Extraction of Nickel(II) in Aqueous Thiocyanate–Perchlorate Solutions with Trioctylphosphine Oxide in Hexane and with 4-Methyl-2-pentanone

Ryokichi MURAI, Shigehisa IWAHORI, and Tatsuya SEKINE

Department of Chemistry, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162

(Received August 23, 1976)

The liquid-liquid partition of nickel(II) between hexane containing trioctylphosphine oxide or 4-methyl-2-pentanone and 1 mol dm^{-3} Na(SCN, ClO_4) solutions at 25 °C was measured. The absorption spectra of the organic and aqueous phases at equilibrium were also measured. From an analysis of these data, the extraction constant and absorption spectrum of each organic species were determined. By comparing the extraction and optical absorption of cobalt(II) complexes in the same systems with the above results for nickel(II), it was concluded that cobalt(II) thiocyanate complexes changed from octahedral to tetrahedral form upon extraction, but that nickel(II) thiocyanate complexes remained in octahedral form throughout.

It is known that cobalt(II) in thiocyanate solutions can be extracted with various oxygen-containing organic solvents. Since the extraction of cobalt(II) in these solutions is much better than that of nickel(II), this thiocyanate method has been recommended for the separation of trace amounts of cobalt(II) from large amounts of nickel(II).[1]

On the other hand, nickel(II) was found to form slightly more stable thiocyanate complexes in aqueous solutions than cobalt(II),[2] and the great difference in the extractability of these metal thiocyanates cannot be attributed to differences in the stabilities of the complexes in aqueous phase.

In order to learn further details of the thiocyanate extraction of these metal ions, solvent extraction and optical absorption measurements were made in aqueous phase for 1 mol dm^{-3} Na(SCN, ClO_4) and in organic phase for hexane containing trioctylphosphine oxide (TOPO) or for 4-metyl-2-pentanone at 25°C.

Experimental

All the reagents were of analytical grade. The TOPO was supplied by Dojindo & Co., Kumamoto. The sodium perchlorate was recrystallized three times from water.

All the distribution experiments and spectrophotometric measurements were performed in a thermostatically-controlled room at 25±0.3 °C. A portion of an aqueous 1 mol dm^{-3} Na(SCN, ClO_4) solution containing 10^{-5} to 10^{-2} mol dm^{-3} of nickel(II) or 10^{-4} to 10^{-2} mol dm^{-3} of cobalt(II) and the same volume of hexane containing TOPO or of 4-methyl-2-pentanone were placed in a stoppered glass tube and the tube was settled on a rotating frame (20 rpm). Since it was found that agitation for 2 h and for 24 h was sufficient to attain equilibrium distributions of cobalt(II) and nickel(II), respectively, agitation for the respective extractions were continued for these periods. The metal content in the organic phase was determined after back extraction into 0.1 mol dm^{-3} perchloric acid, while that in the aqueous phase was determined directly, in both cases, by the atomic absorption method. The optical absorption of the solutions was measured with a spectrophotometer (Hitachi type 139) using glass cells of 10-mm light paths.

Statistical

Throughout this paper, the subscript "org" denotes that in the organic phase while the lack of any subscript denotes that in the aqueous phase. The notation L^- represents the thiocyanate ion.

Since only the M^{2+}, ML^+, and ML_2 species are assumed to be present in the aqueous phase when extraction of higher complexes into the organic phase was possible, the following equation may be written for the distribution ratio:

$$D = ([M(ClO_4)_2]_{org} + [ML(ClO_4)]_{org} + [ML_2]_{org} + [ML_3Na]_{org} + [ML_4Na_2]_{org})([M^{2+}] + [ML^+] + [ML_2])^{-1},$$
$$= (\sum K_{ex,a}[L^-]^a[ClO_4^-]^b)(1+\beta_1[L^-]+\beta_2[L^-]^2)^{-1}, \quad (1)$$

where

$$\beta_n = [ML_n^{2-n}][M^{2+}]^{-1}[L^-]^{-n}, \quad (2)$$

$$K_{ex,a} = [ML_a(ClO_4)_bNa_c]_{org}[M^{2+}]^{-1}[L^-]^{-a}[ClO_4^-]^{-b}. \quad (3)$$

The sodium ion concentration was unity and thus the corresponding term was dropped. Here, $a+b-c=2$. Sodium ions were found in the extracted species only for $a>2$. Perchlorate ions were found only for $a<2$ and in such cases $a+b=2$.

The extraction data can be analyzed in a similar manner to that described in Ref. 3.

The optical absorption of the organic phase at a given wavelength can be written as;

$$E = \sum \varepsilon_a[ML_a(ClO_4)_bNa_c]_{org},$$
$$= \sum \varepsilon_a K_{ex,a}[M^{2+}][L^-]^a[ClO_4^-]^b, \quad (4)$$

where $0 \leq a \leq 4$. The total metal concentration in each phase was obtained by chemical analysis. The concentration of each species in each phase was calculated by Eq. 1 using these total metal concentrations and the stability and extraction constants which had been obtained from the distribution experiments. The molar extinction coefficient of the $M(ClO_4)_2$ species was obtained from an organic phase which was in contact with an aqueous solution containing no thiocyanate and those of the other metal species containing thiocyanate ions were obtained by analysis of the absorption curves of the organic phases which were in contact with aqueous thiocyanate solutions at various concentrations.

Results

Figure 1 gives the extraction curve of nickel(II) with 4-methyl-2-pentanone as a function of the thiocyanate concentration and also the curve for cobalt(II) extraction from a previous study.[4] As is seen in Fig. 1, the shape of the two curves is quite different

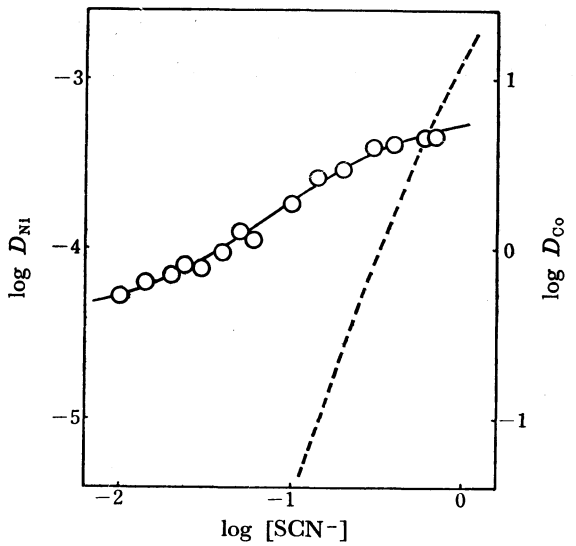

Fig. 1. Exrtaction curve of nickel(II) with 4-methyl-2-pentanone. The solid line was calculated by introducing the values in Table 1(a) and 1(b) into Eq. 1. The dotted curve is that of cobalt(II) in Ref. 4. The left ordinate is for the nickel(II) curve and the right ordinate is for the cobalt(II) curve.

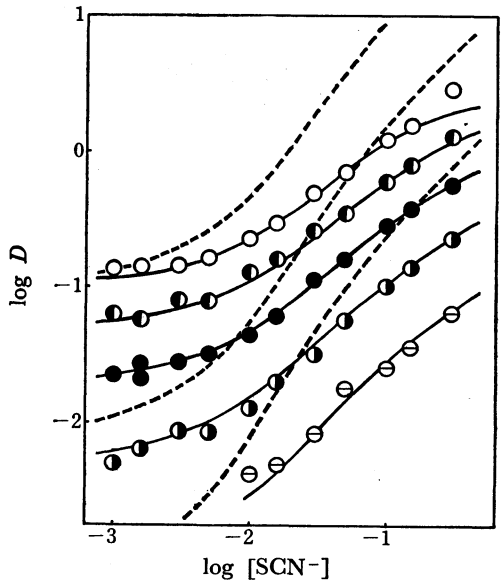

Fig. 2. Extraction curves of nickel(II) into hexane with 0.06 (○), 0.05 (◐), 0.04 (●), 0.03 (◑), and 0.02 (⊖) mol dm^{-3} of TOPO. The solid curves were calculated by introducing the values in Table 1(a) and 1(c) into Eq. 1. The dotted lines from the top to the bottom are curves of cobalt(II) into hexane with 0.04, 0.02, and 0.01 mol dm^{-3} of TOPO in Ref. 4.

and the extraction of nickel(II) is much poorer than that of cobalt(II). Figure 2 shows the extraction curves of nickel(II) with TOPO at various concentrations in hexane as a function of the thiocyanate concentration and also shows the curves for cobalt(II) from a previous study.[4] The shapes of the nickel(II) curves in this figure are similar to those of the curves of cobalt(II). However, the D values for nickel(II) are lower than those for cobalt(II), especially, in the higher thiocyanate concentration region. From an analysis of these distribution data, the extraction constants were obtained, as given in Table 1.

Table 1. Summary of equilibrium constants[a]

(a) Stability constants of aqueous thiocyanate complexes.

	$\log \beta_1$	$\log \beta_2$
Co(II)	1.00	1.32
Ni(II)	1.1	1.6

(b) Extraction constants with 4-methyl-2-pentanone.

	$\log K_{ex0}$	$\log K_{ex1}$	$\log K_{ex2}$	$\log K_{ex3}$	$\log K_{ex4}$
Co(II)	—	—	—	—	2.96
Ni(II)	−4.45	−2.66	−1.54	—	—

(c) Extraction constants with TOPO.

	$[TOPO]_{org}$	$\log K_{ex0}$	$\log K_{ex1}$	$\log K_{ex2}$	$\log K_{ex3}$
Co(II)	0.005	—	−1.00	1.10	0.49
	0.01	—	−0.43	1.80	1.48
	0.02	−2.06	−0.34	2.58	2.48
	0.04	−0.94	1.37	3.32	3.34
	0.08	0.00	2.18	4.00	—
Ni(II)	0.02	−2.62	0.63	0.66	—
	0.03	−2.36	1.10	1.24	—
	0.04	−1.72	1.30	1.64	—
	0.05	−1.18	1.43	1.90	—
	0.06	−0.84	1.58	2.20	—

a) The values in (a) were taken from Refs. 2 and 4, and the values for cobalt(II) in (b) and (c) from Ref. 4.

Table 2. Estimated solvation number of metal species for TOPO extracted into the hexane phase

	$M(ClO_4)_2$	$M(SCN)(ClO_4)$	$M(SCN)_2$	$M(SCN)_3Na$
Co(II)[a]	3	3	*ca.* 2	3
Ni(II)	4	4	3	not extracted

a) Taken from Ref. 4.

The extraction constant with TOPO for each metal species, $K_{ex,a}$, is dependent of the TOPO concentration. From the treatment described in Ref. 3, the solvation number of each species was obtained from the TOPO dependence of the constant, as listed in Table 2.

Figures 3a and 4a show the absorption curves for the organic phase obtained under the conditions described in the captions. Figures 3b and 4b show the absorbance per mole of complex for each extracted species calculated from the data in Figs. 3a and 4a using the procedures described in the statistical section. The absorption curve of cobalt(II) extracted into 4-methyl-2-pentanone has already been reported in Ref. 4(Fig. 7). This curve should be the absorption curve for the $Co(SCN)_4^{2-}$ species in 4-methyl-2-pentanone. The absorption of nickel(II) extracted into this solvent was too weak to be determined because of the low metal concentration due to poor extraction.

The absorption curves of the aqueous phases containing cobalt(II) or nickel(II) in 1 mol dm^{-3} Na(L, ClO_4) solutions were similar to those reported previously, for example (Ref. 6), the cobalt(II) solutions had an absorption peak at 510—520 nm, while the nickel(II) solutions had two peaks at 390—400 and 640—650 nm.

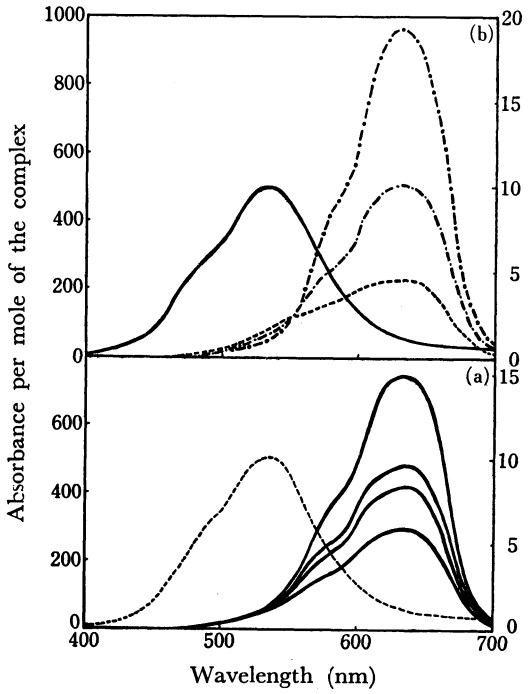

Fig. 3(a). Absorption curve of cobalt(II) extracted into hexane containing 0.04 mol dm^{-3} of TOPO from 1 mol dm^{-3} Na(SCN, ClO_4) aqueous solutions when [SCN^-] was 1, 0.1, 0.03, and 0.01 mol dm^{-3} from the top to the bottom (the absorbance per mole of the complex on the left ordinate). The dotted line is the curve when [SCN^-] was zero (the absorbance per mole of the complex on the right ordinate). Fig. 3(b). Absorption curve of $Co(ClO_4)_2$ ——, $Co(SCN)(ClO_4)$ ----, $Co(SCN)_2$ —·—·—, and $Co(SCN)_3^-$ —•—•— species combined with TOPO molecules in hexane obtained by analysis of the data in Fig. 3(a).

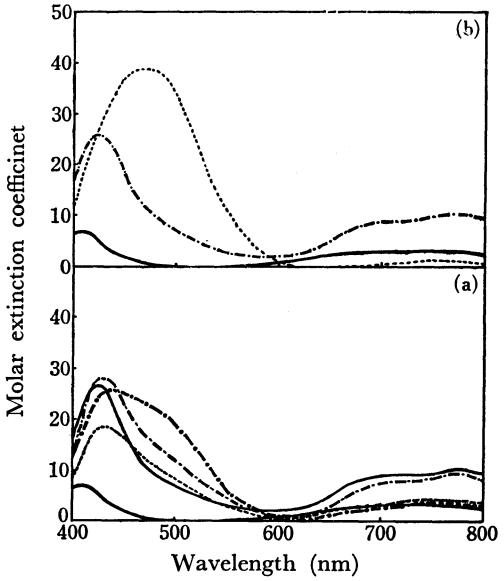

Fig. 4(a). Absorption curve of nickel(II) extracted into hexane containing 0.06 mol dm^{-3} of TOPO from 1 mol dm^{-3} Na(SCN, ClO_4) aqueous solutions when [SCN^-] was 1 ——, 0.3 —·—·—, 0.1 ------, 0.03 —•—•—, and zero —— mol dm^{-3}. Fig. 4(b). Absorption curve of $Ni(ClO_4)_2$ ——, $Ni(SCN)(ClO_4)$ ----, and $Ni(SCN)_2$ —·—·— species combined with TOPO molecules in hexane obtained by analysis of the data in Fig. 4(a).

Discussion

It is known that cobalt(II) in aqueous solutions forms six-coordinated octahedral complexes which color the solution pink and four-coordinated tetrahedral ones which color the solution deep blue, while nickel(II) usually forms six-coordinated octahedral complexes in aqueous solutions except in some cases, such as those having chelating ligands (for example, see Ref. 6). The absorption for the aqueous phase in the present study ([L^-]<1 mol dm^{-3}), as described above, shows that both cobalt(II) and nickel(II) are present in six-coordinated octahedral form in the aqueous phase.

The absorption of the $Co(ClO_4)_2(TOPO)_3$ species in hexane, shown in Fig. 3, indicates that this cobalt(II) should also be in this form. However, it is notable that all the $CoL(ClO_4)(TOPO)_3$, $CoL_2(TOPO)_2$, $NaCoL_3(TOPO)_3$ species absorbed much more strongly and at higher wavelengths than the $Co(ClO_4)_2(TOPO)_3$ species and that all absorptions of these three thiocyanate species can usually assigned to a four-coordinated tetrahedral complex.[6] The absorption curve of the CoL_4^{2-} complex extracted into 4-methyl-2-pentanone together with two sodium ions in a previous study[4] also suggests the extraction of a four-coordinated tetrahedral species for this system.

The absorption curve of the organic phase which had extracted the $Ni(ClO_4)_2(TOPO)_4$, $NiL(ClO_4)(TOPO)_4$, and $NiL_2(TOPO)_3$ species are similar to that of the aqueous phase and thus these species in the organic phase should be of six-coordinated octahedral form.

The atom through which a thiocyanate ion coordinates with the metal ion has been discussed previously.[7] It is not possible to further discuss the position of the extractant in the coordination sphere or the details of the structure of the extracted species only on the basis of the present data. However, the extraction constants in Table 1 show that the extractabilities of the both perchlorates are similar, while the extractabilities of the other cobalt(II) thiocyanate complexes, which are assumed to be tetrahedral, are much higher than those of the other nickel(II) complexes, which are assumed to be octahedral.

An explanation for the higher extraction of the cobalt(II) tetrahedral species over that of the corresponding nickel(II) octahedral species may be that the latter accept water molecules more readily than the former and this stronger hydration hinders the extraction of the nickel(II) octahedral species more than that of the cobalt(II) tetrahedral species. However, much information appears to be necessary in order to explain this complicated phenomenon in more detail.

There have been some recent reports on the absorption spectra of cobalt(II) and nickel(II) perchlorates and thiocyanates in aqueous and nonaqueous solutions[8-10] and these as well as several previous reports[6,7] appear to support the conclusions of the present study.

Poor extraction of nickel(II) from thiocyanate solutions with various oxygen-containing solvents has been reported.[11–15] However, not much is known of the details of the nickel(II) distribution equilibria in these systems.

References

1) E. B. Sandell, "Colorimetric Determination of Traces of Metals," 3rd ed, Interscience, New York, (1959) p. 411.
2) R. Murai, K. Kurakane, and T. Sekine, *Bull. Chem. Soc. Jpn.*, **49**, 335 (1976).
3) H. Moriya and T. Sekine, *Bull. Chem. Soc. Jpn.*, **45**, 1626 (1972).
4) T. Sekine, R. Murai, and M. Iguchi, *Nippon Kagaku Zasshi*, **92**, 412 (1971).
5) T. Sekine and T. Ishii, *Bull. Chem. Soc. Jpn.*, **43**, 2422 (1970).
6) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, John Wiley & Sons, Inc., New York (1972), Chap. 29
7) C. K. Jorgensen, "Inorganic Complexes," Academic Press, London (1963), p. 78.
8) O. Benali-Baitich and E. J. L. Wendling, *J. Inorg. Nucl. Chem.*, **37**, 1217 (1975).
9) Zs. Szabo-Akos, V. Izvekov, and E. Pungor, *Mikrochim. Acta.*, **20**, 187 (1974).
10) A. Miezis, *Acta Chem. Scand.*, **A28**, 407 (1974).
11) R. Rigamonti and E. Spaccamela-Marchetti, *Ann. Chim. (Rome)*, **49**, 106 (1959).
12) E. Spaccamela-Marchetti and M. T. C. Mazza, *Chem. Ind. (Milano)*, **43**, 133 (1961); *Chem. Abstr.*, **55**, 16100 (1961).
13) E. Jackwerth, *Z. Anal. Chem.*, **206**, 335 (1964).
14) A. K. De and A. K. Sen, *Separ. Sci.*, **1**, 641 (1966).
15) S. Tribalat and J. M. Caodero, *C. R. Acad. Sci.*, **258**, 2828 (1964).