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MOLECULAR MODELING, REACTIVITY PARAMETERS AND SPECTROCHEMIC STUDIES OF ε-CAPROLACTAM AND o-PHENANTROLINE

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ABSTRACT

In this work, molecular models were obtained, and the reactivity parameters of ε-caprolactam and o-phenanthroline were calculated to evaluate the interaction in the formation of complex molecular compounds. It was observed that the main electron donor atoms, in the formation of the metal-ligand bond, are centered mainly on the oxygen and nitrogen atoms, respectively, which are sterically more favorable in these species. Conductance measurements in an aqueous solution were obtained to observe the electrolytic behavior of these compounds. Infrared spectra were also recorded to characterize vibrational transitions in identifying these species when present in complex systems. Molecular spectra of absorption in the UV-visible region were recorded to evaluate the spectrochemical properties of these individual ligands and further verify their influence on the formation of complex molecular systems. The parameters evaluated include the molar absorptivity ε, integrated absorption coefficient, oscillator force, and transition dipole moment. It was observed that the ε parameter indicates molecular transitions in the 190 – 300 nm region and the near-infrared, and the oscillator strength is typical of molecules used as dyes and sensitizers for optical light-emitting systems or light-to-electricity converters.

Keywords: *oscillator strength, transition dipole moment, spectrochemical properties*.

1. INTRODUCTION

The ε-caprolactam is a cyclic chain amine with molecular formula $C_6H_{11}NO$, molar mass 113.16 g / mol, soluble in water (50 mg / mL), which in aqueous solution has a pH between 7.0 - 8.5 (333 g/L). In the chemical industry, it has been widely used as a precursor of polymers called nylon 6. More recently, it has been applied in the synthesis of polymeric polyamide compounds (Gong and Yang, 2010), in photochemical-photovoltaic-thermochemical systems (CP-PV-T) for the use of high-efficiency full-spectrum solar energy (Fang *et al,*, 2010), as well as its derivatives, (N-methyl-ε-caprolactam) in the synthesis of light-emitting compounds (Borges *et al*., 2016).

O-phenanthroline is a solid, white, organic heterocyclic compound with the molecular formula $C_{12}H_8N_2$, molar mass 180.21 g/mol, and has a solubility of 3.3 g/L (25 ^oC) in monohydrate form. Although 1,10-phenanthroline is widely used for fast, flexible, and reliable analysis with a high scientific reputation in research, other applications are found, such as; uses cathodic protective buffer layers as a conventional binder to improve the efficiency of organic solar cells (Sun *et al*., 2014), in the study of efficacy in the Luminol chemiluminescence system in Fenton reactions (Mitsuhiro *et al*., 2014), in complex systems with Cu(I) using mixed ligands to amplify luminescent radiative emissions by electron transfer with a high quantum efficiency (Li *et al*., 2012).

This work developed molecular modeling, calculated the reactivity parameters, obtained molar conductivity measurements, recorded infrared and UV-visible spectra, and calculated the spectrochemical properties related to the oscillator strength and induced dipole moment.

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2. MATERIALS AND METHODS

2.1 Molecular Modeling and Reactivity Parameters

Molecular modeling, theoretical reactivity parameters, electrostatic potential cloud, bonding distances, bonding angles, and partial charges were obtained from the WebLab ViewerPro© program. The parameters were calculated using the following expression (Lima *et al*, 2020):

$$\Re = \frac{\int q_i \, d\tau}{\sum_{i=1}^{n} \left| \int q_i \, d\tau \right|}$$

Eq. 01

2.2 Conductance, Conductivity and Molar Conductivity

Molar conductivity measurements were performed for aqueous solutions of millimolar concentration, using a QUIMIS Q-405 conductivity meter, at a temperature of 25.0 ± 1 °C, after calibration of the cell constant with freshly prepared standard solutions millimolar of NaCl and KCl. The molar conductivity was calculated using the expression below:

$$\Lambda_M = \frac{(L_{sol} - L_{solv}).Kc.10^3}{M} = \frac{(k_{sol} - k_{solv}).10^3}{M},$$

Eq. 02

2.3 Spectroscopy in the Infrared Region

The infrared spectra of the two samples were recorded in a PERKIN ELMER FRONTIER equipment, in KBr pellets, in the range of 700 – 4000 cm^{-1} and resolution 4 cm^{-1}.

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2.4 Spectroscopy in the UV-Visible Region

The UV-vis spectra were recorded in a SHIMADZU UV model spectrophotometer in the range of 200 - 1000 nm, quartz cuvette with 1 cm optical path for aqueous ε-caprolactam solutions (1.18×10^{-2} mol L^{-1}), aqueous o-Phenatroline (1.15×10^{-2} mol L^{-1}) and ethanolic o-Phenatroline (1.01×10^{-2} mol L^{-1}). Samples needed to be diluted. The oscillator force f was calculated by Drago's and Figgs method and described methodologies (Lima *et al*., 2020) according to the expressions:

DRAGO: $f = 4{,}6 \times 10^{-9} \int \varepsilon_{(\sigma)} d\sigma$ Eq. 03

FIGGS: $f = 4{,}32 \times 10^{-9} \int \varepsilon_{(\sigma)} d\sigma$ Eq. 04

Area under the absorption band =

$\int A_{(\sigma)} d\sigma = A_{máx}.(1/\lambda_1 - 1/\lambda_2)$ Eq. 05

The transition dipole moment was obtained by the following equation:

$$\mu_{if} = 8{,}422 \times 10^{-22} (m\, s^{-1/2} C) . \sqrt{\frac{f}{\nu}} \quad (C\, m)$$

Eq. 06

3. RESULTS AND DISCUSSION:

3.1 Molecular modeling, obtaining structural data and reactivity parameters.

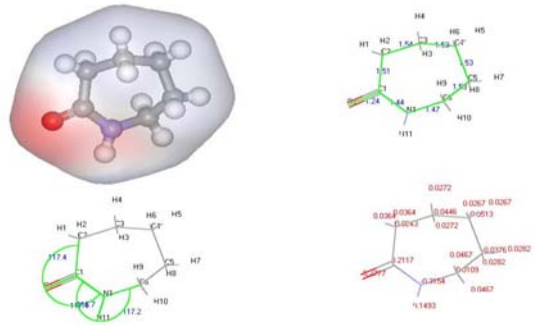

Figure 01 - Modeling obtained for ε-Caprolactam, $C_6H_{11}NO$, using the WebLab ViewerPro program©.

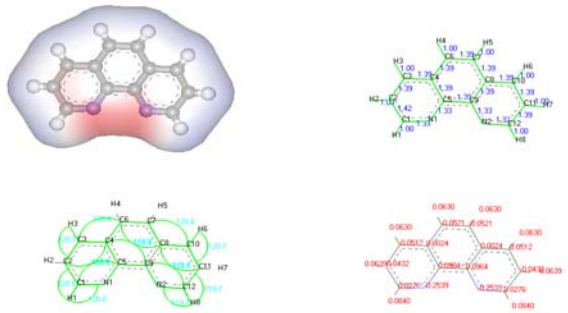

Figure 02 - Modeling obtained for o-Phenanthroline, $C_{12}H_8N_2$, using the WebLab ViewerPro program©.

Table 01 - Partial charges and PRM for ε-Caprolactam, $C_6H_{11}NO$.(main atoms)

Atoms	*Partial charges*		PRM	
	δ^-	δ^+	$\Re^-$	$\Re^+$
O_1	-0,2777		-0,3822	
C_1		0,2117		0,2913
H_1		0,0364		0,0501
H_{10}		0,0467		0,0643
N_1	-0,3154		-0,4341	
H_{11}		0,1493		0,2054

PRM - Molecular Reactivity Parameters

Table 02 - Partial charges and PRM for o-Phenanthroline, $C_{12}H_8N_2$. (main atoms)

	Partial charges		PRM	
Atoms	δ^-	δ^+	$\Re^-$	$\Re^+$
C_1		0,0276		0,0345
C_{12}		0,0276		0,0345
C_5		0,0964		0,1204
C_9		0,0964		0,1204
N_1	-0,2539		-0,3171	
N_2	-0,2539		-0,3171	

PRM - Molecular Reactivity Parameters

3.2 Conductivity measurements and the associated electrolyte type.

Table 03 – Conductivities obtained for millimolar aqueous solutions at 25.0 ± 1 °C.

	k $x10^{-6}$	M Mol/L	Λ_M	Type of electrolyte
H_2O	17,6	55,5	$31,7x10^{-5}$	n-electrol
NaCl	121	0,001	103,4	1:1
KCl	150	0,001	132,4	1:1
ε-capro	34,4	0,001	16,8	n-electrol
o-fen	33,0	0,001	15,4	n-electrol

Units: k (S cm^{-1}); Λ_M (S cm^2 mol^{-1})

3.3 Spectra in the infrared region.

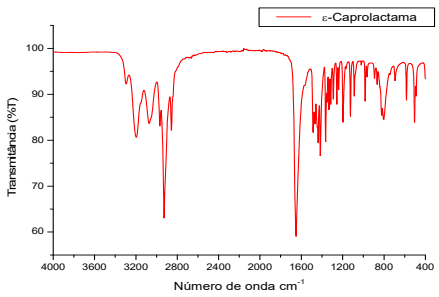

Figure 03 - Infrared spectrum of ε-Caprolactam

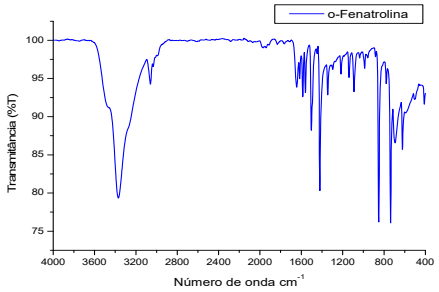

Figure 04 - Infrared spectrum of o-Phenanthroline

Table 04 - Vibrational transition assignments for ε-Caprolactam (main)

vib. modes	Silverstein 2007	Pavia 2010	Cardoso *et al* 2017	Exper
N-H	3350 3180	3300 3100		3294 w 3197 m 3073 m
C=O	1720 1706	1680 1630	1663	1652 s
C-N C-N		 1400	1461	1467 m 1417 m

w (weak); m (medium); s (strong)

Table 05 - Vibrational transition assignments for o-Phenanthroline (main)

vib. modes	Smith, 1961	Martins 2010	Maciel 2015	Exper
νC=N ν_{sim}C=C νC=N νCC νC=C νCN	1616 1585 1558 1508 1418	 1501 1419	1600	1616 m 1586 w 1561 m 1503 s 1421 s
C-N_{arom}	1340			1345 w
δ C=N		621		622 m

w (weak); m (medium); s (strong)

3.4 Spectra in the UV-Visible region in aqueous and ethanolic solution.

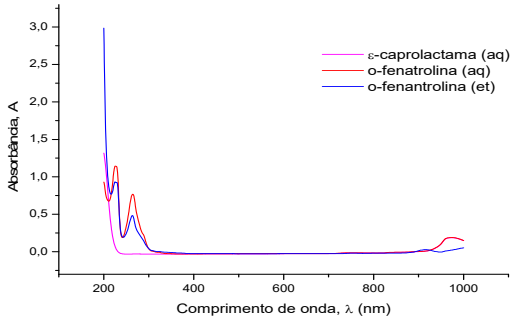

Figure 05 - UV-vis spectrum of ε-caprolactam and o-phenanthroline.

Table 07 - Oscillator strength and ligand transition dipole moment.

Ligand	Range Spectral (nm)	f (x10^{-3}) (adim)		μif x10^{-30} (C m) (Debye)	
		D	F	D	F
ε-cap (aq)	948–999	3,9	3,68	3,0 (0,90)	2,91 (0,872)
o-phe (aq)	948-1000	42	39,2	9,8 (2,9)	9,50 (2,85)
o-phe (et)	900-930	4,5	4,22	3,1 (0,93)	3,22 (0,905)

D – Drago; F – Figgs; 1 Debye = 3,336x10^{-30} C m (aq) aqueous solution, (et) ethanolic solution.

4. CONCLUSIONS

Through molecular modeling and reactivity parameters, elements with higher negative densities corroborate that these species function as a Lewis base and act as electron pumpers in certain systems. Conductivity revealed non-electrolyte characteristics. Infrared spectra identified the main vibrational transitions that are identified in the formation of bonds of these species in complex systems. UV-vis spectra show that they do not absorb into the visible, which may be interesting for better use of energy absorption and conversion phenomena, and that the oscillator strength and transition dipole moment reveal that more energetic transitions confirm that they can acting as optical pumps and those of lower energy show that their outermost electrons can be delocalized with some ease, and these properties and these ligands can be used in the optimization of light-emitting or electron-transfer systems in light-to-electricity converters.

5. ACKNOWLEDGMENTS

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6. REFERENCES

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