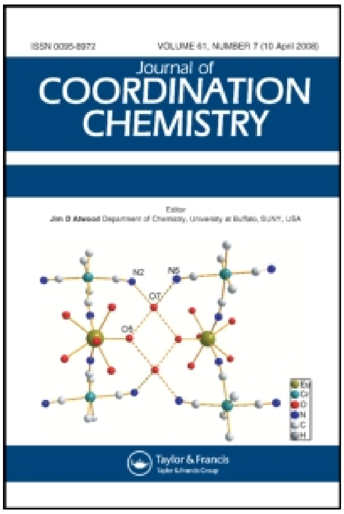

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COMPLEXATION AND COORDINATION SELECTIVITIES OF THE TETRADENTATE LIGAND 7-[(2-HYDROXY-5-SULFOPHENYL) AZO]-8-HYDROXYQUINOLINE-5-SULFONIC ACID WITH Fe(II), Ni(II), Zn(II), Cd(II) AND VO(IV)

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COMPLEXATION AND COORDINATION SELECTIVITIES OF THE TETRADENTATE LIGAND 7-[(2-HYDROXY-5-SULFOPHENYL) AZO]-8-HYDROXYQUINOLINE-5-SULFONIC ACID WITH Fe(II), Ni(II), Zn(II), Cd(II) AND VO(IV)

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The new title tetradentate ligand (SPAHQS), containing both phenylazo and 8-quinolinol fragments, was prepared. Proton-dissociation processes of the ligand and complexing equilibria with Fe(II), Ni(II), Zn(II), Cd(II), and VO(IV) were analyzed spectrophotometrically. Coordination modes of SPAHQS with these metal ions have been investigated by means of polarography and Raman spectroscopy in aqueous solution. It was established that the coordination selectivity of SPAHQS for such metal ions is mainly dependent on steric factors in the chelate ring formed, not on HSAB properties.

KEYWORDS: Tetradentate ligands, equilibria, selectivity, VO(IV), Fe(II), Ni(II), Zn(II), Cd(II)

INTRODUCTION

The coordination selectivity of metal ions with multidentate ligands containing more potentially chelating donor atoms is of fundamental interest in various areas.[1,2] Generally, selectivity would be ascribed to the basicity of a donating atom in the ligands and the kind of metal ion (HSAB properties), or to the size-match of the chelate ring and the steric restrictions of the ligand. The selectivity is, however, not fully and systematically understood at the present time.

In previous papers,[3] the selectivity of multidentate pyridylazo ligands, 7-[(3,5-dichloro(or bromo)-2-pyridyl)azo]-8-hydroxyquinoline-5-sulfonic acid (X_2PAHQS) toward a series of metal ions was studied in detail. As a result, it was concluded that

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coordination selectivities of X_2PAHQS were mainly dependent on the HSAB properties[4] of the chelate sites and the metal ions.[3]

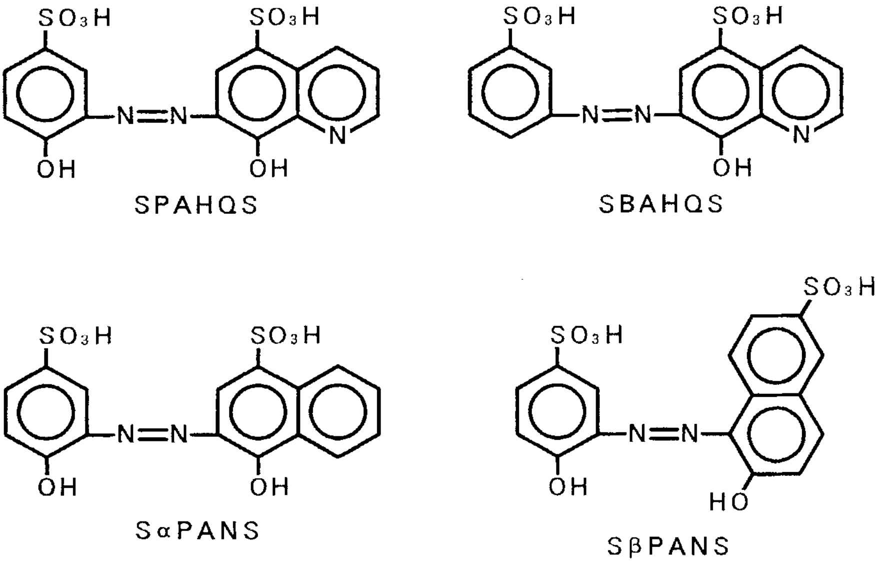
Here, we extend our study to a newly prepared tetradentate ligand, 7-[(2-hydroxy-5-sulfophenyl)azo]-8-hydroxyquinoline-5-sulfonic acid (SPAHQS), which contains a harder -OH group, as compared with the N-atom in the pyridine ring of X_2PAHQS.[3] This paper describes first the proton-dissociation of SPAHQS and of analogous ligands (*vide infra*), and complexing equilibria analyzed spectrophotometrically, then coordination selectivities to VO(IV) as a hard acid, to Fe(II), Ni(II), and Zn(II) as border line acids, and to Cd(II) as a soft acid, in aqueous solution. Selectivities are mainly determined by polarography and Raman spectroscopy.

For comparative studies, 7-[(5-sulfophenyl)azo]-8-hydroxyquinoline-5-sulfonic acid(SBAHQS) was newly prepared to investigate the coordination ability of the O-atom of a phenolate in SPAHQS. In addition, 2-[(hydroxy-5-sulfophenyl)azo]-1-hydroxynaphthalene-4-sulfonic acid (SαPANS), and 1-[(2-hydroxy-5-sulfophenyl)azo]-2-hydroxynaphthalene-6-sulfonic acid (SβPANS), as analogues of SαPANS, were also prepared to examine the function of the N-atom of the 8-quinolinol moiety in SPAHQS, as shown in Scheme 1.

EXPERIMENTAL

Reagents

SPAHQS was synthesized as follows. Commercial 2-aminophenol-4-sulfonic acid was diazotizated by the usual method.[5] To an aqueous solution containing



Scheme 1 Chemical formulae of the new ligands.

diazotizated phenol, commercial 8-hydroxyquinoline-5-sulfonic acid, with sodium hydroxide, was added. A crude product was then obtained by heating the solution for about 24 h at 60°C. The product was purified by recrystallization from water, then dried *in vacuo*. Yield, 54%; mp (decomp)>300°C. Found: C, 38.11; H, 1.91; N, 8.72%. Calcd. for $C_{15}H_9N_3S_2O_8Na_2$: C, 38.39; H, 1.93; N, 8.95%. IR ($\nu_{N=N}$): 1372 cm^{-1}. ^1H NMR (D_2O): δ = 7.12 (1H, d, J = 9.0 Hz, H-3'), 7.74 (1H, d, J = 3.0 Hz, H-6'), 7.98 (1H, dd, J = 7.2 and 2.7 Hz, H-3), 8.39 (1H, s, H-6), 8.65 (1H, dd, J = 7.2 and 1.8 Hz, H-4), 8.86 (1H, dd, J = 7.2 and 1.8 Hz, H=2'), 9.24 (1H, dd, J = 9.0 and 2.0 Hz, H-4'). The other three ligands were synthesized by a similar procedure. SBAHQS was recrystallized from water. Yield, 66%; mp (decomp) >300°C. Found: C, 34.96; H, 2.04; N, 8.12%. Calcd. for $C_{15}H_9N_3S_2O_7Na_2 \cdot H_2O \cdot 3/2NaCl$: C, 35.12; H, 1.96; N, 8.19%. IR ($\nu_{N=N}$): 1382 cm^{-1}. ^1H NMR (D_2O): δ = 6.92 (1H, dd, J = 9.0 and 5.4 Hz, H-3), 7.22 (1H, s, H-6), 7.30 (1H, t, J = 7.2 Hz, H-5'), 7.4-7.6 (3H, m, H-4, H-4', H-6), 8.17 (1H, d, J = 6.3 Hz, H-2), 8.24 (1H, d, J = 3.0 Hz, H-2'). SαPANS was purified by washing with ethanol. Yield, 51%; mp (decomp)>300°C. Found: C, 34.23; H, 3.81; N, 2.98%. Calcd. for $C_{16}H_{10}N_2S_2O_8Na_2 \cdot 4C_2H_5OH \cdot 3/2\ NaClO_4$: C, 34.47; H, 4.10; N, 3.25%. IR($\nu_{N=N}$):1385 cm^{-1}. ^1H NMR (D_2O): δ = 1.2 (12H, t, J = 7.0 Hz, 4 × CH_3 of $4C_2H_5OH$), 3.7 (8H, q, J = 7.0 Hz, 4 × CH_2 of $4C_2H_5OH$), 6.5-8.2 (8H, m, aromatic H's). SβPANS was purified by washing with ethanol and acetone. Yield, 27%; mp (decomp) >300°C. Found: C, 38.69; H, 5.66; N, 1.97%. Calcd. for $C_{16}H_{10}N_2S_2O_8Na_2 \cdot 4(CH_3)_2CO\text{–}\cdot 6C_2H_5OH \cdot 2NaClO_4$: C, 38.63; H, 5.35; N, 2.25%. IR ($\nu_{N=N}$): 1386 cm^{-1}. ^1H NMR (D_2O): δ = 1.2 (18H, t, J = 7.0 Hz, 6 × CH_3 of $6C_2H_5OH$), 2.2 (24H, s, 8 × CH_3 of $4(CH_3)_2CO$), 3.7 (12H, q, J = 7.0 Hz, 6 × CH_2 of $6C_2H_5OH$), 7.1-8.5 (8H, m, aromatic H's). The melting points of the products (>300°C) suggest that all the ligands were in the form of sodium salts ($-SO_3Na$). Except for SPAHQS, the ligands contained NaCl or $NaClO_4$, as shown above. Aqueous Ni(II), Zn(II), Cd(II) and VO(IV) solutions were prepared as perchlorates.[3] Aqueous Fe(II) stock solution was prepared from $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$, and was acidified with perchloric acid in order to prevent hydrolysis of Fe(II). Absence of traces of Fe(III) in the stock solution was checked by investigating its reaction with thiocyanate. The concentrations of the metal ions were determined by the usual EDTA-titration. All other chemicals, of analytical or equivalent grade, were used without further purification.

Measurements

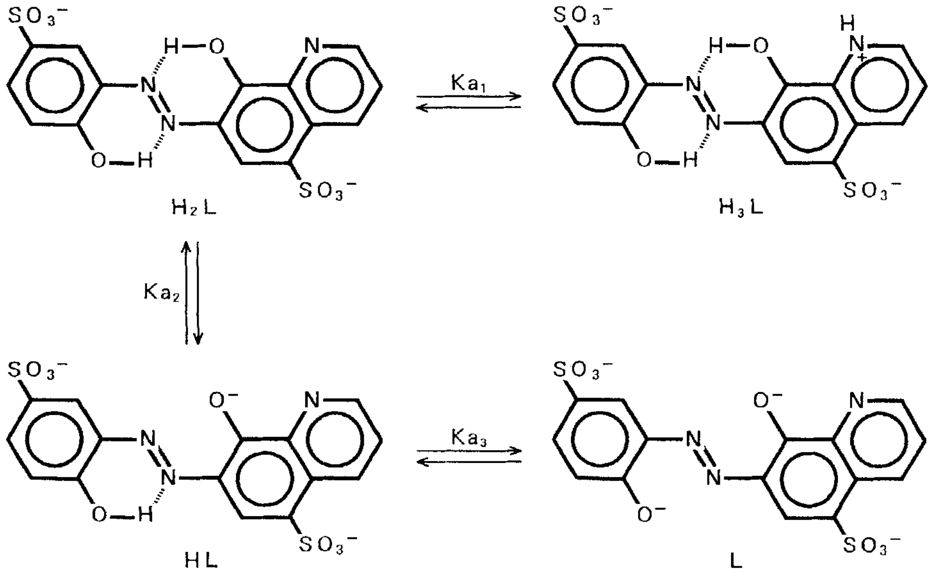
^1H NMR spectra were obtained on a JEOL JNM-EX90 FT NMR spectrometer. IR spectra were recorded on a JASCO A-102 spectrometer (KBr disk). Dissociation constants of the ligands and formation constants of the complexes were obtained spectrophotometrically using a Hitachi 220A recording spectrophotometer, and polarograms were recorded on a Yanaco P-1100 polarographic analyzer in aqueous solution.[3a] Electronic absorption spectra were recorded on a Hitachi U-4000 spectrophotometer. Raman spectra were recorded on a JASCO R-800 spectrometer equipped with an NEC GLG 3200 Ar^+ laser as exciting light source. The excitation wavelengths were 457.9 nm for SPAHQS and its Ni(II) complex, and 476.5 nm for SBAHQS and its Ni(II) complex.

RESULTS AND DISCUSSION

Proton Dissociation Constants of the Ligands

The proton-dissociation processes of SPAHQS, as an example for the ligands synthesized, are shown in Scheme 2. The sequence of dissociations for SPAHQS is considered to be at first that from HN^+ in 8-quinolinol, then from HO in 8-quinolinolate, and finally from HO in the phenol moiety, on the basis of a mutual comparison of these values and with those of analogous ligands,[2,6] and judging from literature values[7] obtained under the same conditions for each component of SPAHQS: pK_{a2} = 8.95–9.90 for 8-quinolinol, and pK_a = 9.98 for phenol, respectively. That is, in the lower pH range, two hydroxy groups form weak intramolecular hydrogen bonds with N-atoms in azo groups, simultaneously. With increasing pH, the HO proton in 8-quinolinol is dissociated prior to that of the phenolate, since the hydrogen bond formed between the former proton and the azo group is weaker than that of the latter due to the large bulkiness of the aromatic rings. After the dissociation of this proton, a comparatively strong hydrogen bond would be formed between the residual HO group in the phenolate and an N-atom in the azo group. Thus the pK_a values of the HO group in the phenolate ring are much larger than that of the quinolinolate (Table 1).

For SαPANS and SβPANS, likewise, the sequence of proton dissociation is thought to be at first from HO in the naphtholate (pK_{a1}), then from HO in the phenolate (pK_{a2}), because of hydrogen bond formation as shown in Scheme 3. The pK_{a1} values for SαPANS and SβPANS are quite similar in magnitude, owing to the fact that no hydrogen bond forms between the HO group in the naphtholate ring and the azo group. The difference of pK_{a2} values between SαPANS and SβPANS

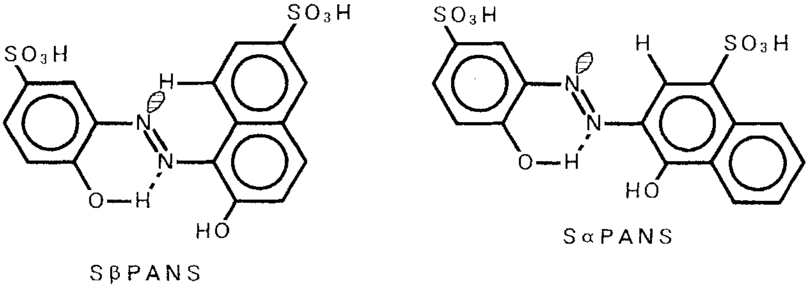


Scheme 2 Proton dissociations in SPAHQS.

Table 1 Dissociation Constants.[a]

Ligand	pK_{a1}	pK_{a2}	pK_{a3}
SPAHQS	2.67	6.73	9.22
SBAHQS	2.80[b]	7.35[c]	
SαPANS	6.42[d]	10.69[e]	
SβPANS	6.51[d]	11.59[e]	

[a] Aq. soln., μ = 0.1 ($NaClO_4$), 25.0 ± 0.5°C.
[b] Quinoline.
[c] Quinolinolate.
[d] Naphtholate.
[e] Phenolate. All experimental errors are within ±0.05 pK_{ai} units.



Scheme 3 Intramolecular hydrogen bond and dipole-dipole interactions in the ligands.

amounts to *ca* 1. This difference is interpreted as illustrated in Scheme 3, *i.e.*, hydrogen bonding of SβPANS is additionally stabilized by ring formation due to dipole-dipole interaction between the naphtholate ring hydrogen atom and a lone pair on the N-atom in the azo group (fit for both direction and bond distance for dipole-dipole interaction of lone pair[3]). For SαPANS, neither spatial direction of the lone pair of electrons nor bond distance could make a strong dipole-dipole interaction as revealed by molecular models.

All dissociation constants obtained spectrophotometrically were calculated by the Hildebrand-Reilly method.[8]

Complexing Equilibria and Calculation of Stability Constants

Except for the Cd(II)-SαPANS and -SβPANS systems, all the aqueous solutions containing the ligands and metal ions (ligand: metal ion = 1: 10 ~ 1: 50 mixture) showed spectroscopic changes with pH variation having clear isosbestic points in the pH ranges as shown in Table 2. For the Cd(II)-SαPANS and -SβPANS sets, colour changes with metal complexation were too slight to observe, and these sets had no clear isosbestic points. The released protons upon complexation were determined by the Hildebrand-Reilly method.[8] In addition, the compositions of the complexes (metal to ligand) were analyzed by the continuous variation method. With Ni(II) and Cd(II) complexation with SPAHQS, two kinds of equilibria, *i.e.*, one in the lower pH range and the other in the higher pH range, were observed as shown in Fig. 1. For the other metal-ligand sets, there was only one simple equilibrium observed.

Table 2 Complexing pH Range, Equilibrium Mode, Maximum Wavenumber and Molar Absorptivity, and Stability Constants of VO(IV), Fe(II), Ni(II), Zn(II), and Cd(II) Complexes.[a]

Ligand	pH Range	Equilibrium	$\tilde{\nu}_{max}/10^3cm^{-1}$ $(\varepsilon_{max}/10^4)$	$\log\beta_{[M(HL)]}$	$\log\beta_{[ML]}$
SPAHQS	0-2.79	$VO + H_3L \Leftrightarrow VO(HL) + 2H$	22.3 (1.69)	16.31	
	0-4.00	$Fe + H_3L \Leftrightarrow Fe(HL) + 2H$	21.2 (1.53)	10.73	
	0-3.40	$Ni + H_3L \Leftrightarrow Ni(HL) + 2H$	21.1 (2.09)	14.13	
	5.78-8.45	$Ni(HL) \Leftrightarrow NiL + H$	19.8 (1.03)		16.03
	1.01-4.15	$Zn + H_3L \Leftrightarrow Zn(HL) + 2H$	21.3 (1.97)	12.20	
	3.83-6.92	$Cd + H_2L \Leftrightarrow Cd(HL) + H$	21.1 (2.29)	6.54	
	6.93-9.27	$Cd(HL) \Leftrightarrow CdL + H$	19.6 (1.44)		7.52
SBAHQS	0-3.57	$VO + H_2L \Leftrightarrow VOL + 2H$	24.8 (1.29)		15.07
	0-5.24	$Fc + H_2L \Leftrightarrow FeL + 2H$	24.4 (0.85)		9.70
	0.69-4.80	$Ni + H_2L \Leftrightarrow NiL + 2H$	23.0 (1.28)		12.46
	0.64-4.88	$Zn + H_2L \Leftrightarrow ZnL + 2H$	24.1 (1.22)		11.15
	5.09-7.59	$Cd + HL \Leftrightarrow CdL + H$	22.5 (1.22)		6.32
SαPANS	0-3.42	$VO + H_2L \Leftrightarrow VOL + 2H$	19.6 (0.77)		32.27
	2.11-5.39	$Fe + H_2L \Leftrightarrow FeL + 2H$	20.8 (0.64)		21.71
	2.05-5.33	$Ni + H_2L \Leftrightarrow NiL + 2H$	19.9 (1.15)		23.51
	3.27-5.85	$Zn + H_2L \Leftrightarrow ZnL + 2H$	20.0 (1.04)		18.05
SβPANS	0.28-2.70	$VO + H_2L \Leftrightarrow VOL + 2H$	20.7 (0.49)		34.28
	3.06-4.76	$Fe + H_2L \Leftrightarrow FeL + 2H$	21.2 (0.47)		23.87
	0-4.12	$Ni + H_2L \Leftrightarrow NiL + 2H$	20.8 (0.58)		26.00
	3.16-6.68	$Zn + H_2L \Leftrightarrow ZnL + 2H$	21.0 (0.52)		19.40

[a] Aq. soln., $\mu = 0.1$ ($NaClO_4$), 25.0 ± 0.5°C. Experimental errors are within ±0.1 log β units.

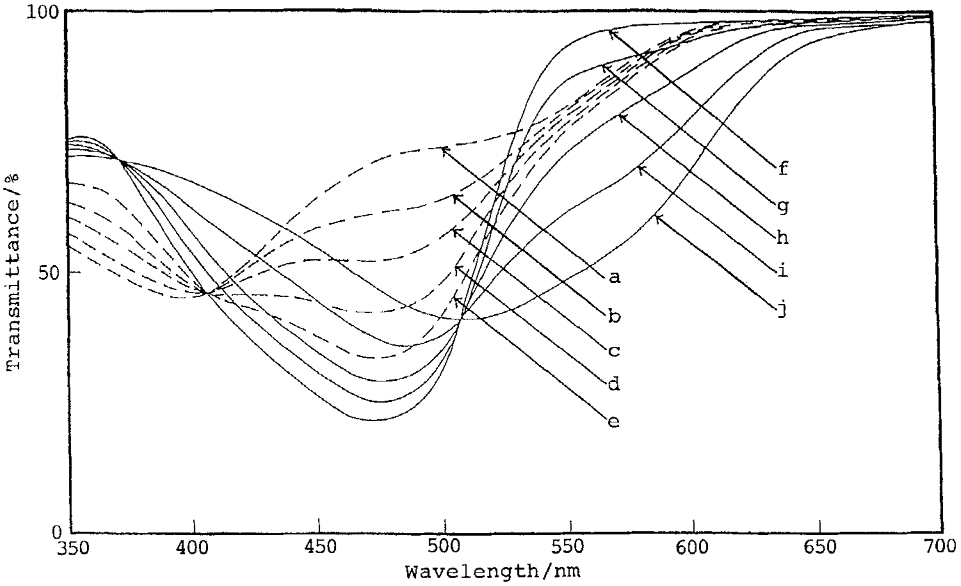


Figure 1 Absorption spectra of mixtures of Ni(II) and SPAHQS in aqueous solution at various pH values; pH:a = 0-0.64; b = 1.02; c = 1.86; d = 2.06; e = 2.32; f = 3.09-5.58; g = 6.63; h = 7.08; i = 7.50; j = 8.45-10.97; C_L = 3.01×10^{-5} mol dm^{-3}, C_{Ni} = 3.00×10^{-4} mol dm^{-3}, $\mu = 0.1$ ($NaClO_4$), 25.0 ± 0.5°C.

Stability constants were calculated using the following equations, where C_M stands for the initial concentrations of metal ions.

In equilibria for SPAHQS of the type $M + H_3L \rightleftharpoons M(HL) + 2H^+$, equation (*1*) was used,

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

For SPAHQS for $M(HL) \rightleftharpoons ML + H^+$, equation (*2*) was used,

$$\log\beta_{ML} = \log([ML]/[M]\,[L]) = \log([M]/[M(HL)]) + \log\beta_{M(HL)} - pH + pK_{a3} \qquad (2)$$

where $\log\beta_{M(HL)}$ corresponds to constants obtained from equation (1).

In case of the reaction $M + H_2L \rightleftharpoons M(HL) + H^+$ for SPAHQS, the stability constants were calculated from equation (*3*).

$$\log\beta_{M(HL)} = \log([M(HL)]/[M][HL]) = \log([M(HL)]/[H_2L]) - pH - \log C_M + pK_{a2} \qquad (3)$$

For the equilibria $M + H_2L \rightleftharpoons ML + 2H^+$ in the SBAHQS, SαPANS and SβPANS cases, equation(*4*) was used for the calculation of stability constants.

$$\log\beta_{ML} = \log([ML]/[M]\,[L]) = \log([ML]/[H_2L]) - 2pH - \log C_M + pK_{a1} + pK_{a2} \qquad (4)$$

Finally, in the case of $M + HL \rightleftharpoons ML + H^+$ for SBAHQS, the stability constant was calculated by using equation (*5*).

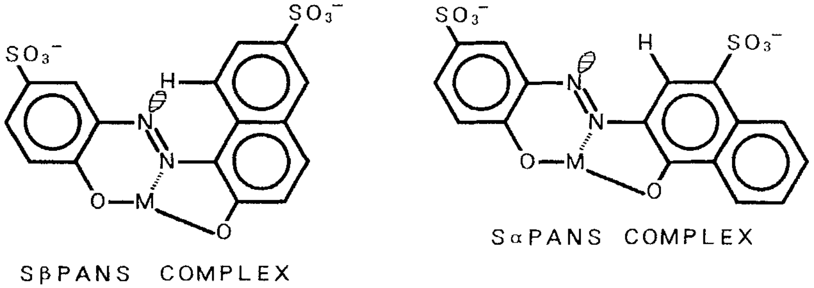
$$\log\beta_{ML} = \log([ML]/[M][L]) = \log([ML]/[HL]) - pH - \log C_M + pK_{a2} \qquad (5)$$

In any case, the released proton number upon complexations is determined graphically from a slope of the straight line between pH *vs* the first term of the right hand side in each equation.

The stability constants, corrected for reaction coefficients of the metal ions[9] are listed in Table 2. For complexes with SPAHQS and SBAHQS, direct comparison can not be made, owing to different compositions of the complexes (M(HL) for SPAHQS and ML for SBAHQS). It is likely, however, that the constants for SPAHQS complexes are larger than those for SBAHQS complexes, for all the metal ions. This can be explained by the conjugate effect of the phenol group of SPAHQS. Constants for the SβPANS complexes were larger than those of SαPANS for all metal ions. This is attributed to a stabilization effect (dipole-dipole interaction) as shown in Scheme 3. Furthermore, larger stability constants for SαPANS and SβPANS complexes, as compared with those of SPAHQS and SBAHQS complexes are interpreted in terms of the chelate effect. For complexation of SαPANS and SβPANS it is suggested that these ligands act as O, N, O-terdentates; thus, two five- and six-membered chelate rings are assumed to be formed (Scheme 4).

Polarograms of Ligands and Their Metal Complexes

To ascertain the coordination mode of the multidentate ligands containing the azo group with metal ions, measurements of reduction potentials for the azo group of the free ligand and metal complexes are quite useful in order to judge whether the N-atom in the azo group participates in bonding.[3]



Scheme 4 Five- and six-membered chelate ring formation.

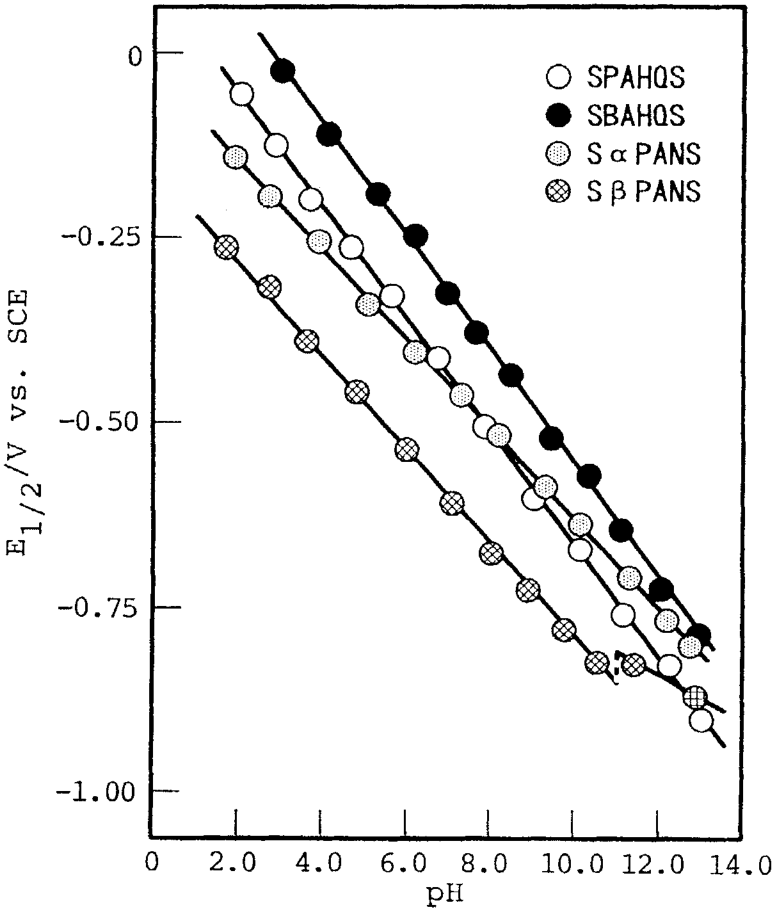


Figure 2 Relation between pH and half wave potentials of ligands; SPAHQS: $E_{1/2} = -0.074\mathrm{pH} + 0.088$ ($r = 0.999$); SBAHQS: $E_{1/2} = -0.075\mathrm{pH} + 0.187$ ($r = 0.998$); SαPANS: $E_{1/2} = -0.054\mathrm{pH} - 0.088$ ($r = 0.997$); SβPANS: $E_{1/2} = -0.055\mathrm{pH} - 0.079$ (pH = 2-11.5, $r = 0.989$), $E_{1/2} = -0.029\mathrm{pH} - 0.337$ (pH = 11.5 - 13); $C_L = 2.50 \times 10^{-4}$ mol dm^{-3}, $\mu = 0.1$ (KNO_3), 0.01% gelatin, 24 ± 2°C. The curve for SβPANS is shifted by 0.15 unit downward for clarity.

Figure 2 shows the relation between pH and reduction potential of the azo group in the ligands. A linear relation holds for all ligands over the pH range studied. It is noteworthy for S*β*PANS, however, that the potentials at *ca* pH > 11-12 are markedly shifted toward the positive region, because proton dissociation from HO in the phenolate ring will occur after destroying the strong hydrogen bond between the proton of HO and the N-atom of the azo group. Thus, the azo group is easily reduced at this pH.[10] For the other three ligands, the potentials were dependent on pH values, but independent of the kinds of ligand species because the hydrogen bond is weaker than that in S*β*PANS. The potentials of SPAHQS were on the negative side, as compared with SBAHQS. This can be interpreted by an electronegativity rule[11] for the reduction of organic compounds.

Figure 3 shows plots of pH *vs* reduction potential of azo groups in the metal complexes of SPAHQS and SBAHQS, where solid lines (a) and (b) represent free

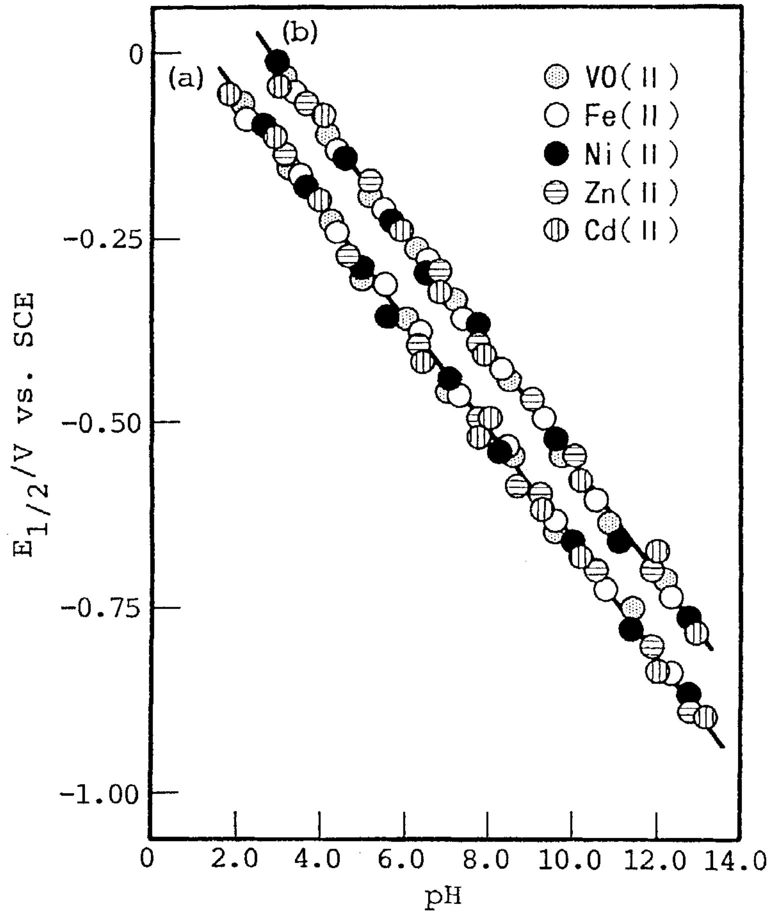


Figure 3 Relation between pH and half wave potentials of metal complexes with SPAHQS and SBAHQS; $C_L = 2.50 \times 10^{-4}$ mol dm^{-3}, $C_M = 2.50 \times 10^{-4}$ mol dm^{-3}, $\mu = 0.1$ (KNO_3), 0.01% gelatin, 24 ± 2°C.

SPAHQS and SBAHQS, respectively. It can be seen from this Figure that the potentials of all the metal complexes fall on the appropriate line. Therefore, this result strongly indicates that neither the N-atom of the azo group in SPAHQS nor in SBAHQS participates in metal complexation. In other words, complexation occurs only by the 8-quinolinol moiety, forming a five-membered N,O-chelate ring.[12]

The potential variations with pH for metal complexes with SαPANS are shown in Figure 4. Potentials of the complexes with Fe(II), Ni(II) and Zn(II) are markedly shifted to the negative side as compared with those of free SαPANS (a further negative shift at *ca* pH>9 for the Zn(II) complex is not yet understood). Variations for the Fe(II) complex are characteristic, *i.e.*, the potentials at pH < 4 are almost the same as those of free SαPANS, and at pH 4-9 they are shifted to the negative region (azo group is stabilized by hydrogen bond formation).[11,13,14] At pH > 9 the

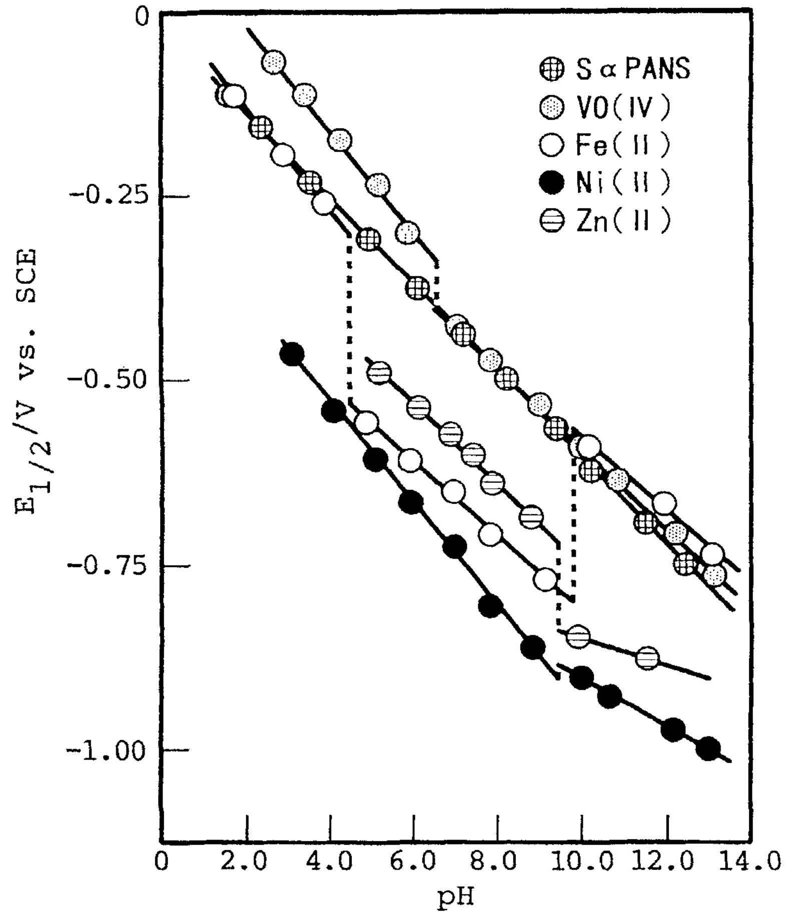


Figure 4 Relation between pH and half wave potentials of SαPANS and its metal complexes. The experimental conditions are the same as those in Fig. 3.

potentials lie again on the line for free SαPANS. In the final step at pH > 9, the Fe(II) complex is assumed to be dissociated (hydrolyzed). In the VO(IV) complex the potentials at pH < 6 are remarkably shifted to the positive side on complexation, due to the influence of the considerable electron-attracting ability of the VO(IV) ion[14] attached to the azo group.[11] At pH > 6, potentials of the VO(IV) complex lie again on the line of free SαPANS. This means that the VO(IV) complex is dissociated at these pH values.[16]

For potential variations with pH of the complexes with SβPANS, similar behaviour may be inferred. Accordingly, these observations also strongly demonstrate that, in complexes with SαPANS and SβPANS, O, N, O- (O-atom in the phenolate, N-atom adjacent to azo group in naptholate ring, O-atom in naptholate) chelates containing one five- and one six-membered ring are formed, as illustrated in Scheme 4.

Raman Spectra

Raman bands due to the azo group in the various compounds are known to be observed in the 1200-1700 cm^{-1} region.[17] Figure 5 shows Raman spectra of free SPAHQS in D_2O and H_2O solutions at several pH values (with excitation wavelength 457.9 nm). The spectrum (a) for D_2O solution at pD = 0.69, where two intramolecular hydrogen bonds between D and azo group as illustrated in Scheme 2 are formed, shows characteristic peaks at 1389, 1455, and 1596 cm^{-1}. For the H_2O solution of SPAHQS at pH = 0.90 (a'), the above peaks are shifted to higher wavenumber, *i.e.*, 1409, 1476, and 1624 cm^{-1}, respectively. In the spectrum (b), observed in D_2O solution at pD = 13.47, two intramolecular hydrogen bonds are destroyed and Raman peaks at 1380 and 1423 cm^{-1} are observed. For H_2O solution at pH = 12.16 (b'), peaks at 1379 and 1422 cm^{-1} are quite close to those found in D_2O solution (b). This means theat the Raman bands located in the region 1200–1700 cm^{-1} are attributable to stretching vibrations of the azo group in SPAHQS. Accordingly, the observations show that Raman spectroscopy can give useful information concerning coordination selectivity of the N-atom in the azo group towards metal ions, in addition to information from the polarographic method described above. As a representative example, the spectra of Ni(II) complexes with SPAHQS and SBAHQS in aqueous solution, in which SBAHQS is known to coordinate to Ni(II) by the N,O-bidentate of the 8-quinolinol moiety, are shown in Figure 6. The spectra of free SPAHQS at pH = 10.22 (a) and its Ni(II) complex at pH = 10.11 (a') are almost the same. This result strongly indicates that there is no participation of the N-atom of the azo group in coordination with Ni(II). This is reinforced by the Raman spectra of free SBAHQS at pH = 9.06 (b) with an excitation wavelength of 476.5 nm and of its Ni(II) complex at pH = 5.44 (b'), because of lack of differences in the number of peaks, frequencies, and general spectroscopic features.

For SαPANS and SβPANS, which are confirmed to act as O, N, O-terdentates with metal ions, no Raman spectra were obtained because of strong background fluorescence.

Finally, the compositions of all the complexes (metal: ligand) listed in Table 2 were 1:1. Accordingly, the formation of a tetrahedral structure for these complexes is not anticipated because of steric restrictions, since the three coordination sites, (O,N,O-) and (N, O-), lie in the same plane. For example, the electronic absorption

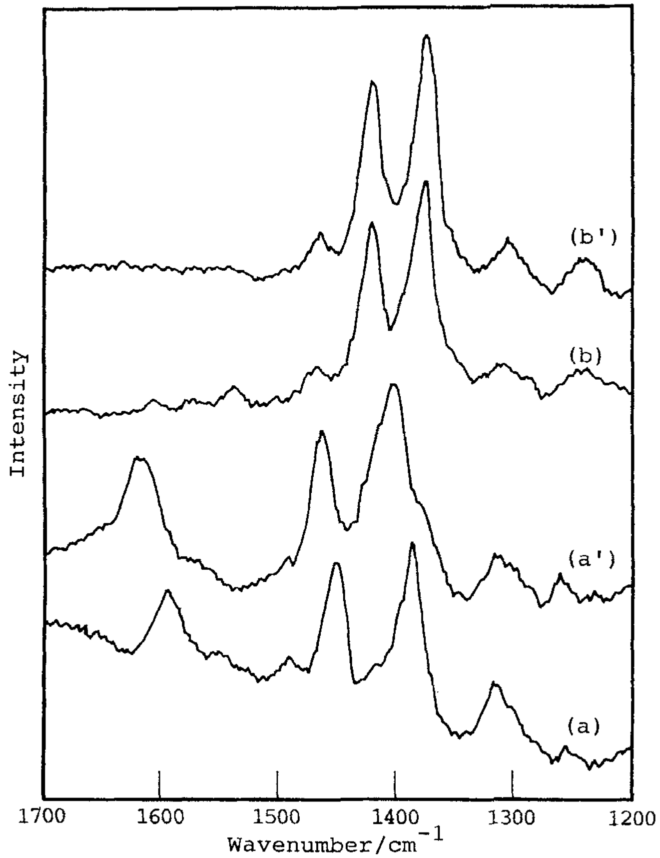


Figure 5 Raman spectra of SPAHQS in (a) D_2O at pD = 0.69; (a') H_2O at pH = 0.90; (b) D_2O at pD = 13.47; (b') H_2O at pH = 12.16.

spectra of the Ni(II) complexes with SPAHQS and SBAHQS show a band at *ca* 1100 nm, and with SαPANS and SβPANS at *ca* 820 nm, respectively; these are assigned to $d \rightarrow d$ transitions for high-spin d^8 electronic configurations. Accordingly, the formation of four-coordinated, square-planar structures is excluded by the appearance of these bands in the near infrared region.[18] If the structure is assumed to be six-coordinate, octahedral, three water molecules from solvent are coordinated (as [NiL $(H_2O)_3$]) for SαPANS and SβPANS, and four water molecules (as [NiHL $(H_2O)_4$] for SPAHQS and SBAHQS. For the other metal complexes, octahedral structures are formed.

In conclusion, the ligand SPAHQS selectively coordinates to Fe(II), Ni(II), Zn(II), Cd(II), and VO(IV) with the same N, O-bidentate of the 8-quinolinol fragment. This is caused by steric factors, especially the large strain in the five- and six-membered chelate rings in the O,N,O-terdentate (as evidenced by molecular models). That is, in contrast to the ligand X_2PAHQS[3] whose coordination selectivity is mainly dependent on HSAB properties,[4] the selectivity of SPAHQS towards metal ions is

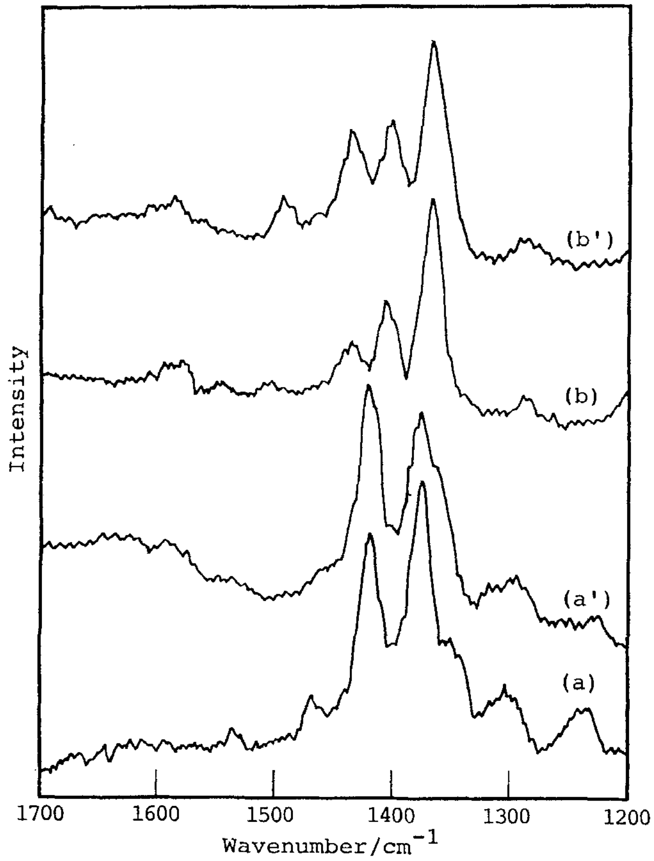


Figure 6 Raman spectra of free SPAHQS and SBAHQS and their Ni(II) complexes in aqueous soln.; (a) free SPAHQS at pH = 10.22; (a') SPAHQS-Ni(II) complex at pH = 10.11; (b) free SBAHQS at pH = 9.06; (b') SBAHQS-Ni(II) complex at pH = 5.44.

governed by steric factors, because the hardness (or softness) of the O,N,O-site is almost the same as that of the N,O-site.

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