enough room around itself to accommodate all or part of a seventh molecule at the transition state, contrary to the more compact Zn^{2+} ion. We can say accordingly that the isoelectronic octahedral divalent and trivalent cations of the second row, being larger than their first-row analogues, will probably all react with much more associative character than their first-row counterparts.

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Registry No. $Cd(H_2O)_6^{2+}$, 14752-06-8; $Zn(H_2O)_6^{2+}$, 15906-01-1; $Cd(H_2O)_4bpy^{2+}$, 61917-96-2; $Zn(H_2O)_4bpy^{2+}$, 61918-16-9; bpy, 366-18-7.

Supplementary Material Available: Equilibrium measurements (Tables SI, SII, and SVII–SIX) and observed first-order rate constants (Tables SIII–SVI, SX, and SXI) (11 pages). Ordering information is given on any current masthead page.

Contribution from the Coordination Chemistry Laboratories, Institute for Molecular Science, Myodaiji, Okazaki 444, Japan, and Department of Chemistry, Niigata University, 8050 Igarashi, Niigata 950-21, Japan

Calorimetric Study of Thiocyanato Complexes of the Cobalt(II) Ion in Micellar Solutions of a Nonionic Surfactant

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Complex formation equilibria between cobalt(II) and thiocyanate ions have been studied calorimetrically in an aqueous solution and in micellar solutions of the nonionic surfactant Triton X-100 containing $MClO_4$ (M = Li, Na, NH_4) as ionic media at 25 °C. Calorimetric data were well explained in terms of the formation of $[Co(NCS)]^+$ and $[Co(NCS)_2]$ and of $[Co(NCS)]^+$, $[Co(NCS)_2]$, and $[Co(NCS)_4]^{2-}$ in water and in micellar solutions, respectively. The formation of $[Co(NCS)_3]^-$ was found to be practically negligible in any of the solutions examined. The formation constant and enthalpy of formation of $[Co(NCS)_4]^{2-}$ change with the concentration of the surfactant and with the ionic media in the micellar solutions, while those of $[Co(NCS)]^+$ remain practically constant. It is suggested that the $[Co(NCS)]^+$ complex is formed only in the aqueous phase, while $[Co(NCS)_4]^{2-}$ is formed mainly in micelles as ion pairs.

Introduction

One of the present authors[1-5] studied liquid–liquid extraction of metal ions with poly(ethylene glycol) and poly(oxyethylene)-type nonionic surfactants as extractants. In aqueous solution of a nonionic surfactant, neutral micelles are formed above the critical micelle concentration (cmc) of the surfactant; the polar hydrophilic groups, such as those of poly(oxyethylene), are directed toward the aqueous bulk phase and the hydrophobic hydrocarbon chains are directed away from the aqueous phase to make up the central cores of micelles. It has been elucidated from the liquid–liquid extraction experiments[1-5] that metal ions such as Co(II), Zn(II), Mo(II), and U(VI) are highly extractable from their thiocyanate micellar solutions by inert polar solvents such as 1,2-dichloroethane and nitrobenzene and that Cd(II), Hg(II), and Pb(II) ions are extractable from their iodide solutions, while Mn(II) and Ni(II) ions as well as alkali-metal and alkaline-earth-metal ions are hardly extracted from either thiocyanate or iodide solution. In the cobalt(II) thiocyanate system with the nonionic surfactant Triton X-100 ($C_8H_{15}C_6H_4(C_2H_4O)_nH$ (n = 10)), it was suggested that the metal ion is extracted by an organic solvent in the form of $M_2[Co(NCS)_4]\cdot 2$(Triton X-100) (M^+ = alkali-metal ions or NH_4^+). The same conclusion was drawn for the zinc(II) thiocyanate system. The distribution ratios D of the Zn(II) ion with various MSCN micellar solutions increased in the order LiNCS < NaNCS < NH_4NCS < KNCS (the respective log D values are –0.5, 1.0, 1.7, and 2.3 in micellar solutions of 0.1% w/v Triton X-100 for example), i.e. in the order of decreasing hydration energies of the monovalent cations. Although the complex formation equilibria between cobalt(II) and thiocyanate ions in micellar solutions have not been investigated, cobalt(II) thiocyanate micellar solutions of Triton X-100 show absorption spectra originating from the tetrahedral $[Co(NCS)_4]^{2-}$ complex. It is thus supposed that the $[Co(NCS)_4]^{2-}$ complex is present in the form of the $M_2[Co(NCS)_4]$ ion pairs in micelles of Triton X-100 that have a polar surface zone of poly(oxyethylene) groups with an effective dielectric constant of $\epsilon \simeq 30$.[6]

In order to throw more light on the mechanism of extraction of metal(II) ions with nonionic surfactants, we have investigated complex formation equilibria between cobalt(II) and thiocyanate ions in micellar solutions of the nonionic surfactant Triton X-100. Although such a surfactant solution, on the macroscopic scale, is homogeneous as an aqueous–organic mixed solvent, it might microscopically be a pseudo-two-phase system consisting of micellar and aqueous bulk phases, as will be discussed later. A calorimetric titration procedure that has been used for studying complex formation equilibria of metal ions in various nonaqueous solvents was employed in this work.[7]

Experimental Section

Calorimetric measurements were carried out in a room thermostated at 25 ± 0.5 °C. Test solutions were prepared by dissolving cobalt(II) perchlorate hexahydrate crystals in an aqueous Triton X-100 solution of a given concentration over the range 1–10% w/w. As the cmc of Triton X-100 is about 2.5×10^{-4} mol dm^{-3}, the surfactant molecules were present mostly as micelles in the solutions. The ionic strength of the test solutions was kept at 0.5 mol dm^{-3} throughout the measurements by using $MClO_4$ (M = Li, Na, NH_4). A cobalt(II) perchlorate solution (50 cm^3) was placed in a stainless steel vessel, the inside wall of which was coated with Teflon, and the vessel was inserted into an aluminum block thermostated at 25 ± 0.0001 °C in an air bath. The concentration of cobalt(II) perchlorate in the initial solutions was varied over the range 5–40 mmol dm^{-3}. This solution was titrated with a 0.5 mol dm^{-3} MNCS (M = NH_4, Na, Li) solution by using an autoburet (APB-118, Kyoto Electronics). Heats observed at each titration point were about 1 J with a certainty of ±0.02 J. The heat of reaction thus determined was corrected for heats of dilution of the titrant, which had been determined by separate experiments and found to be very small. Micellar solutions remained

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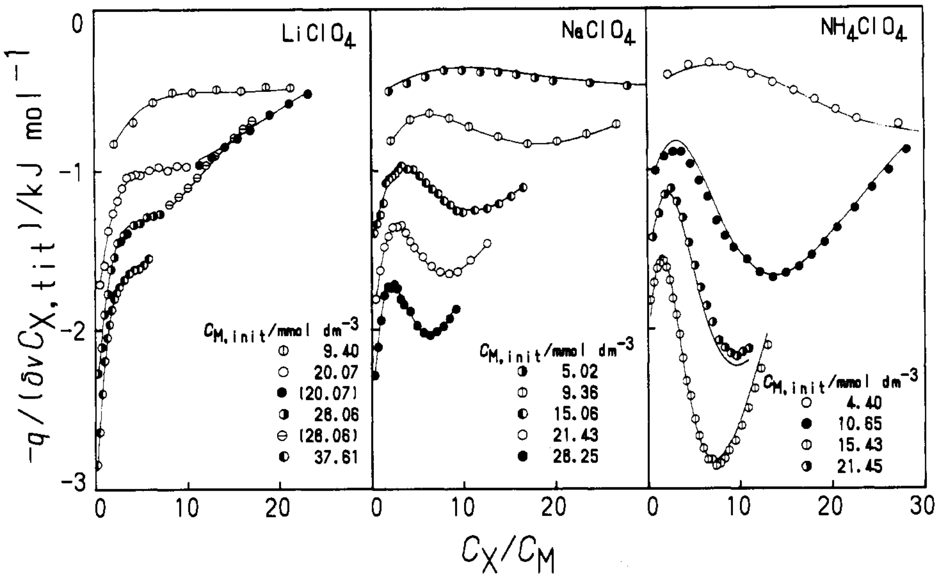

Figure 1. Calorimetric titration curves in micellar solutions of 10% w/w Triton X-100 containing $Co(ClO_4)_2$ and MNCS (M = Li, Na, NH_4) at 25 °C. Concentrations of cobalt(II) ions, $C_{M,init}$/mmol dm^{-3}, in the initial solutions are given. Solid lines show the curves calculated by using the constants in Table I.

apparently homogeneous in the course of titrations under the experimental conditions.[8] All the measurements were carried out by using a fully automatic on-line system for titration calorimetry developed at the Institute for Molecular Science.[9]

Analysis of Heat Data. In order to explain the calorimetric titration curves obtained, we assumed the formation of mononuclear $[Co(NCS)_n]^{(2-n)+}$ complexes with various n's according to eq 1. A heat of

$$Co^{2+} + nNCS^- = [Co(NCS)_n]^{(2-n)+} \tag{1}$$

$$\beta_n = [Co(NCS)_n{}^{(2-n)+}]/[Co^{2+}][NCS^-]^n \tag{2}$$

reaction q_i observed at the ith titration point is then expressed as follows by using the overall formation constants β_n in eq 2 and the corresponding overall enthalpies of formation $\Delta H°_{\beta n}$ of the $[Co(NCS)_n]^{(2-n)+}$ complexes:

$$q_i = -(V_i\sum\beta_n(\Delta H°_{\beta n})m_i x_i^n - V_{i-1}\sum\beta_n(\Delta H°_{\beta n})m_{i-1}x_{i-1}^n) \tag{3}$$

where V denotes the volume of the test solution and m and x stand for the concentrations of free Co^{2+} and SCN^- ions, respectively. The total concentrations of the metal and ligand ions in solution, C_M and C_X, respectively, are represented on the basis of the mass-balance equations as follows:

$$C_{M,i} = m_i + \sum\beta_n m_i x_i^n \tag{4}$$

$$C_{X,i} = x_i + \sum n\beta_n m_i x_i^n \tag{5}$$

Formation constants and enthalpies were simultaneously determined by minimizing the error-square sum, $U = \sum(q_{i,obsd} - q_{i,calcd})^2$, by using the least-squares program developed in our laboratory.

Cobalt(II) perchlorate hexahydrate, LiNCS, NaNCS, and NH_4NCS of reagent grade were dried in vacuo and used without further purification. Triton X-100 was used as purchased.

Results

Calorimetric data obtained in micellar solutions of 10% w/w Triton X-100 containing LiNCS, NaNCS, or NH_4NCS are depicted in Figure 1. As the heat of reaction q at each titration point depends on the volume of an aliquot of the titrant added δv and the concentration of ligand ions in the titrant $C_{X,tit}$, the $-q/(\delta v C_{X,tit})$ value is plotted against the ratio of the total concentrations of the ligand to the metal ion in solution C_X/C_M. The calorimetric data were explained in terms of the formation of $[Co(NCS)_n]^{(2-n)+}$ with various n's in solution. In the course of the analysis of the data obtained in the LiNCS solution, among various sets of the complexes examined, the set (1,2,4) assuming the formation of $[Co(NCS)]^+$, $[Co(NCS)_2]$, and $[Co(NCS)_4]^{2-}$ gave the minimum value of the Hamilton R factor (0.01455). The set (1,4) eliminating $[Co(NCS)_2]$ from the set (1,2,4) also gave a relatively small value of the R factor (0.0184). Further, the data obtained in the NaNCS solution were well explained in terms of either set (1,2,4) or (1,4), while the data obtained in the NH_4NCS solution were explained in terms of the sole set (1,4). It is noted that the formation of $[Co(NCS)_3]^-$ is practically negligible in the micellar solutions. Considering the fact that the $[Co(NCS)_2]$ complex is appreciably formed in water and also in micellar solutions of lower concentrations of the surfactant, as described in a later section, we take into account the formation of this complex, although its formation is suppressed in the solutions of 10% w/w Triton X-100 owing to the extensive formation of $[Co(NCS)_4]^{2-}$. The formation of $[Co(NCS)_4]^{2-}$ is especially favorable in the NH_4NCS micellar solution, while the formation of $[Co(NCS)_2]$ is hardly confirmed in this solution. The final results of the thermodynamic quantities obtained in solutions of 10% w/w Triton X-100 are summarized in Table I. The titration curves calculated by using the constants in Table I in each solution are shown by the solid lines in Figure 1, which well reproduce the experimental points.

Table I. Overall Formation Constants, log (β_n/mol^{-n} dm^{3n}), Enthalpies, $\Delta H°_{\beta n}$/kJ mol^{-1}, and Entropies, $\Delta S°_{\beta n}$/J K^{-1} mol^{-1}, of $[Co(NCS)_n]^{(2-n)+}$ in Micellar Solutions of 10% w/w Triton X-100 Containing MSCN (M = Li, Na, NH_4) at 25 °C[a]

	LiNCS (1,2,4)	NaNCS (1,2,4)	NH_4NCS (1,4)
log β_1	1.00 (0.15)	0.97 (0.11)	0.88 (0.16)
log β_2	1.07 (0.64)	1.17 (0.33)	
log β_4	3.12 (0.11)	3.41 (0.05)	3.72 (0.11)
$\Delta H°_{\beta 1}$	−11.0 (2.8)	−11.6 (2.4)	−14.6 (4.4)
$\Delta H°_{\beta 2}$	−31 (38)	−24 (18)	
$\Delta H°_{\beta 4}$	−32.6 (2.1)	−41.6 (1.6)	−49.8 (0.9)
$\Delta S°_{\beta 1}$	−18	−20	−32
$\Delta S°_{\beta 2}$	−84	−58	
$\Delta S°_{\beta 4}$	−50	−74	−96
U^b	0.0162	0.0064	0.0924
R^c	0.0145	0.0082	0.0329
N^d	73	86	96

[a] Values in parentheses refer to three standard deviations. [b] Error-square sum. [c] The Hamilton R factor. [d] The number of data points.

Calorimetric data obtained in water and in the micellar solutions of Triton X-100 of varying concentrations are shown in Figure

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(8) Phase separation takes place in cobalt(II) thiocyanate solutions of lower concentration ratio of the surfactant Triton X-100 to cobalt(II) ion, especially in the presence of K^+ ions.

(9) The procedure for analyzing temperature-change data in this system is essentially the same as that described in ref 7. Procedures for automatic titration, temperature control, and data acquisition have been very much improved to determine small heats of reaction with high accuracy in this calorimetry system.

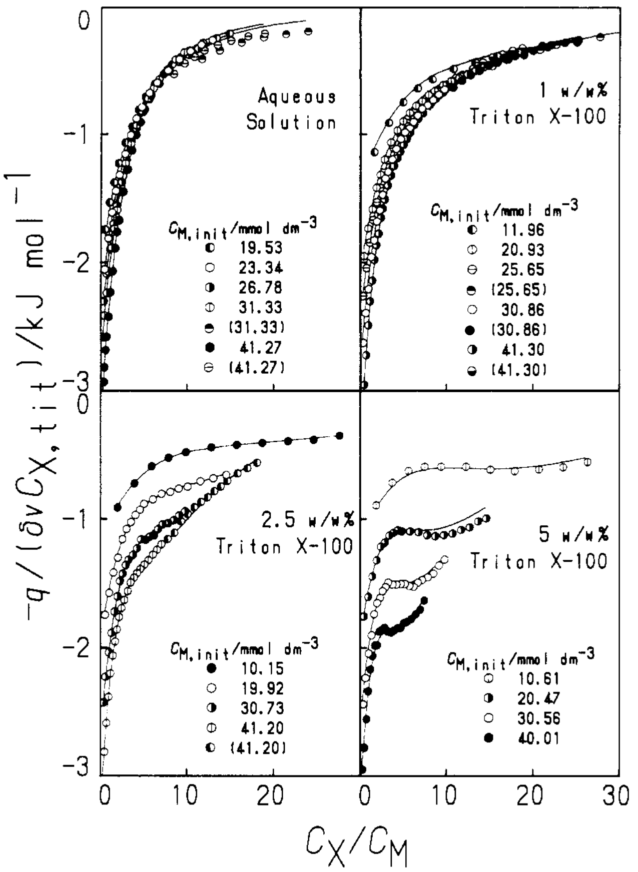

Figure 2. Calorimetric titration curves in micellar solutions of Triton X-100 of varying concentrations containing $Co(ClO_4)_2$ and NaNCS at 25 °C. Concentrations of cobalt(II) ions, $C_{M,init}$/mmol dm^{-3}, in the initial solutions are given. Solid lines show the curves calculated by using the constants in Table II.

Table II. Overall Formation Constants, log (β_n/mol^{-n} dm^{3n}), Enthalpies, $\Delta H°_{\beta n}$/kJ mol^{-1}, and Entropies, $\Delta S°_{\beta n}$/J K^{-1} mol^{-1}, of $[Co(NCS)_n]^{(2-n)+}$ in Micellar Solutions of Triton X-100 of Various Concentrations Containing $NaClO_4$ as an Ionic Medium at 25 °C[a]

	Triton X-100 content/(% w/w)			
	0.0	1.0	2.5	5.0
log β_1	1.20 (0.21)	1.04 (0.15)	1.04 (0.10)	1.0[e]
log β_2	1.57 (0.33)	1.63 (0.32)	1.50 (0.26)	1.2 (1.2)
log β_4		2.82 (0.26)	2.89 (0.12)	3.11 (0.27)
$\Delta H°_{\beta 1}$	-8.10 (2.7)	-10.7 (2.7)	-10.3 (1.8)	-10.8 (0.6)
$\Delta H°_{\beta 2}$	-22.5 (1.8)	-16 (7)	-18 (7)	-26 (56)
$\Delta H°_{\beta 4}$		-28.3 (1.8)	-36.8 (1.8)	-37.1 (0.6)
$\Delta S°_{\beta 1}$	-4	-16	-15	-17
$\Delta S°_{\beta 2}$	-45	-22	-32	-64
$\Delta S°_{\beta 4}$		-41	-68	-65
U[b]	0.0606	0.0544	0.0137	0.268
R[c]	0.0320	0.0266	0.0138	0.0450
N[d]	102	128	85	102

[a] Values in parentheses refer to three standard deviations. [b] Error-square sum. [c] The Hamilton R factor. [d] The number of data points. [e] The log β_1 value is fixed to be 1.0.

2. The calorimetric data obtained are satisfactorily explained in terms of the formation of $[Co(NCS)]^+$ and $[Co(NCS)_2]$ and of $[Co(NCS)]^+$, $[Co(NCS)_2]$, and $[Co(NCS)_4]^{2-}$ in water and in the micellar solutions, respectively, over the C_X/C_M range examined. The final results of the formation constants and enthalpies are listed in Table II. As seen in Figure 2, the solid curves calculated by using the constants in Table II well reproduce the experimental points in each solution. The distribution of the $[Co(NCS)_n]^{(2-n)+}$ complexes is depicted in Figure 3.

Discussion

Thermodynamic Quantities in Water. The formation constant of $[Co(NCS)]^+$ in water containing various ionic media has so far been determined by various methods.[10] The log K_1 values have been reported to be 1.00[11] and 0.95[12] in the 1 mol dm^{-3} $NaClO_4$ solution and 1.27[13] in the 3 mol dm^{-3} $LiClO_4$ solution. The value of 1.20 ± 0.2 (the uncertainty is 3σ) in the 0.5 mol dm^{-3} $NaClO_4$ solution in this study is in good agreement with the values previously obtained. The stepwise formation constant log K_2 of formation of $[Co(NCS)_2]$ is 0.37. We note that the $[Co(NCS)_3]^-$ and $[Co(NCS)_4]^{2-}$ complexes were not found in water.

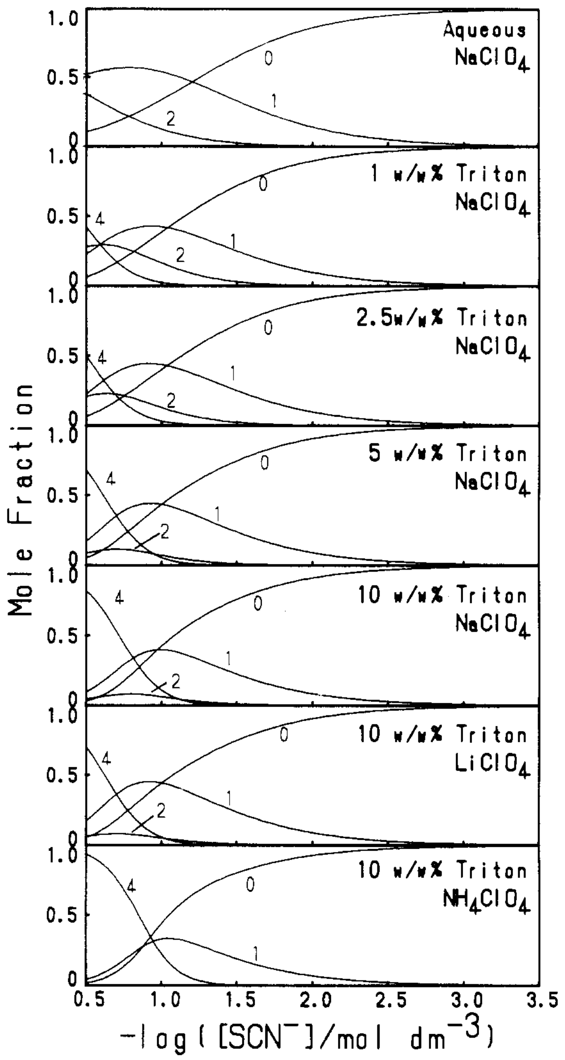

Figure 3. Distribution of the thiocyanate complexes of cobalt(II) in various micellar solutions of Triton X-100 at 25 °C. The number represents n within the $[Co(NCS)_n]^{(2-n)+}$ complex.

Ionic Medium Effect. As seen in Table I, the log β_1 and $\Delta H°_{\beta 1}$ values of $[Co(NCS)]^+$ in micellar solutions of 10% w/w Triton X-100 containing various ionic media are similar to those in the surfactant-free aqueous solution. The result suggests that the $[Co(NCS)]^+$ complex is mainly formed in the aqueous plase. The log β_1 values of the complex in the micellar solutions should be larger by about 0.05 than those in water because of the decreased volume fraction of the aqueous phase in the micellar solutions. However, the increment of the log β_1 values is not appreciable in this measurement.

The formation of $[Co(NCS)_2]$ is not enhanced, but even suppressed, in the micellar solutions. Therefore, we suppose that the

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$[Co(NCS)_2]$ complex is formed mostly in the aqueous phase as well as $[Co(NCS)]^+$.

The formation of $[Co(NCS)_4]^{2-}$ is extensive in the micellar solutions but not in water, as noted in a preceding section, and the result suggests that the complex forms in the micellar phase. This is not unexpected, because the tetrakis(thiocyanato) complexes of bivalent transition-metal ions form in aprotic solvents.[14] As seen in Table I, the log β_4 value is larger in the order of decreasing hydration energies of medium cations, $Li^+ > Na^+ > NH_4^+$. The corresponding $\Delta H°_{\beta 4}$ and $\Delta S°_{\beta 4}$ values become more negative in the same order of medium cations. These results may be ascribed to the formation of the ion pairs $M_2[Co(NCS)_4]$ (M = Li, Na, NH_4) in micelles with a low effective dielectric constant.[6] The enthalpies of formation of the ion pairs may be less negative with increasing hydration energies of the medium cations beause of the rupture of the $M–OH_2$ bonds, i.e. the liberation of water molecules around the hydrated medium cations. The corresponding entropies may also become less negative because the number of water molecules liberated from the solvation shells, including second and third shells, may become larger as the hydration energies of the medium cations increase.

The cobalt(II) ion is coordinated with four nitrogen atoms within the tetrahedral $[Co(NCS)_4]^{2-}$ complex,[15] and the complex thus interacts with the bulk substance mainly through the ligand sulfur atoms. Consequently, the $[Co(NCS)_4]^{2-}$ complex prefers the hydrophobic environment to the hydrogen-bonding water owing to the poor hydrogen-bonding ability of the ligand sulfur atom. The $[Co(NCS)_4]^{2-}$ complex is thus preferably formed in the micellar phase; i.e., the cobalt(II) ion is easily extractable by inert polar solvents from its thiocyanate micellar solution. The same conclusion is drawn for the $[Zn(NCS)_4]^{2-}$ complex.

On the other hand, the thiocyanate ion binds to soft Hg(II) and Pb(II) ions through its sulfur atom,[16] and thus the thiocyanato complexes of these metal(II) ions interact with the bulk through the ligand nitrogen atoms. The ligand nitrogen atom favorably forms hydrogen bonds with water, and thus the $[Hg(SCN)_4]^{2-}$ and $[Pb(SCN)_4]^{2-}$ complexes may prefer the aqueous phase; i.e., Hg(II) and Pb(II) ions are hardly extractable from their thiocyanate solutions with Triton X-100. On the contrary, these metal ions are easily extracted from their iodide solutions because of the poor hydrogen-bonding ability of the ligand ion.

Although Mn(II) and Ni(II) ions, as well as Co(II) and Zn(II) ions, may be coordinated with the N atom of SCN^- ions within their thiocyanato complexes, they are hardly extractable. This may be due to the weak complexation of Mn(II) and Ni(II) with thiocyanate ions, implying that the $[Mn(NCS)_4]^{2-}$ and $[Ni(NCS)_4]^{2-}$ complexes may not be formed in sufficient amounts in micelles. In fact, the formation constants of $[Mn(NCS)_4]^{2-}$ and $[Ni(NCS)_4]^{2-}$ in *N,N*-dimethylformamide are significantly smaller than those of $[Co(NCS)_4]^{2-}$ and $[Zn(NCS)_4]^{2-}$ (log β_4 = 5.61, 6.41, and 13.31 for Mn(II), Ni(II), and Zn(II), respectively).[17]

Dependence on the Surfactant Concentration. The $[Co(NCS)_4]^{2-}$ complex was found to be appreciably formed even in a solution of 1% w/w Triton X-100. The formation constant of $[Co(NCS)_4]^{2-}$ increases and the corresponding enthalpies and entropies become more negative with increasing concentrations of the surfactant. Unfortunately, since the thermodynamic quantities of formation of $[Co(NCS)_4]^{2-}$ and $M_2[Co(NCS)_4]$ in water are unknown, it is difficult to attribute the enthalpy and entropy values obtained for $[Co(NCS)_4]^{2-}$ in the micellar solutions to a specific interaction.

If we consider the formation of $[Co(NCS)_4]^{2-}$ only in the micellar phase, its observed formation constant may change with the volume fraction y of the surfactant according to eq 6.[18] From

$$\beta_4 = (\text{const})y/(1-y)^5 \tag{6}$$

eq 6, the log β_4 values at $y = 0.025$, 0.05, and 0.1 are calculated to be 3.25, 3.61, and 4.03, respectively, on the basis of the log β_4 value of 2.82 at $y = 0.01$. The $\beta_{4,\text{exptl}}/\beta_{4,\text{calcd}}$ ratios are thus 0.43, 0.32, and 0.24 at $y = 0.025$, 0.05, and 0.1, respectively, the values being appreciably smaller than 1. Evidently, the result cannot be explained in terms of the change in the volume fraction of the surfactant alone. The affinity of $M_2[Co(NCS)_4]$ for micelles may change with the concentration of the ion pair in the micelles.

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Registry No. $[Co(NCS)_4]^{2-}$, 18904-81-9; Triton X-100, 9002-93-1.

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(18) The average concentration of species i, $[i]_{av}$, in a micellar solution of the surfactant volume fraction y is expressed as $[i]_{av} = (1-y)[i]_{aq} + y[i]_m$, by using the concentrations $[i]_{aq}$ and $[i]_m$ in the aqueous and micellar phases, respectively, provided that the concentration of surfactant is much higher than the cmc. In this system we assume the complex formation equilibria $Co^{2+}(aq) + 4SCN^-(aq) = [Co(NCS)_4]^{2-}(aq)$ and $2Na^+(aq) + [Co(NCS)_4]^{2-}(aq) = Na_2[Co(NCS)_4](m)$ in a micellar solution. As each micellar solution involves 0.5 mol dm^{-3} Na^+ as a medium cation, the following equation may hold: $[Co(NCS)_4{}^{2-}]_m = K_d[Co(nNCS)_4{}^{2-}]_{aq} = K_d\beta_4'[Co^{2+}]_{aq}[NCS^-]_{aq}{}^4$, where β_4' denotes the overall formation constant of the $[Co(NCS)_4]^{2-}$ complex in aqueous solution and K_d is a constant. If $[Co(NCS)_4{}^{2-}]_{aq} \ll [Co(NCS)_4{}^{2-}]_m$, $[Co^{2+}]_{eq} \gg [Co^{2+}]_m$, and $[NCS^-]_{aq} \gg [NCS^-]_m$, then the apparent formation constant β_4 is represented as $\beta_4 = [Co(NCS)_4{}^{2-}]_{av}/[Co^{2+}]_{av}[NCS^-]_{av}{}^4 = K_d\beta_4'y/(1-y)^5$.