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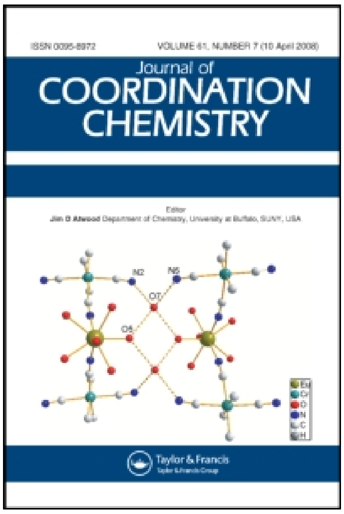

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COMPLEXES OF 2-[(2-HYDROXY-5-CHLOROPHENYL)AZO]-1,8-DIHYDROXYNAPHTHALENE-3,6-DISULFONIC ACID WITH VO(IV), Ni(II) AND Cd(II)

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Acid dissociation constants of the title multidentate ligand (PACA) consisting of both chlorophenolylazo and chromotropic acid fragments were elucidated as $pK_{a1} = 7.27$ (from HO– at the 1-position of the chromotropic acid moiety) and $pK_{a2} = 10.54$ (from HO– in the chlorophenol moiety), by a comparison with an analogous ligand, 2-[(3-chlorophenyl)azo]-1,8-dihydroxynaphthalene-3,6-disulfonic acid(BACA). Coordination modes of VO(IV), Ni(II), and Cd(II) with PACA, BACA, and 2-[(3-chlorophenyl)azo]-1-hydroxynaphthalene-3,6-disulfonic acid(BARGA) were studied by means of spectroscopy and polarography in aqueous solution. Stability constants of the PACA complexes [M(HL)] with VO(IV), Ni(II), and Cd(II) are governed by HSAB properties.

KEYWORDS: Multidentates, coordination selectivity, VO(IV), Ni(II), Cd(II), stability constants

INTRODUCTION

In previous papers the coordination selectivity of the multidentate ligand, 7-[(3,5-dihalo-2-pyridyl)azo]-8-hydroxyquinoline-5-sulfonic acid (X_2PAHQS) toward various metal ions chosen from a standpoint of HSAB properties was studied in detail in aqueous solution[1–3] by means of absorption spectroscopy, polarography and Raman spectroscopy.

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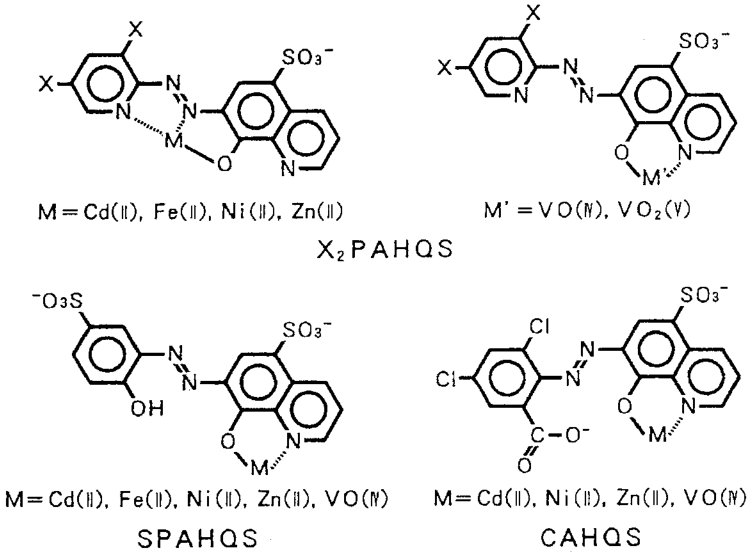
In the X_2PAHQS case, it was shown that X_2PAHQS coordinated selectively using N,N,O-sites toward Cd(II)[1] as a soft acid, and Fe(II),[3] Ni(II)[1] and Zn(II)[1] as border line acids. By N,N,O-complexation, two five-membered rings, scarcely strained (by inspection of molecular models), are formed as shown in Scheme 1. For VO(IV)[2] and VO_2(V)[3] as hard acids, X_2PAHQS coordinated selectively using N,O-bidentate sites in the 8-quinolinol moiety. Thus, in the case of X_2PAHQS, selectivity is mainly governed by HSAB properties.

Secondly, we reported the coordination selectivity of the multidentate ligand, 7-[(2-hydroxy-5-sulfophenyl)azo]-8-hydroxyquinoline-5-sulfonic acid(SPAHQS,[4] Scheme 1), toward Cd(II), Fe(II), Ni(II), Zn(II), and VO(IV) in aqueous solution to investigate the effects of variation of ring-members. That is, if SPAHQS acts as an O,N,O-terdentate ligand, the chelate formed is expected to have one five-membered and one six-membered ring. As a result, it was shown that SPAHQS coordinated selectively by N,O-bidentate sites in the 8-quinolinol moiety regardless of hardness (or softness) of the metal ion and of ligating atoms in SPAHQS, *i.e.*, in the case of SPAHQS, selectivity is governed by steric restrictions on chelate rings formed.

Finally, we reported coordination modes of a new multidentate ligand 7-[(3,5-dichloro-2-carboxyphenyl)azo]-8-hydroxyquinoline-5-sulfonic acid(CAHQS,[5] Scheme 1) in aqueous solution to explore the effect of ring-member variation on selectivity toward Ni(II), Zn(II), Cd(II) and VO(IV). If CAHQS acts as a terdentate ligand toward metal ions by using O,N,O- (O-atom in carboxylate, N-atom of azo group, O-atom in 8-quinolinol) sites, two six-membered rings would be formed. The study showed that all metal ions coordinated selectively to N,O-bidentate sites of the 8-quinolinol fragment regardless of metal ion's hardness (or softness) as in the SPAHQS[4] case (also illustrated in Scheme 1). In other words, the selectivity of CAHQS toward metal ions is also governed mainly by steric restrictions.



M = Cd(II), Fe(II), Ni(II), Zn(II)   M' = VO(IV), VO_2(V)

X_2PAHQS

M = Cd(II), Fe(II), Ni(II), Zn(II), VO(IV)   M = Cd(II), Ni(II), Zn(II), VO(IV)

SPAHQS   CAHQS

Scheme 1 Metal chelates of X_2PAHQS, SPAHQS and CAHQS.

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Here we extend our study to the ligand PACA (Scheme 2), which has a hard HO– group instead of a relatively soft N-atom (in the 8-quinolinol fragment in X_2PAHQS, SPAHQS, and CAHQS) to investigate the influence of this hard environment of PACA toward VO(IV) (hard acid), Ni(II) (border line acid) and Cd(II) (soft acid). This paper describes first the proton dissociation processes of PACA and of analogous ligands (*vide infra*), then the coordination selectivities of these ligands toward the above metal ions by means of spectrophotometry and polarography, and finally complexing modes and the stability constants of the metal complexes. For comparative studies, 2-[(3-chlorophenyl)azo]-1,8-dihydroxynaphthalene-3,6-disulfonic acid(BACA) was prepared to examining the coordination ability of the O-atom in the chlorophenol fragment of PACA. In addition, 2-[(5-chlorophenyl)azo]-1-hydroxynaphthalene-3,6-disulfonic acid(BARGA) was also prepared to study the effect of an O-atom at the 8-position in the chromotropic acid moiety in BACA on complexation, as shown in Scheme 2.

EXPERIMENTAL

Reagents

Reagent grade PACA was commercially obtained (Tokyo Kasei) and was used without further purification. BACA was synthesized through a coupling reaction. Commercial 3-chloroaniline (10 mmol) was dissolved in 250 cm^3 of a mixture (1 : 1) of dilute hydrochloric acid (pH 1–2) and methanol at 0°C. The aniline was diazotizated by dropwise addition of an aqueous solution (20 cm^3) of sodium nitrite (20 mmol) to the above mixture. Small amounts of an aqueous alkaline solution (pH 9–10) of 1,8-dihydroxynaphthalene-3,6-disulfonic acid (10 mmol) were added to the above solution containing the diazonium salt. The mixture was refluxed for 24 h at 60°C, then the solution was evaporated to dryness to give a crude product. The product was washed with acetone (100 cm^3), purified by recrystallization from water, then dried over silica gel. Yield, 36%; mp (decomp) >300°C. Found: C,

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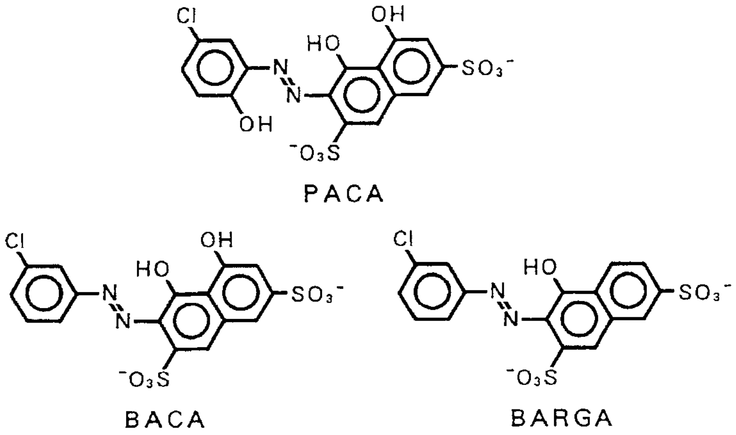

PACA

BACA

BARGA

Scheme 2 Chemical formulae of PACA, BACA and BARGA.

33.73; H, 2.52; N, 5.15%. Calcd. for $C_{16}H_9N_2O_8S_2ClNa_2 \cdot 3.5H_2O$: C, 33.96; H, 2.85; N, 4.95%. IR: 1379 cm^{-1} ($\nu_{N=N}$). ^1H NMR (DMSO-d_6): $\delta = 14.87$ (1H, s, OH), 12.63 (1H, s, OH), 8.07–7.22 (6H, m, aromatic H's), 7.61 (1H, s, H-4).

BARGA was synthesized by a procedure similar to that for BACA, except 1-hydroxynaphthalene-3,6-disulfonic acid was used instead of 1,8-dihydroxynaphthalene-3,6-disulfonic acid as a coupling component. Yield, 28%; mp (decomp) >300°C. Found: C, 34.41; H, 2.71; N, 5.02%. Calcd. for $C_{16}H_9N_2O_7SClNa_2 \cdot 4H_2O$: C, 34.39; H, 3.07; N, 5.01%. IR: 1383 cm^{-1} ($\nu_{N=N}$). ^1H NMR (DMSO-d_6): $\delta = 16.03$ (1H, s, OH), 8.72–7.50 (7H, m, aromatic H's), 7.66 (1H, s, H-4).

Aqueous VO(IV), Ni(II), and Cd(II) solutions were prepared as perchlorates. The concentrations of the metal ions were determined by the usual EDTA titration. All other chemicals used were of analytical or equivalent grade.

Measurements

^1H NMR spectra were obtained on a JEOL PMX60-SI NMR spectrometer. IR spectra were recorded on a JASCO A-102 spectrophotometer (KBr disk). Dissociation constants of the ligands and stability constants of the complexes were obtained spectrophotometrically on a Hitachi 220A recording spectrometer. Polarograms were recorded on a Yanaco P-1100 polarographic analyzer in an aqueous solution containing 0.1 mol dm^{-3} KNO_3 as supporting electrolyte, and 0.01% gelatin as a maximum suppressor. A three-electrode cell was used, in which the working electrode was a dropping mercury electrode (DME); the auxiliary electrode was a platinum coil. A saturated calomel electrode (SCE) was used as the reference. The DME had the following characteristics: $m = 2.02$ mg s^{-1}, $t = 1.00$ s/drop at −0.5V *vs* SCE, in electrolytic solution at pH 7.0. The pH of the sample solutions for both spectrophotometric and polarographic measurements was adjusted by an appropriate buffer solution, and was read on an Hitachi-Horiba F-13 pH meter immediately after the measurements.

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RESULTS AND DISCUSSION

Electronic spectra and dissociation constants of PACA

Figure 1 shows electronic spectra of PACA at various pH values. The fully protonated species (curve a) gives two dominant peaks at 18,500 cm^{-1} corresponding to the $\pi^* \leftarrow \pi$ transition of the azo group[6,7] and around 32,500 cm^{-1} due to chromotropic acid.[8,9] The absorption bands are shifted bathochromically upon deprotonation (curves b–d). Among them, the shift in the 16,900–19,100 cm^{-1} region reflects deprotonation of HO– at the 1-position in the chromotropic acid fragment, whereas the shift in the 31,000–33,000 cm^{-1} region reflects deprotonation at the chlorophenolate oxygen atom.[8]

Miyata *et al.*[10,11] deduced acid dissociation processes for PACA, which was used as a colorimetric reagent for alkali earth metal ions. In their reports, the sequence of dissociation of the two protons was not determined.

In this study, it was found that the first dissociation would occur from HO– in the chromotropic acid fragment, judging from a comparison between $pK_{a1} = 7.27$

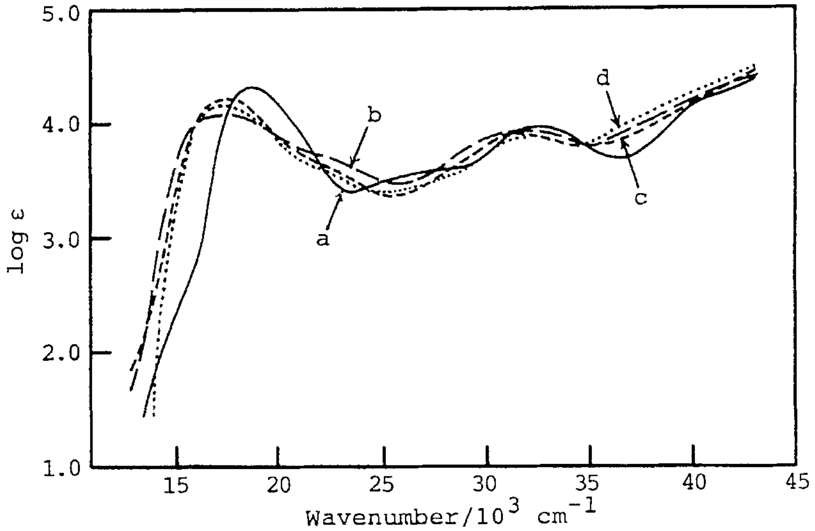

Figure 1 Absorption spectra of PACA in aqueous solution; pH: a = 5.15 (species H_3L); b = 8.21 (species H_2L); c = 11.15 (species HL); d > 14; 25.0 ± 0.5°C.

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for PACA and pK_{a1} = 8.21 for BACA which has no chlorophenolic proton, as summarized in Table 1. Successively, the dissociation from HO– in the chlorophenol moiety would occur as illustrated in Scheme 3. The dissociation from HO– in the 8-position in the chromotropic acid moiety (pK_{a3}) is considered to be very difficult, as reported in the literature[12,13] (15.6 for chromotropic acid itself, and 14.64 for phenylazochromotropic acid). Actually, the pK_{a3} value in this study was too large to determine in aqueous solution. The dissociation constant of BARGA (10.47) is consistent with the literature value 10.66 for 1-hydroxy-2-(phenylazo)-naphthalene-3,6-disulfonic acid[13] which has no chlorine in comparison with BARGA.

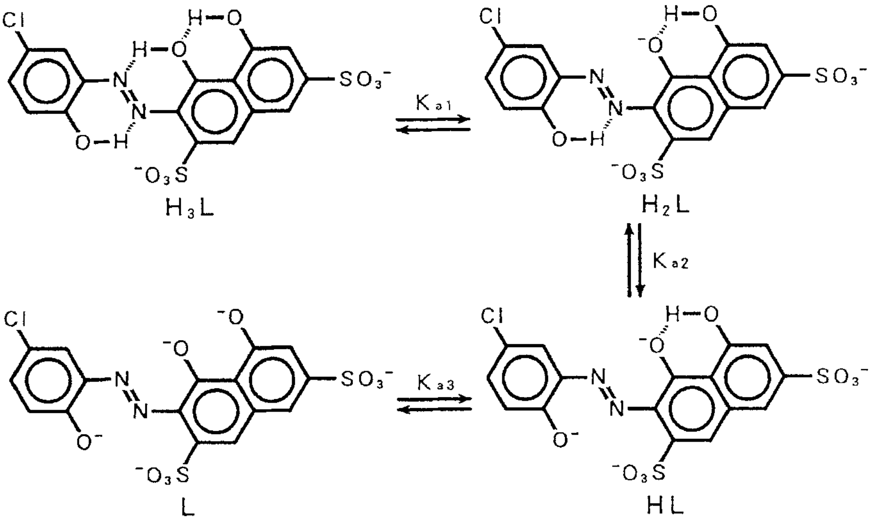
Polarograms of ligands and their metal complexes

To investigate the coordination mode of the ligands containing azo groups against metal ions, comparison of reduction potentials for the azo group in the free ligand and in the metal complexes is quite useful to judge whether the N-atom in the azo group coordinates to metal ion or not.[1–3,7,8] Figure 2 shows potential variations of the azo groups for free ligands and their metal complexes with pH over *ca* 2–12. A

Table 1 Dissociation constants.[a]

Ligand	pK_{a1}	pK_{a2}	pK_{a3}
PACA	7.27	10.54	>14
BACA	8.21[b]	>14	
BARGA	10.47		

[a] Aqueous solution, μ = 0.1($NaClO_4$), 25.0 ± 0.5°C. [b] 1-hydroxy moiety. Errors are within ±0.05 in pK_{ai} units.



Scheme 3 Proton dissociation processes of PACA.

linear relation for free PACA ($E_{1/2}$ = -0.05pH $-$ 0.08, r = 0.998) was found through the pH range studied. The potentials for the VO(IV) complex at pH< 3 are almost the same as those for free PACA, then at pH 3–9 they are shifted to a negative region ($E_{1/2}$ = -0.06pH $-$ 0.09, r = 0.997), showing stabilization by a ngative shift effect.[1,17–19] At pH> 9 the potentials lie again on the line of free PACA. This means that the VO(IV) complex is dissociated by the hydrolysis of the VO(IV) ion,[2,3,8] *e.g.*, to give $(VOOH)_2^{2+}$, $VO(OH)_2$ and so on. Likewise, potential

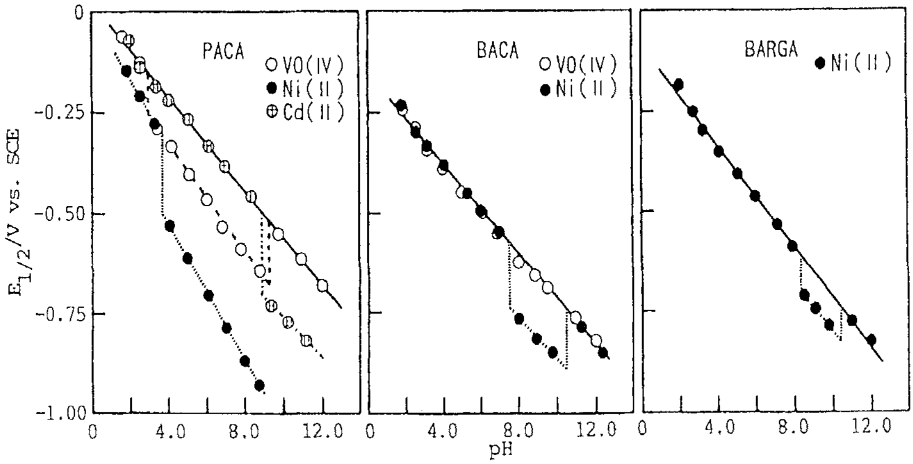


Figure 2 Relation between pH and half-wave potentials of PACA, BACA, and BARGA and their metal complexes; [ligand] = [metal] = 2.00×10^{-4} mol dm^{-3}, μ = 0.1 ($NaClO_4$), 0.01% gelatin, 24 ± 2°C. The solid lines depict the reduction potentials of free ligands.

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variations for the Cd(II)-PACA complex at pH> 8.3 are also shifted to the negative side by the same effect.[1,17–19] For the Ni(II)-PACA complexation, the relation at pH< 3 is represented by $E_{1/2} = -0.09\ \mathrm{pH} + 0.01$ ($r = 0.997$), whose slope in this pH range is different from that for free PACA. This slope difference is not explained at the present stage. In any case, for the PACA complexation with VO(IV), Ni(II), and Cd(II), these polarographic results strongly indicate that PACA coordinates as a terdentate by using O,N,O–(O-atom in chlorophenolate, N-atom of azo group, O-atom at 1-position in chromotropic acid) sites.

Potential variations of the azo groups for free BACA and its VO(IV) and Ni(II) complexes are illustrated in Figure 2. For free BACA, a linear relation ($E_{1/2} = -0.06\mathrm{pH} - 0.17$, $r = 0.996$) was observed. Potential variations of the VO(IV)–BACA complex lie on the straight line for BACA itself at any pH, showing that no bonding of N-atom in the azo group with VO(IV) take place. Thus, as one of the possible structures for the BACA–VO(IV) complex, an O,O-chelate is assumed to be formed as illustrated in Scheme 4, because released proton number upon complexation is 2 (see Table 2), hydrolysis of VO(IV) is not great at pH 2.34 – 4.23 and a similar structure for the Cu(II)-chromotropic acid complex is reported.[20] On the other hand, for the Ni(II)–BACA complex, the potentials at pH 7.5–10.5 are shifted negatively. Namely, the N-atom of the azo group is used for chelation.

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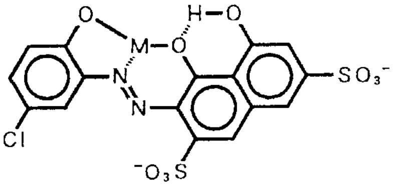
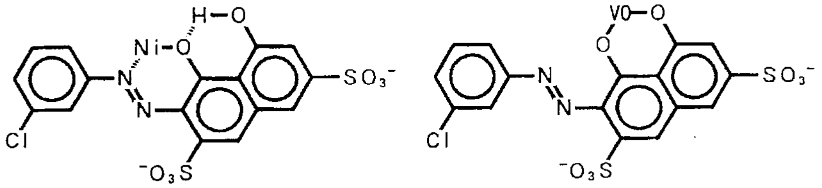
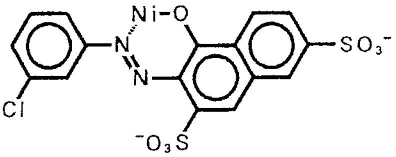


M : VO (IV), Ni (II), Cd (II)

PACA Complexes



BACA Complexes



BARGA–Ni Comlex

Scheme 4 Structures of metal complexes.

Table 2 Complexing pH range, equilibrium mode, maximum wavenumber (molar absorptivity), and stability constants for complexes.[a]

Ligand	pH Range	Equilibrium	$\tilde{\nu}_{max}/10^3 cm^{-1}(\varepsilon_{max}/10^4)^b$	$\log\beta^c$
PACA	0.90–4.23	$VO + H_3L \Leftrightarrow VO(HL) + 2H$	17.6(1.36)	30.28
	5.95–7.88	$VO(HL) + H_3L \Leftrightarrow VO(HL)_2 + 2H$	17.5(1.12)	39.35
	3.01–5.38	$Ni + H_3L \Leftrightarrow Ni(HL) + 2H$	18.2(1.96)	22.30
	5.50–7.34	$Cd + H_3L \Leftrightarrow Cd(HL) + 2H$	18.1(1.54)	12.85
BACA	2.34–4.23	$VO + H_2L \Leftrightarrow VOL + 2H$	19.8(2.59)	33.72
	5.98–8.02	$Ni + H_2L \Leftrightarrow Ni(HL) + H$	19.8(1.81)	5.58
	8.09–9.27	$Ni(HL)(H_2O)_2 \Leftrightarrow Ni(HL)(OH)_2 + 2H$	19.2(2.05)	16.28
BARGA	6.64–9.58	$Ni + HL \Leftrightarrow NiL + H$	20.6(1.69)	7.96

[a] Aqueous solution, $\mu = 0.1(NaClO_4)$, 25.0 ± 0.5°C. [b] $\pi^* \leftarrow \pi$ absorption of azo group. [c] See definitions of β in text. All errors are within ±0.05 in $\log\beta$ units.

For free BARGA, a linear relation ($E_{1/2} = -0.05pH - 0.21$, $r = 0.996$) was obtained. For the Ni(II)-BARGA complex, a negative shift at pH 8.0–10.5 was seen. This shift also demonstrates coordination between the N-atom in the azo group and Ni(II).

Complexing Equilibria, Calculation of Stability Constants, and Structure of Complexes

Aqueous solutions containing the ligands and metal ions (ligand:metal ion = 1:10 ~ 1:33) showed spectroscopic changes with pH variation, having clear isosbestic points in the pH ranges as shown in Table 2. All of the released proton numbers upon complexation were determined graphically from the slope of the straight line by plots between either pH in equations (*1*), (*3*)–(*6*) or α_L in equation (*2*) *vs* the first term of the right hand side in each equation (*vide infra*). Furthermore, all compositions (M:L) were confirmed by the continuous variation method, in all equilibrations.

On the basis of the acid dissociation constants of the ligands, the stability constants of the complexes with PACA of the type $M + H_3L \Leftrightarrow M(HL) + 2H$ ($M = VO(IV)$, Ni(II), and Cd(II)) are calculated by equation (*1*), where C_M stands for the initial metal ion concentration.

$$\log\beta_{M(HL)} = \log\{[M(HL)]/[H_3L]\} - 2pH - \log C_M + pK_{a1} + pK_{a2} \qquad (1)$$

From the polarographic results, the metal ions in M(HL) coordinate with O,N,O-sites in PACA. Thus, a structure has one five- and two six-membered rings including a hydrogen bond ring as shown in Scheme 4. For the set VO(IV)-PACA, the presence of another equilibrium at pH 5.95–7.88 of the type $VO(HL) + H_3L \Leftrightarrow VO(HL)_2 + 2H$ was confirmed. The stability constant of the complex $VO(HL)_2$ is obtained from equation (*2*).

$$\log\beta_{VO(HL)_2} = \log\{[VO(HL)_2]/[VO(HL)]\} - \log(C_L/\alpha_L) + \log\beta_{VO(HL)} \qquad (2)$$

Here $C_L = ([H_3L] + [H_2L] + [HL])$, $\alpha_L = \{([H]^2/K_{a1}\cdot K_{a2}) + ([H]/K_{a2}) + 1\}$, and $\beta_{VO(HL)}$ corresponds to that in equation (*1*).

In case of the reaction with BACA, $VO + H_2L \Leftrightarrow VOL + 2H$, the stability constant was calculated from equation (*3*).

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$$\log\beta_{VOL} = \log([VOL]/[H_2L]) - 2pH - \log C_{VO} + pK_{a1} + pK_{a2} \quad (3)$$

On the basis of the polarographic results, VO(IV) in the VO(IV)-BACA complex is thought to coordinate to O,O-sites as shown in Scheme 4. It can be seen from Table 2 that, in the Ni(II)-BACA complexation, there are two equilibria, *i.e.*, one at pH 5.98–8.02 and the other in the region pH 8.09–9.27.

Figure 3 shows spectra of a mixture of Ni(II) and BACA at various pH values. The changes at pH 5.98–8.02, having isosbestic points at 440 and 553 nm, correspond to an equilibrium $Ni + H_2L \Leftrightarrow Ni(HL) + H$. In this case, the stability constant of Ni(HL) is calculated by equation (*4*). Ni(II) in Ni(HL) coordinates to N,O-sites of BACA, based on the polarographic data, and thus two six-membered rings involving a hydrogen bond are formed, as illustrated in Scheme 4.

$$\log\beta_{Ni(HL)} = \log\{[Ni(HL)]/[H_2L]\} - pH - \log C_{Ni} + pK_{a1} \quad (4)$$

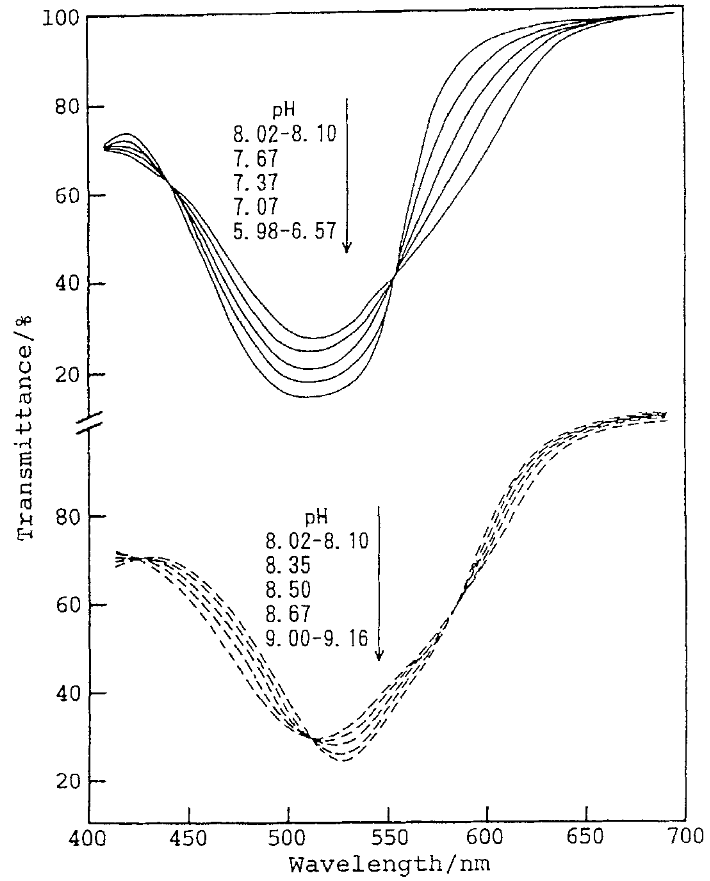

Figure 3 Absorption spectra of mixtures of Ni(II) and BACA in aqueous solution at various pH values; $[Ni^{2+}] = 3.00 \times 10^{-4}$ mol dm^{-3}, $[BACA] = 3.12 \times 10^{-5}$ mol dm^{-3}, $\mu = 0.1(NaClO_4)$, 25.0 ± 0.5°C.

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The structural difference of the BACA complexes with VO(IV) and Ni(II) may be explained as follows. Hard VO(IV) commonly prefers to bind with relatively hard O,O-sites without using the N-atom of the azo group, whereas Ni(II) as a border line acid is prone to bind to N,O-sites by using the relatively soft N-atom of the azo group. As is shown also in Figure 3, the spectra of the Ni(II)-BACA mixture at pH 8.09–9.27 show clear isosbestic points at 420, 510, and 580 nm. These changes would be due to a hydrolysis equilibrium[18] of the Ni(II) complex, $Ni(HL)(H_2O)_2 \Leftrightarrow Ni(HL)(OH)_2 + 2H$, in which released proton numbers, composition of the complex, and species of BACA were carefully determined. In this case, the stability constant of $Ni(HL)(OH)_2$ is obtained from equation (*5*).

$$\log\beta_{Ni(HL)(OH)_2} = \{[Ni(HL)(OH)_2]/[Ni(HL)]\} + \log\beta_{Ni(HL)} - 2pH + 2pK_w \qquad (5)$$

In equation (*5*), the value of $\beta_{Ni(HL)}$ corresponds to that in equation (*4*), and $pK_w = 14$ is adopted for the calculation. No data for Cd(II)-BACA were listed in Table 2, because neither color changes due to complexation nor isosbestic points attributed to complexation equilibria were observed at any pH.

Finally, in case of $Ni + HL \Leftrightarrow NiL + H$ with BARGA, the stability constant was calculated by equation (*6*).

$$\log\beta_{NiL} = \log([NiL]/[HL]) - pH - \log C_{Ni} + pK_{a1} \qquad (6)$$

The structure of the Ni(II)-BARGA complex which has one six-membered ring using N,O-sites, is represented on the basis of the polarographic results in Scheme 4. Although some hydroxo-complex formation for Ni(II)-BARGA at pH> 10 was observed, no data which can be used to calculate a stability constant were obtained. Furthermore, no complexation of VO(IV) or Cd(II) with BARGA was observed under these conditions.

The stability constants corrected finally for the side reaction coefficient[19] of the metal ions are listed in Table 2. The magnitude of the stability constants of M(HL) with PACA is in the order VO(IV) > Ni(II) > Cd(II), where each difference in $\Delta\log\beta$ amounts to 8~9. This finding is in accord with the decreasing order of hardness of the metal ions studied. In other words, the coordination ability of PACA toward metal ions is mainly governed by HSAB properties.

We described previously[4,5] that Raman spectroscopy is quite useful to judge whether the N-atom in the azo group coordinates to metal ion or not (by measuring —N=N— vibrations in the region 1,200–1,700 cm^{-1}.[21] A study of Raman spectra, however, was unsuccessful because of strong background fluorescence from the ligands used in this study.

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