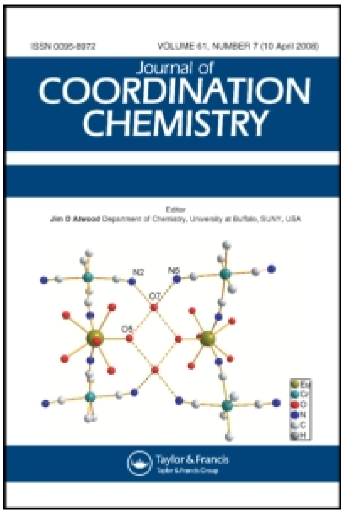

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COORDINATION SELECTIVITIES IN IRON(II) AND VANADIUM(V) COMPLEXES WITH THE MULTIDENTATE LIGANDS, 7-[(3,5-DIHALO-2-PYRIDYL)AZO]-8-HYDROXYQUINOLINE-5-SULFONIC ACID

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COORDINATION SELECTIVITIES IN IRON(II) AND VANADIUM(V) COMPLEXES WITH THE MULTIDENTATE LIGANDS, 7-[(3,5-DIHALO-2-PYRIDYL)AZO]-8-HYDROXYQUINOLINE-5-SULFONIC ACID

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The reactions of Fe(II) and V(V) with the title ligands were studied in aqueous solutions by focussing on the coordination selectivity of chelate sites using polarographic and spectrophotometric methods. Fe(II) ion, as a borderline acid, selectively coordinated to the comparatively soft N,N,O-terdentate chelate site containing an azo group; V(V) ion as a hard acid selectively bound to the relatively hard N,O-chelate site in the 8-quinolinol moiety. The complexing reactions of the two metal ions with the ligands 2-[(3,5-dihalo-2-pyridyl)azo]-1-hydroxynaphthalene-4-sulfonic acid, 1-[(3,5-dihalo-2-pyridyl)azo]-2-hydroxynaphthalene-6-sulfonic acid, and 7-[(4-chloro or unsubstituted phenyl)azo]-8-hydroxyquinoline-5-sulfonic acid were also studied for the comparative discussion.

Keywords: Coordination selectivity, Fe(II), V(V), multidentate ligands

INTRODUCTION

The selectivity of coordination modes of multidentate ligands containing two groups of potentially chelating donor atoms have become of interest for a variety of metal ions.[1,2] In our previous papers, the coordination behaviour of the new multidentate ligands, 7-[(3,5-dihalo-2-pyridyl)azo]-8-hydroxyquinoline-5-sulfonic acid (X_2PAHQS, X = Cl or Br, see Scheme), toward metal ions were studied in aqueous solution.[3] As a result, Ni(II), Zn(II), and Cd(II) ions, which are classified as soft or borderline acids, have been found to coordinate selectively to the N,N,O-terdentate moiety containing an azo group.[3a] On the contrary, VO(IV) (hard acid) bound selectively to the N,O-skeleton in the hydroxyquinoline (HQS) moiety.[3b]

In order to look more closely at the nature of the coordination selectivity of these multidentate ligands, in this work, the coordination selectivity of X_2PAHQS to Fe(II)

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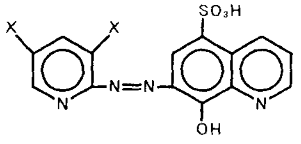
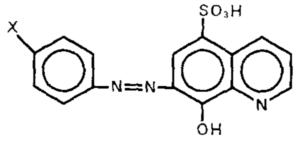
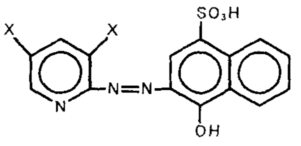


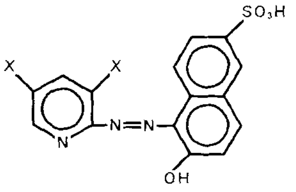
X_2PAHQS(X=Cl, Br)



BAHQS(X=H) ; ClBAHQS(X=Cl)



$X_2\alpha$PANS(X=Cl, Br)



$X_2\beta$PANS(X=Cl, Br)

and V(V) ions was investigated in detail. In the present work, Fe(II) ion was chosen as representative of a borderline acid, and V(V) of a hard acid. The Fe(II) case is interesting because it was expected to show an absorption band in near infrared region ascribable to metal-to-ligand charge transfer (CT) when coordinating to an N,N,O-terdentate containing an azo group.[2b,4] Tanaka *et al.*[5] have reported in detail complexation equilibria for V(V) with 8-quinolinol (which is an important fragment in X_2PAHQS). On the other hand, although pyridylazo ligands are very useful for the spectrophotometric determinations of trace amount of V(V) ion,[6] there are few publications concerned with complexation equilibria of pyridylazo ligands with V(V). Accordingly, V(V) is of interest in its reaction with these multidentate ligands. For the comparative study, the reaction of Fe(II) and V(V) with the ligands (see Scheme), 2-[(3,5-dihalo-2-pyridyl)azo]-1-hydroxynaphthalene-4-sulfonic acid ($X_2\alpha$PANS), 1-[(3,5-dihalo-2-pyridyl)azo]-2-hydroxynaphthalene-6-sulfonic acid ($X_2\beta$PANS), and 7-[(4-chloro{or unsubstituted}phenyl)azo]-8-hydroxyquinoline-5-sulfonic acid (BAHQS or ClBAHQS) were also investigated.

EXPERIMENTAL

Reagents

Eight ligands used in this study were synthesized by the methods described in our previous paper.[3a]

An 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). The stock solution was standardized by EDTA titration. Absence of traces of Fe(III) in the stock solution was checked by investigating its reaction with thiocyanate. An aqueous V(V) solution was made as dioxovanadium(V) perchlorate. Pure ammonium metavanadate was dissolved in sodium hydroxide solution. The solution was then heated while bubbling with nitrogen gas to expel ammonia. After cooling, perchloric acid was added to obtain a dioxovanadium(V) perchlorate solution. Vanadium(V) was reduced by sulfur dioxide and the resulting vanadium(IV) was titrated with a standard potassium permanganate solution.

All other reagents, of analytical or equivalent grade, were used without further purification.

Measurements

Polarograms were recorded on a Yanaco P-1100 Polarographic Analyzer and absorption spectra were measured on a Hitachi 220A recording spectrophotometer, as described in previous papers.[3]

RESULTS AND DISCUSSION

Coordination Modes in Fe(II) and V(V) Complexes

Figure 1 shows plots of reduction potentials of the azo groups of the ligands and their Fe(II) complexes *vs* pH. In the case of Cl_2PAHQS, the reduction potentials in the Fe(II) complexes (curve 1′) were markedly shifted (about 0.18 V) to the negative side, compared with those of the free ligands (curve 1) at the same pH values, showing the stabilization of azo group by a negative-shift effect.[3,7–10] Reduction potentials of curve 1′ at pH > 10 coincided with those of curve 1 due to free Cl_2PAHQS produced by hydrolysis of the Fe(II)-complex (*cf.* Table I). For the Fe(II)–$Cl_2\alpha$PANS complex (curve 2′), potentials were negatively shifted (about 0.09 V) compared with those of the ligand (curve 2), and potentials of curve 2′ at pH > 10 were also similar to those of the free ligand (curve 2) produced by hydrolysis of the complex. In the case of Fe(II)–$Cl_2\beta$PANS complex (curve 3′), the potentials were also negatively shifted (about 0.18 V) from those of the free ligand (curve 3), and hydrolysis of the complex occurred above pH 12 (*cf.* Table I). These negative shifts strongly indicate complex (ring) formation by the N-atom of the azo group.[3a] The reason for a parallel shift of reduction potentials for free $Cl_2\beta$PANS (curve 3) from pH 11 has already been explained in detail from the viewpoint of intramolecular dipole–dipole interactions.[3a] On the other hand, reduction potentials of the azo group in the Fe(II)–BAHQS complex (curve 4′) were almost the same as those of free BAHQS (curve 4), suggesting that azo group do not participate in complexation.[3] In other words, complexation occurred only through the HQS moiety, since BAHQS has no chelating donor atom in the phenyl ring.

Figure 2 shows the electronic absorption spectra of the ligands and their Fe(II) complexes. As can be seen, for Cl_2PAHQS (series a), $Cl_2\alpha$PANS (series b) and $Cl_2\beta$PANS (series c) ligands, absorption maxima (*ca* $20 \times 10^3\ \mathrm{cm}^{-1}$ for a-1, $21 \times 10^3\ \mathrm{cm}^{-1}$ for b-1 and c-1) ascribable to $\pi \rightarrow \pi^*$ transitions of the azo group in the free ligands are shifted upon Fe(II) complexation to lower wavenumber. In addition, a peak around $14 \times 10^3\ \mathrm{cm}^{-1}$ appears in the lowest-energy region, and which can be assigned to metal to ligand CT bands.[11] On the other hand, in the case of BAHQS (series d), the absorption maximum of the azo group in the free ligand (*ca* $20 \times 10^3\ \mathrm{cm}^{-1}$) is shifted higher upon complexation. Furthermore, no CT

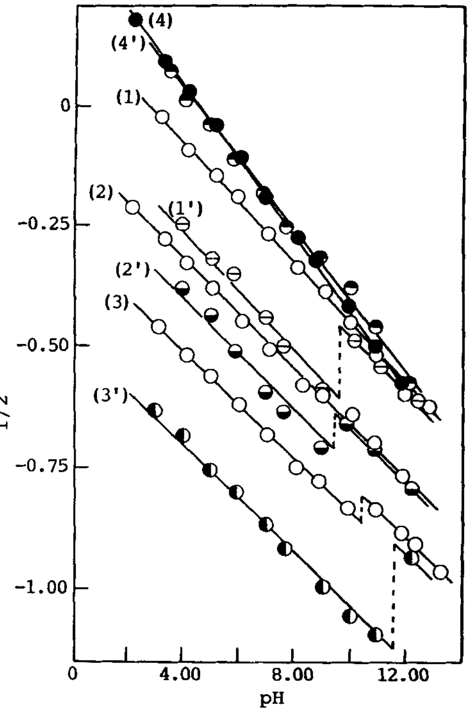


FIGURE 1 Relation between pH and half-wave potentials of ligands and their Fe(II) complexes. (1) Cl_2PAHQS; (1') Cl_2PAHQS + Fe(II); (2) $Cl_2\alpha PANS$; (2') $Cl_2\alpha PANS$ + Fe(II); (3) $Cl_2\beta PANS$; (3') $Cl_2\beta PANS$ + Fe(II); (4) BAHQS; (4') BAHQS + Fe(II). $C_L = 2.50 \times 10^{-4}$ mol dm^{-3}, $C_{Fe} = 2.50 \times 10^{-3}$ mol dm^{-3}, $\mu = 0.1$ (KNO_3), 0.01% gelatin, 24 ± 2°C. Curves (2) and (2') are shifted by 0.15 units downward, (3) and (3') by 0.30 units downward, and (4) and (4') by 0.20 units upwards, for clarity, respectively.

TABLE I

Complexing pH range, equilibrium mode, and stability constants for iron(II) complexes[a]

Ligand	pH range	Equilibrium	log β_1[b]	log β_2[c]
Cl_2PAHQS	0–2.95	$Fe + 2H_2L \Leftrightarrow Fe(HL')_2$[d] + 2H		27.74
Br_2PAHQS	0–3.00	$Fe + 2H_2L \Leftrightarrow Fe(HL')_2$[d] + 2H		27.73
BAHQS	0–4.73	$Fe + H_2L \Leftrightarrow FeL + 2H$	13.76	
ClBAHQS	0–4.53	$Fe + H_2L \Leftrightarrow FeL + 2H$	13.49	
$Cl_2\alpha PANS$	0–3.45	$Fe + 2HL \Leftrightarrow FeL_2 + 2H$		25.85
$Br_2\alpha PANS$	0–3.43	$Fe + 2HL \Leftrightarrow FeL_2 + 2H$		25.81
$Cl_2\beta PANS$	1.20–4.10	$Fe + 2HL \Leftrightarrow FeL_2 + 2H$		34.14
$Br_2\beta PANS$	1.20–4.13	$Fe + 2HL \Leftrightarrow FeL_2 + 2H$		34.08

[a] Aq. soln., $\mu = 0.1$ (KNO_3), 25.0 ± 0.5°C.

[b] $\beta_1 = [FeL]/[Fe][L]$.

[c] For X_2PAHQS $\beta_2 = [Fe(HL')_2]/[Fe][HL']^2$, for $X_2\alpha PANS$ and $X_2\beta PANS$ $\beta_2 = [FeL_2]/[Fe][L]^2$. Experimental errors are within ±0.10 log units.

[d] HL' is the ligand species which retains a proton combined with the nitrogen atom of the quinoline group, but with the phenolic proton released, judging from pK_a values.

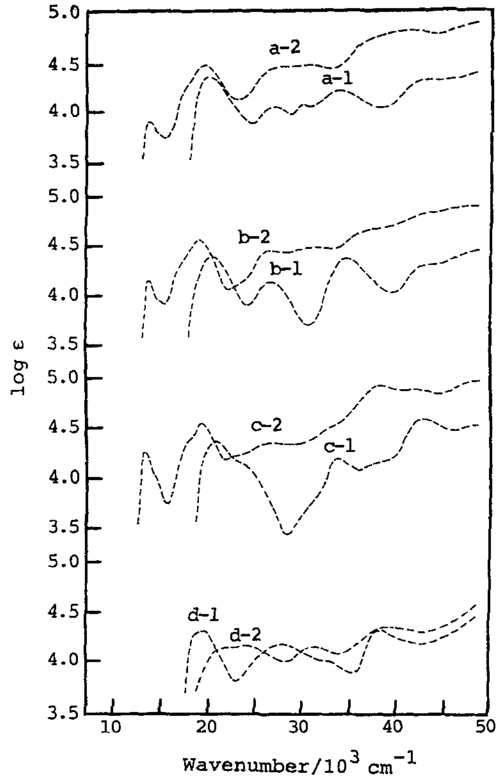


FIGURE 2 Absorption spectra of ligands and their Fe(II) complexes. Curve a-1: HL of Cl_2PAHQS at pH = 4.20; a-2: FeL_2 with Cl_2PAHQS at pH = 4.29; b-1: HL of $Cl_2\alpha PANS$ at pH = 4.80; b-2: FeL_2 with $Cl_2\alpha PANS$ at pH = 5.43; c-1: HL of $Cl_2\beta PANS$ at pH = 5.30; c-2: FeL_2 with $Cl_2\beta PANS$ at pH = 5.49; d-1: H_2L of ClBAHQS at pH = 0.01; d-2: FeL with ClBAHQS at pH = 4.40. $C_L = 1.00 \times 10^{-5}$ mol dm^{-3}, $C_{Fe} = 1.00 \times 10^{-4}$ mol dm^{-3}, 25.0 ± 0.5°C.

bands are observed in the near infrared region for the Fe(II)–ClBAHQS complex (d-2).

From the above, it is apparent that in the Fe(II)–Cl_2PAHQS complex, the Fe(II) ion is coordinated to Cl_2PAHQS as an N,N,O-terdentate using the N-atom of the azo group. This is also true for $Cl_2\alpha PANS$ and $Cl_2\beta PANS$ ligands.[3,7–10] However, in the BAHQS complex, the Fe(II) ion is coordinated to an N,O-bidentate (HQS moiety).[12]

For the V(V) complexes, it is evident from Figure 3 that for Cl_2PAHQS (curves (1) and (1′)) and BAHQS (curves (4) and (4′)) trends of reduction potentials *vs* pH for the free ligand and the V(V) complexes are quite similar. Accordingly, in the complexation of V(V) with these two ligands, no participation of the azo group is suggested. In other words, complexation occurs *via* the N,O-bidentate of the HQS moiety.[12] On the other hand, for $Cl_2\alpha PANS$ and $Cl_2\beta PANS$, reduction potentials of the azo groups were greatly shifted to the positive on complexation (curves (2′) and (3′)). This might be due to the considerable electron-attracting ability of the V(V) ion attached to the azo groups, resulting in easy reduction of the azo group.[3b]

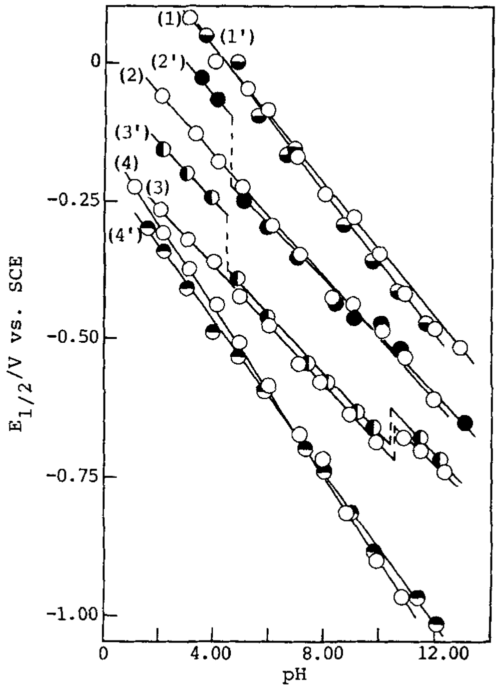


FIGURE 3 Relation between pH and half-wave potentials of ligands and their V(V) complexes. (1) Cl_2PAHQS; (1') Cl_2PAHQS + V(V); (2) $Cl_2\alpha$PANS; (2') $Cl_2\alpha$PANS + V(V); (3) $Cl_2\beta$PANS; (3') $Cl_2\beta$PANS + V(V); (4) BAHQS; (4') BAHQS + V(V). $C_L = 2.50 \times 10^{-4}$ mol dm^{-3}, $C_V = 2.50 \times 10^{-3}$ mol dm^{-3}, $\mu = 0.1$ (KNO_3), 0.01% gelatin, 24 ± 2°C. Curves (3) and (3') are shifted by 0.10 units downward, (4) and (4') by 0.20 units downward, and (1) and (1') by 0.10 units upward, for clarity, respectively.

This can be explained by the electronegativity rule[7] for reduction of organic compounds. However, in the region with pH > 4.5, reduction potentials of the azo groups for free ligands and their V(V) complexes were almost the same. This indicates that the complexes dissociate under these conditions (*cf.* Table II).

Figure 4 shows electronic spectra of the V(V) complexes. V(V) complexes with $Cl_2\beta$PANS (series c) and $Cl_2\alpha$PANS (series d) show a similar spectroscopic trend upon complexation; the absorption maximum of the azo group in the complexes is shifted to lower wavenumber as compared with the ligand species, and it is clearly split into two peaks. Accordingly, it was considered that N,N,O-terdentate chelate rings were formed in these complexes.[3b] The Cl_2PAHQS system (series a) is different to the $Cl_2\alpha$PANS and $Cl_2\beta$PANS systems, but the change is similar to that of the ClBAHQS system (series b). The maximum absorption of the azo groups of free ClBAHQS and Cl_2PAHQS were shifted to higher values on complexation and showed a single maximum absorption peak, thus suggesting that the azo groups do not participate in bonding.[3b] It should be emphasized that these results are in good agreement with the above polarographic studies.

TABLE II

Complexing pH range, equilibrium mode, and stability constants for vanadium(V) complexes[a]

Ligand	pH range	Equilibrium	log β[b]
Cl_2PAHQS	0–2.96	$VO_2 + H_2L + 2H_2O \Leftrightarrow VO(OH)_2L(OH_2) + 2H$	16.34
	4.90–9.43	$VO(OH)_2L(OH_2) + H_2O \Leftrightarrow L + P$[c]	
Br_2PAHQS	0–2.96	$VO_2 + H_2L + 2H_2O \Leftrightarrow VO(OH)_2L(OH_2) + 2H$	16.38
	4.89–9.49	$VO(OH)_2L(OH_2) + H_2O \Leftrightarrow L + P$[c]	
BAHQS	0–2.99	$VO_2 + H_2L + 2H_2O \Leftrightarrow VO(OH)_2L(OH_2) + 2H$	17.07
	5.35–10.97	$VO(OH)_2L(OH_2) + H_2O \Leftrightarrow L + P$[c]	
ClBAHQS	0–2.97	$VO_2 + H_2L + 2H_2O \Leftrightarrow VO(OH)_2L(OH_2) + 2H$	16.86
	5.36–10.27	$VO(OH)_2L(OH_2) + H_2O \Leftrightarrow L + P$[c]	
$Cl_2\alpha$PANS	0.62–3.10	$VO_2 + HL + H_2O \Leftrightarrow VO(OH)_2L + H$	16.12
	3.23–5.23	$VO(OH)_2L + H_2O \Leftrightarrow HL + P$[c]	
$Br_2\alpha$PANS	0.60–3.00	$VO_2 + HL + H_2O \Leftrightarrow VO(OH)_2L + H$	15.97
	3.24–5.41	$VO(OH)_2L + H_2O \Leftrightarrow HL + P$[c]	
$Cl_2\beta$PANS	0.63–3.03	$VO_2 + HL + H_2O \Leftrightarrow VO(OH)_2L + H$	21.91
	3.24–5.49	$VO(OH)_2L + H_2O \Leftrightarrow HL + P$[c]	
$Br_2\beta$PANS	0.71–3.03	$VO_2 + HL + H_2O \Leftrightarrow VO(OH)_2L + H$	21.96
	3.24–5.40	$VO(OH)_2L + H_2O \Leftrightarrow HL + P$[c]	

[a] Aq. soln., $\mu = 0.1$ (KNO_3), 25.0 ± 0.5°C.

[b] For X_2PAHQS, BAHQS and ClBAHQS complexes, $\beta = [VO(OH)_2L(OH_2)]/[VO(OH)_2(OH_2)][L]$,[5] for $X_2\alpha$PANS and $X_2\beta$PANS complexes, $\beta = [VO(OH)_2L]/[VO(OH)_2][L]$.[5] Experimental errors are within ±0.10 log units.

[c] P represents products of hydrolysis of vanadium(V) ion, $VO_2(OH)_2(OH_2)_2$, $VO_2(OH)(OH_2)_2$, *etc.*[5]

Complexing Equilibria and Stability Constants for the Fe(II) and V(V) Complexes

All of the aqueous solutions containing Fe(II) and the eight ligands showed spectroscopic changes having clear isosbestic points (with pH variation), demonstrating the presence of a complexing equilibrium. On the basis of the complexing pH ranges and the coordination modes described above, these equilibria were analyzed using the following equations.

For the 1:2 (metal to ligand) Fe(II)-X_2PAHQS cases, equation (*1*) was used.[3a]

$$\log\beta_2 = \log([Fe(HL')_2]/[H_2L]) - 2pH - \log(C_{Fe} + [HL]/3 - C_L/3) - \log(C_L/3 - [HL]/3) + 2pK_{a3}, \qquad (1)$$

Here, $\beta_2 = [Fe(HL')_2]/[Fe][HL']^2$ (the meaning of HL′ is explained in Table I), $[HL] = C_L/(1 + [H]/K_{a2} + K_{a3}/[H])$, and C_{Fe} and C_L are the total concentration of Fe(II) and X_2PAHQS, respectively. K_{a2} and K_{a3} are the dissociation constants from the N-atom in HQS and from HO– in HQS, respectively. According to (*1*), plots of $\log([Fe(HL')_2]/[H_2L])$ *vs* pH give a straight line with a slope of 2.

For the 1:1 Fe(II)-BAHQS and -ClBAHQS systems, equation (*2*) was used.[3a]

$$\log\beta_1 = \log([FeL]/[H_2L]) - 2pH - \log(C_{Fe} + [HL]/2 - C_L/2) + 2pK_{a1} + 2pK_{a2} \qquad (2)$$

Here, $\beta_1 = [FeL]/[Fe][L]$, $[HL] = (1 + [H]/K_{a1} + K_{a2}/[H])$, and K_{a1} and K_{a2} are dissociation constants from the heterocyclic N-atom in HQS and from HO– in HQS, respectively. From (*2*), plots of $\log([FeL]/[H_2L])$ *vs* pH give a straight line with a slope of 2.

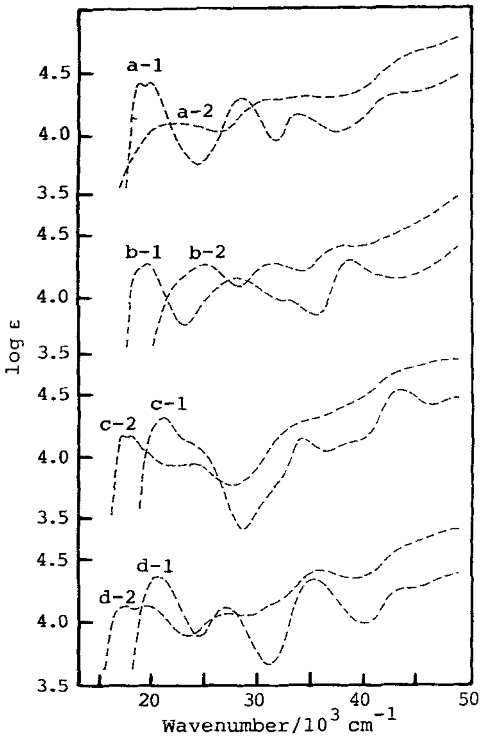


FIGURE 4 Absorption spectra of ligands and their V(V) complexes. Curve a-1: H_2L of Cl_2PAHQS at pH = 0.01; a-2: $VO(OH)_2L(OH_2)$ with Cl_2PAHQS at pH = 3.14; b-1: H_2L of ClBAHQS at pH = 0.01; b-2: $VO(OH)_2L(OH_2)$ with ClBAHQS at pH = 3.03; c-1: HL of $Cl_2\beta PANS$ at pH = 4.80; c-2: $VO(OH)_2L$ with $Cl_2\beta PANS$ at pH = 3.03; d-1: HL of $Cl_2\alpha PANS$ at pH = 4.80; d-2: $VO(OH)_2L$ with $Cl_2\alpha PANS$ at pH = 3.10. $C_L = 1.00 \times 10^{-5}$ mol dm^{-3}, $C_V = 1.00 \times 10^{-4}$ mol dm^{-3}, 25.0 ± 0.5°C.

For the 1:1 V(V)-X_2PAHQS systems formed in the region pH 0–3, the formation constants ($\beta = [VL]/[V][L]$) were calculated from (*3*),[3b]

$$\log \beta = \log([VL]/[H_2L]) - 2pH - \log(C_V + [HL]/2 - C_L/2) + 2pK_{a2} + 2pK_{a3} \qquad (3)$$

where VL is the hydroxo complex[5] $VO(OH)_2L(OH_2)$ and C_V is the total concentration of V(V). According to (*3*), the slope of plots of $\log([VL]/[H_2L])$ *vs* pH is 2.

For the 1:1 V(V)-$X_2\alpha PANS$ and -$X_2\beta PANS$ cases when pH ~ 3, (*4*) was used.[3a]

$$\log \beta = \log([VL']/[HL]) - pH - \log(C_V - C_L/2) + pK_{a2} \qquad (4)$$

Here, $\beta = [VL']/[V][L]$, and VL' is $VO(OH)_2L$.[5] In this case, plots of $\log([VL']/[HL])$ *vs* pH give a straight line with a slope of unity.

The formation constants for the 1:1 complexes of V(V) with BAHQS and ClBAHQS were obtained using equation (*5*).[3b]

$$\log \beta = \log([VL]/[H_2L]) - 2pH - \log(C_V + [HL]/2 - C_L/2) + 2pK_{a1} + 2pK_{a2}. \qquad (5)$$

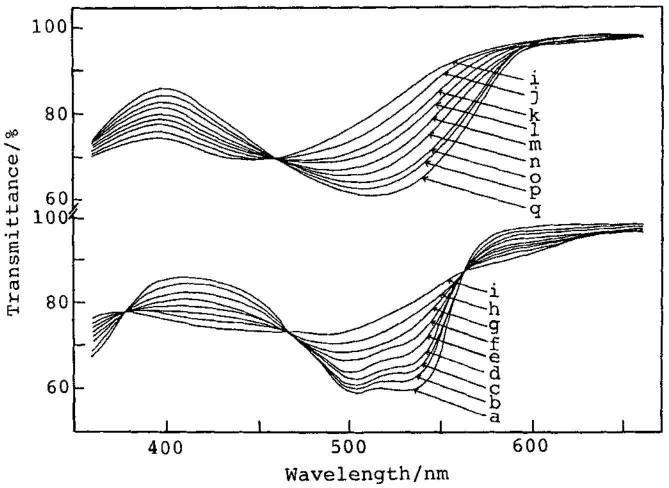


FIGURE 5 Absorption spectra of mixture of V(V) and Cl_2PAHQS in aqueous solution at various pH values. pH: a = 0; b = 1.27; c = 1.55; d = 1.63; e = 1.83; f = 2.02; g = 2.33; h = 2.56; i = 2.96–4.90; j = 6.33; k = 6.70; l = 7.02; m = 7.24; n = 7.56; o = 7.84; p = 7.95; q = 9.43–12.28. $C_L = 1.00 \times 10^{-5}$ mol dm^{-3}, $C_V = 1.00 \times 10^{-4}$ mol dm^{-3}, 25.0 ± 0.5°C.

in which, $\beta = [VL]/[V][L]$ and the meaning of VL is the same as in (*3*). K_{a1} has the same meaning as in (*1*). Plots of $\log([VL]/[H_2L])$ *vs* pH give a straight line with a slope of 2.

Though the compositions were mainly determined by the Hildebrand–Reilly method[13] ((1) to (5)), they were confirmed by the continuous variation method as well. It is noteworthy that despite conditions where $[Fe] \gg [ligand]$ (10:1), the formation of 1:2 (Fe:ligand) complexes were observed in the cases of X_2PAHQS, $X_2\alpha PANS$ and $X_2\beta PANS$. Therefore, if the structures of the complexes are assumed to be octahedral, two N,N,O-terdentates coordinate to Fe(II) forming complexes with four five-membered fused chelate rings; compositions are shown in Table I. In Tables I and II, data for the bromide derivatives are also listed. As can be seen, there are no significant differences between chloro- and bromo-derivatives, reflecting values of Hammet constants (σ_p: Cl = 0.23, Br = 0.23; σ_m: Cl = 0.37, Br = 0.39).

It can be seen from Table II that the V(V) complexes are involved with two equilibria at lower and higher pH ranges, respectively. As a typical example, Figure 5 shows spectra of a mixture of V(V) and Cl_2PAHQS at various pH values. The changes with pH from curves a to i and i to q show clear isosbestic points at 378, 466, 561 and 458 nm, demonstrating the equilibria[5] $VO_2 + H_2L + 2H_2O \Leftrightarrow VO(OH)_2L(OH_2) + 2H$ (spectra a to i) and $VO(OH)_2L(OH_2) + H_2O \Leftrightarrow L + P$ (spectra i to q), respectively. The changes from i to q reflect the hydrolysis $VO(OH)_2L(OH_2)$ complexes accompanied by liberation of L (*cf.* Table II). It is known that V(V) is easily hydrolyzed to form hydroxyl complexes at higher pH, the product (P in the above) being thought to consist of various species.[5] As shown in Figure 6, in the visible region up to about 28,000 cm^{-1}, spectrum (1) (corresponding to the spectrum of species q in Figure 5) is the same as that of the ligand itself (spectrum (2)). In the UV region, however, spectrum (1) gave a new absorption band at 37,000 cm^{-1}, assignable to the absorption of the hydrolyzed species P at

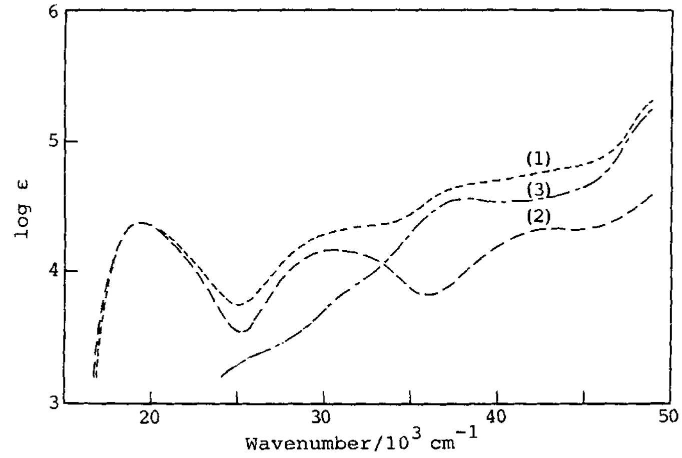


FIGURE 6 Absorption spectra of aqueous solutions of mixtures of V(V) and Cl_2PAHQS (curve 1: V(V) + L + OH^-, at pH = 11.67), Cl_2PAHQS (curve 2: L, at pH = 11.00) and of hydroxide with V(V) (curve 3: $VO_2(OH)_2(OH_2)_2$, $VO_2(OH)(OH_2)_2$, *etc.*,[5] at pH = 11.91). $C_L = 1.00 \times 10^{-5}$ mol dm^{-3}, $C_V = 1.00 \times 10^{-4}$ mol dm^{-3}, 25.0 ± 0.5°C.

pH = 12, judging from spectrum (3). Thus it was evident that spectrum (1) is due to the sum of contributions from L produced by the hydrolysis of the V(V)–Cl_2PAHQS complex and the product P. It was found that $VO(OH)_2L(OH_2)$ complexes with Cl_2PAHQS were stable in the region pH = 3.00–4.90. Spectroscopic changes were used to calculate stability constants for the complexes. On the basis of the complexing pH ranges and the coordination modes described above, these equilibria were analyzed using (*3*), since the complexing pH ranges in the lower pH regions (*cf.* Table II) and coordination modes of the V(V) complexes were similar to those of VO(IV) complexes.[3b] All the species in Table II might be six-coordinated and octahedral.

The formation constants for the Fe(II) and V(V) complexes, corrected using side-reaction coefficients of ligands and metal ions taking data from Refs. 14 and 15, are listed in Tables I and II, respectively. It can be seen from these Tables that the $\log \beta_1$ values for the Fe(II) complexes are in the order BAHQS > ClBAHQS, and $\log \beta$ values of V(V) complexes in the order BAHQS > ClBAHQS > X_2PAHQS. These orders can be explained by taking into account effects of the halogen or nitrogen atoms in the ligands. The $\log \beta$ values for V(V)–$X_2\alpha PANS$ species are of similar magnitude to those of thiazolylazo complexes with V(V), which also contain N,N,O-chelate rings.[16] On the other hand, the stability constants for $X_2\beta PANS$ complexes with both Fe(II) and V(V) ions are larger than those for $X_2\alpha PANS$. This can be interpreted in terms of dipole–dipole interactions in the $X_2\beta PANS$ complexes as described in Ref. 3a.

Characterization of the Oxidation State of the Iron in the Complexes

It is well known that Fe(II) ion is easily oxidized to Fe(III). In order to make sure of the oxidation state of iron in the complexes obtained in this study, reactions of

Fe(III) with the eight ligands were also investigated under the same experimental conditions. As a result, it was shown that spectroscopic changes having no isosbestic point with variation of pH were observed. Accordingly, complexing equilibria of Fe(III) could not be analyzed. Furthermore, it was found from measurements of ESR spectra (recorded at 77 K on a JES-FE-3X spectrometer) of the Fe(II) complexes with the eight ligands that all solutions were ESR silent, thus showing the absence of Fe(III). Thus, the iron in the complexes of this study is not oxidized to Fe(III) upon complexation.

CONCLUSIONS

In the reactions of the multidentate ligands X_2PAHQS, Fe(II) selectively coordinates to the comparatively soft chelate sites (N,N,O-terdentate containing an azo group), forming four five-membered chelate rings from pH = 3–10. On the contrary, V(V) ion is bound selectively to the comparatively hard chelate site (N,O-bidentate in HQS moiety), forming one five-membered chelate ring from pH = 3–5.

So far as the Cd(II), Ni(II), Zn(II), Fe(II), VO(IV), and V(V) complexes with X_2PAHQS ligands were concerned (*cf.* Ref. 3), the coordination selectivity of the ligands to the metal ions in aqueous solution would be mainly dependent on the HSAB (Hard and Soft Acids and Bases)[17] properties of the chelate sites and the metal ions. That is to say, the metal ions which are classified as soft or borderline acids are found to coordinate selectively to the comparatively soft chelate site, and the metal ions belong to the hard acids selectively coordinate to the comparatively hard chelate site.

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REFERENCES

1. (a) P. M. May and R. A. Bulman, *Prog. Med. Chem.*, **20**, 226 (1983); (b) R. A. Bulman, *Struct. Bonding*, **67**, 91 (1987).
2. K. Hayashi, K. Okamoto, J. Hidaka and H. Einaga, *J. Chem. Soc., Dalton Trans.*, 1377 (1982); (b) M. Noritake, K. Okamoto, J. Hidaka and H. Einaga, *Bull. Chem. Soc. Jpn.*, **63**, 353 (1990), and references therein.
3. (a) H. Huang, H. Chikushi, M. Nakamura and F. Kai, *Bull. Chem. Soc. Jpn.*, **63**, 1985 (1990); (b) H. Huang, Y. Asai, M. Hirohata, M. Nakamura and F. Kai, *Nippon Kagaku Kaishi*, 1348 (1990).
4. K. Ueda, N. Kobayashi and Y. Yamamoto, *Analyst*, **111**, 733 (1975).
5. A. Yuchi, S. Yamada and M. Tanaka, *Bull. Chem. Soc. Jpn.*, **52**, 1643 (1979).
6. (a) T. Iwamoto, *Bull. Chem. Soc. Jpn.*, **34**, 605 (1961); (b) T. Yotsuyanagi and K. Aomura, *Talanta*, **16**, 1611 (1969); (c) Y. Shijo and T. Takeuchi, *Bunseki Kagaku*, **14**, 115 (1965); (d) M. Kawamoto, H. Mochizuki, R. Kajiyama and K. Ichihashi, *ibid.*, **14**, 348 (1965); (e) O. Budevsky and R. Pribil, *Talanta*, **11**, 1313 (1964).
7. S. Koide, "Polarography", in "Kagakuno Ryouiki Zoukan No. 69", Ed. T. Fujinaga and M. Maruyama (Nankoudou, Tokyo, 1965), Vol. 3, p. 83.
8. T. Takahashi and N. Tanaka, *Nippon Kagaku Zasshi*, **91**, 339 (1970).
9. G. W. Latimer, Jr., *Talanta*, **15**, 1 (1968).

10. L. Holleck, J. M. Abd El Kader and A. M. Shams El Din, *J. Electroanal. Chem.*, **20**, 287 (1969).
11. K. Yamazaki and H. Yamadera, "Mukikagaku Zensho, Bekkan, Sakutai (Jyo)" (Maruzen, Tokyo, 1977), p. 117.
12. T. Yoshida, *Nippon Kagaku Kaishi*, **9**, 1710 (1973).
13. G. P. Hildebrand and C. N. Reilly, *Anal. Chem.*, **29**, 258 (1957).
14. Dissociation Constants of Ligands; X_2PAHQS: pK_{a2} (quinoline-N, $H_2L \Leftrightarrow HL + H) = 2.23$ ($X = Cl$), 2.21 ($X = Br$); pK_{a3} (quinolinolate-OH, $HL \Leftrightarrow L + H) = 7.23$ ($X = Cl$), 7.25 ($X = Br$); $X_2\alpha$PANS; pK_{a2} (naphtholate-OH, $HL \Leftrightarrow L + H) = 7.99$ ($X = Cl$), 7.91 ($X = Br$); $X_2\beta$PANS: $pK_{a2} = 10.70$ ($X = Cl$), 10.73 ($X = Br$); XBAHQS: pK_{a1} (quinoline-N, $H_2L \Leftrightarrow HL + H) = 2.93$ ($X = H$), 2.77 ($X = Cl$); pK_{a2} (quinolinolate-OH, $HL \Leftrightarrow L + H) = 7.40$ ($X = H$), 7.32 ($X = Cl$).
15. R. M. Smith and A. E. Martell, "Critical Stability Constants" (Plenum Press, New York, 1989).
16. J. J. Arias, F. Jimenez and F. G. Montelongo, *An. Quim., Ser. B*, **76**, 452 (1980).
17. R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).