Solvochromism and Thermochromism of Cobalt(II) Complexes Solubilized in Reversed Micelles

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Configurational change takes place between tetrahedral and octahedral species, when cobalt(II) complexes are cosolubilized in reversed micelles formed by the cationic or ampholytic detergents in chloroform. This is accompanied by the elimination-addition reaction of ligand water from and to the metal ion in the reversed micellar core. The phenomenon is interpreted in terms of solvochromism and thermochromism. The nature and state of "*naked*" metal ion and "*free*" water molecule afforded in a highly restricted field of reversed micelles have been discussed on the basis of equilibrium constants and thermodynamic parameters for the configurational change, particular attention being given to the structure of micelles. Their resemblance to the active site of metalloenzymes is also discussed.

The resemblance of reversed micelles to hydrophobic pockets of enzymes or biomembranes has attracted much attention.1) One of specific features of the reversed micelles is that some reversed micelles can solubilize a considerably large amount of water in their interior cores. Earlier works on fluorescent properties,2) relaxation mechanisms in NMR,3) electronic spectra,4) and kinetics of reactions occurring in the micellar core5) have demonstrated that the nature of water solubilized in reversed micelles differs a great deal from that of ordinary bulk water. Careful survey of these studies aroused our interest to investigate the properties of water in various reversed micelles paying particular attention to the coordination chemistry and metal ion catalysis. Elimination and addition of water molecules from and to the metal ion cosolubilized in the reversed micelles should be closely related to the nature of water present in a highly restricted field.

Cobalt(II) ion is only one of d^7 transition metal ions which show relatively easy octahedral-tetrahedral configuration change accompanied by the addition-elimination of ligands.6) An octahedrally coordinated cobalt(II) ion should have three spin allowed d-d transitions, which are from the ground state, $^4T_1(F)$, to the states $^4T_2(\nu_1)$, $^4A_2(\nu_2)$, and $^4T_1(P)(\nu_3)$. The visible absorption of hexaaquacobalt(II) ion, $[Co(H_2O)_6]^{2+}$, is weak and the aqueous solution shows pale pink color. On the other hand, the visible absorption band of tetrahedrally coordinated cobalt(II) ion lies in the red part of the spectrum, giving intense blue color. This absorption band stems from the d-d transition from the $^4A_2$ ground state to the $^4T_1(P)$ state, and its fine structure results from spin-orbit coupling.7) The octahedral-tetrahedral configuration change takes place in two ways. When cobalt(II) chloride is dissolved in water, octahedrally coordinated ion is formed. In alcohols or acetone, a blue color due to the tetrahedral species, $CoCl_2L_2$, is observed.8,10c) This is interpreted in terms of the solvochromic effect. On the other hand, Swift and Connick found evidence of a tetrahedral species, $[Co(H_2O)_4]^{2+}$, near 100 °C by NMR relaxation studies.9) Aqueous solutions of cobalt(II) chloride and bromide show a reversible color change from pink to violet in the temperature range 100—200 °C.10) This was discussed in terms of the thermochromic effect.

Wells obtained an interesting result on the interior water pool of phosphatidylcholine micelles in ether by use of cobalt(II) chloride, attention being given to the correlation between the nature of bound water and the activity of phospholipase A_2 on the membrane surfaces.11) In this work, we have studied the solvochromic and thermochromic behavior of the cobalt(II) complexes and the properties of bound and free water in the restricted field formed by various reversed micelles.

Experimental

Materials. Analytical grade samples of cobalt(II) chloride $CoCl_2 \cdot 6H_2O$, (Wako Pure Chemical Ind. Ltd.) and nitrate, $Co(NO_3)_2 \cdot 6H_2O$, (Nakarai Chemicals Ltd.) were used without further purification. The concentrations of their aqueous solutions were determined by the usual procedures with EDTA.

Commercial hexadecyltrimethylammonium bromide (CTAB)12) and sodium 1,2-bis(2-ethylhexyloxycarbonyl)-1-ethanesulfonate (AOT)13) were purified by recrystallization. Dodecylammonium propionate (DAP) was prepared and purified.14) *N*,*N*-Dimethyl-*N*,*N*-dioctadecylammonium chloride (QD) was supplied by the Tokyo Institute of Kao Soap Co., Ltd. Egg lecithin was extracted from egg yolk and purified.15)

Reagent grade chloroform was distilled and stored over a Linde type 4A molecular sieve, the water content of which being less than 4 ppm. Chloroform was chosen as the solvent since it is the only solvent which affords the completely homogeneous systems of reversed micelles cosolubilizing water and cobalt(II) complexes.

Spectrophotometric Measurements. All the visible and near infrared spectra were measured on a Hitachi 323 or Hitachi 124 recording spectrophotometer equipped with a thermoregulated cell compartment. Three milliliters of the detergent solution (about 0.20 M, M=mol dm^{-3}) in chloroform was placed in a cuvette. After the injection of 3.0 μl of aqueous cobalt(II) solution (about 3.0 M) into the cell, it was shaken on a Vortex mixer and kept in the thermostatted cell compartment for 20 min to attain equilibrium.

Results and Discussion

Solvochromic Effect. In aqueous solution the cobalt(II) ion is octahedrally complexed with water to afford $[Co(H_2O)_6]^{2+}$, giving pink coloration to the

Table 1. Spectral data for tetrahedral cobalt(II) complexes in various reversed micelles

Micelles[a]	DAP		QD		CTAB		AOT		EL[c]		In water	
Salt[b]	I	II	I	II	I	II	I	II	I	II	I	II
Doublets cm^{-1} (ε)											20200[d] (5)	20200[d] (5)
ν_3 Band cm^{-1} (ε)	19200 (127)$_{sh}$	19200 (119)$_{sh}$	18700 (9)	18700 (8)	14600 (479)	15400 (324)	18900 (10)	18900 (13)	17200 (9)	18300 (1)		
	17200 (177)	17200 (165)	15700 (474)	15700 (443)	14400 (550)	14900 (716)			16700 (12)	17200 (1)		
			14300 (738)	14300 (670)	13900 (801)	14100 (1000)			16200 (13)	16700 (1)		
						13700 (1105)			15700 (14)	15900 (1)		
									15300 (14)			
ν_2 Band cm^{-1} (ε)	8403 (26)	8403 (20)	6061—4202 (92.3—69.2)	5917 (91.8)	5814—4255 (88.8)	5848—4545 (115.6)			7037—5128 (14)	4505 (1.4)	7843 (1.4)	7843 (1.4)
	4505 (16)	4878—4651 (14)		5348 (91.8)		4274 (115.6)					6494 (1.2)	6711—6494 (1.2)
	4444 (16)	4464 (19)		4808—4545 (61.2)								
	4255 (18)			4274 (20.4)								

a) Concentrations of water and detergent are 55.5×10^{-3} and 0.20 M, respectively, in all runs. b) I: $CoCl_2$, II: $Co(NO_3)_2$. c) EL stands for egg lecithin. d) Octahedral complex.

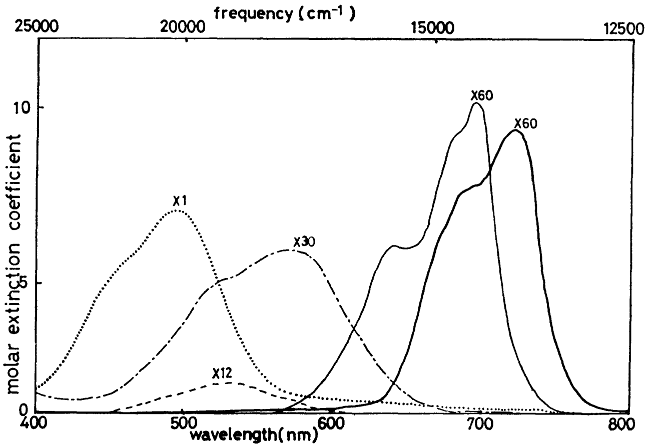

Fig. 1. Visible spectra of $CoCl_2$ in pure water (······) and in reversed micelles formed by AOT (----), DAP (— — —), QD (——), and CTAB (——) in chloroform at 25 °C.

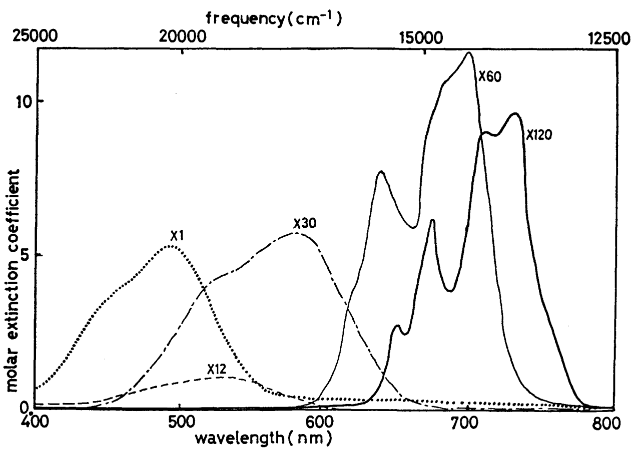

Fig. 2. Visible spectra of $Co(NO_3)_2$ in pure water (······) and in reversed micelles formed by AOT (----), DAP (——), QD (——), and CTAB (——) in chloroform at 25 °C.

solution. When the concentrated aqueous solution of $CoCl_2$ or $Co(NO_3)_2$ is injected into the solutions of certain detergents in chloroform, it is readily dissolved, giving intense blue or violet solutions. Their visible spectra differ with detergent. When the cobalt(II) ion is cosolubilized in the DAP reversed micelles, the coloration is violet, while in the CTAB or QD micelles it is intensely blue. However, in AOT micelles, no color change from pink to blue is observed due to the cosolubilization of the cobalt(II) ion. In the anionic reversed micelles such as AOT, it is possible that the detergent molecules themselves coordinate to the metal ion forming stable octahedral complexes. The spectra in different reversed micelles are shown in Figs. 1 and 2. Spectral data are summarized in Table 1 for cobalt(II) chloride and nitrate.

The visible spectra of the cobalt(II) complexes in the CTAB or QD reversed micelles closely resemble those for the tetrahedral complex, $[CoX_4]^{2-}$, as reported by Cotton and his co-workers.[7] These cationic detergents carry halogen as counter anions. Thus the species formed in the micellar core may be $[CoBr_4]^{2-}$

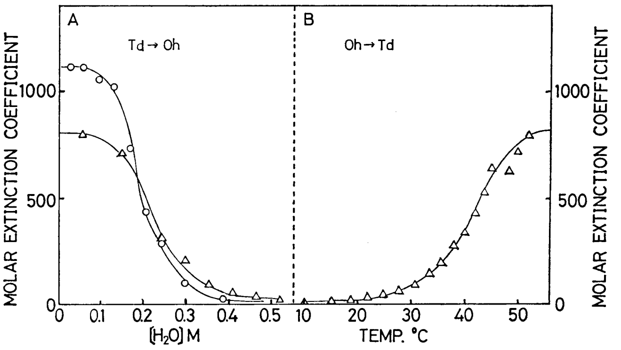

Fig. 3. The solvochromic effect with water (A) and thermochromic effect (B) for the configurational change of cobalt(II) complexes in the CTAB reversed micelles. —○—; $Co(NO_3)_2$, —△—; $CoCl_2$.

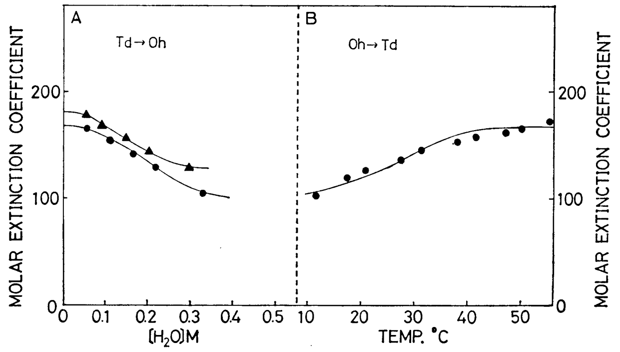

Fig. 4. The solvochromic effect with water (A) and thermochromic effect (B) for the configurational change of cobalt(II) complexes in the DAP reversed micelles. —▲—; $CoCl_2$, —●—; $Co(NO_3)_2$.

in the CTAB micelles and $[CoCl_4]^{2-}$ in the QD micelles. However, in view of the slight difference between the visible spectra of cobalt(II) chloride and nitrate in the CTAB micelles, we can not disregard the possibility of the coexistence of other mixed complexes[10c] such as $[Co(NO_3)_2Cl_2]^{2-}$, $[Co(NO_3)_2Br_2]^{2-}$, or $[CoCl_2Br_2]^{2-}$. The structures of complexes formed in each case can not be clarified at present. Contrary to what would be expected from the cloud expanding effect of ligands, halide ions are more strongly coordinating to the metal ion pushing away water molecules in the reversed micellar core.[16] This would be responsible for the effect of the very restricted field of the reversed micelles. Antipora-Karataeva and Vainshtein observed a similar phenomenon in different solvents such as methanol, ethanol, acetone, and ethyl methyl ketone, and pointed out the importance of chloride ion since solutions of $Co(NO_3)_2$ never become blue.[17] We found that even nitrate shows exactly the same phenomenon as that observed with chloride (Figs. 1 and 2).

When water is added to the reversed micelles cosolubilizing metal ions, the blue or violet color fades as reflected by the decrease in the molar absorbancy of the tetrahedral complex. Finally the solution becomes pale pink again, indicating the reproduction of an octahedral species. This configurational change from the tetrahedral complex to the octahedral one causes the spectral change with isosbestic points. As seen in Figs. 3-A and 4-A, configurational changes occur sigmoidally with water concentration. With both DAP and CTAB micelles, inflection points were observed around the point where the molar ratio of water to the detergent molecule is about unity. Inflection was more enhanced in the cationic CTAB reversed micelles than in the DAP micelles. The most plausible mechanism for the phenomena can be interpreted by the "two step hydration mechanism."[3,11] When water is first introduced into the reversed micelles, water tends to interact more strongly with the polar head group of the detergent rather than with the metal ion. Upon completion of the first hydration in the micellar core, water molecules start to coordinate to the metal ion, affording a octahedral complex with a concomitant decrease in intensity in red region of visible spectra. The strength of interaction of water in the first hydration stage with detergents should be affected by the kind of detergent molecule. Water molecules in the second hydration stage would behave differently from those of the first, *i.e.*, those tightly bound to detergents. The hydrolysis of norleucine *p*-nitrophenyl ester was significantly promoted by the copper(II) ion in the AOT reversed micelles.[18] The catalytic effect becomes maximum at the point where the water content is almost equivalent to the detergent concentration. When water concentration is less than that at the maximum, the formation constants of the complex between the copper(II) ion and substrate are surprisingly large ($\log K_f = 8$—9 at 25 °C). At the maximum of catalytic effect in the reversed micelles, nucleophilic rate constants with water k_{H_2O} increase by about 10^3-fold as compared with those in bulk water.[18] This is closely related to the configurational change of metal complex in the reversed micelles. During the course of first hydration stage, the metal ion can easily form a complex with the substrate ester using vacant coordination sites of the metal ion. In the second hydration stage, water molecules start to coordinate to the metal ions or attack the substrate activated on complex formation with the metal ion. The "free" water molecules should be very reactive. The water further added in the second hydration stage finally tends to resemble pure bulk water.[3,11] A similar conclusion regarding the state of water in the AOT reversed micelles has recently been attained by Wong and his co-workers in NMR relaxion studies of water.[3]

Thermochromic Effect. When the pink solution was warmed after the completion of second hydration in the reversed micellar sphere, the intensely blue color appeared again. The thermochromism looks like a mirror image of the solvochromism shown in Fig. 3. The configurational change between the tetrahedral and octahedral complexes with temperatures was certainly reversible; upon cooling the solution, the original pink color appeared again. It is noteworthy that in the reversed micellar systems the reversible change of configuration occurs even at 10—60 °C, while much higher temperatures are necessary in aqueous solutions.[9,10]

Evaluation of Equilibrium Constant. The configu-

Table 2. Equilibrium constants and thermodynamic parameters for the configurational change of the cobalt(II) complexes in reversed micelles

In DAP reversed micelles;

$$\underset{\mathrm{T_d}}{\mathrm{CoL_2X_2}} + 2\mathrm{L} \overset{K_1}{\rightleftharpoons} \underset{\mathrm{O_h}}{\mathrm{CoL_4X_2}}$$

$\ln K_1 = 1.17 \pm 0.18$ (25 °C) for chloride
$\ln K_1 = 1.10 \pm 0.06$ (25 °C) for nitrate
$\Delta G^0 = -0.69 \pm 0.11$ kcal mol^{-1}
$\Delta H^0 = -10.8 \pm 0.3$ kcal mol^{-1}
$\Delta S^0 = -33.6 \pm 1.0$ e.u.

In CTAB reversed micelles;

$$\underset{\mathrm{T_d}}{[\mathrm{CoX_4}]^{2-}} + 2\mathrm{L} \overset{K_2}{\rightleftharpoons} \underset{\mathrm{O_h}}{[\mathrm{CoX_4L_2}]^{2-}}$$

$\ln K_2 = 6.64 \pm 0.50$ (25 °C) for nitrate
$\ln K_2 = 6.23 \pm 0.22$ (25 °C) for chloride
$\Delta G^0 = -3.69 \pm 0.13$ kcal mol^{-1}
$\Delta H^0 = -27.2 \pm 0.7$ kcal mol^{-1}
$\Delta S^0 = -72.2 \pm 2.2$ e.u.

rational change of the cobalt(II) complexes in the reversed micelles can be classified as follows.

(I) In the DAP micelles:

$$\underset{\mathrm{T_d}}{\mathrm{CoL_2X_2}} + 2\mathrm{L} \overset{K_1}{\rightleftharpoons} \underset{\mathrm{O_h}}{\mathrm{CoL_4X_2}}, \qquad (1)$$

where L is water and X is the halide ions or NO_3^-.

(II) In the CTAB micelles:

$$\underset{\mathrm{T_d}}{[\mathrm{CoX_4}]^{2-}} + 2\mathrm{L} \overset{K_2}{\rightleftharpoons} \underset{\mathrm{O_h}}{[\mathrm{CoX_4L_2}]^{2-}}. \qquad (2)$$

In the CTAB or QD micelles, other mixed complexes such as $[CoX_2Y_2]^{2-}$ or $[CoX_2Y_2L_2]^{2-}$ may be formed. Even if this is the case, the equilibrium of addition-elimination of water will be essentially similar to Eq. 2. Equilibrium constants K_1 and K_2 for the addition reactions (Eqs. 1 and 2) could be calculated by the procedure of Sacconi *et al.*[19)]

$$K_1 = \frac{[\mathrm{CoL_4X_2}]}{[\mathrm{CoL_2X_2}][\mathrm{L}]^2} \qquad (3)$$

$$K_2 = \frac{[\mathrm{CoX_4L_2}^{2-}]}{[\mathrm{CoX_4}^{2-}][\mathrm{L}]^2} \qquad (4)$$

Modifying these we get the following equation which will be valid for different water concentrations:

$$\ln\frac{1-\alpha}{\alpha} = \ln K - 2\ln[\mathrm{L}]_\mathrm{f}, \qquad (5)$$

where α is the fraction of the tetrahedral complex of the total concentration of cobalt(II) ion adopted and $[L]_f$ is the concentration of the "free" ligand, the difference between the concentration of water initially added and twice the concentration of the adduct, the octahedral species. Figure 5 shows the reliability of equilibria 1 and 2. The maximum of the $\approx$17200 cm^{-1} band of the tetrahedral complexes was used for the concentration measurement. Corrections for the overlap by the absorption of the octahedral complexes are negligible because of the very much smaller molar extinction coefficients of the octahedral complexes (Table 1). From a comparison of the respective equilibrium constants for the two different types of micellar systems (Table 2), it seems that the second hydration occurs more easily in the CTAB reversed micelles than in the DAP micelles.

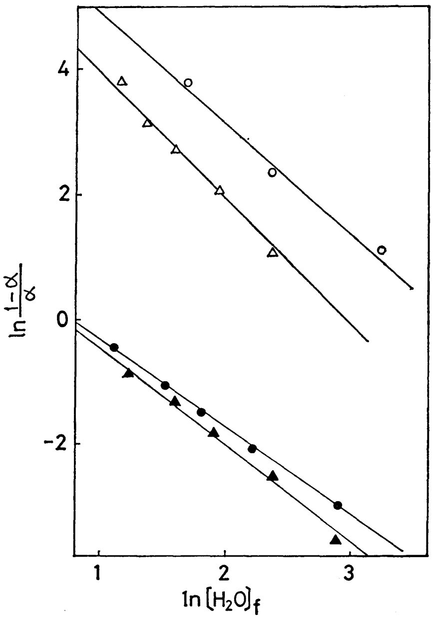

Fig. 5. Plots of $\ln(1-\alpha)/\alpha$ against $\ln[H_2O]_f$ related with the Eq. 5 in the text; $Co(NO_3)_2$(○) and $CoCl_2$(△) in the CTAB reversed micelles; $Co(NO_3)_2$(▲) and $CoCl_2$(●) in the DAP reversed micelles.

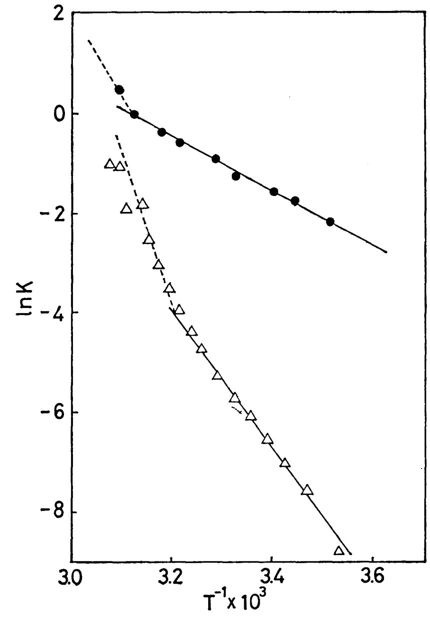

Fig. 6. Plots of $\ln K$ against $1/T$ for the thermochromism in the DAP reversed micelles cosolubilizing $Co(NO_3)_2$(●) and in the CTAB reversed micelles cosolubilizing $CoCl_2$(△).

The standard molar thermodynamic parameters are evaluated by means of the usual relationships $\Delta G^0 = -RT\ln K = \Delta H^0 - T\cdot\Delta S^0$ using the data of thermo-

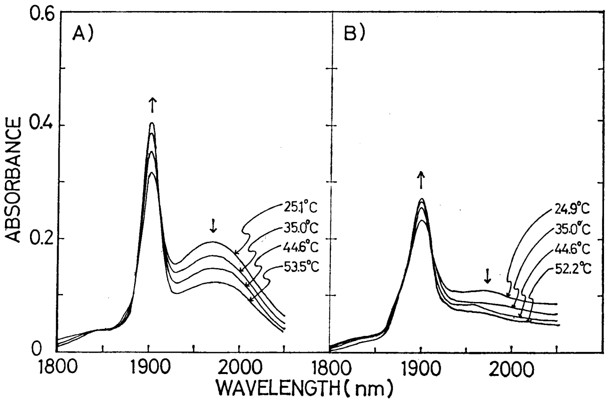

Fig. 7. The temperature effect on the near infrared spectra of water (0.203 M) solubilized in the 0.20 M CTAB (A) and in the 0.20 M DAP (B) reversed micelles formed in chloroform at different temperatures.

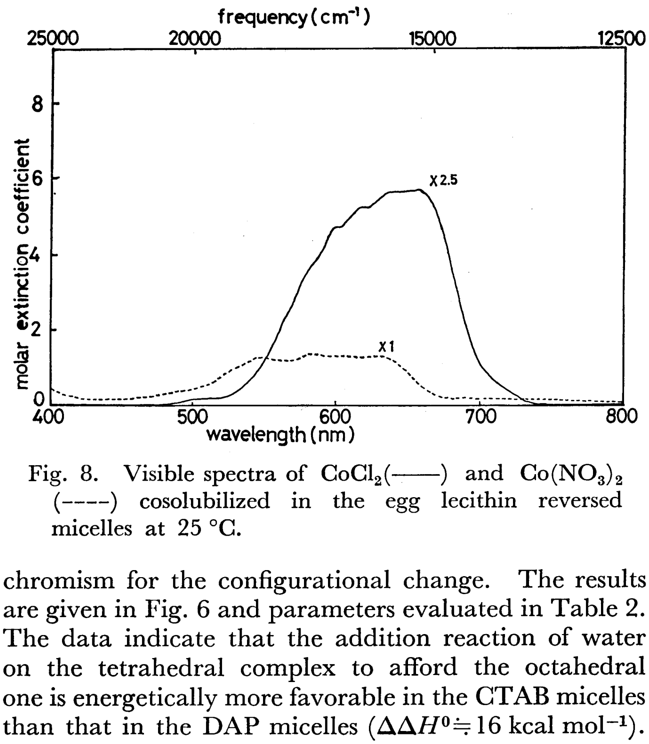

Fig. 8. Visible spectra of $CoCl_2$(——) and $Co(NO_3)_2$ (----) cosolubilized in the egg lecithin reversed micelles at 25 °C.

chromism for the configurational change. The results are given in Fig. 6 and parameters evaluated in Table 2. The data indicate that the addition reaction of water on the tetrahedral complex to afford the octahedral one is energetically more favorable in the CTAB micelles than that in the DAP micelles ($\Delta\Delta H^0 \fallingdotseq 16$ kcal mol^{-1}). On the basis of unfavorable entropy, on the other hand, we can imagine that the CTAB micelles may provide the more rigid hydration shell than the DAP micelles ($\Delta\Delta S^0 \fallingdotseq 38$ e.u.). Negative values of ΔG^0 are essential to form the more stable octahedral complexes. The values of parameters strongly resemble those obtained for the configurational equilibrium[10c] between Co(isoquinoline)$_2$Cl$_2$ and Co(isoquinoline)$_4$Cl$_2$,[20] Co(py)$_2$X$_2$ and Co(py)$_4$X$_2$[21,22] in chloroform, or $[Co(H_2O)_4]^{2+}$ and $[Co(H_2O)_6]^{2+}$ in aqueous solution.[23] Plots of $1/T$ against $\ln K$ indicate the presence of two energetically distinct equilibria. It was more obvious in the CTAB reversed micellar systems. The equilibrium in the partition of water molecules between the micellar core and bulk phase may play a role.

The near infrared spectra of water in the CTAB and DAP reversed micelles were determined over the range 1800—2000 nm. The water solubilized in the reversed micelles shows a relatively sharp band at 1902 nm and a broad band around 1970—1980 nm. The former band is ascribed to the free water dispersed in the bulk phase, and the latter to the water strongly bound to detergent molecules.[24] With temperature rise from 25 to 55 °C, the intensity of the band of free water increases, while that of the bound water decreases (Fig. 7). Rise in temperature causes the increase in the mobility of the water molecule encapsulated in the micellar core, resulting in easier dispersion into the bulk phase of organic solvent. The temperature effect on the equilibrium depends on the kind of micelle. It is more drastic in the CTAB micelles than in the DAP micelles. The results are in line with those observed in the thermochromism of the cobalt(II) complexes. The infrared spectra of the CTAB micellar system are sharper, relative amounts of bound water in the micellar core to those of free water in bulk appearing to be larger in the CTAB micelles than in the DAP ones.

The IR data might reflect the fact that in the micellar sphere the water interacts more strongly with CTAB than with DAP. The behavior of water molecules in the micelles closely correlates with the thermochromism and solvochromism of the cobalt(II) complexes.

Egg Lecithin Reversed Micelles. In all the reversed micelles except for egg lecithin micelles, no specific difference was observed in visible spectra between the chloride and nitrate. In the egg lecithin reversed micelles, however, there is much difference, especially in absorption maximum, as shown in Fig. 8. When cobalt(II) chloride was cosolubilized in the egg lecithin micelles, it gave a blue solution with a broad absorption at 620—670 nm, which was identical with the result in the phosphatidylcholine micelles obtained by Wells.[11] When nitrate was introduced into the same micelles, on the other hand, the broad absorption was observed at 540—640 nm range, its molar absorptivity being relatively small. In both cases, however, solvochromism and thermochromism were observed, though not distinctly.

We might conclude that in a very restricted field formed by reversed micelles, specifically reactive water molecule and "*naked*" metal ion can be afforded, where the situation resembles the hydrophobic pocket of metalloenzymes.

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