

Electrochemically Active Ligands Useful for the Indirect Analysis of Lanthanides

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Electrochemical determination of lanthanides was not widely used because of the unfavorable half-wave potentials especially in aqueous media. Only Sm^{3+} , Eu^{3+} and Yb^{3+} were successfully determined.¹ Also very similar electronic structure of lanthanide produced very close half-wave potentials such a way that it was almost impossible to separate one from the others by direct electrochemical analysis. In order to overcome these problems, indirect measurements through complexation of lanthanides were developed. Willard and Dean² first reported that the polarographic wave of Eriochrome Violet B showed two waves when aluminum ion was added. Florence³ and Palmer⁴ have applied this azo dye for the determinations of lanthanides. Thakur⁵ reported the possibility using a dihydroxyazo dye for the determination of gadolinium with cathode ray polarography. Then, various many other electrochemically active ligands, such as triphenylmethane dyes^{6,7}, crown ether⁸, cryptands containing a ferrocene unit⁹, diphthalocyanine¹⁰, and diethylenetriaminepentaacetic acid¹¹ have been used for the indirect measurement of lanthanides.

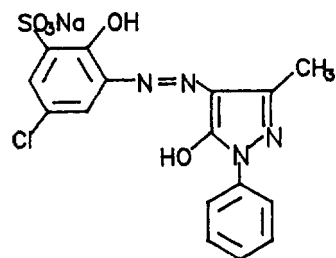
Either the decrease of current from ligand's electrochemical reaction or the increase of complex's wave was measured for lanthanide analysis in these methods. Here, we are reporting that we have found new ligands which are electrochemically active and able to form complexes with lanthanides.

A Bioanalytical System model BAS100A electrochemical analyzer and hanging mercury drop electrode (PAR, 303) were used in this experiment for linear sweep polarography.

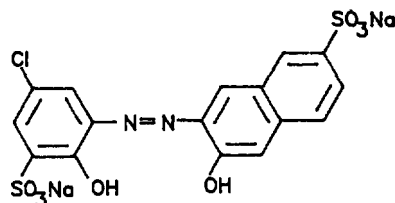
Requirements of new ligands for the indirect determination of lanthanide are firstly, they must have electrochemically active group and secondly, they should have unpaired electrons in their structure for complexation. In addition, the presence of chromophores with rather high molar absorptivity in UV/VIS region was considered to acceptable one in our case so that the spectroscopic experiments could be independently performed. Also they should have reasonable solubility in water.

Considering the above points, azo compounds containing either hydroxide or carboxylic oxygen and quinone or hydroquinone compounds with side phenol group were some on the list to be searched.

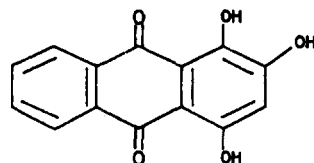
Figure 1 shows the structure of three new ligands which satisfy the requirements. They are Mordant Red 19 (MR19, 5-hydroxy-3-methyl-1-phenyl-4-[(5-chloro-2-hydroxy-3-sulfophenyl)azo]-pyrazole, sodium salt), Mordant Blue 9 (MB9, 6-[(5-chloro-2-hydroxy-3-sulfophenyl)azo]-5-hydroxy-1-naphthalene-sulfonic acid, disodium salt), and Purpurin (1,2,4-trihydroxy-9,10-anthracenedione). First two have hydroxyazo group and the third one has quinone with side phenol group



Mordant Red 19



Mordant Blue 9



Purpurin

Figure 1. Structure of ligands.

in the structure.

Linear sweep polarograms of a solution containing each of the above ligand in the presence of La^{3+} in pH 9.2 ammonia buffer are shown in Figure 2. The concentration of the ligand was maintained such a way that both free ligand and its complex were presented. All showed the presence of sharp and narrow reduction peaks due to ligand itself as well as its lanthanum complex, and the linear dependence of the peak current to scan rate indicating the adsorptive nature of both ligand and complex. Also they showed the shift of peak potential of complexes to cathodic direction in the presence of La^{3+} , indicating the complexes were more difficult to be reduced than the ligands themselves. The magnitude of peak potential difference and absorption maximum of these ligands are shown in Table 1. The ΔE , changed from 75 to 135 mV depending on the ligand in the case of La^{3+} .

Gao and Zhang⁶ observed that the ΔE , varied from 170 mV for La^{3+} to 42 mV for Lu^{3+} with *o*-Cresolphthalexon while less than 15 mV for all lanthanides with Thymolphthalexon. It is interesting to notice that the ΔE , value was decreasing with increasing the atomic number of lanthanide in the case of *o*-Cresolphthalexon. There was only 45 mV difference in La^{3+} , but it increased to 234 mV for Lu^{3+} with Eriochrome Violet B³. This trend is exactly the opposite compared to the results of Zhang. But there was no explanation to this discrepancy. Comparing these data, three new ligands we are reporting have a wide potential difference between ligand and complex so that it would be easier to investigate for themselves are well as it would be possible to apply

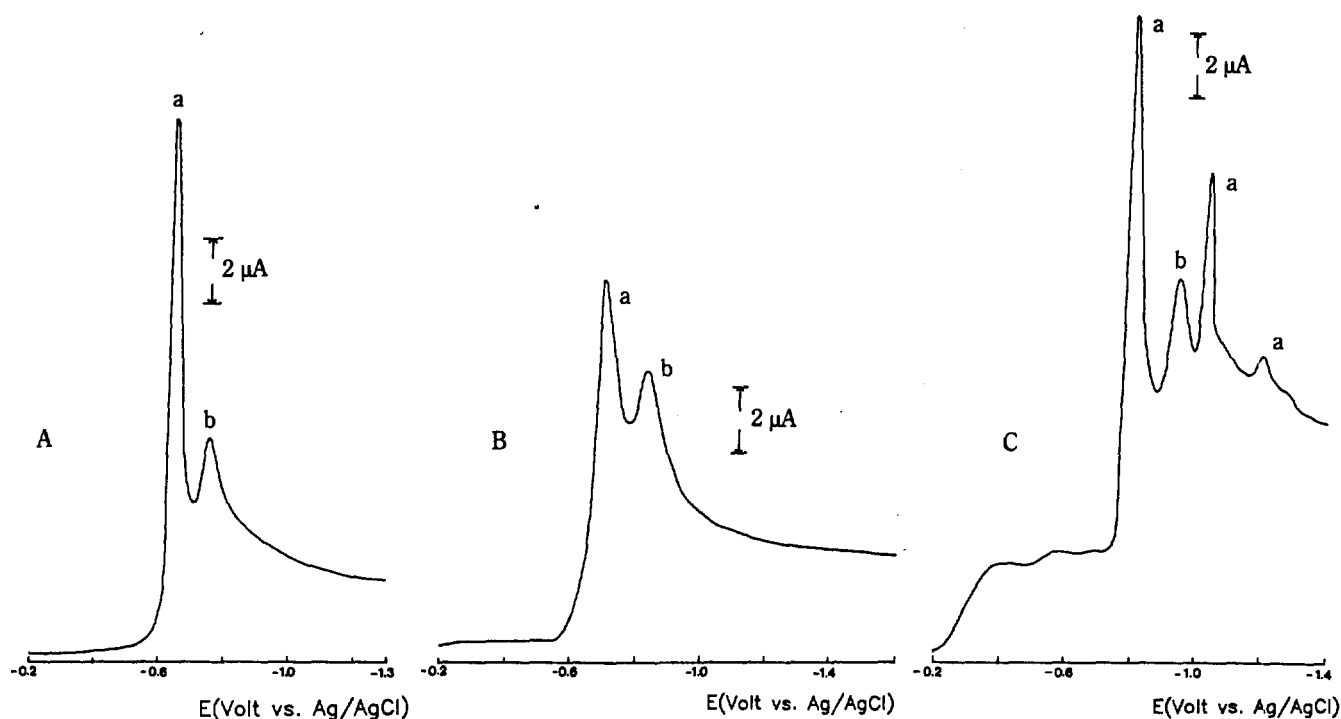


Figure 2. Linear sweep polarograms. A: Mordant Red 19, B: Mordant Blue 9, C: Purpurin Solution; 1.0×10^{-3} M Ligand + La^{3+} in 0.1 M NaCl, pH=9.2, Scan Rate=100 mV/sec. a and b represent ligand and complex, respectively.

Table 1. Electrochemical Parameters of La^{3+} -Ligand System

Ligands	$-E_p$, ligand (mV)	$-E_p$, complex (mV)	ΔE_p (mV)	λ_{max}^a (nm)
Mordant Red 19	670	745	75	472
Mordant Blue 9	710	840	130	516
Purpurin	810	945	135	485
	1040			

^a λ_{max} of ligand. ^bMolar absorptivity, $\text{cm}^{-1}\text{M}^{-1}$. Scan Rate=100 mV/sec.

them for the selective determination of lanthanide in a certain mixture. Detailed electrochemical behaviors, composition of the complex, and analytical applications are under investigation and will be reported later.

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An Effective Diastereofacial Control by Built-in Oxazolidinone Ring System: An Application to the Total Synthesis of α -Allokainic Acid

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α -Allokainic acid **1**, isolated from the algae, *Digenea Simplex*¹ and *Centrocerus clavulatum*² has attracted considerable attention due to its neuroexcitatory activity, although its activity is much less than that of kainic acid³. Structurally α -allo-