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Potentiometric and Spectrophotometric Studies of the Complexation of Lanthanum(III) with Adrenaline, Noradrenaline, and Dopamine

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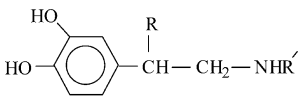
ABSTRACT: The interaction of lanthanum(III) with the catecholamines adrenaline (AD), noradrenaline (NAD), and dopamine (DP) has been investigated by potentiometric and spectrophotometric methods at 298.15 K in an I = 0.2 M KCl ionic medium. The protonation constants for the ligands and the stability constants of the La(III) complexes are calculated from the potentiometric data using "BEST" software. The LaHL and $La(HL)_2$ complexes are reported in 1:1 and 1:2 molar ratios from the potentiometric and spectrophotometric data. The species distribution diagrams were also calculated. In all of the catecholamine systems, the coordination of the ligands to La(III) occurs via the phenolate sites (O; OH), but one of the phenolate protons does not dissociate. With respect to the ligands, the stability constants of the La(III) complexes decrease in the following order: dopamine > adrenaline > noradrenaline. The stability constants of these lanthanum(III) complexes are lower than the analogous Y(III) complexes due to the lower ionic potential of La(III).

INTRODUCTION

Lanthanum is always found in nature with the other lanthanides. Its ionic radius is 1.17 Å for a coordination number of 9, and its chemical properties are very similar to the later lanthanides (with ionic radii of (1.00 to 1.17) Å).[1] We recently reported the interactions of lanthanum(III) with catecholates[2] and salicylates,[3] such as 1,2-dihydroxybenzene-3,5-disulfonate (TIRON), 4-nitrocatechol, 5-sulfosalicylic acid, and 5-nitrosalicylic acid. We proposed that in the lanthanum(III)−catecholate and lanthanum(III)−salicylate complexes two phenolic hydroxyl groups bind La(III), but two phenolic hydroxyl groups are deprotonated.

Like catecholates and salicylates, catecholamines also have a catechol ring. Moreover, catecholamines are bioenergetic amines that play an important role as neurotransmitters in the central nervous system (CNS).[4] They are compounds with amines attached to a benzene ring possessing two hydroxyl groups. The most important endogenously produced compounds within this group are adrenaline (AD), noradrenaline (NAD), and dopamine (DP). The structural formulas are shown in Figure 1. We investigated the stability constants of the



Dopamine, R = R' = H

Adrenaline, R = OH, R' = CH_3

Noradrenaline, R = OH, R' = H

Figure 1. Structures of the ligands used in this study.

binary complexes of Y(III) ions with adrenaline (AD), noradrenaline (NAD), and dopamine (DP) at 298.15 K in an I = 0.2 M KCl ionic medium[5] by the potentiometric method. We calculated the protonation constants of the ligands and the stability constants of the binary complexes using the BEST software. Wu et al. investigated complexes of lanthanum(III) with adrenaline by a potentiometric method and a quantum chemical ab initio method under physiological conditions (at 335 K and an ionic strength of 0.15 M NaCl) to clarify neuroendocrine effects and the underlying mechanism of lanthanides.[6] Gao et al. determined the stability constant for a complex of promethium(III) with adrenaline by a potentiometric titration under equivalent physiological conditions.[7] In the literature, information about the interactions of trivalent metal ions and catecholamines is generally uncommon. However, no research has been published concerning the interactions of lanthanum(III) with dopamine and noradrenaline.

We will continue to study with biologically important ligands, as in our previous work.[5,8] In this study, due to their importance in biological systems, the protonation constants of adrenaline, noradrenaline, and dopamine and the stability constants of the binary complexes that these ligands form with La(III) have been determined at 298.15 K in an 0.2 M KCl ionic medium using potentiometric and spectrophotometric methods. The protonation constants of the ligands and the stability constants of the complexes were calculated with the BEST software.[9] The concentration distribution curves of each complex species in solution were also evaluated by the SPE software.[9]

MATERIALS AND METHODS

Materials. All of the catecholamine hydrochlorides (dopamine, adrenaline, and noradrenaline) were purchased

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from Sigma. These ligands were used without further purification. A lanthanum(III) chloride solution was prepared by dissolving lanthanum oxide (99.9 %) in concentrated HCl (Merck, 37 % purity). The stock solution of lanthanum(III) chloride was standardized complexometrically by the disodium salt of ethylenediaminetetraacetic acid (Na_2EDTA, 99 %) using a suitable indicator.[10] The excess acid in the La(III) stock solution was determined by potentiometric titrations as described previously.[2,3] A carbonate-free KOH (Fluka, 86 % purity) solution was prepared and standardized potentiometrically against the primary standard, potassium hydrogen phthalate (Merck, 99.9 %).[11,12] A hydrochloric acid solution (0.1 M) was prepared and standardized by titration against the potassium hydroxide standard. The potassium chloride, which was used as a background electrolyte, was received from Merck and was of p.a. reagent grade. The ionic strength of each solution was adjusted to 0.2 M by the addition of KCl as the supporting electrolyte. All solutions were prepared with analytical grade water (R = 18 MΩ) using grade A glassware.

Potentiometric Measurements. Potentiometric titrations were carried out using a Schott TitroLine Alpha Plus automatic titrator equipped with a Schott combined pH electrode. The titrator was connected to a computer, and the automatic titrations were performed using a suitable computer program to control the titrant delivery. The pH meter was calibrated daily using standard buffer solutions (Mettler Toledo) with pH values of 4.01, 6.98, and 8.96 at 298.15 K. The potentiometric cell was calibrated before each experiment to allow the measurement of the hydrogen ion concentration rather than its activity. For this purpose, standardized HCl solution was titrated with KOH solution. From the titration data in the acidic region, an equation was obtained (E (mV) = E°_{cell} + S log [H^+] + E_j). In this equation, E°_{cell} is the standard potential in this cell; S is electrode slope; and E_j is the liquid junction potential value that depends only on the ionic strength. When the potential values were measured in the ligand or metal + ligand solutions, pH values were calculated from the potential value using the above equation. From the titration data in the basic region, the K_w values were calculated from several separate series of [H^+] and [OH^-] measurements in 0.2 M KCl.[9,10] The calculated K_w value is 13.66.

All titrations were carried out in solutions contained in a double-walled glass vessel. The titration cell was thermostatted at (298.15 ± 0.1) K using a VWR 11405. The titrations were performed in an inert atmosphere in which nitrogen gas was bubbled through the titrated solutions before and during the pH measurements.

The ionic strength of the solutions was held constant (at 0.2 M) using a KCl solution, and a total volume of 50 mL was used for each titration. Potentiometric titrations were caried out using four different metal concentrations ($2.0 \cdot 10^{-3}$ M to $4.0 \cdot 10^{-3}$ M). The potentiometric measurements were performed by titrating 50 mL of the titrant solution with the standard KOH solutions until the formation of slightly insoluble species was noted. The overall experimental procedure involved the potentiometric titrations of the following solutions:

(a) 5 mL of 0.1 M HCl + 5 mL of 2 M KCl (for cell calibration)
(b) 5 mL of 0.1 M HCl + 0.1 mmol of ligand + 5 mL of 2 M KCl (for the determination of the protonation constants of the ligands)
(c) 5 mL of 0.1 M HCl + 0.2 mmol of ligand + 5 mL of 2 M KCl (for the determination of the protonation constants of the ligands)
(d) 5 mL of 0.1 M HCl + 0.1 mmol of ligand + 10 mL of 0.01 M (0.1 mmol) lanthanum(III) + 5 mL of 2 M KCl (for the determination of the stability constants of the ML complexes)
(e) 5 mL of 0.1 M HCl + 0.2 mmol of ligand + 10 mL of 0.01 M (0.1 mmol) lanthanum(III) + 5 mL of 2 M KCl (for the determination of the stability constants of the ML_2 complexes)
(f) 5 mL of 0.1 M HCl + 10 mL of 0.01 M (0.1 mmol) lanthanum(III) + 5 mL of 2 M KCl (for a pH range where hydrolysis of the La(III) ion occurs)

The computations of the protonation constants of the ligands and the stability constants of the binary complexes of La(III) from potentiometric data were carried out using the BEST[9] 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. All of the protonation and binary system titrations contained at least 99 experimental points between pH 2.0 and 11.0. In the calculations of each, the sigma fit (σ_{fit}) was found to be lower than 0.03 which is considered to be an acceptable fit. The protonation and stability constants reported in this paper were obtained as average values of least three titrations. The results were given with the standard deviation values calculated at a 95 % confidence interval. The potentiometric results were analyzed using the SPE software,[9] and the distributions of the complex species were drawn for all La(III)−catecholamine systems.

Spectrophotometric Measurements. The spectrophotometric studies were performed using a GBS Cintra 303 UV−visible spectrophotometer connected with a Peltier thermocell and a Heidolph Pumpdrive 5201 peristaltic pump. The system used for the potentiometric titrations (i.e., the automatic titrator, titration cell, nitrogen gas, and thermostat) was combined with the spectrophotometer and the peristaltic pump. The automatic titrator was used to measure the pH and for the addition of the base to the solution. The spectra of the solutions containing the catecholamines or the La(III)−catecholamine complexes at different molar ratios were taken separately between pH 3.5 and 10.5 within the range of (200 to 400) nm.

RESULTS AND DISCUSSION

Potentiometric Studies. *Protonation Constants of the Ligands.* The structural formulas of the investigated ligands are given in Figure 1. The protonation constants of the ligands were reinvestigated potentiometrically in an aqueous medium at 298.15 K and I = 0.2 M KCl. The values obtained (Table 1) are in a good agreement with the previous studies.[13−16] Individual titration curves of dopamine, adrenaline, and noradrenaline are shown in Figures 2, 3, and 4. In the titration curves of ligands, one inflection point was observed. In the one buffer zone along the inflection point, the number of titrated protons is two per ligand. For dopamine, adrenaline, and noradrenaline, the first proton is released from the phenolic hydroxyl followed by the one ammonium proton, $-NH_3^+$.[15] The other phenolic hydroxyl is too weakly acidic, and it ionizes only in a very basic solution. All ligands are shown as H_2LH^+;

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Table 1. Protonation Constants (log $K \pm \sigma^b$)^c of Dopamine, Adrenaline, and Noradrenaline at T = 298.15 K in an I = 0.2 M KCl Ionic Medium

	log K		
equilibrium	dopamine	adrenaline	noradrenaline
$L^{2-} + H^+ \rightleftharpoons HL^-$	12.62 ± 0.20[a]	13.13 ± 0.11[a]	12.93 ± 0.06[a]
	12.8[14]	13.15[15]	12.9[13]
$HL^- + H^+ \rightleftharpoons H_2L$	10.32 ± 0.01[a]	9.84 ± 0.04[a]	9.53 ± 0.04[a]
	10.41[16]	9.87[15]	9.53[13]
$H_2L + H^+ \rightleftharpoons H_3L^+$	8.85 ± 0.01[a]	8.63 ± 0.02[a]	8.58 ± 0.03[a]
	8.89[16]	8.63[15]	8.58[13]

[a]This work and previous work (ref 5). [b]Standard deviation. [c]± 95 % confidence interval.

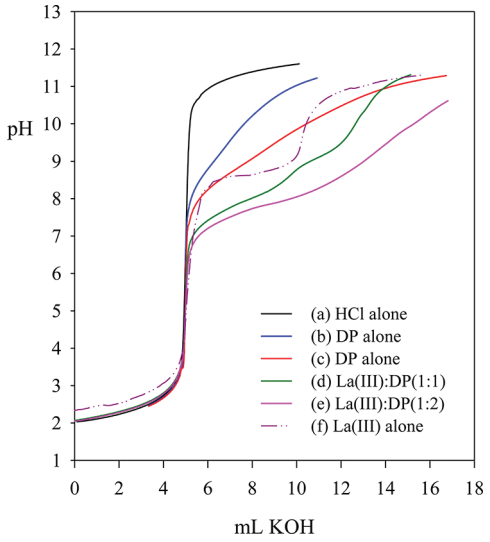

Figure 2. Potentiometric titration curves for the La(III)−DP system at 298.15 K and I = 0.2 M KCl: (a) $1.0 \cdot 10^{-2}$ M HCl; (b) solution a + $4.0 \cdot 10^{-3}$ M DP; (c) solution a + $8.0 \cdot 10^{-3}$ M DP; (d) solution a + $4.0 \cdot 10^{-3}$ M La(III) + $4.0 \cdot 10^{-3}$ M DP; (e) solution a + $4.0 \cdot 10^{-3}$ M La(III) + $8.0 \cdot 10^{-3}$ M DP; (f) solution a + $3.0 \cdot 10^{-3}$ M La(III).

here, the protons on the left side of L are the phenolic hydroxyl protons, and the "H" on the right side is the amine proton.

Complexes of La(III) with Dopamine, Adrenaline, and Noradrenaline. The potentiometric titrations of the La(III)−catecholamine systems were performed at 298.15 K in an 0.2 M KCl ionic medium. Solid catecholamine hydrochlorides were added to the La(III) solutions with a molar ratio of (1:1) or (1:2). Two inflection points were observed at m = 2.0 and 3.0 on the titration curves of the (1:1) La(III)−catecholamine systems, where m is the number of moles of base added per mole of metal (Figures 2, 3, and 4). In addition, the inflections were located in a lower pH region than the titration curves of the catecholamines alone (Figures 2, 3, and 4). In all of the catecholamine systems, the difference between the titration curves of the ligand and metal−ligand solutions (ΔpH) is 2. Experimental data have shown that, in the m = 0.0 to 2.0 buffer zone, the LaHL complex forms between pH 6.1 and pH 8.2. The potentiometric titrations of the (1:2) La(III)−catecholamine systems were carried out under the same experimental conditions. In these curves, only one inflection point was observed at m = 4.0 (Figures 2, 3, and 4). The titration of four protons in each of these systems indicates that the $La(HL)_2$ complex forms gradually. Moreover, no precipitation was

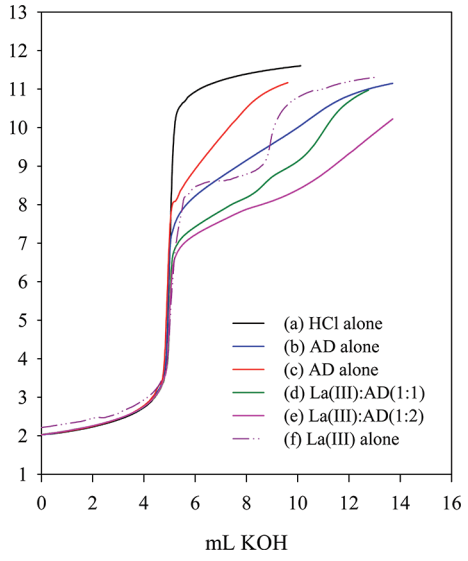

Figure 3. Potentiometric titration curves for the La(III)−AD system at 298.15 K and I = 0.2 M KCl: (a) $1.0 \cdot 10^{-2}$ M HCl; (b) solution a + $3.0 \cdot 10^{-3}$ M AD; (c) solution a + $6.0 \cdot 10^{-3}$ M AD; (d) solution a + $3.0 \cdot 10^{-3}$ M La(III) + $3.0 \cdot 10^{-3}$ M AD; (e) solution a + $3.0 \cdot 10^{-3}$ M La(III) + $6.0 \cdot 10^{-3}$ M AD; (f) solution a + $3.0 \cdot 10^{-3}$ M La(III).

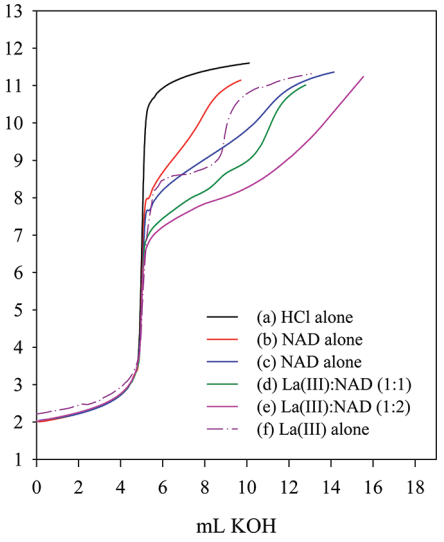

Figure 4. Potentiometric titration curves for the La(III)−NAD system at 298.15 K and I = 0.2 M KCl: (a) $1.0 \cdot 10^{-2}$ M HCl; (b) solution a + $3.0 \cdot 10^{-3}$ M NAD; (c) solution a + $6.0 \cdot 10^{-3}$ M NAD; (d) solution a + $3.0 \cdot 10^{-3}$ M La(III) + $3.0 \cdot 10^{-3}$ M NAD; (e) solution a + $3.0 \cdot 10^{-3}$ M La(III) + $6.0 \cdot 10^{-3}$ M NAD; (f) solution a + $3.0 \cdot 10^{-3}$ M La(III).

observed in any of the titrations. The equilibria involved in this system can be described by the following equations, where β is the overall stability constants of the complex, K is the stepwise stability constant, and L = dopamine, adrenaline, and noradrenaline.

$$La + HL \overset{\beta_{LaHL}}{\rightleftharpoons} LaHL \qquad \beta_{LaHL} = \frac{[LaHL]}{[La][HL]} \tag{1}$$

$$LaHL + HL \overset{K_{La(HL)_2}}{\rightleftharpoons} La(HL)_2 \qquad K_{La(HL)_2} = \frac{[La(HL)_2]}{[LaHL][HL]} \tag{2}$$

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Table 2. Stability Constants ($\log \beta \pm \sigma^b$)^c of La(III) Complexes of Dopamine, Adrenaline, and Noradrenaline at T = 298.15 K in an I = 0.2 M KCl Ionic Medium

	ligand	$\log \beta_{MHL}$	$\log K_{M(HL)_2}$	$\log \beta_{M(HL)_2}$
La(III)	dopamine	6.35 ± 0.03[a]	5.35 ± 0.20[a]	11.7 ± 0.2[a]
	adrenaline	5.96 ± 0.06[a]	4.54 ± 0.20[a]	10.5 ± 0.2[a]
	noradrenaline	5.64 ± 0.03[a]	4.06 ± 0.11[a]	9.70 ± 0.11[a]
Y(III)	dopamine	7.95[5]	6.89[5]	14.84[5]
	adrenaline	7.40[5]	6.38[5]	13.78[5]
	noradrenaline	7.07[5]	6.08[5]	13.15[5]

[a]This work. [b]Standard deviation. [c]± 95 % confidence interval.

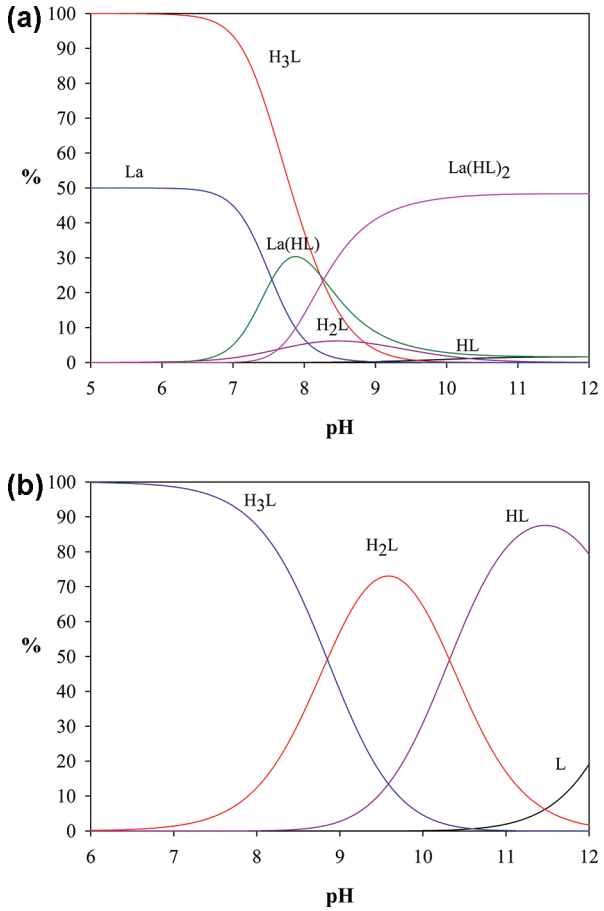

Figure 5. Distribution of species as a function of pH for the systems (a) La(III)−DP in the ratio 1:2 and (b) DP alone, at 298.15 K and I = 0.2 M KCl.

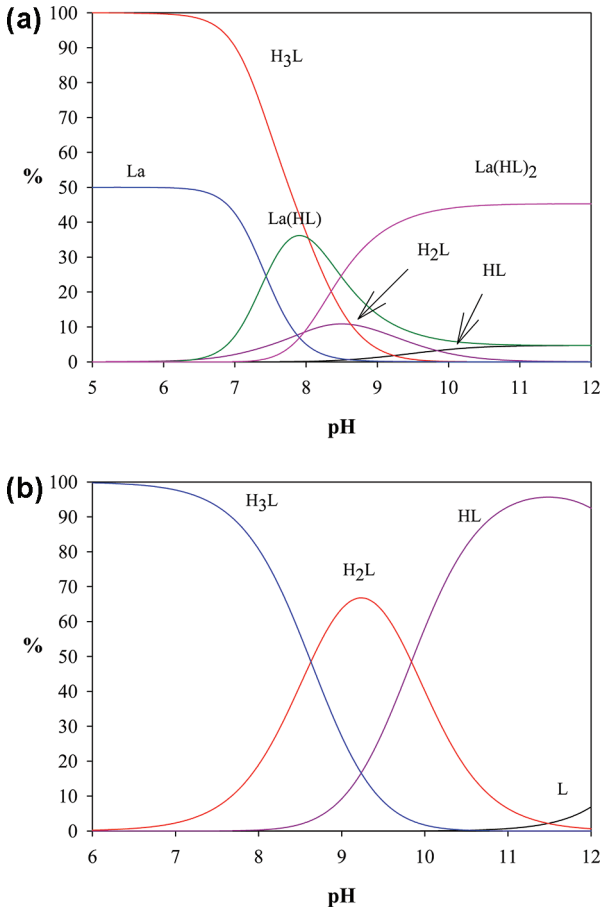

Figure 6. Distribution of species as a function of pH for the systems (a) La(III)−AD in the ratio 1:2 and (b) AD alone, at 298.15 K and I = 0.2 M KCl.

$$La + 2HL \overset{\beta_{La(HL)_2}}{\rightleftharpoons} La(HL)_2$$

$$\beta_{La(HL)_2} = \frac{[La(HL)_2]}{[La][HL]^2} \quad (3)$$

In the (1:2) molar ratio potentiometric titrations, the stability constants of the complexes (LaHL and $La(HL)_2$) were calculated by the BEST software. However, the software indicated that other complexes (LaL, LaL_2, etc.) were present at parts per million concentrations in the medium. The stepwise and overall stability constants of these complexes are listed in Table 2. It was observed that the stability sequence of the LaHL and $La(HL)_2$ complexes formed by La(III) with the catecholamines is dopamine > adrenaline > noradrenaline.

The catecholamines are tridentate ligands containing one amino and one catechol group. The first protonation of the aromatic ring is that of the first phenolate of the catecholate group. The second and third protonations are those of the amino group and the second phenolate of the catecholate group, respectively. Dopamine, containing one catechol and one amino group, has the simplest structure of the catecholamines studied here. The adrenaline and noradrenaline ligands contain aliphatic hydroxyl (−OH) groups outside the aromatic ring. In addition, adrenaline contains a methyl ($-CH_3$) group connected to the amino group. As a result of the inductive effects of these substituents, the second and third protonation constants of dopamine are higher than the corresponding protonation constants of adrenaline and noradrenaline. The high second and third protonation constants of dopamine show that the bonds between the ligand and the protons are more

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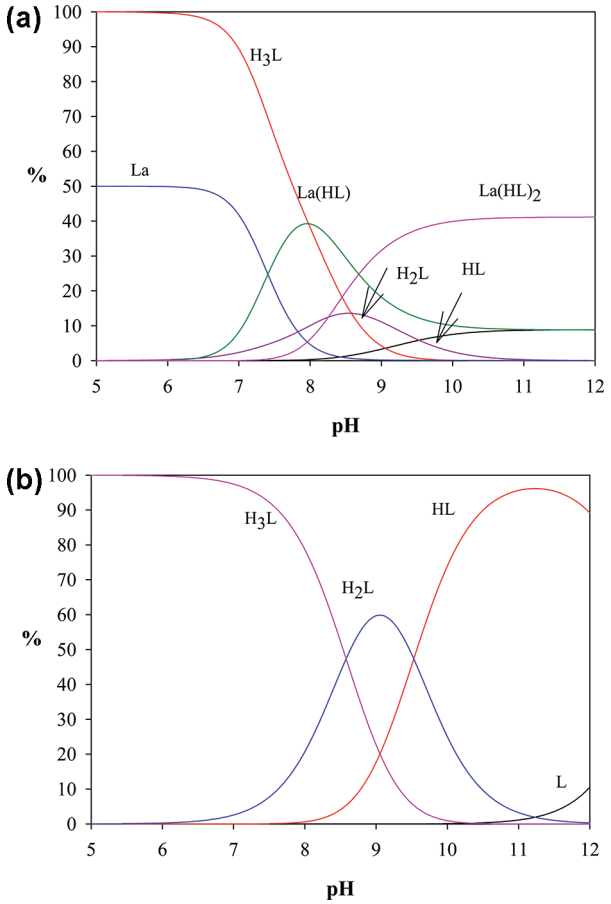

Figure 7. Distribution of species as a function of pH for the systems (a) La(III)−NAD in the ratio 1:2 and (b) NAD alone, at 298.15 K and I = 0.2 M KCl.

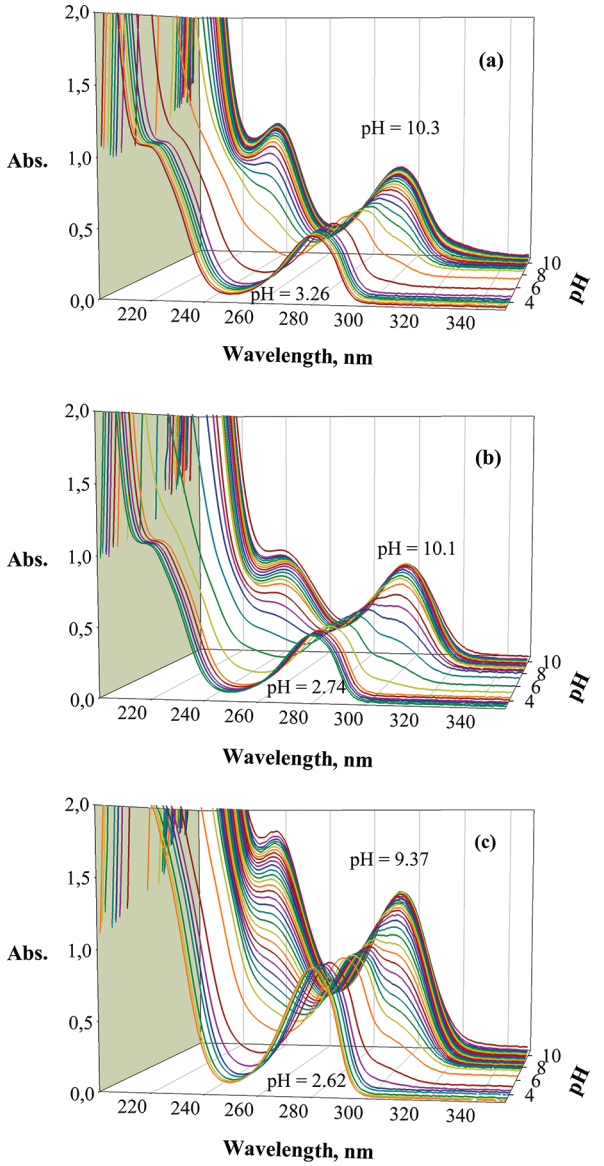

Figure 8. Electronic spectra obtained for the La(III)−DP system as a function of pH at 298.15 K and I = 0.2 M KCl: (a) DP alone, $[L_T]$ = $1{\cdot}10^{-4}$ M; (b) La(III)−DP system, $[L_T]/[M_T]$ = 1, $[M_T]$ = $1{\cdot}10^{-4}$ M; (c) La(III)−DP system, $[L_T]/[M_T]$ = 2, $[M_T]$ = $1{\cdot}10^{-4}$ M.

powerful. The formation of strong metal−ligand bonds may be expected from ligands that form strong bonds with protons. In this study, we found that the stability constants of the La(III) complexes with dopamine are higher than those of the other complexes.

The La(III) ion is a hard Lewis acid, as is the Y(III) ion. Stable complexes are expected when high-valent metal ions bind with ligands containing hard donor atoms, such as oxygen. Previously, we reported the formation of stable complexes of La(III) and Y(III) with catechol-containing ligands in aqueous solutions. The number of protons released in the La(III)−catechol solutions was found to be two protons per metal ion. In the La(III)−catechol systems, we showed that the ligands on the metal ion are bonded to both of the phenolic hydroxyl groups, creating a five-membered chelate ring. However, in the La(III)−catecholamine solutions, the number of protons released from the ligand is also two per metal ion. This indicates that one phenolic proton and one amino proton were dissociated. The experimental data show that the La(III) ion again forms a five-membered ring with the ligand, but in this case, the second phenolic proton is not dissociated, as it is in the Y(III)−catecholamine systems. The complexes of La(III) with the catecholamines take the form of LaHL and $La(HL)_2$, where the proton to the left of the L is the undissociated phenolic proton.

As the catecholamines have two phenolic protons and one amino proton, their interactions with metals may be estimated using various binding models. Previous studies have concluded that the catecholamines bind with the two phenolic hydroxyl group connected to M(II) and Al(III) ions.[6,7,16,17] Wu et al. investigated the complexes formed in a La(III)−adrenaline system with potentiometric and ab initio methods.[6] The result of the calculations made with ab initio methods indicated that the catecholamines can bond to the La(III) ion without losing a phenolic proton. They found that the stability constants of the LaHL and $La(HL)_2$ complexes, log β_1 and log β_2, were 5.91 and 10.73, respectively, at 310.15 K in a 0.15 M NaCl ionic medium. We found that the complexes formed in the Y(III)−dopamine, Y(III)−adrenaline, and Y(III)−noradrenaline systems with the potentiometric method at 298.15 K in an 0.2 M KCl ionic medium.[5] For the Y(III)−dopamine system, we calculated that the stability constants of the Y(HL) and $Y(HL)_2$ complexes, log β_1 and log β_2, were 7.95 and 14.84, respectively. For the Y(III)−adrenaline system, log β_1 and log β_2 were 7.40 and 13.78. For the Y(III)−noradrenaline system, log β_1 and log

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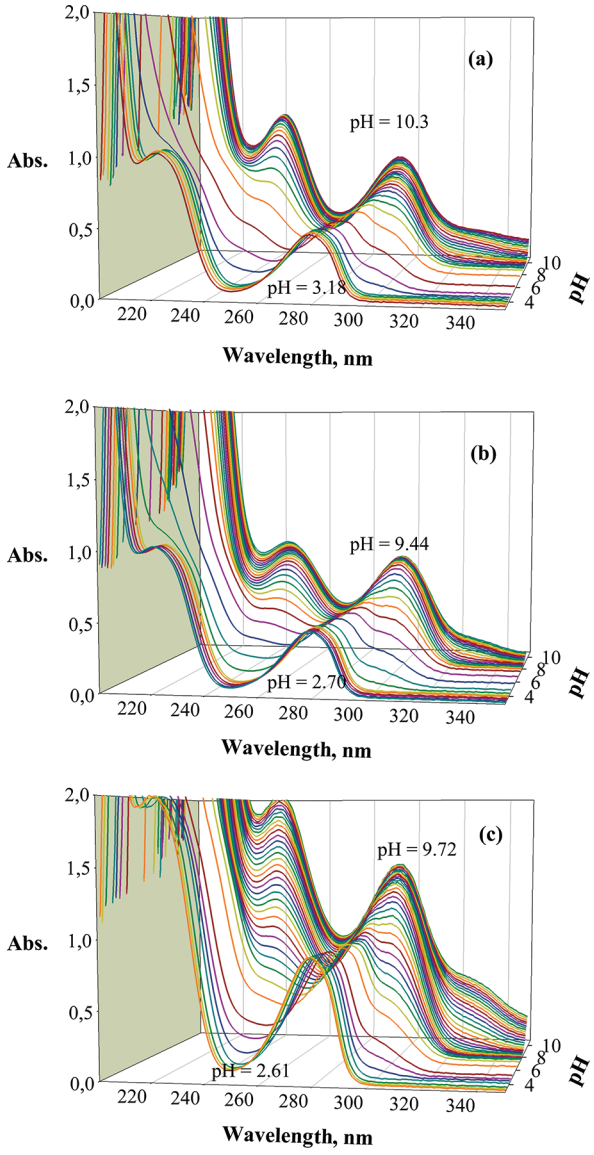

Figure 9. Electronic spectra obtained for the La(III)−AD system as a function of pH at 298.15 K and I = 0.2 M KCl: (a) AD alone, $[L_T]$ = $1{\cdot}10^{-4}$ M; (b) La(III)−AD system, $[L_T]/[M_T]$ = 1, $[M_T]$ = $1{\cdot}10^{-4}$ M; (c) La(III)−AD system, $[L_T]/[M_T]$ = 2, $[M_T]$ = $1{\cdot}10^{-4}$ M.

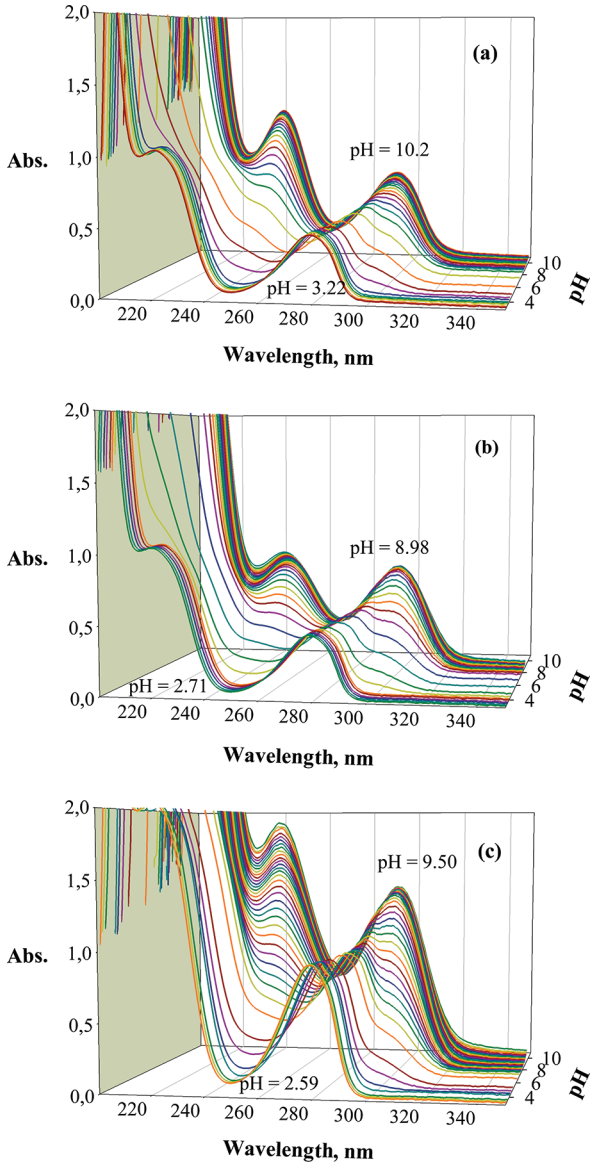

Figure 10. Electronic spectra obtained for the La(III)−NAD system as a function of pH at 298.15 K and I = 0.2 M KCl: (a) NAD alone, $[L_T]$ = $1{\cdot}10^{-4}$ M; (b) La(III)−NAD system, $[L_T]/[M_T]$ = 1, $[M_T]$ = $1{\cdot}10^{-4}$ M; (c) La(III)−NAD system, $[L_T]/[M_T]$ = 2, $[M_T]$ = $1{\cdot}10^{-4}$ M.

β_2 were 7.07 and 13.15 at 298.15 K in an 0.2 M KCl ionic medium.[5]

Distribution Diagrams. The concentration distributions of the complex species in all of the La(III)−catecholamine systems could be obtained using the SPE software. The distributions are shown in Figures 5, 6, and 7. The LaHL and $La(HL)_2$ complexes reach their maximum concentrations in the basic region for all systems.

The concentration distribution curves are drawn for the catecholamine systems (in the absence of metal) in Figures 5a, 6a, and 7a. In these systems, while the H_3L concentration decreases, H_2L starts to form at pH ca. 6.8 and reaches a maximum concentration of ca. 73 % in the dopamine solution, ca. 66 % in the adrenaline solution, and 60 % in the noradrenaline solution between pH values of ca. 9.0 and 9.5. In the dopamine system, at pH 11.0, HL reaches a maximum of ca. 88 %. However, in the adrenaline and noradrenaline systems, the concentration of HL is 96 % at the same pH. In all of the La(III)−catecholamine systems, the LaHL complex starts to form at a pH of ca. 7.9 (Figures 5b, 6b, and 7b). At a basic pH value (i.e., pH 8.0), the concentrations of the LaHL complex for the La(III)−DP, La(III)−AD, and La(III)−NAD systems are ca. 30 %, ca. 36 %, and ca. 40 %, respectively. For the same systems, at pH 10, the concentrations of the $La(HL)_2$ complex are ca. 47 %, ca. 43 %, and ca. 40 %, respectively (Figures 5b, 6b, and 7b).

Spectrophotometric Studies. Spectrophotometric titrations of the catecholamines and the La(III)−catecholamine systems were carried out at 298.15 K in an 0.2 M KCl ionic medium under an atmosphere of nitrogen gas. The recorded electronic spectra at different pH values are shown in Figures 8, 9, and 10.

The spectra of the dopamine ligand in the acidic region (pH 3.26 to 5.55) exhibit a shoulder at 218 nm and a λ_{max} at 279 nm, as shown in Figure 8(a). In this region, the protons are not yet dissociated, and the dopamine is in the form of H_3L. In the

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basic region, from pH 7 to 10.12, the observed values for λ_{max} were red-shifted as the deprotonation occurred. The red-shift is caused by the decrease in the energy of the $\pi \rightarrow \pi^*$ electron transitions of the benzene ring with the loss of one of the dopamine protons. No coloration was observed in the solution until pH 10.12. Above pH 10.12, the solution started to become yellow in color. At pH 10.12, two λ_{max} are observed at 239 nm (A = 1.08815) and 294 nm (A = 0.72090). The spectra of a solution of (1:1) La(III)−DP are shown in Figure 8(b). Because there is no ligand field interaction with the La(III) ion, the peak was assigned to the intraligand transition. In the spectra, a redshift was observed from pH 5.01 to 9.28. The peak shift and the variation in the position of the peak in comparison with the free ligand peak indicate the formation of metal complexes. The increase in absorbance continued up to pH 9.28. At pH 9.28, the absorbance maxima were measured as 0.74 and 0.76 at (239 and 294) nm, respectively. As shown in Figure 8(c), the spectra of (1:2) La(III)−DP red-shifted from pH 4.23 to 9.37. The absorbance continued to increase up to pH 9.37. At pH 9.37, the absorbance maxima were measured as 1.61 and 1.30 at (239 and 294) nm, respectively.

The spectra of the adrenaline and noradrenaline ligands in the acidic region show a λ_{max} at 279 nm and a shoulder at 221 nm (Figures 9(a) and 10(a)). In the spectra recorded in the basic region, at pH 9.60, the shoulder and the λ_{max} were red-shifted, and two λ_{max} were observed at (243 and 292) nm. The spectra for the (1:1) and (1:2) molar ratios of La(III)−AD and La(III)−NAD are shown in Figures 9(b), 9(c), 10(b), and 10(c). As in the La(III)−DP system, starting from approximately pH 4.5, a red-shift and an increase in the absorbance values were observed. In the basic region, in all of the spectra of the La(III)−AD and La(III)−NAD systems, the λ_{max} are 250 and 298 nm. After pH 9.0, the absorbance values increased very little.

CONCLUSIONS

In this study, equilibrium measurements were performed to study the interactions of adrenaline, noradrenaline, and dopamine with La(III) in 1:1 and 1:2 molar ratios at 298.15 K in an 0.2 M KCl ionic medium.

The coordination of adrenaline, noradrenaline, and dopamine to La(III) occurs via the phenolate sites (O; OH), and the complexes formed are formulated as LaHL and $La(HL)_2$. In terms of the ligands, the stability sequence of the La(III) complexes is dopamine > adrenaline > noradrenaline, in agreement with the analogous Y(III) complexes. Dopamine and noradrenaline are primary amines, and noradrenaline possesses a hydroxyl group on the β-carbon atom; however, adrenaline is a secondary amine, which has a methyl group on the nitrogen of the terminal amino moiety. Therefore, the stabilities of the complexes formed by La(III) with dopamine are higher than those of the adrenaline and noradrenaline complexes. As a result of the higher ionic radius of La(III) compared with Y(III), the stability of the La(III) complexes is weaker than corresponding Y(III) complexes.

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