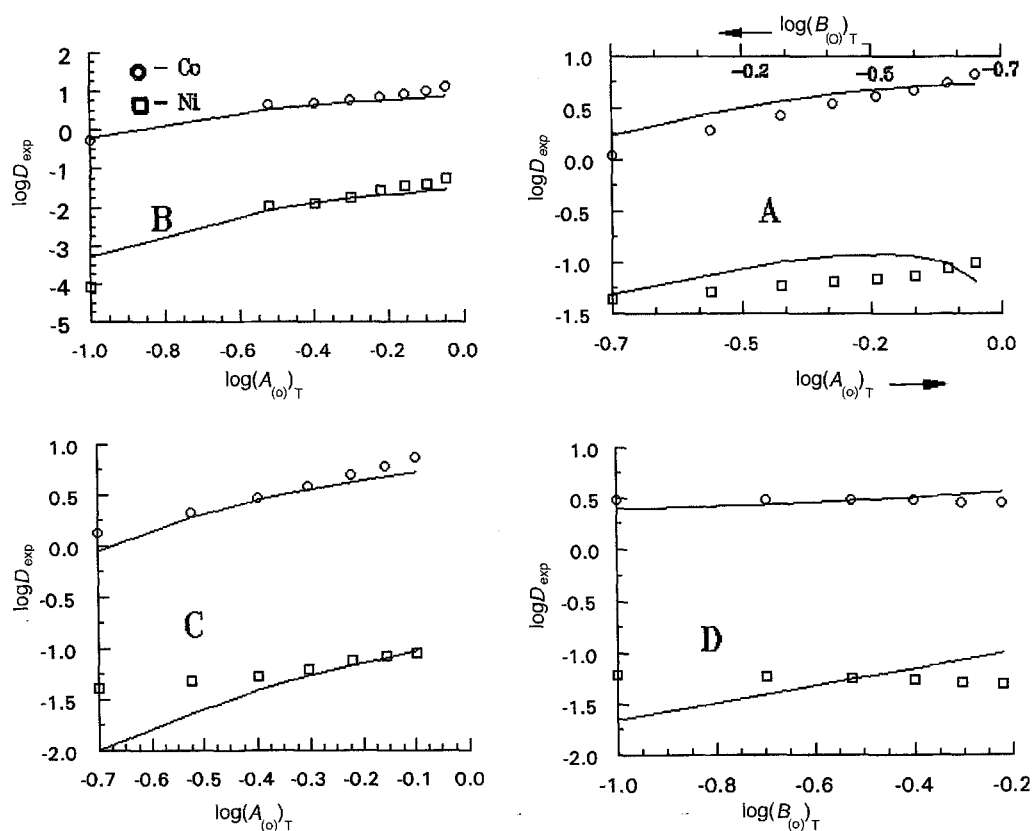


Fig. 1. Change of $\log D_{exp}$ (points) and $\log D_{calc}$ (lines) with rising extractant concentration for *Aliquat 336-TBP*; A: $(A_{(o)})_T = 0.2 - 0.9 M$, $(B_{(o)})_T = 0.8 - 0.1 M$; B: $(A_{(o)})_T = 0.1 - 0.9 M$; C: $(A_{(o)})_T = 0.2 - 0.8 M$, $(B_{(o)})_T = 0.2 M$; D: $(A_{(o)})_T = 0.4 M$, $(B_{(o)})_T = 0.1 - 0.6 M$

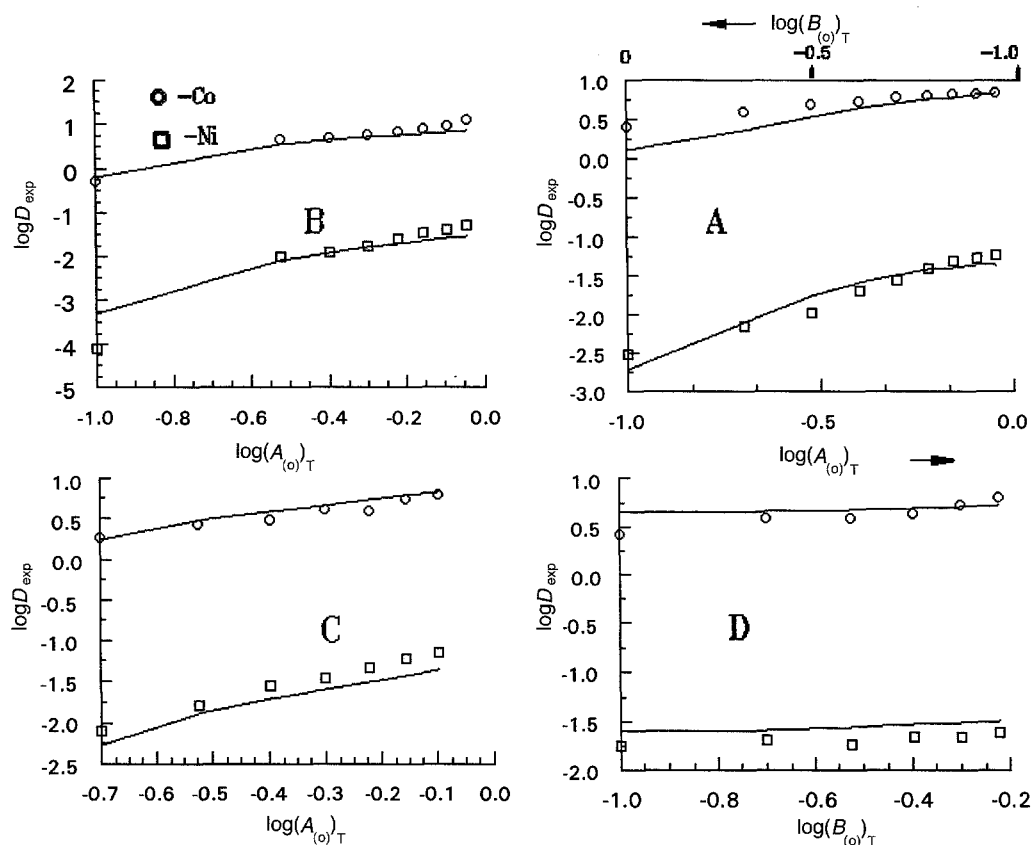
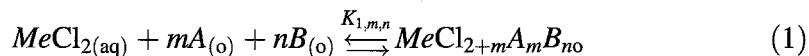


Fig. 2. Change of $\log D_{\text{exp}}$ and $\log D_{\text{calc}}$ with increasing extractant concentration for *Aliquat 336-TOPO*; A: $(A_{(o)})_T = 0.1 - 0.9M$, $(B_{(o)})_T = 0.9 - 0.1M$; B: $(A_{(o)})_T = 0.1 - 0.9M$; C: $(A_{(o)})_T = 0.2 - 0.8M$, $(B_{(o)})_T = 0.2M$; D: $(A_{(o)})_T = 0.4M$, $(B_{(o)})_T = 0.3 - 0.8M$

$MeCl_{2+m}A_mB_n$ and is defined by Eq. (2). Note that the concentration of chlorides is included in the value of the extraction constant.



$$K_{1,m,n} = [MeCl_{2+m}A_mB_n] [MeCl_{2(aq)}]^{-1} [A_{(o)}]^{-m} [B_{(o)}]^{-n} \quad (2)$$

The distribution ratio of the metal D_{exp} can be written as $D_{\text{exp}} = c_{(o)}/c_{(aq)}$. Taking into account Eq. (2) and fact that the sum of the complex species exists in the organic phase, we obtain

$$D_{\text{calc}} = \sum_{i=0}^m \sum_{j=0}^n K_{1,i,j} [A_{(o)}]^i [B_{(o)}]^j. \quad (3)$$

Apart from the equilibria concerning the metal extraction, the interaction between molecules of extraction reagents (*A* and *B*) has to be taken into consideration. The adduct formation constants $k_{i,j}$ are defined as

$$k_{i,j} = [(A)_i(B)_j] [A_{(o)}]^{-i} [B_{(o)}]^{-j}. \quad (4)$$

Table 1. Extraction constants of $MeCl_{2+i}A_iB_j$ in the synergistic systems *Aliquat 336-TBP* and *Aliquat 336-TOPO* (n.f.: species not found by computer treatment; max: maximum of the extraction constant)

$MeCl_{2+i}A_iB_j$ (defined as $Me\ 1 : i : j$)	Extraction constant $K_{1,i,j}$	
	<i>TBP</i>	<i>TOPO</i>
Ni 1:3:0		0.32 ± 0.66
Ni 1:4:0		2.54 ± 0.33
Ni 1:5:0		$(4.519 \pm 1.52) \times 10^6$
Ni 1:2:1		n.f.
Ni 1:2:2		n.f.
Ni 1:2:3		n.f.
Ni 1:4:1	$(7.108 \pm 0.600) \times 10^6$	$(4.317 \pm 0.160) \times 10^6$
Ni 1:4:2	$(4.168 \pm 0.160) \times 10^6$	$(1.353 \pm 0.140) \times 10^4$
Ni 1:4:3	$(6.993 \pm 0.160) \times 10^5$	$(2.01 \pm 0.130) \times 10^7$
Ni 1:5:1	$(1.11 \pm 0.170) \times 10^8$	$(8.163 \pm 0.150) \times 10^5$
Ni 1:0:2	0.99 ± 0.14	0.008 ± 0.1
Co 1:3:0		0.58×10^6 (max)
Co 1:4:0		289 (max)
Co 1:5:0		$(0.9 \pm 0.565) \times 10^6$
Co 1:2:1	$(0.512 \pm 0.252) \times 10^5$	n.f.
Co 1:2:2	1.905 ± 0.33	$(0.325 \pm 0.662) \times 10^5$
Co 1:2:3	n.f.	$(0.335 \pm 0.61) \times 10^8$
Co 1:0:2	100 (max)	321 ± 0.2
Co 1:0:3	n.f.	3420 ± 50

The values in square brackets refer to the equilibrium concentrations of particular species occurring in the organic phase.

Equilibria in the organic phase

The change of D_{exp} for *Aliquat 336-TBP* and *Aliquat 336-TOPO* systems are given in Figs. 1 and 2. Four alternatives were taken into consideration:

- 1) constant sum of concentrations A and B (part A),
- 2) system with pure A (part B),
- 3) change of concentration of A at constant concentration of B (part C), and
- 4) change of concentration of B at constant concentration of A (part D). Notice that increasing *TOPO* concentration (Fig. 2, part D) results in increasing of Co extraction in contrast to the *TBP* case (Fig. 1, part D).

The complex equilibria in the organic phase were detected and estimated quantitatively using the computer program LETAGROP [12] which looks for the best compatibility (best fit) between D_{exp} and D_{calc} , defined as the least square sum $\sum (D_{\text{exp}} - D_{\text{calc}})^2$. At the same time, the calculated total concentrations of metals and extraction reagents are compared with their real concentrations. This operation allows to find the equilibrium concentrations $[A_{(o)}]$ and $[B_{(o)}]$ together with the $k_{i,j}$ values.

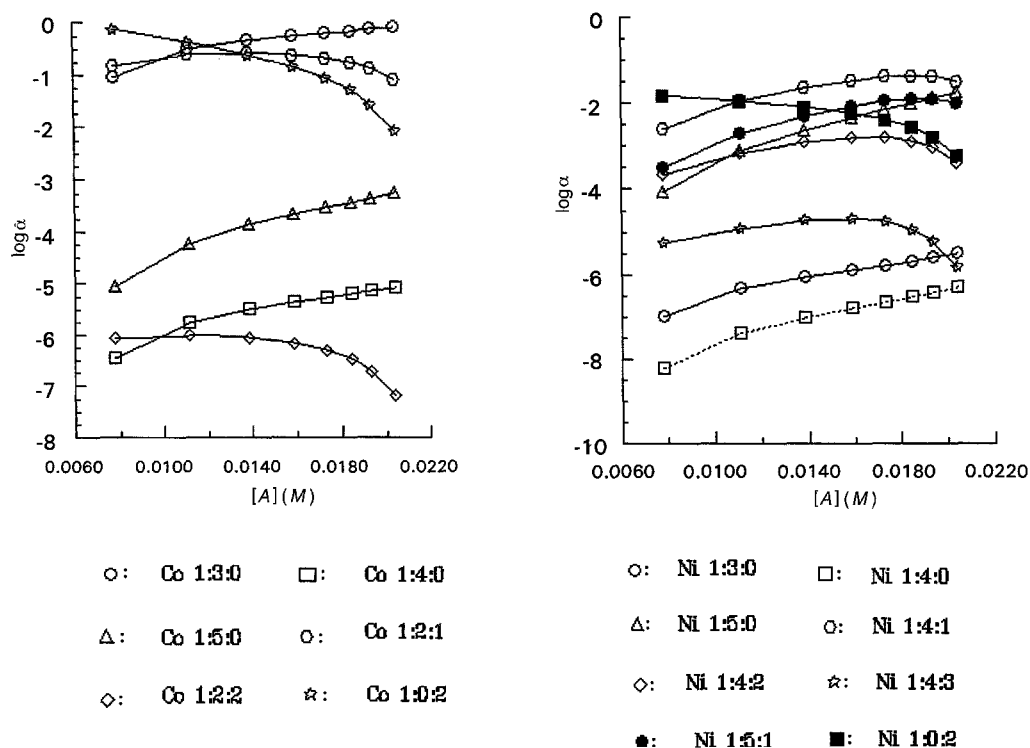


Fig. 3. Change of molar fractions of particular complex species of Co and Ni in the organic phase with rising $[A]$ in the synergistic mixture *Aliquat 336-TBP* ($(A_{(o)})_T = 0.2 - 0.9M$, $(B_{(o)})_T = 0.8 - 0.1M$)

In the first step of the computer calculation, the adduct formation constants $k_{i,j}$ were optimized. The calculations reveal that A exists in the organic phase as self-adducts of the form A_6 with a formation constant $k_{6,0}$ of 0.71×10^9 , whereas *TBP* forms dimers with a dimerization constants $k_{2,0}$ of 4.6. The following adducts of A with *TBP* were found: AB ($k_{1,1} = 27.9$) and AB_2 ($k_{1,2} = 329$). *TOPO* forms dimers with a dimerization constant $k_{2,0}$ of 290 and adducts AB_2 and AB_3 ($k_{1,2} = 20$, $k_{1,3} = 10000$).

In the second step of the computer program, the values of self-adduct and adduct formation constants $k_{i,j}$ were kept unchanged, and the values of extraction constants $K_{1,i,j}$ were optimized (Table 1). The contribution of the particular complex metal species to the overall concentration of the metal in the organic phase (Figs. 3 and 4) was estimated using Eq. (5), where $c_{1,i,j} = K_{1,i,j} [MeCl_2(aq)] \cdot [A_{(o)}]^i [B_{(o)}]^j$.

$$\alpha = c_{1,i,j} \left(\sum_{i=0}^m \sum_{j=0}^n K_{1,i,j} [MeCl_2(aq)] [A_{(o)}]^i [B_{(o)}]^j \right)^{-1} \quad (5)$$

In the organic phase, Co exists predominantly in the form of complexes: $CoCl_5A_3$, $CoCl_4A_2B$, and $CoCl_2B_2$ (marked in Fig. 3 as Co 1:3:0, Co 1:2:1, and Co

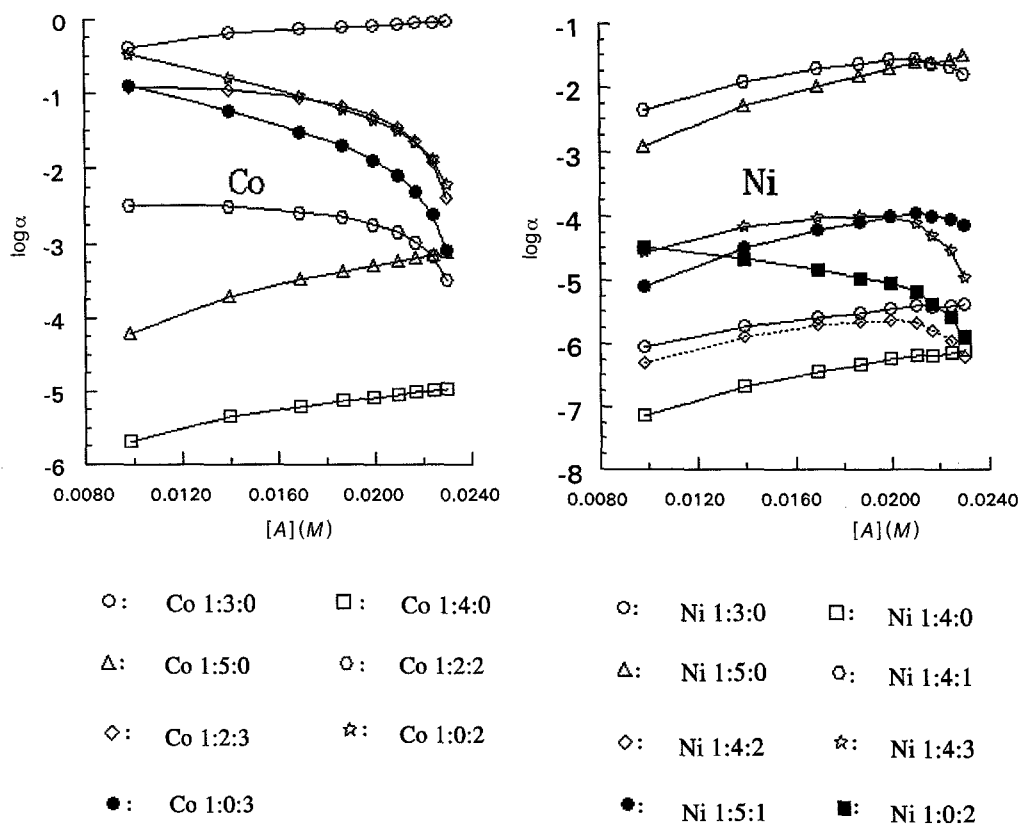


Fig. 4. Change of molar fractions of particular complex species of Co and Ni in the organic phase with rising $[A]$ in the synergistic mixture *Aliquat 336-TOPO* ($(A_{(o)})_T = 0.1 - 0.9M$, $(B_{(o)})_T = 0.9 - 0.1M$)

1:0:2). The remaining forms of Co with minor contribution to the overall concentration are $CoCl_6A_4$, $CoCl_7A_5$, and $CoCl_4A_2B_2$ (marked in Fig. 3 as Co 1:4:0, Co 1:5:0, and Co 1:2:2). Nickel exists in the organic phase in the predominant forms $NiCl_6A_4B$, $NiCl_7A_5B$, and $NiCl_2B_2$.

In the case of *Aliquat 336-TOPO* (Fig. 4), Co exists in the organic phase in the form of $CoCl_5A_3$, $CoCl_4A_2B_3$, $CoCl_2B_2$, and $CoCl_2B_3$. The predominant forms of Ni are $NiCl_6A_4B$ and $NiCl_7A_5$. In contrast to *Aliquat 336-TBP*, the system with *TOPO* therefore contains more synergistic species of Co in the organic phase and at the same time less forms of Ni.

Separation efficiency of the Co/Ni extraction

The separation factors $\beta_{Co/Ni}$ for the *Aliquat 336-TBP* system are given in Fig. 5. Increasing *TBP* concentration in *Aliquat 336-TBP* results in a decrease of $\beta_{Co/Ni}$ values (see Fig. 5, part A). The highest values of $\beta_{Co/Ni}$ (above 200) were found for pure *Aliquat 336* (Fig. 5, part B).

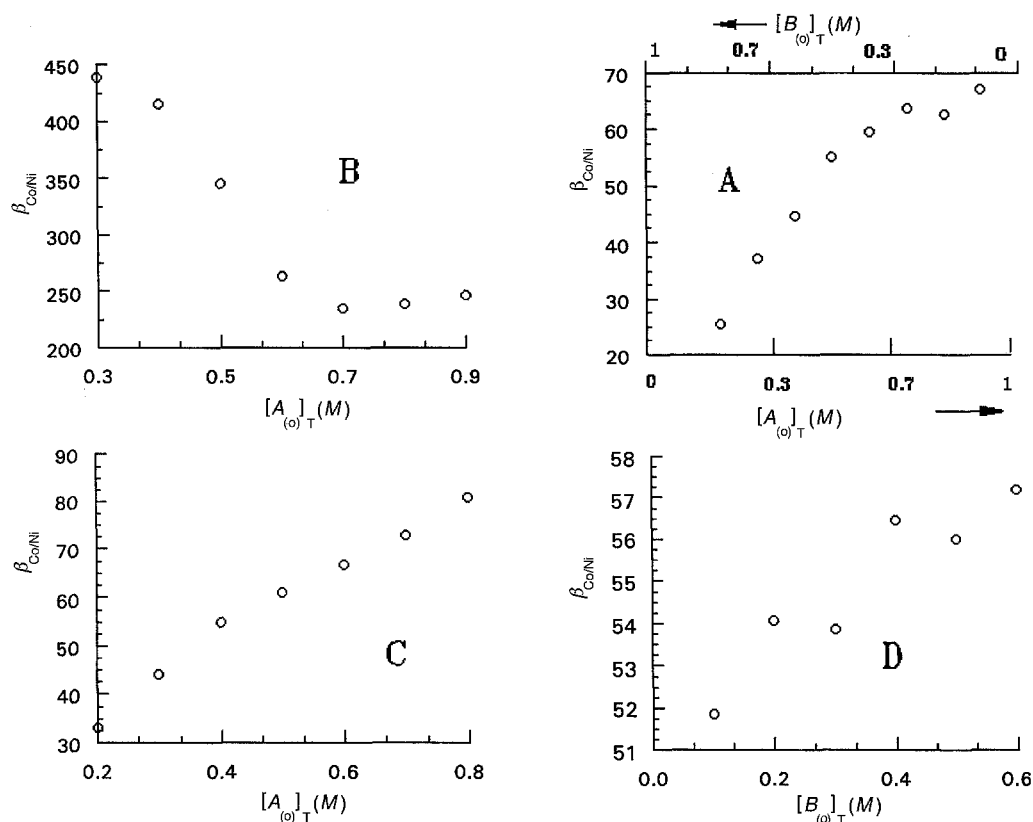


Fig. 5. Change of the separation factors $\beta_{\text{Co/Ni}}$ with rising extractant concentration in *Aliquat 336-TBP*; A: $(A_{(o)})_T = 0.2 - 0.9M$, $(B_{(o)})_T = 0.8 - 0.1M$; B: $(A_{(o)})_T = 0.1 - 0.9M$; C: $(A_{(o)})_T = 0.2 - 0.8M$, $(B_{(o)})_T = 0.2M$; D: $(A_{(o)})_T = 0.4M$, $(B_{(o)})_T = 0.1 - 0.6M$

In the case of *Aliquat 336-TOPO*, an increase of the *TOPO* concentration in *Aliquat 336-TOPO* results in an evident increase of $\beta_{\text{Co/Ni}}$ values (Fig. 6, part C). The opposite is the case when the concentration of *A* is increased (Fig. 6, parts A and B). This is easily understandable taking into account the aforementioned tendency of Co to form many synergistic complex species in *Aliquat 336-TOPO* and the relatively low values of the extraction constants of Ni complex species. The extraction system *Aliquat 336-TOPO* can therefore be strongly recommended for the separation of Co and Ni from chloride media with regard to the high values of $\beta_{\text{Co/Ni}}$ preserved for a wide range of *TOPO* concentrations.

Experimental

Chemicals

Stock solutions of Co/Ni chlorides were prepared by dissolution of the metal salts in 4 M NaCl. In all experiments described in this paper, the initial concentration of both Ni and Co in the aqueous phase was 0.1 M.

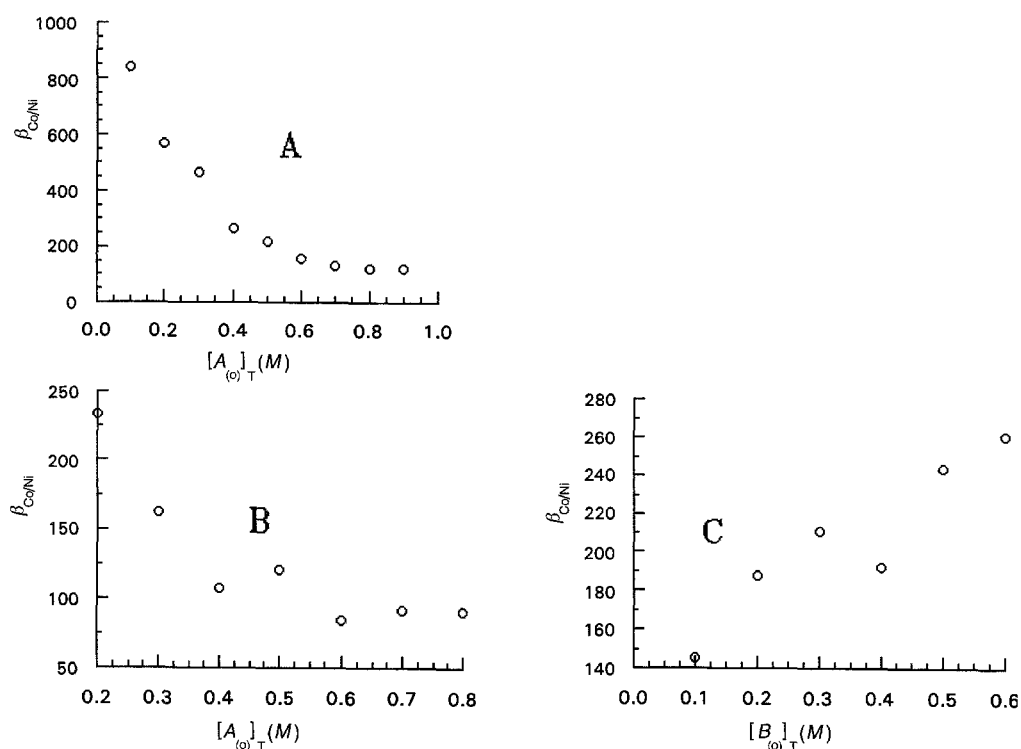


Fig. 6. Change of the separation factors $\beta_{\text{Co/Ni}}$ with rising extractant concentration in *Aliquat 336-TOPO*; A: $(A_{(o)})_T = 0.1 - 0.9M$, $(B_{(o)})_T = 0.9 - 0.1M$; B: $(A_{(o)})_T = 0.2 - 0.8M$, $(B_{(o)})_T = 0.2M$; C: $(A_{(o)})_T = 0.4M$, $(B_{(o)})_T = 0.3 - 0.8M$

Tri-*n*-octylmethylammonium chloride (Merck, 90% purity, concentration checked argentometrically) in xylene (Merck, reagent grade) with *TBP* or *TOPO* (Merck, reagent grade) as additives was used as the organic phase. The concentration of the extraction reagents ranged from 0.1 to 0.9 M.

Distribution experiments

The organic and aqueous phases were equilibrated (volume ratio = 1) for 10 min in small glass tubes with stoppers at room temperature (17°C). The phases were separated by gravity, and a sample of the aqueous phase was taken for the Co/Ni determination by atomic flame absorption spectrometry. The concentration of the elements in the organic phase was determined in the same way after reextraction of the elements from the organic phase with water (volume ratio = 1).

Nomenclature

A: tri-*n*-octylmethylammonium chloride (*Aliquat 336*); B: *TBP* or *TOPO*; *MeCl*₂: CoCl₂ or NiCl₂; *D*_{exp}: experimental distribution coefficient; *D*_{calc}: calculated distribution coefficient; $\beta_{\text{Co/Ni}}$: Co/Ni separation factor; *MeCl*₂+*iA**B*_{*j*}: complex species of Co or Ni with the ratio *Me*:*A*:*B* = 1 : *i* : *j*; *K*_{1,*i,j*}: extraction constant of *MeCl*₂+*iA**B*_{*j*}; *K*_{*i,j*}: adduct formation constant of *A*_{*i*}*B*_{*j*}; α : molar fraction of *MeCl*₂+*iA**B*_{*j*} with respect to its contribution to the total concentration of the metal in the organic phase; *c*_(o): total molar concentration of the metal in the organic phase; *c*_(aq): total molar

concentration of the metal in the aqueous phase; $C_{1,i,j}$: molar concentration of $MeCl_{2+i}A_iB_j$ in the organic phase; $(A_{(o)})T$, $(B_{(o)})T$: total concentrations of A and B in the organic phase; $[A_{(o)}]$, $[B_{(o)}]$: equilibrium concentrations of A and B in the organic phase.

References

- [1] Preston JS, du Preez AC (1988) Mintek Report No M378
- [2] Preston JS (1983) *Hydrometallurgy* **10**: 187
- [3] Szymanowski J (1990) *Ekstrakcja miedzi hydroksyoksymami*, Panstwowe Wydawnictwo Naukowe, Warszawa, p 155
- [4] Cox M (1992) In: Rydberg J, Musikas C, Choppin GR (eds) *Principles and Practices of Solvent Extraction*. Marcel Dekker, New York, p 360
- [5] Serga V (1993) *Latv Khim* **6**: 676
- [6] Sung-Sih L (1994) *Hwahak Koaghak* **32**: 300
- [7] Martinez M (1993) *Hydrometallurgy* **33**(1–2): 95
- [8] Noirot PA, Saoud M, Debreuille-Gresse MF, Wozniak M (1992) *Process Metall (Solvent Extr 1990, Pt. A)* **7A**: 195
- [9] Kachanovich IV (1994) *Zh Neorg Khim* **39**(2): 347
- [10] Mufazzel SM (1995) *J Radioanal Nucl Chem* **189**(1): 83
- [11] Majdan M, Kolarik Z (1993) *Solv Extr Ion Exch* **11**(2): 331
- [12] Liem DH (1971) *Acta Chem Scand* **25**: 1521

Received July 29, 1996. Accepted September 12, 1996