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Thermochromism of Metal Complexes of Cresolphthalein Dye. Solvent Effect on Temperature-Dependence and Reversibility

Masato Nanasawa,* Mitsuo Wada, and Hiroyoshi Kamogawa
Department of Applied Chemistry and Biotechnology, Faculty of Engineering,
Yamanashi University, Takeda-4, Kofu 400

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Synopsis. The thermochromism of metal complexes of cresolphthalein dye was studied in organic solvents in the presence of pyridine derivatives. Remarkable thermochromic changes were observed for complexes with nickel(II) and magnesium(II) ion; a large temperature dependence was found in a polar aprotic solvent.

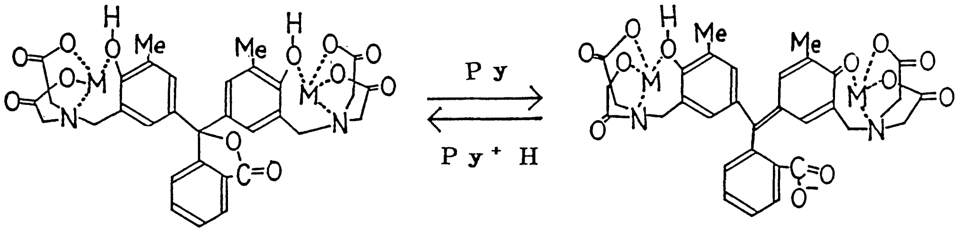
Organic erasable-direct-read-after-write (EDRAW) media have received much attention regarding their application to recording devices with high storage density and responsibility. These include heating-mode recording system employing the abrasive recording of pigments,[1] phase conversion of liquid crystals,[2] and color change of thermochromic compounds.[3] The thermochromism of metal complexes with triphenylmethane dyes observed in aqueous buffer solution[4,5] was also possible in the solid state, and its thermochromic behavior was found to depend distinctly on the kind of polymer matrix employed.[3] This paper describes the thermochromism of cresolphthalein (PC) complexon with various bivalent metal ions and discusses the solvent effect on its temperature-dependence and reversibility.

Results and Discussion

The 2:1-metal complexes of the multidentate ligands of triphenylmethane dyes indicate thermochromism by protolytic equilibrium.[3,4] The reversible color change of a PC-dye was investigated in H_2O, ethylene glycol (EG), and *N*-methylpyrrolidone (NMP) containing pyridine derivatives as organic base, using metal ions having four coordination number such as Cd(II), Co(II), Cu(II), Mg(II), Mn(II), Ni(II), Pb(II), and Zn(II).

Metal ions, Co(II) and Cu(II), formed a complex with an organic solvent to induce an intensive color, and the complex of Fe(III) ion revealed a strong absorption at 517 nm (ε=1600 dm^3 mol^{-1} cm^{-1}) in NMP and 532 nm (ε=1400) in EG without the addition of the pyridine derivative. The color development of a PC-metal complex was observed only slightly in the case of PC-Zn(II) possessing a large value of stability constant against PC-dye ($K_{\text{stab.}}$).[6] The magnitude of the absorptivity difference between 25 and 80 °C was in the following order: Ni(II), Mg(II)$\gg$Cd(II)$>$Mn(II), Pb(II)$>$Zn(II).[7] Proton dissociation of PC-metal complexes to induce thermochromism is not correlated to the value of $K_{\text{stab.}}$, but seems to relate to the affinity constant against OH^- ions (K_{OH}) and the metal ionic radius.[8] An intensive reversible color change was obtained with metal ions possessing 2.5—4.0 of pK_{OH} value and approximately 0.7 Å ionic radius.

In Fig. 1, the absorbances of the PC-Mg complex are plotted against the proton dissociation constants of the conjugated acid of pyridine derivatives (K_{py}).[9] The absorbance at 25 °C increased with an increase in the pK_{py} value, and also increased in the order NMP$<$EG$<H_2O$. This order is consistent with the values of the proton dissociation constant of relatively low molecular weight phenol derivatives.[10] Since color development takes place by the dissociation of the phenolic proton from a PC-metal complex, its absorbance depends on the stability of a combination of metalloquinonoid anion (PC^--M) and the protonated pyridinium derivatives (Py^+H). Since the salt comprising PC^--M and a pyridinium cation with higher pK_{py} is more stable, its absorbance is large at 25 °C. However, upon heating, a marked increase in the absorbance was observed for the solution of PC-Mg(II) in NMP. Table 1 shows the acid dissociation constant of a PC-metal complex (K_c) and the thermodynamic parameter ΔH and ΔS for the following equation: $\text{PC-M} \rightleftarrows \text{PC}^-\text{-M}+H^+$ (2). The value of K_c was determined by the following equation $\log K_c = \log K + \log K_{py}$ (3), where K indicates the equilibrium constant for Eq. 1. The values of ΔH and ΔS were determined by plotting the value of $\log K_c$ against



$$\text{PC-M}+\text{Py} \rightleftarrows \text{PC}^-\text{-M}+\text{Py}^+\text{H} \quad (1)$$

Scheme 1.

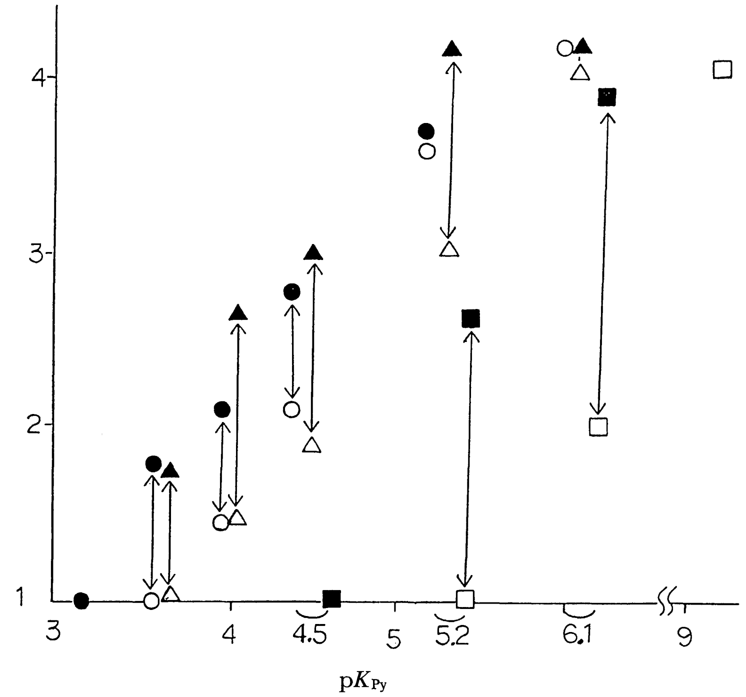


Fig. 1. Temperature-Dependence of PC-Mg(II) Complex with Pyridine Derivatives. ○⟷● indicates the reversible absorption difference at 566 nm between 25 and 80 °C in H_2O; △⟷▲ at 573 nm in EG; □⟷■ at 576 nm in NMP. PC-dye, 1.5×10^{-3} mol dm^{-3}; metal ions, 9×10^{-3}; pyridine derivative, 7.5×10^{-2} mol dm^{-3}.

Table 1. Thermodynamic Parameters for the Proton Dissociation of PC-Metal in Different Solvents[a]

	PC-Ni(II)			PC-Mg(II)		
	H_2O	EG	NMP	H_2O	EG	NMP
p(K_c[b]/mol dm^{-1})	6.6	7.9	10.2	7.8	8.5	10.7
ΔH[c]/kJ mol^{-1}	27	55	78	29	51	75
ΔS[c]/JK^{-1} mol^{-1}	−37	−15	37	−13	−20	30
ΔG_{298}/kJ mol^{-1}	38	37	36	31	42	31
ΔG_{333}	40	28	15	33	37	16
$\Delta\Delta G$[d]	−2	9	21	−2	5	15

a) Calculated for the Eq. 2: PC-dye, 1.5×10^{-3} mol dm^{-3}; metal ions, 9×10^{-3} mol dm^{-3}; 3-Acetylaminopyridine, 7.5×10^{-2} mol dm^{-3} for PC-Ni(II), 4-Acetylaminopyridine for PC-Mg(II). b) Calculated from Eq. 3 at 25 °C. c) Average values for the range 25—80 °C, deviation ±5% in H_2O; ±15% in EG; ±35% in HMP. d) Difference in ΔG-values between 25 °C and 60 °C.

Table 2. Rate Constants for the Reversible Reaction of PC-Ni(II) in Different Solvents[a]

	H_2O	EG	NMP
k_1/dm^3 mol^{-1} s^{-1}	8.4×10^{-4}	5.1×10^{-4}	1.5×10^{-5}
k_{-1}/dm^3 mol^{-1} s^{-1}	2.2×10^{-1}	1.0×10^{-1}	1.2×10^{-3}
k_{-1}/k_1	3.8×10^{-3}	5.1×10^{-3}	1.3×10^{-2}

a) at 60 °C, PC-dye, 1.5×10^{-3} mol dm^{-3}; Ni(II) ions, 9×10^{-3} mol dm^{-3}; N-methylniconinamide, 7.5×10^{-2} mol dm^{-3}.

$1/T$. However, the plot of $\log k_c$-$1/T$ in an organic solvent does not give a straight line, but the gradient increases with a decrease in $1/T$. Although the value of ΔH, or ΔS, was calculated by supposing that the variation of ΔS, or ΔH, with the temperature would be small in the same solvent,[11,12] the errors of both values in EG and NMP amounted to more than 15- and 35 percent, respectively. Accordingly, the values of the Gibbs function are shown in Table 1.

The value of pK_c of PC-dye with Ni(II) and Mg(II) is of the order $H_2O<EG<NMP$. This order is different from those of the phenol derivatives having a relatively bulky molecular size.[10] Presumably, PC-metal is fully solvated with the H-donor solvent at complexed sites, so that difference in solvation for its conjugated base is small. The values of ΔH of PC-Ni(II) and -Mg(II) in H_2O resemble that of Xylenol orange(XO) with Cu(II) ion.[5] Although the deviation of the estimated values of ΔH and ΔS were large for the equilibrium reaction in EG and NMP, the ΔH-value increased in the order $H_2O<EG<NMP$. These results correspond to the intensive reversible color change observed for Eq. 1. The ΔS-value is large compared with that of XO-Cu in buffer solution of sodium perchlorate. The difference might be caused by a color development obtained by using the pyridine derivatives as proton acceptor.

The reversibility of the thermochromism of a PC-metal complex is also affected by the kind of solvent. Table 2 shows the reaction rate at 60 °C for Eq. 1.

The amount of the pyridine derivative employed was 50-molar equivalent for the PC-metal complex, so that the rate constants were estimated for the forward reaction(k_1) as the first order and the reverse(k_{-1}) one as the second order.[13] The value of $\Delta\Delta G$ (temperature-dependence) and the ratio of k_1 to k_{-1} (fixing of colored species) were large in a polar aprotic solvent. Since a protic solvent solvates the PC^{-}–M and $Py^{+}H$ combination strongly and increases the anion content, strong absorption is induced even at a low temperature.[14] On the other hand, a polar aprotic solvent appears to predominantly solvate the pyridinium cation formed by protonation at an elevated temperature, as compared with an undissociated metallophthalein having a bulky molecular size. This causes a large temperature dependence of thermochromism in an aprotic solvent. The predominant solvation with an aprotic solvent stabilizes the pyridinium cation, so that proton recombination may be retarded in a polar aprotic solvent.[15]

Experimental

Solvents were purified by distillation under reduced pressure. All chemicals were used as supplied. Visible absorption spectra were recorded on a Hitachi 200-10 and a Shimadzu UV-160 spectrophotometer. Absorbance was measured for 1.5×10^{-3} mol dm^{-3} dye solution (2:98 H_2O-solvent) containing 9×10^{-3} mol dm^{-3} metal nitrate and 7.5×10^{-2} mol dm^{-3} pyridine derivative at a given temperature.

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