Distribution Thermodynamics of Metal Complexes in Micelles of Nonionic Surfactants

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The completion of cobalt(II), nickel(II), copper(II), and zinc(II) with thiocyanate ions has been studied in micellar solutions of nonionic surfactant Triton X-100 by titration spectrophotometry and calorimetry. The complexation has been also studied by varying length of POE (polyoxyethylene) chain. With regard to Co(II), the [Co(NCS)₄]²⁻, which hardly forms in aqueous phase, is extensively formed in micelles. With Zn(II), the [Zn(NCS)₃]⁻ and [Zn(NCS)₄]²⁻ are formed in micelles. With Ni(II), no completion occurs in micelles. In the case of Cu(II), the formation of [Cu(NCS)₂]⁺ is concluded in both micelles and aqueous phase. The complexation behavior of [Co(NCS)₄]²⁻ and [Cu(NCS)₂]⁺ depends significantly on the length of POE chain, suggesting that these complexes exist both in the relatively hydrophilic POE site and hydrophobic core site.

Keywords Spectrophotometry, Calorimetry, Nonionic surfactant, Metal-ion complexation

Micelles are considered as organic micro spheres in aqueous solution, provide new reaction media, and have thus been widely used for separation or extraction of metal ions, as well as biologically important proteins and enzymes. The nonionic surfactant Triton is consisted of hydrophobic iso-octylphenylether and relatively hydrophilic polyoxyethylene (POE) groups, which forms spherical micelles with the average aggregation number and size of 140 and 4.3 nm, respectively, in an aqueous solution. Sotobayashi et al reported solvent extraction of metal ions using POE type nonionic surfactant as a coextractant. Although a micellar solution is apparently homogeneous, it separates into two phases at an elevated temperature (above the cloud point), and metal ions also distribute into the surfactant-rich phase. So far, the interaction of alkaline metal and thiocyanate ions with POE, and the interaction of chloride ion with POE have been reported. However, still little is known on the interaction between ion and nonionic micelles.

In this work, therefore, we studied the complexation of some transition metal(II) with thiocyanate ions by precise titration spectrophotometry and calorimetry in aqueous and micellar solutions of a nonionic surfactant Triton X-100 (the average chain length of 9.7), X-114(7.5), X-305(30), and X-405(40).

Experimental

Reagents

Triton X-100, X-114, X-305 and X-405 of reagent grade (Kishida) were purified by solvent extraction using dichloromethane which was finally removed by evaporation. All chemicals used were purified and dried over P₂O₅ under vacuum in a desiccator.

Measurements

Electronic spectra were measured by an automatic spectrophotometric titration system, with a spectrophotometer (Hitachi-340 or U3500). A flow cell with a path length of 1.0 cm was connected with a titration vessel through Teflon and glass tubes. A test solution thermostatated at 25°C (±0.01) was circulated through a flow cell by using a Teflon pump. An initial test solution of M(ClO₄)₂ (M = Co(II), Ni(II), Cu(II)) containing a supporting electrolyte NaClO₄ (I = 0.4 moldm⁻³) and a given concentration of a surfactant was titrated with an NaSCN solution containing the same concentrations of NaClO₄ and surfactant. Measured electronic spectra were recorded over the wavelength
range 300-850 nm, and the data at selected 50 wavelengths over the range 400-710 nm and 300-850 nm were employed for data analysis.

Calorimetric measurements were carried out by a fully automatic titration and data acquisition system combined with a twin-type isoperibol calorimeter (Tokyo Riko). A test solution (30 cm³) was placed in a Teflon vessel, which was inserted in an aluminum block thermostated at 25.0±0.1°C with a fluctuation ±0.0001°C in an air bath. Aliquots of the titrant solution were added from an autoburet (APB-118, Kyoto electronics), and heat of complexation at each titration point was measured with a certainty of ±0.02J and corrected for heats of dilution of the titrant obtained in advance.

**Data Analysis**

The binding constant $K_{M*}$ for the association reaction between a species A and a micelle M* (eq.(1)) is defined by eq. (2);

$$A + M^* = AM^* \quad (1)$$

$$K_{M*} = \frac{[AM^*]}{[A][M^*]} \quad (2)$$

The concentration of micelles is given as:

$$[M^*] = \frac{(C_S - c.m.c.)/n^*}{(3)}$$

where $C_S$, c.m.c. and $n^*$ denote a total concentration of the surfactant, a critical micellar concentration of the surfactant and an aggregation number of the surfactant per one micelle. The binding constant $K^*$ for a surfactant molecule for the same reaction is given by

$$K^* = \frac{[A^*]/[A]CS = K_{M*}/n^*}{} \quad (4)$$

if $C_S>>c.m.c.$

The metal-ion complexation is thus described as:

$$M + nL + mS = [ML_nS_m] \quad (m = 0 \text{ or } 1) \quad (5)$$

$$\beta_{nm} = \frac{[ML_nS_m]}{[M][L]^n[S]^m} \quad (6)$$

where $m=0$ and $m=1$ denote that the complex is formed in an aqueous solution and in micelles, respectively. An absorbance $A_j$ and a heat $q_i$ are represented as:

$$A_j = \Sigma e_m(\lambda_j)\beta_{nm}[M][L]^n[S]^m + a_d(\lambda_j)[M] + q_i(\lambda_i)L \quad (7)$$

$$q_i = \Sigma \beta_{nm}\Delta H_{nm}^0(V_i[M]_i[L]^n[S]^m - V_i[M]_i[L]_i[S]^n) \quad (8)$$

The formation constants, molar extinction coefficients and enthalpies are obtained by minimizing the error-square sums, $U=\Sigma (q_{i,\text{calc}}-q_{i,\text{obs}})$ or $U=\Sigma A_j(\lambda_j - A_j(\lambda))$, by using nonlinear least square programs MQCAL and MQSPEC.  

**Results and Discussion**

**Comparison between metal(II)-NCS systems**

Thermodynamic parameters of formation of some first transition metal(II) thiocyanato complexes in micellar solutions are summarized in Table 1. With cobalt(II), the formation of $[Co(NCS)]^+$, $[Co(NCS)_2]^-$ and $[Co(NCS)_3S]$ was established, where S indicates that the complex is formed in micelles, and their formation constants, enthalpies and entropies were obtained. With nickel(II), the formation of sole $[Ni(NCS)]^+$ and $[Ni(NCS)_2]$ was established. With zinc(II), the formation of $[Zn(NCS)]^+$, $[Zn(NCS)_2]^-$ and $[Zn(NCS)_3S]$ was established. With copper(II), the formation of $[Cu(NCS)]^+$, $[Cu(NCS)_2]$ and $[Cu(NCS)_3S]$ was established.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\log K$</th>
<th>$\Delta H^\circ$</th>
<th>$\Delta S^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(II)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$M^{2+}(aq) + L^-(aq) = [ML]^+(aq)$</td>
<td>1.2</td>
<td>-7.8</td>
<td>-3</td>
</tr>
<tr>
<td>$[ML]^+(aq) + L^-(aq) = <a href="aq">ML_2</a>$</td>
<td>0.6</td>
<td>-11</td>
<td>-28</td>
</tr>
<tr>
<td>$<a href="aq">ML_2</a> + 2L^-(aq) = [ML_3]^2$ (micelle)</td>
<td>2.5</td>
<td>-32</td>
<td>-61</td>
</tr>
<tr>
<td>Ni(II)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$M^{2+}(aq) + L^-(aq) = [ML]^+(aq)$</td>
<td>1.3</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>$[ML]^+(aq) + L^-(aq) = <a href="aq">ML_2</a>$</td>
<td>0.3</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Cu(II)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$M^{2+}(aq) + L^-(aq) = [ML]^+(aq)$</td>
<td>1.8</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>$[ML]^+(aq) + L^-(aq) = <a href="aq">ML_2</a>$</td>
<td>1.0</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>$<a href="aq">ML_2</a> + L^-(aq) = [ML_3]^2$ (micelle)</td>
<td>2.4</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Zn(II)</td>
<td></td>
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</tr>
<tr>
<td>$M^{2+}(aq) + L^-(aq) = [ML]^+(aq)$</td>
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<td>-7</td>
<td>-13</td>
</tr>
<tr>
<td>$[ML]^+(aq) + 2L^-(aq) = [ML_2]^+(aq)$</td>
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<td>2</td>
<td>31</td>
</tr>
<tr>
<td>$[ML_2]^+(aq) + 2L^-(aq) = [ML_3]^2$ (micelle)</td>
<td>4.3</td>
<td>-28</td>
<td>-12</td>
</tr>
<tr>
<td>$[ML_3]^2$ (micelle)</td>
<td>3.0</td>
<td>-30</td>
<td>-44</td>
</tr>
<tr>
<td>$[ML_3]^2$ (aq) + $L^-(aq) = [ML_3]^2$ (micelle)</td>
<td>3.8</td>
<td>-74</td>
<td>-176</td>
</tr>
</tbody>
</table>

With $d^7$ cobalt(II) and $d^{10}$ zinc(II) ions, $[M(NCS)_4]^{2-}$ is favorably formed in micelles. The SCN$^-$ ion binds to these metal ions with the N end and directs the S end outward. This may be the primary reason for the favorable formation of these complexes in rather
water-deficit micellar pseudo-phase, because the sulfur atom prefers a hydrophobic environment. However, the [Ni(NCS)₄]²⁻ is not formed in micelles. This is not unexpected if we take into account the six-coordinate [Ni(NCS)₄(DMF)₂]²⁻ in DMF,¹⁰ as the corresponding structure with two bound water molecules may be unfavorable in micelles. Note that the [M(NCS)₄]²⁻ (M = Co, Zn) is tetrahedrally four-coordinated with no bound solvent molecule in DMF.¹¹,¹²

The [Zn(NCS)₃]⁺, which is also tetrahedrally four-coordinated with a bound water molecule, is also extensively formed in micelles. This indicates that such a complex with one coordinating water molecule can stay in micelles. However, note that the corresponding [Co(NCS)₃]⁺ is hardly formed. As in DMF, the formation of the complex may be competitively suppressed owing to the more favorable formation of [Co(NCS)₄]²⁻. The six-coordinated mono- and dithiocyanato complexes may not be usually formed in micelles, probably owing to their strong hydrophilic nature. However, the [Cu(NCS)₂]⁺ is found to form in both aqueous and micellar pseudo-phases. According to the electronic spectra, the complex has essentially the same geometry, a distorted octahedral six-coordination. The axial interaction may be weak due to the Jahn-Teller effect for copper(II), which may reduce largely the hydrophilic nature of the complex to allow an inclusion of the [Cu(NCS)₂]⁺ complex in micelles. The band of [Cu(NCS)₂S] at 372 nm in micelles is slightly shifted to a longer wavelength by 18 nm from that of [Cu(NCS)₂] (354 nm) in aqueous solution. The corresponding band of [Cu(NCS)₂] appears at 395 nm in DMF.¹⁰ The LMCT energy thus decreases in the order water > micelle > DMF, the order of decreasing hydrophilic nature of solvent.

**Thermodynamic parameters**

Both the reaction enthalpy and entropy values are significantly negative, and the complexation is driven mainly by the enthalpy term in a micellar solution, unlike in DMF, where the values are positive and the complexation is driven by the entropy term.¹³ In micelles, unlike DMF, as the anionic complexes may form ion pairs. Therefore, we can not simply compare the values in the micellar solution and DMF. The complexation in micelles may be described as:

\[
\text{Zn}^{2⁺}(aq) + 2\text{Na}⁺(aq) + 4\text{SCN}^-(aq) = \text{Na}_2[\text{Zn(NCS)}_4](\text{micelle})
\]

which can be rewritten as the sum of following three reactions:

\[
\text{Zn}^{2⁺}(aq) + 4\text{SCN}^-(aq) = [\text{Zn(NCS)}_4](aq) \quad (10)
\]

\[
2\text{Na}⁺(aq) + [\text{Zn(NCS)}_4](aq) = \text{Na}_2[\text{Zn(NCS)}_4](aq) \quad (11)
\]

\[
\text{Na}_2[\text{Zn(NCS)}_4](aq) = \text{Na}_2[\text{Zn(NCS)}_4](\text{micelle}) \quad (12)
\]

The observed negative enthalpy and entropy in micellar solution cannot be ascribed to those of complexation in water. Indeed in water, the enthalpy and entropy values for reaction (10) have been determined to be -12.8 kJ mol⁻¹ and 5 J K⁻¹ mol⁻¹, respectively,¹⁴ which is significantly less negative than those in micelles. As the ion-pair formation is weak in aqueous solution, the enthalpy and entropy of formation of possibly solvent separated ion-pair may be generally small and positive due to desolvation of ions (ΔH° > TΔS° > 0).¹⁵ Taking into account these facts, we propose that the significantly negative enthalpy and entropy values are ascribed to those of transfer of the Na₂[Zn(NCS)₄] ion pair.

**Dependence on the POE Chain Length**

The binding constants with micelles, β₄₁/β₂₀ for the [Co(NCS)₄]²⁻ and β₂₁/β₂₀ for the [Cu(NCS)₂]⁺, are plotted against the average number of POE chain

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**Fig. 1** Variation of (a) β₄₁/β₂₀ for cobalt(II) thiocyanato complexes and (b) β₂₁/β₂₀ for copper(II) thiocyanato complexes as a function of the POE chain length, n*
length $n^*$ in Fig. 1. All experimental points fell on the straight line. As seen, the extrapolated values at $n^* = 0$ are not zero. Thermodynamic parameters, $\Delta G_{\text{pnm}}^o$, $\Delta H_{\text{pnm}}^o / \text{kJmol}^{-1}$ and $\Delta S_{\text{pnm}}^o / \text{JK}^{-1}\text{mol}^{-1}$, for the cobalt(II) thiocyanato complexation in micellar solutions are listed in Table 2. The $\Delta H_{\text{p41/p30}}^o$ value ($= \Delta H_{\text{p41}}^o - \Delta H_{\text{p30}}^o$) are plotted against $n^*$ in Fig. 2. As seen, the $\Delta H_{\text{p41}}^o$ increases with increasing length of the POE chain. These facts cannot explain simply by taking into account a single homogeneous phase for a micelle.

These might be explained by assuming that (i) a micelle is consisted of two pseudo-phases, the hydrophilic POE moiety and hydrophobic core, (ii) micelles consist of practically the same number of surfactant molecules and (iii) the volume of the hydrophilic POE moiety increases linearly with increasing $n^*$. On the basis of the assumption, we obtain the relationship between $n^*$ and $\beta_n/\beta_{0n}$.

$\Delta H_{\text{p41/p30}}^o = (1-x)\Delta H_{\text{p41/p30,philic}}^o + x\Delta H_{\text{p41/p30,phobic}}^o$ (14)

where $D_{\text{philic}}$ and $D_{\text{phobic}}$ stand for the distribution coefficients of a complex to the hydrophilic POE moiety and to the hydrophobic core, respectively, from an aqueous pseudo-phase, $V_{\text{OE}}^o$ and $V_{\text{phobic}}$ the molar volume of an oxyethylene unit and of hydrophobic core, respectively, and $x = (\beta_{41}/\beta_{30})_n^* = (\beta_{41}/\beta_{30})_o^*$. The values of $\Delta H_{\text{p41/p30,philic}}^o$ and $\Delta H_{\text{p41/p30,phobic}}^o$ thus obtained are -15 kJ mol$^{-1}$ and -70 kJ mol$^{-1}$, respectively, indicates that the hydrophobic core site possess a more strong affinity for the metal complex than the hydrophilic POE site.

References