Study on the Interaction of Yttrium(III) with Adrenaline, Noradrenaline, and Dopamine

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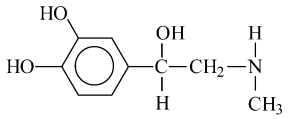
Yttrium(III) equilibria in the presence of catecholamines adrenaline (AD), noradrenaline (NAD), and dopamine (DP) have been investigated by potentiometric titration in aqueous solution in $I = 0.20$ mol·dm^{-3} KCl ionic medium and at 298.15 K. The complexation model for Y(III)−catecholamine systems has been established by the "BEST" software from the potentiometric data. The types of complexes in the yttrium(III)−catecholamine systems have been ascertained, and the protonation constants for catecholamines and the stability constants for yttrium(III) complexes with catecholamines have been obtained. The stability constants of YHL^{2+}- and $Y(HL)_2^{+}$-type complexes are reported. Catecholamines can form stable yttrium(III) complexes with the phenolic hydroxyl groups of catecholamines as the binding site to yttrium(III). In terms of the ligands, the stability of complexes ranks in an order such as dopamine > adrenaline > noradrenaline. The stability constants of Y(III)−adrenaline complexes are higher than their La(III) complexes due to the higher ionic potential of Y(III). The ionic radii of Ca(II) and Y(III) are roughly equal, but Y(III) has a higher charge than Ca(II). Therefore, Y(III)−catecholamine complexes are relatively more stable than Ca(II)−catecholamine complexes. This result may be utilized for in vitro and in vivo studies.

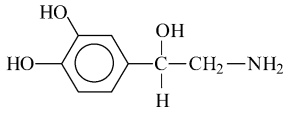
Introduction

Yttrium is always found in nature with lanthanides. Its ionic radius is 1.04 Å for coordination number 6, and its chemical properties are very similar to the later lanthanides ((1.00 to 1.17) Å).[1] Recently, some authors have studied the equilibria of catecholate complexes of many transition metals and lanthanides.[2−22] In our previous papers, the interactions of Y(III)[2,3] and La(III)[4] with catecholates were reported, i.e., 1,2-dihydroxybenzene-3,5-disulfonate (TIRON) and 4-nitrocatechol. We proposed that in the Y(III)−catecholate and La(III)−catecholate complexes two phenolic hydroxyl groups serve as binding sites for Y(III), but two phenolic hydroxyl groups are deprotonated. The stability constants of Y(III) complexes of TIRON are higher than those of La(III) due to the higher ionic potential of Y(III).

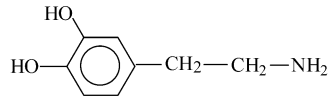
The catecholamines are bioenergetic amines that play quite an important role as neurotransmitters in the central nervous system (CNS).[23] They are compounds with amines attached to a benzene ring possessing two hydroxyl groups. The most important endogenously produced compounds of this group are adrenaline (AD), noradrenaline (NAD), and dopamine (DP). The structural formulas are shown in Figure 1. These ligands are written as H_2LH^+, where phenolic protons are written on the left side of L. The catecholamine complexes of many transition metals have been reported in the literature,[2−20] but information about the interactions of lanthanide(III) and catecholamines is restricted. Wu et al.[21] investigated complexes of lanthanum(III) with adrenaline by a potentiometric method and a quantum chemical ab initio method under physiological conditions (335 K and an ionic strength of 0.15 mol·dm^{-3} NaCl), to clarify neuroendocrine effects and the underlying mechanism of lanthanides. They calculated the stability constants of the LaL and LaL_2 complexes and defined that adrenaline is coordinated to lanthanum(III) via its phenolic hydroxyl group (only one phenolic hydroxyl group is deprotonated). Furthermore, Gao et al.[22] determined the stability constant for a complex of promethium(III) with adrenaline by a potentiometric titration under physiological conditions (335 K and an ionic strength of 0.15 mol·dm^{-3} NaCl). However, no research has been published concerning the interaction of yttrium(III) with catecholamines. As a continuation of our studies on the interaction of yttrium(III) with ligands including the catechol group, we have investigated the interaction of yttrium(III) with adrenaline, noradrenaline, and dopamine by a potentiometric method. The calculation of the protonation constants of adrenaline, noradrenaline, and dopamine and the stability constants of Y(III) complexes were carried out using a recently developed computer program.[24]



4-[1-Hydroxy-2-(methylamino)ethyl]-1,2-benzenediol; adrenaline (AD)



1-[3,4-Dihydroxyphenyl]-2-amino)ethanol]; noradrenaline (NAD)



(3,4-dihydroxyphenyl)ethylamine; dopamine (DP)

Figure 1. Structures and IUPAC names of the ligands studied.

Experimental

Chemicals. All of the catecholamine hydrochlorides (dopamine, adrenaline, and noradenaline) were purchased from Sigma. These ligands were used without further purification. Yttri-

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um(III) chloride solution was prepared by dissolving yttrium oxide (99.9 %) in concentrated HCl. The stock solution of yttrium(III) chloride was standardized complexometrically by EDTA titration using a suitable indicator.[25] The excess acid in the Y(III) stock solution was determined by potentiometric titrations described previously.[6] A carbonate-free KOH solution (0.1 mol·dm^{-3}) was prepared and standardized potentiometrically against the primary standard, potassium hydrogen phthalate.[26,27] All reagents were of AR grade. A hydrochloride solution (0.1 mol·dm^{-3}) was prepared and then standardized by titration against a potassium hydroxide standard. The potassium chloride, which was used as a background electrolyte, was a Merck p.a. reagent. The ionic strength of each solution was adjusted to 0.20 mol·dm^{-3} by the addition of KCl as the supporting electrolyte. All solutions were prepared with analytical grade water (R = 18 MΩ) using grade A glassware.

Apparatus and Procedure. Potentiometric pH measurements were performed by means of a Schott−Gerate automatic titrator model TitroLine Alpha Plus (Germany, Deutschland) with a combined pH electrode (Mettler Toledo) which is connected to a computer. The apparatus was connected to a PC, and automatic titrations were performed using a suitable computer program to control titrant delivery. All titrations were carried out in solutions contained in a double-wall glass vessel at 298.15 K. The titrations were performed in an inert atmosphere where nitrogen gas was bubbled through the titrated solutions before and during the pH measurements. The ionic strength was kept constant (0.20 mol·dm^{-3}) using a KCl solution, and a total volume of 50 cm^{-3} was used for each titration. Metal to ligand ratios in the titrant solution were always 1:1 ≤ Y(III)/H_2LH^+ ≤ 1:10.

The different solutions titrated were as follows:

(a) 5 mL of 0.1 mol·dm^{-3} HCl + 5 mL of 2.0 mol·dm^{-3} KCl (for cell calibration)

(b) solution a + n × 2 mL of 0.005 mol·dm^{-3} H_2LH^+; n = 2 to 10 (for the determination of the dissociation constants)

(c) solution b + 10 mL of 0.001 mol·dm^{-3} Y(III) salts (for the determination of the formation constants of Y(III) complexes)

Potentiometric measurements were carried out by titrating 50 mL of the titrant solution with standard KOH solutions until the formation of scarcely soluble species was noted. The potentiometric cell was calibrated before each experiment so as to measure the hydrogen ion concentration rather than its activity. The K_w values were calculated from several separate series of [H^+] and [OH^-] measurements in 0.2 mol·dm^{-3} KCl.[25,26]

Calculations. The computations of the protonation constants of ligands and the formation constants of Y(III) complexes from potentiometric data were carried out by the BEST software. The BEST software was used to minimize the standard deviation of the fit (σ_{fit}) between the observed and calculated pH values for the overall titration data.

Results and Discussion

Protonation Constants of Catecholamines. Protonation constants of adrenaline, noradrenaline, and dopamine were determined potentiometrically in I = 0.2 mol·dm^{-3} KCl ionic medium at 298.15 K. Individual titration curves of adrenaline, noadrenaline, and dopamine are shown as b curves in Figures 2, 3, and 4, respectively. Only a single inflection point was observed in the titration curves of the ligands. In the buffer zone along the inflection point, the number of titrated protons is two per ligand. Ligands have two deprotonable phenolic hydroxyl and one amine proton. In previous studies, many researchers have reported that the first ionizing proton is a phenolic hydroxyl; the second is an amine; and the third proton is the other phenolic hydroxyl proton. In this study, all ligands are shown as H_2LH^+; here, protons on the left side of L are phenolic hydroxyl protons, and on the right side is the amine proton. Protonation constants of ligands are calculated from potentiometric data by the BEST software; calculated data in conjunction

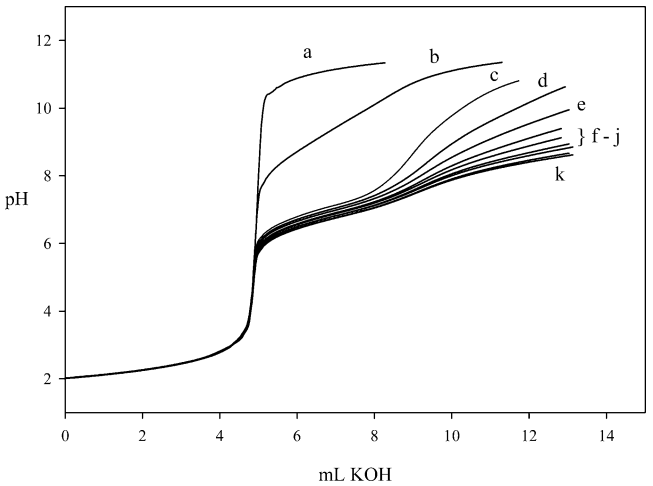

Figure 2. pH against volume of 0.1 mol·dm^{-3} KOH for the Y(III)−AD system at 298.15 K and I = 0.2 mol·dm^{-3} KCl: (a) 1.0·10^{-2} mol·dm^{-3} HCl; (b) solution a + 4.0·10^{-3} mol·dm^{-3} AD; (c) solution a + 2.0·10^{-3} mol·dm^{-3} Y(III) + 4.0·10^{-3} mol·dm^{-3} AD; (d) solution a + 2.0·10^{-3} mol·dm^{-3} Y(III) + 6.0·10^{-3} mol·dm^{-3} AD; (e) solution a + 2.0·10^{-3} mol·dm^{-3} Y(III) + 8.0·10^{-3} mol·dm^{-3} AD; (f) solution a + 2.0·10^{-3} mol·dm^{-3} Y(III) + 1.0·10^{-2} mol·dm^{-3} AD; (g) solution a + 2.0·10^{-3} mol·dm^{-3} Y(III) + 1.2·10^{-2} mol·dm^{-3} AD; (h) solution a + 2.0·10^{-3} mol·dm^{-3} Y(III) + 1.4·10^{-2} mol·dm^{-3} AD; (i) solution a + 2.0·10^{-3} mol·dm^{-3} Y(III) + 1.6·10^{-2} mol·dm^{-3} AD; (j) solution a + 2.0·10^{-3} mol·dm^{-3} Y(III) + 1.8·10^{-2} mol·dm^{-3} AD; (k) solution a + 2.0·10^{-3} mol·dm^{-3} Y(III) + 2.0·10^{-2} mol·dm^{-3} AD.

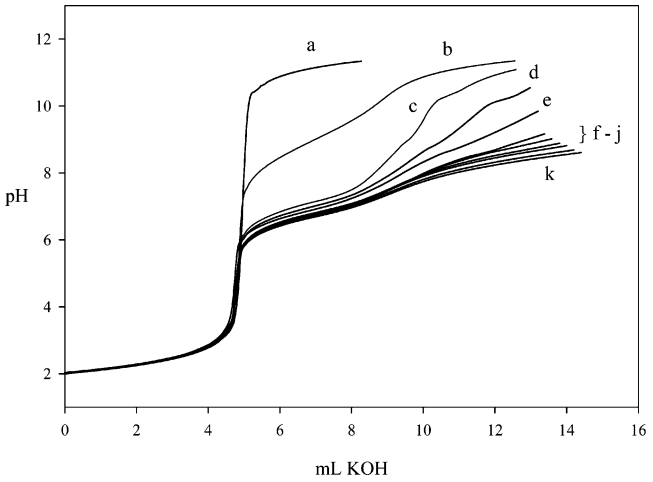

Figure 3. pH against volume of 0.1 mol·dm^{-3} KOH for the Y(III)−NAD system at 298.15 K and I = 0.2 mol·dm^{-3} KCl: (a) 1.0·10^{-2} mol·dm^{-3} HCl; (b) solution a + 4.0·10^{-3} mol·dm^{-3} NAD; (c) solution a + 2.0·10^{-3} mol·dm^{-3} Y(III) + 4.0·10^{-3} mol·dm^{-3} NAD; (d) solution a + 2.0·10^{-3} mol·dm^{-3} Y(III) + 6.0·10^{-3} mol·dm^{-3} NAD; (e) solution a + 2.0·10^{-3} mol·dm^{-3} Y(III) + 8.0·10^{-3} mol·dm^{-3} NAD; (f) solution a + 2.0·10^{-3} mol·dm^{-3} Y(III) + 1.0·10^{-2} mol·dm^{-3} NAD; (g) solution a + 2.0·10^{-3} mol·dm^{-3} Y(III) + 1.2·10^{-2} mol·dm^{-3} NAD; (h) solution a + 2.0·10^{-3} mol·dm^{-3} Y(III) + 1.4·10^{-2} mol·dm^{-3} NAD; (i) solution a + 2.0·10^{-3} mol·dm^{-3} Y(III) + 1.6·10^{-2} mol·dm^{-3} NAD; (j) solution a + 2.0·10^{-3} mol·dm^{-3} Y(III) + 1.8·10^{-2} mol·dm^{-3} NAD; (k) solution a + 2.0·10^{-3} mol·dm^{-3} Y(III) + 2.0·10^{-2} mol·dm^{-3} NAD.

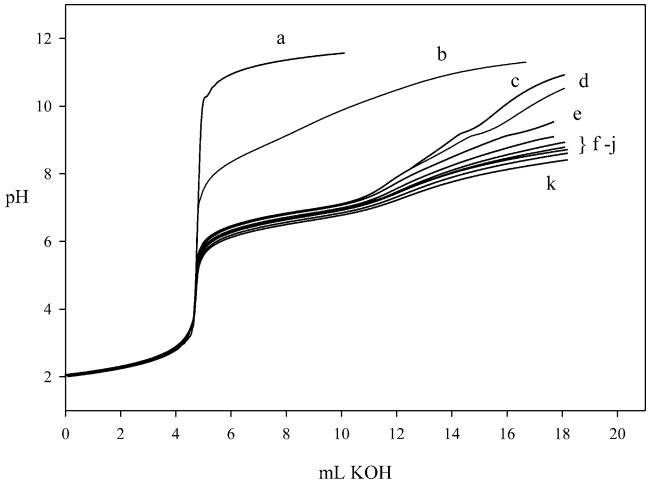

Figure 4. pH against volume of 0.1 mol·dm^{-3} KOH for the Y(III)−DP system at 298.15 K and I = 0.2 mol·dm^{-3} KCl: (a) 1.0·10^{-2} mol·dm^{-3} HCl; (b) solution a + 8.0·10^{-3} mol·dm^{-3} DP; (c) solution a + 4.0·10^{-3} mol·dm^{-3} Y(III) + 8.0·10^{-3} mol·dm^{-3} DP; (d) solution a + 4.0·10^{-3} mol·dm^{-3} Y(III) + 1.2·10^{-2} mol·dm^{-3} DP; (e) solution a + 4.0·10^{-3} mol·dm^{-3} Y(III) + 1.6·10^{-2} mol·dm^{-3} DP; (f) solution a + 4.0·10^{-3} mol·dm^{-3} Y(III) + 2.0·10^{-2} mol·dm^{-3} DP; (g) solution a + 4.0·10^{-3} mol·dm^{-3} Y(III) + 2.4·10^{-2} mol·dm^{-3} DP; (h) solution a + 4.0·10^{-3} mol·dm^{-3} Y(III) + 2.8·10^{-2} mol·dm^{-3} DP; (i) solution a + 4.0·10^{-3} mol·dm^{-3} Y(III) + 3.2·10^{-2} mol·dm^{-3} DP; (j) solution a + 4.0·10^{-3} mol·dm^{-3} Y(III) + 3.6·10^{-2} mol·dm^{-3} DP; (k) solution a + 4.0·10^{-3} mol·dm^{-3} Y(III) + 4.0·10^{-2} mol·dm^{-3} DP.

Table 1. Protonation Constants (log $K \pm \sigma^a$)^b of Adrenaline, Noradrenaline, and Dopamine at Ionic Strength I = 0.2 mol·dm^{-3} KCl at T = 298.15 K

ligand	pK_1	pK_2	pK_3
adrenaline	13.13 ± 0.11^c	9.84 ± 0.04^c	8.63 ± 0.02^c
	-	9.76[21]	8.45[21]
	13.15[15]	9.87[15]	8.63[15]
	12.1[14]	10.01[14]	8.74[14]
	13.1[13]	9.84[13]	8.64[13]
noradrenaline	12.93 ± 0.06^c	9.53 ± 0.04^c	8.58 ± 0.03^c
	12.9[13]	9.53[13]	8.58[13]
dopamine	12.62 ± 0.20^c	10.32 ± 0.01^c	8.85 ± 0.01^c
	13.1[20]	10.41[20]	8.89[20]
	12.8[14]	10.55[14]	9.05[14]
Tiron	12.57[3]	7.65[3]	

^{a} Standard deviation. ^{b} ± 95 % confidence interval. ^{c} This work.

with literature data are presented in Table 1. Values listed in this table can be described by the following equations.

$$L^{2-} + H^+ \rightleftharpoons HL^- \qquad K_1 = \frac{[HL^-]}{[L^{2-}][H^+]} \qquad \text{(i)}$$

$$HL^- + H^+ \rightleftharpoons HLH \qquad K_2 = \frac{[HLH]}{[HL^-][H^+]} \qquad \text{(ii)}$$

$$HLH + H^+ \rightleftharpoons H_2LH^+ \qquad K_3 = \frac{[H_2LH^+]}{[HLH][H^+]} \qquad \text{(iii)}$$

Formation Constants of the Y(III) Complexes. Potentiometric titrations of the Y(III)−catecholamine system were conducted in various molar ratios ranging from 1:2 to 1:10 in I = 0.2 mol·dm^{-3} KCl ionic medium at 298.15 K. Titration curves against consumed base volume are shown in Figure 2, 3, and 4, curves c to k. In all catecholamine systems, the difference between titration curves of the ligand and metal−ligand solutions (ΔpH) is 2. A single inflection point was observed in titration curves obtained by various metal/ligand molar ratios. In the buffer zone along the inflection point, the number of titrated protons is four per metal ion. The equilibria involved in this region can be described by the following equations.

Table 2. Stability Constants (log $\beta \pm \sigma^a$)^b of Y(III) Complexes of Adrenaline, Noradrenaline, and Dopamine at Ionic Strength I = 0.2 mol·dm^{-3} KCl at T = 298.15 K

catecholamines	log β_1	log β_2
adrenaline	7.40 ± 0.01^c	13.78 ± 0.04^c
noradrenaline	7.07 ± 0.02^c	13.15 ± 0.02^c
dopamine	7.95 ± 0.02^c	14.84 ± 0.05^c

^{a} Standard deviation. ^{b} ± 95 % confidence interval. ^{c} This work

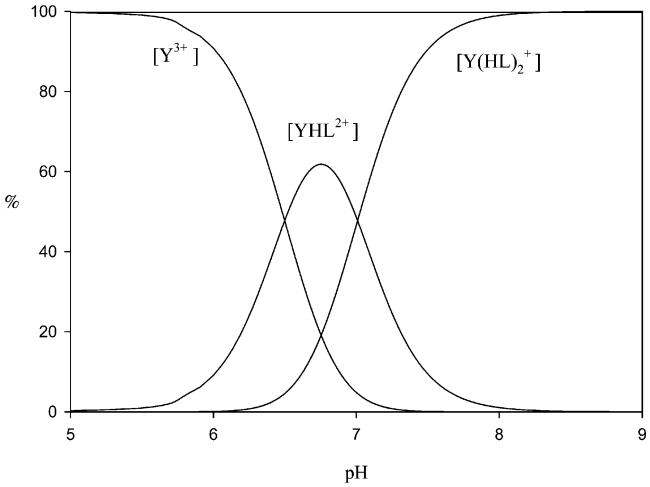

Figure 5. Complex type distribution curves for the Y(III)−AD system at a metal ion−ligand ratio of 1:4 (T_Y = 3.0·10^{-3} mol·dm^{-3}).

$$Y^{3+} + HL^- \rightleftharpoons YHL^{2+} \qquad \beta_1 = \frac{[YHL^{2+}]}{[Y^{3+}][HL^-]} \qquad \text{(iv)}$$

$$Y^{3+} + 2HL^- \rightleftharpoons Y(HL)_2^+ \qquad \beta_2 = \frac{[Y(HL)_2^+]}{[Y^{3+}][HL^-]^2} \qquad \text{(v)}$$

Moreover, in all titrations, pH readings in metal/ligand molar ratios exceeding 1:5 were relatively more stable, and no precipitation could be observed during the titration. In potentiometric titrations made in various molar ratios, complexes (such as YLH, $Y(LH)_2$, YL, YL_2, YLH_{-1}, YHL, and $Y(HL)_2$) which may occur in the medium were examined by the BEST software. Stability constants of YHL^{2+} and $Y(HL)_2^+$ complexes could be calculated by the BEST software in various metal/ligand molar ratios ranging from 1:5 to 1:10; however, the software demonstrated that other complexes were in parts per million level within the medium. In all stability constant calculations, sigma fit (σ_{fit}) was found to be lower than 0.03. Stability constants found in Y(III)−catecholamine systems with different molar ratios and various concentrations are presented in Table 2.

Figures 5, 6, and 7 show the distribution of Y(III) and its coordination species that occur in the Y(III)−catecholamine systems as a function of defined concentration. Thus, the major complex type resulted from Y(III)−adrenaline, Y(III)−noradrenaline, and Y(III)−dopamine systems in acidic, neutral, and basic pH ranges for all systems defined by potentiometry as follows: YHL^{2+} and $Y(HL)_2^+$. When distribution curves are drawn for three different systems of the Y(III) ion, complex derivatives of the Y(III)−noradrenaline system are seen in the most acidic region. It is observed that complex derivatives of

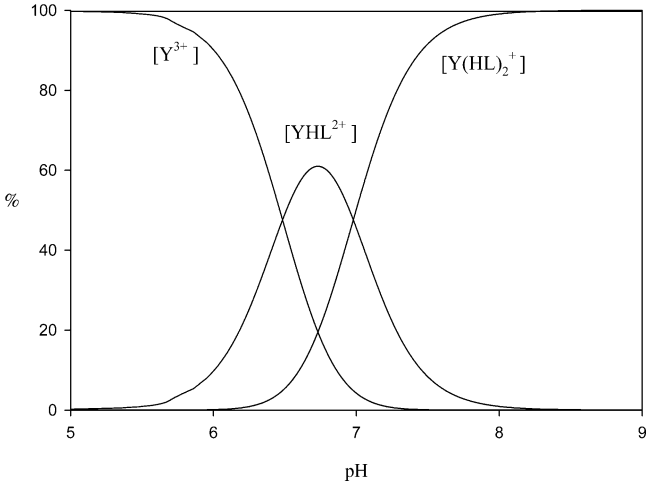

Figure 6. Complex type distribution curves for the Y(III)−NAD system at a metal ion−ligand ratio of 1:4 ($T_Y = 3.0 \cdot 10^{-3}$ mol·dm^{-3}).

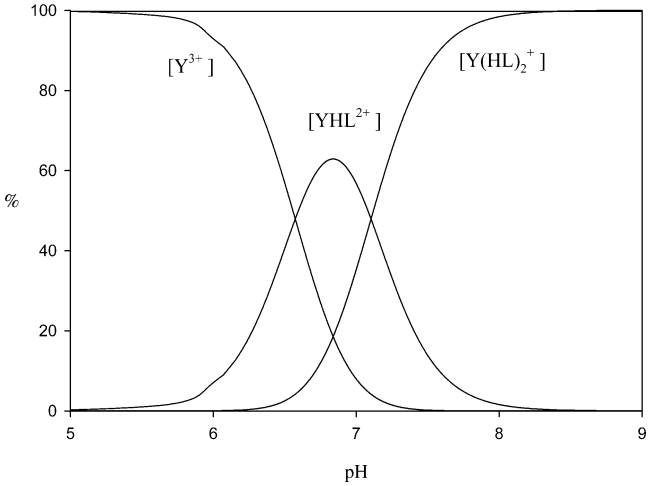

Figure 7. Complex type distribution curves for the Y(III)−DP system at a metal ion−ligand ratio of 1:4 ($T_Y = 3.0 \cdot 10^{-3}$ mol·dm^{-3}).

the Y(III)−adrenaline system occur in a more basic region and that complex derivatives of the Y(III)−dopamine system occur in the most basic region. The reason for this observation is: noradrenaline has an electron-attracting aliphatic hydroxyl group; adrenaline has both an aliphatic hydroxyl group and a methyl group; and dopamine has no substituent.

Y(III) is a hard acid, and it is known to form stable complexes with ligands which have a hard donor atom such as oxygen. In our previous studies, it was reported that the Y(III) ion forms stable complexes with a ligand where oxygen is the donor. In one of the said studies, interaction of disodium 1,2-dihydroxybenzene-3,5-disulfonate (Tiron), a catechole derivate, with the Y(III) ion was examined in $I = 0.1$ M $NaClO_4$ at 298.15 K. The number of protons decomposed in a 1:1 molar Y(III)−Tiron solution was found to be two per metal ion, and the stability constant of the ML complex was found to be $\log \beta_1 = 14.11$.[2] As the constant was always found to be 3 for higher molar ratios, the stability constant was found to be $\log \beta_2 = 43.97$ considering the presence of the M_2L_3 dinuclear complex in the medium. It was reported that in the Y(III)−Tiron system Tiron bound to Y(III) by both phenolic hydroxyls and that a five-membered chelate ring was formed. The stability constant of the LaL complex formed by La(III) ions and Tiron was found to be 13.11, and it was reported that the complex demonstrated behavior similar to that of Y(III).[4]

With regard to protonation constants presented in Table 1, it is obvious that the first two protons of the three deprotonable protons of ligands are relatively more acidic. In their studies, many researchers reported that most acidic protons were found in phenolic hydroxyl and amino groups, in decreasing order.[13−15,20,21] Additionally, it is believed that phenolic hydroxyl groups of ligands bind to Y(III) more easily. Consequently, phenolic hydroxyl groups are a donor for catecholamines. In this study, titration curves obtained in 1:2 or higher metal/ligand molar ratios showed that four protons were titrated per metal ion along the inflection point. It was decided that coordination resulting in formation of a nine-membered chelate by interaction of ligand and Y(III) can be related to phenolic hydroxyl and amino groups or both. However, such a chelate ring would be highly unstable because the amino group of the ligand is too far from the phenolic hydroxyl group to form a stable chelate ring. As a consequence, it was recommended that catecholamines bind to Y(III) only by phenolic hydroxyl groups and that the second phenolic hydroxyl group can participate in chelate ring formation without deprotonating. Complexes formed by Y(III) with catecholeamines were shown as YHL^{2+} and $Y(HL)_2^+$; here, the proton located on the left side of L belongs to the second phenolic hydroxyl.

As catecholamines have three donor atoms, various binding models can be observed in their interaction with metals. It was recommended that coordination of catecholamines with Cu(II), Co(II), Ni(II), Mn(II), and Zn(II) ions was through two phenolic hydroxyl groups.[16] Chakrawarti et al. examined stability constants of complexes formed by adrenaline and noradrenaline in conjunction with soil alkali metals by a potentiometric method.[17,18] Stability constants of complexes formed by the Ca(II) ion with adrenaline are found to be $\log \beta_1 = 5.96$ and $\log \beta_2 = 7.99$, and for noradrenaline, they were found to be $\log \beta_1 = 5.67$ and $\log \beta_2 = 7.05$. Researchers indicated that adrenaline and noradrenaline are bound to the Ca(II) ion through two phenolic hydroxyl protons, but only one phenolic hydroxyl proton was deprotonated. Also, in their study conducted in 2005, Wu et al. examined the interaction of the La(III) ion with adrenaline by potentiometric and "ab initio" methods.[21] The stability constant of the LaL complex formed in the La(III)−adrenaline system was found to be $\log \beta_1 = 5.91$, and the stability constant of the LaL_2 complex was found to be $\log \beta_2 = 10.73$. Researchers reported that the La(III) ion binds to adrenaline through a phenolic hydroxyl group as does the Ca(II) ion and that only one of two phenolic hydroxyl groups was deprotonated.

In the Y(III)−catecholamine system, the Y(III) ion demonstrated behavior similar to that of the Ca(II) and La(III) ions. In previous studies where Y(III),[2] La(III),[4] and Ca(II)[4] ions formed complexes with Tiron, one of the catechole derivatives, similar behavior was reported. In the said complexes, it was reported that binding was through phenolic hydroxyl groups and that two phenolic hydroxyl protons deprotonated.

Conclusion

1. In acidic and neutral pH ranges, the coordination of Y(III) to adrenaline, noradrenaline, and dopamine occurs either in 1:2 or higher molar ratios, presumably via phenolate sites (O; OH) to form YHL^{2+}- and $Y(HL)_2^+$-type complexes.

2. Dopamine and noradrenaline are primary amines, but noradrenaline possesses a hydroxyl group on the β-carbon atom. Consequently, the stabilities of complexes formed by Y(III) with dopamine are higher than its noradrenaline complexes.

3. Adrenaline is a secondary amine which has a methyl group on the nitrogen of the terminal amino group. Furthermore, the protonation constants of adrenaline and its Y(III) complexes are higher than those of noradrenaline.

4. The stability order of Y(III)−catecholamine complexes is as follows: dopamine > adrenaline > noradrenaline.

5. As a result of the smaller ionic radius of Y(III) than La(III), adrenaline complexes of Y(III) are stronger than corresponding La(III) complexes.

6. Due to the higher ionic potential of Y(III), its adrenaline and noradrenaline complexes are more stable than Ca(II)−adrenaline and Ca(II)−noradrenaline complexes. This result may be utilized for in vitro and in vivo studies, since ionic radii of Ca(II) and Y(III) are roughly equal.

7. In complexes formed by Y(III), La(III), and Ca(II) ions with catechols and catecholamines, it was observed that binding was through two phenolates, but only one proton deprotonated from only one of the phenolic hydroxyls in the catecholamines.

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