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ABOUT THE KINETICS AND MECHANISM OF THE REACTIONS OF 4-(2-PYRIDYLAZO)-RESORCINOL, WITH ZN^{2+}, CU^{2+} AND ZN^{2+}+CU^{2+} EQUIMOLAR MIXTURES, IN AQUEOUS SOLUTIONS

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Abstract

The kinetics and mechanism of the reactions between 4-(2-pyridylazo)-resorcinol and Zn^{2+}, Cu^{2+} and Zn^{2+}+Cu^{2+} equimolar mixtures were studied. The reactions were performed in aqueous solution (pH = 8.5, borate buffer) and monitored spectrophotometrically at 500 nm using stopped-flow technique. Spectral and kinetic data indicate that the Zn^{2+}+Cu^{2+} equimolar mixture behaves as an unique species and it can be attributed to the interactions of Zn^{2+} and of Cu^{2+} with water molecules in the aqueous solution. A mechanism is proposed and the rate constants are calculated.

Keywords: PAR, zinc, copper, kinetics, mechanism

Introduction

Since 1960, derivatives of 2-pyridylazo have been extensively studied for analytical purposes. A very important example is 4-(2-pyridylazo)-resorcinol, PAR. This is an excellent metallochromic indicator and also very useful as a chromogenic agent for the quantitative determination of over 50 elements, including at trace levels [10].

PAR, $C_{11}H_9N_3O_2$, is commercially available as the free dye in the protonated form (represented as H_2L) or as the monosodium ($NaHL.H_2O$) or disodium salt ($Na_2L.2H_2O$). The sequence shows the proton dissociation scheme of PAR in aqueous solution. The dissociation constant are pK_1 (N+H) = 3.1, pK_2 (*p*-OH) = 5.6 and pK_3 (*o*-OH) = 11.9. Two protonated species, H_4L^{2+} and H_5L^{3+}, can exist in 50 and 90% sulfuric acid solution respectively [10,1].

$$H_3L^+ \underset{pK_1}{\rightleftharpoons} H_2L \underset{pK_2}{\rightleftharpoons} HL^- \underset{pK_3}{\rightleftharpoons} L^{2-}$$

yellow	yellow	orange	red
pH < 2.5	3.0 < pH < 5.5	6.0 < pH < 12.5	pH > 12.5

PAR behaves as a terdentate or a bidentate ligand to form soluble or insoluble colored complexes with cations of Mg, Al, Ca, Sr, Ba, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Y, Zr, Nb, Ru, Rh, Pd, Ag, Cd, In, Sn, Hf, Ta, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Th, U, Np and the lanthanides at specific pH values. The Cu^{2+} complex is formed at pH values higher than 5 and the complex with Zn^{2+} is formed at pH values higher than 8. Most PAR complexes are red or red-violet and, in some cases, the color changes with pH [10]. In the case of divalent cations, the complex formed is uncharged, coordination-saturated [10], with a cation to ligand ratio equal to 1:2, $M(HL)_2$(2). For complexes of PAR with Cu^{2+} and Zn^{2+}, in aqueous solution at 25°C, with ionic

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strength = 0.1 mol L^{-1}, the logarithm of the first stability constants (K_{MHL}) are 14.8 and 10.5 respectively. The logarithm of the second stability constant (K_{MHL2}) are 9.1 and 6.6 respectively [1].

Aqueous solutions are the most common medium for chemical reactions but, for simplification purposes, individual interactions of the reactive species with water are usually neglected. Usually, kinetic-mechanistic studies of the complexation of metal transition cations have been performed in the presence of only one species of cation and not in conditions where a mixture of cations reacts with the ligand. Nevertheless, in nature and in analytical sample matrixes, complexation reactions occur with cations and ligands that are in the presence of water and other species, including other cations than can be complexed [9].

The effect of the interactions among water molecules, among water and reacting species, among water and other species, *etc*., are usually neglected due to simplification purposes. However, in some cases, this simplification can hide the actual mechanism of the reaction and the actual nature of the complex formed. Despite the fact that these interactions in water solutions can be considered weak, in some cases they are detectable and can be understood according to the characteristics of the species involved [9, 7]. In a study of the mechanism of the reaction of Cu^{2+}, of Zn^{2+} and of Zn^{2+}+Cu^{2+} equimolar mixtures with Zincon [9], it was shown that the water molecules in the solvation shells of the ions probably determinate the mechanism and the equilibrium of the reaction.

The aim of the present work was to show that some weak interactions in aqueous solutions can actually influence the kinetics and the equilibrium of chemical reactions. This knowledge could help to understand and to prevent interference, in kinetic and in equilibrium analytical procedures, that can be caused by these weak interactions. Certainly, it could also be applied to other fields of the Chemistry although this is out of the scope of the present work.

Experimental

Materials

All reagents were of analytical grade and solutions were prepared with water obtained from an all-glass distillation apparatus. KCl was used to maintain constant ionic strength (1.00 mol L^{-1}) in all working solutions. A (1.528±0.001)×10^{-2} mol L^{-1} stock solution of zinc chloride was prepared by dissolving metallic zinc in 6.0 mol L^{-1} HCl. Working Zn^{2+} solutions were prepared by dilution. A (1.550±0.005)×10^{-2} mol L^{-1} stock solution of copper sulfate was prepared by dissolving $CuSO_4.5H_2O$ in distilled water followed by standardization by the iodometric method [13]. Working Cu^{2+} solutions were prepared by dilution with distilled water. Working solutions of Zn^{2+}+Cu^{2+} equimolar mixtures were prepared by dilution of mixtures of appropriate volumes of the above stock solutions with distilled water. Buffer solutions (pH = 8.5) were obtained by mixing 50.0 ml of 0.10 mol L^{-1} H_3BO_3 prepared in 1.00 mol L^{-1} KCl solution with 10.0 ml of 0.10 mol L^{-1} NaOH solution [14]. PAR solutions were prepared daily by direct weighing of the monosodium salt for dissolution in the buffer solution.

Spectra

The visible electronic spectra were determined with a HP-8452 Diode Array Spectrophotometer and a 1.00 cm path quartz cell. The following solutions were used: 3.03×10^{-5} mol L^{-1} $Zn(HL)_2$; 2.96×10^{-5} mol L^{-1} $Cu(HL)_2$ and (1.50+1.50)×10^{-5} mol L^{-1} $[(Zn+Cu)(HL)_2]$.

Kinetics

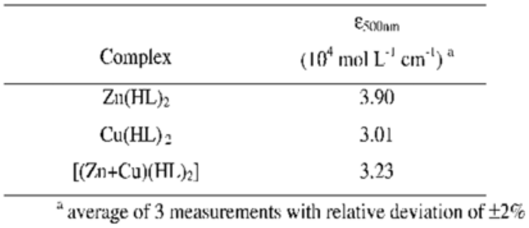
The reactions were monitored spectrophotometrically at 500 nm, at (25.0 ± 0.1) °C, using a stopped-flow apparatus built in our laboratory [8, 11,12]. In order to study the influence of the concentration of the metal and of the ligand on the reaction, two series of experiments were performed for each metal and for the equimolar mixture of zinc and copper. **Series I**: to study the influence of the metal concentration on the reaction rate, where the concentration of the metal varied from 5×10^{-6} to 8×10^{-5} mol L^{-1} and the PAR concentration was fixed near 8×10^{-4} mol L^{-1}. **Series II**: to study the influence of PAR concentration on the reaction rate, where the concentration of PAR varied from 4×10^{-5} to 1×10^{-4} mol L^{-1} and the metal concentration was fixed near 5×10^{-4} mol L^{-1}. In both series, both sulfate and chloride solutions were tested to verify a possible effect of the anion on the kinetics. The results are the average of at least five individual determinations obtained in immediate succession.

The reaction rate constants were determined considering the initial <20% of the total variation of absorbance. Experimental readings were taken on an interfaced PC and rates were calculated using a program in QuickBasic 3.0 especially developed for this work, including unweighted-average smoothing.

The stopped-flow experiments were done with the PAR solutions buffered at pH = 8.5 and an ionic strength of 1.00 mol L^{-1} (KCl). The Zn^{2+} and Cu^{2+} solutions were prepared only with distilled water and enough KCl to obtain the desired ionic strength. No precipitation was observed during the course of these experiments.

Results and Discussion

The electronic spectra of the aqueous solutions of PAR complexes, $M(HL)^2$, where M is Zn^{2+}, Cu^{2+} and Zn^{2+}+ Cu^{2+} equimolar mixture are shown in FIGURE 1 - Electronic spectra of aqueous solutions of (a) $[Cu(HL)_2]$ 2.96 x 10^{-5} mol L^{-1}; (b) mixture $[(Zn+Cu)(HL)_2]$ $(1.50+1.50)\times10^{-5}$ mol L^{-1}; (c) $[Zn(HL)_2]$ 3.03×10^{-5} mol L^{-1}. Distilled water was used as reference. The values of the molar absorptivity, ε, were calculated at 500 nm, for the $M(HL)_2$ complexes and they are presented in Table 1. It is noted that the molar absorptivity of the Zn^{2+} + Cu^{2+} equimolar mixture complex is not the mean of the two independent complexes of copper and of zinc but is closer to that of the copper complex. This is confirmed by inspection of the spectrum of the equimolar Zn^{2+}+ Cu^{2+} mixture PAR complex (Figure 1) which resembles to that of Cu^{2+} complex. This suggests that Cu^{2+} presents a higher influence on the structure of the complex than Zn^{2+} and, as a consequence, this cation should influence the kinetic behavior of the mixture more than Zn^{2+}.

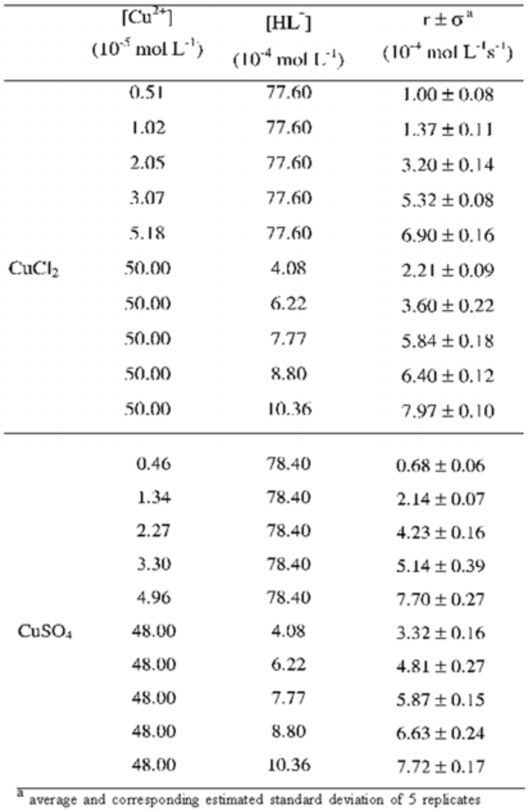


Complex	ε_{500nm} (10^4 mol L^{-1} cm^{-1}) [a]
$Zn(HL)_2$	3.90
$Cu(HL)_2$	3.01
$[(Zn+Cu)(HL)_2]$	3.23

[a] average of 3 measurements with relative deviation of ±2%

Table 1. Molar absorptivity of Cu^{2+}, Zn^{2+} and Zn^{2+}+ Cu^{2+} complexes with monoprotonated PAR, HL^-, in aqueous solution; pH = 8.5 (borate buffer)

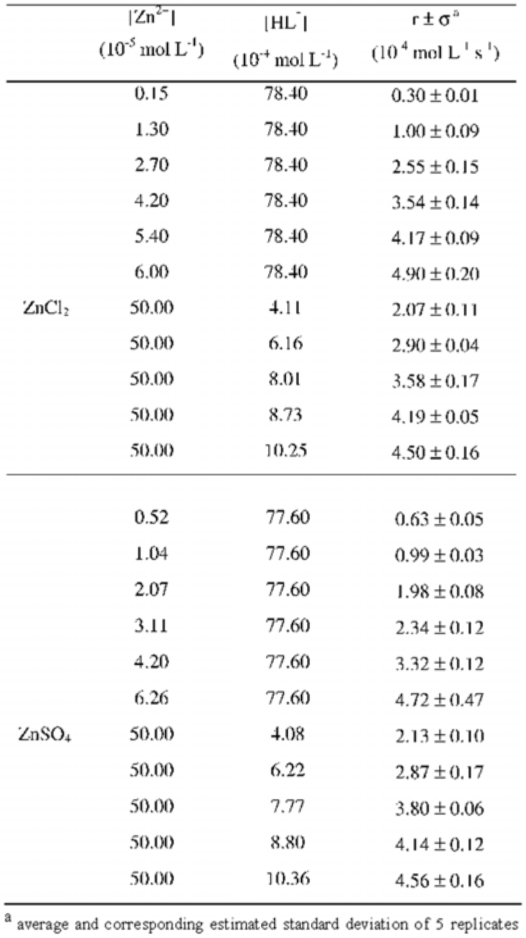
Tables 2 to 7 show the experimental rates obtained from the kinetic experiments at the indicated concentrations of reagents. It can be observed that the reaction rate increases with the increasing of the concentration of the reagents. The reaction rate constants and the order of reaction were determined from these data. The data fit a first order rate treatment with respect to each reagent in the concentration range studied.



	$[Cu^{2+}]$ (10^{-5} mol L^{-1})	$[HL^-]$ (10^{-4} mol L^{-1})	$r\pm\sigma$ [a] (10^{-4} mol $L^{-1}s^{-1}$)
$CuCl_2$	0.51	77.60	1.00 ± 0.08
	1.02	77.60	1.37 ± 0.11
	2.05	77.60	3.20 ± 0.14
	3.07	77.60	5.32 ± 0.08
	5.18	77.60	6.90 ± 0.16
	50.00	4.08	2.21 ± 0.09
	50.00	6.22	3.60 ± 0.22
	50.00	7.77	5.84 ± 0.18
	50.00	8.80	6.40 ± 0.12
	50.00	10.36	7.97 ± 0.10
$CuSO_4$	0.46	78.40	0.68 ± 0.06
	1.34	78.40	2.14 ± 0.07
	2.27	78.40	4.23 ± 0.16
	3.30	78.40	5.14 ± 0.39
	4.96	78.40	7.70 ± 0.27
	48.00	4.08	3.32 ± 0.16
	48.00	6.22	4.81 ± 0.27
	48.00	7.77	5.87 ± 0.15
	48.00	8.80	6.63 ± 0.24
	48.00	10.36	7.72 ± 0.17

[a] average and corresponding estimated standard deviation of 5 replicates

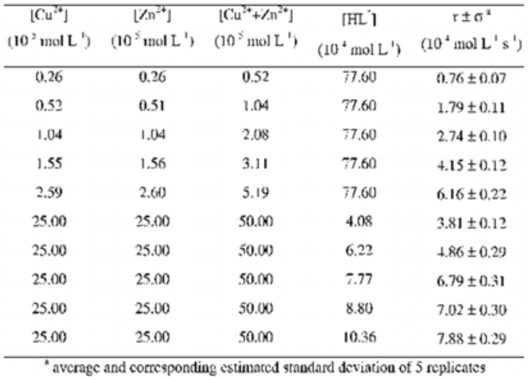
Table 2: Initial reaction rates for aqueous $CuCl_2$ and $CuSO_4$ solutions with aqueous monoprotonated PAR, HL^-, solutions, at 25.0±0.1°C, in borate buffer, pH = 8.5.



	$[Zn^{2+}]$ (10^{-5} mol L^{-1})	$[HL^-]$ (10^{-4} mol L^{-1})	$r \pm \sigma^a$ (10^{-4} mol L^{-1} s^{-1})
$ZnCl_2$	0.15	78.40	0.30 ± 0.01
	1.30	78.40	1.00 ± 0.09
	2.70	78.40	2.55 ± 0.15
	4.20	78.40	3.54 ± 0.14
	5.40	78.40	4.17 ± 0.09
	6.00	78.40	4.90 ± 0.20
	50.00	4.11	2.07 ± 0.11
	50.00	6.16	2.90 ± 0.04
	50.00	8.01	3.58 ± 0.17
	50.00	8.73	4.19 ± 0.05
	50.00	10.25	4.50 ± 0.16
$ZnSO_4$	0.52	77.60	0.63 ± 0.05
	1.04	77.60	0.99 ± 0.03
	2.07	77.60	1.98 ± 0.08
	3.11	77.60	2.34 ± 0.12
	4.20	77.60	3.32 ± 0.12
	6.26	77.60	4.72 ± 0.47
	50.00	4.08	2.13 ± 0.10
	50.00	6.22	2.87 ± 0.17
	50.00	7.77	3.80 ± 0.06
	50.00	8.80	4.14 ± 0.12
	50.00	10.36	4.56 ± 0.16

[a] average and corresponding estimated standard deviation of 5 replicates

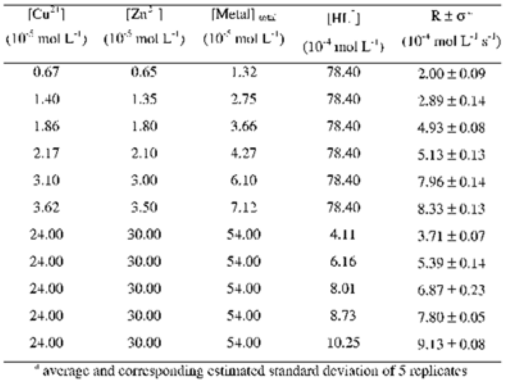
Table 3: Initial reaction rates for aqueous $ZnCl_2$ and $ZnSO_4$ solutions with aqueous monoprotonated PAR, HL^-, solutions, at 25.0±0.1°C, in borate buffer, pH = 8.5.



$[Cu^{2+}]$ (10^{-5} mol L^{-1})	$[Zn^{2+}]$ (10^{-5} mol L^{-1})	$[Cu^{2+}+Zn^{2+}]$ (10^{-5} mol L^{-1})	$[HL^-]$ (10^{-4} mol L^{-1})	$r \pm \sigma^a$ (10^{-4} mol L^{-1} s^{-1})
0.26	0.26	0.52	77.60	0.76 ± 0.07
0.52	0.51	1.04	77.60	1.79 ± 0.11
1.04	1.04	2.08	77.60	2.74 ± 0.10
1.55	1.56	3.11	77.60	4.15 ± 0.12
2.59	2.60	5.19	77.60	6.16 ± 0.22
25.00	25.00	50.00	4.08	3.81 ± 0.12
25.00	25.00	50.00	6.22	4.86 ± 0.29
25.00	25.00	50.00	7.77	6.79 ± 0.31
25.00	25.00	50.00	8.80	7.02 ± 0.30
25.00	25.00	50.00	10.36	7.88 ± 0.29

[a] average and corresponding estimated standard deviation of 5 replicates

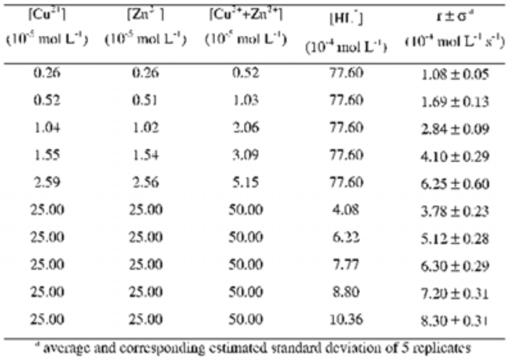
Table 4: Initial rate reaction for aqueous $CuCl_2$ + $ZnCl_2$ solutions with aqueous monoprotonated PAR, HL^-, solutions, at 25.0±0.1°C, in borate buffer, pH = 8.5.



$[Cu^{2+}]$ (10^{-5} mol L^{-1})	$[Zn^{2+}]$ (10^{-5} mol L^{-1})	$[Metal]_{total}$ (10^{-5} mol L^{-1})	$[HL^-]$ (10^{-4} mol L^{-1})	$R \pm \sigma^a$ (10^{-4} mol L^{-1} s^{-1})
0.67	0.65	1.32	78.40	2.00 ± 0.09
1.40	1.35	2.75	78.40	2.89 ± 0.14
1.86	1.80	3.66	78.40	4.93 ± 0.08
2.17	2.10	4.27	78.40	5.13 ± 0.13
3.10	3.00	6.10	78.40	7.96 ± 0.14
3.62	3.50	7.12	78.40	8.33 ± 0.13
24.00	30.00	54.00	4.11	3.71 ± 0.07
24.00	30.00	54.00	6.16	5.39 ± 0.14
24.00	30.00	54.00	8.01	6.87 ± 0.23
24.00	30.00	54.00	8.73	7.80 ± 0.05
24.00	30.00	54.00	10.25	9.13 ± 0.08

[a] average and corresponding estimated standard deviation of 5 replicates

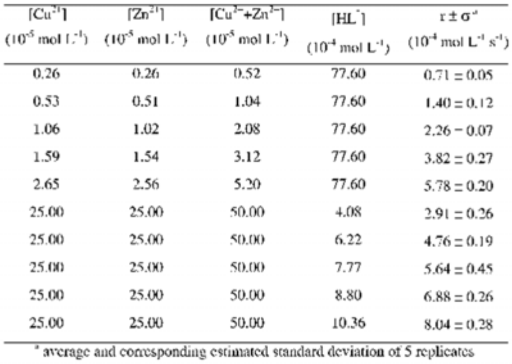
Table 5: Initial rate reaction for aqueous $CuSO_4$ + $ZnCl_2$ solutions with aqueous monoprotonated PAR, HL^-, solutions, at 25.0±0.1°C, in borate buffer, pH = 8.5.



$[Cu^{2+}]$ (10^{-5} mol L^{-1})	$[Zn^{2+}]$ (10^{-5} mol L^{-1})	$[Cu^{2+}+Zn^{2+}]$ (10^{-5} mol L^{-1})	$[HL^-]$ (10^{-4} mol L^{-1})	$r \pm \sigma^a$ (10^{-4} mol L^{-1} s^{-1})
0.26	0.26	0.52	77.60	1.08 ± 0.05
0.52	0.51	1.03	77.60	1.69 ± 0.13
1.04	1.02	2.06	77.60	2.84 ± 0.09
1.55	1.54	3.09	77.60	4.10 ± 0.29
2.59	2.56	5.15	77.60	6.25 ± 0.60
25.00	25.00	50.00	4.08	3.78 ± 0.23
25.00	25.00	50.00	6.22	5.12 ± 0.28
25.00	25.00	50.00	7.77	6.30 ± 0.29
25.00	25.00	50.00	8.80	7.20 ± 0.31
25.00	25.00	50.00	10.36	8.30 ± 0.31

[a] average and corresponding estimated standard deviation of 5 replicates

Table 6: Initial rate reaction for aqueous $CuCl_2$ + $ZnSO_4$ solutions with aqueous monoprotonated PAR, HL^-, solutions, at 25.0±0.1°C, in borate buffer, pH = 8.5.



$[Cu^{2+}]$ (10^{-5} mol L^{-1})	$[Zn^{2+}]$ (10^{-5} mol L^{-1})	$[Cu^{2+}+Zn^{2+}]$ (10^{-5} mol L^{-1})	$[HL^-]$ (10^{-4} mol L^{-1})	$r \pm \sigma^a$ (10^{-4} mol L^{-1} s^{-1})
0.26	0.26	0.52	77.60	0.71 ± 0.05
0.53	0.51	1.04	77.60	1.40 ± 0.12
1.06	1.02	2.08	77.60	2.26 ± 0.07
1.59	1.54	3.12	77.60	3.82 ± 0.27
2.65	2.56	5.20	77.60	5.78 ± 0.20
25.00	25.00	50.00	4.08	2.91 ± 0.26
25.00	25.00	50.00	6.22	4.76 ± 0.19
25.00	25.00	50.00	7.77	5.64 ± 0.45
25.00	25.00	50.00	8.80	6.88 ± 0.26
25.00	25.00	50.00	10.36	8.04 ± 0.28

[a] average and corresponding estimated standard deviation of 5 replicates

Table 7: Initial rate reaction for aqueous CuSO4 + ZnSO4 solutions with aqueous monoprotonated PAR, HL-, solutions, at 25.0±0.1°C, in borate buffer, pH = 8.5.

The monitored species, $M(HL)_2$, is the product of the reaction whose concentrations can be directly associated to the consumption of the less concentrated reagent, A = ligand or metal cation. The excess reagent concentration, B, can be assumed as constant during the reaction, so its value can be included in the observed constant.

$$M^{2+} + HL^{-} \quad M(HL)^{+} \quad \text{slow rate} = r_1$$

$$M(HL)^{+} + HL^{-} \quad M(HL)_2 \text{fast rate} = r_2$$

Considering that the reaction is overall second order and that the rate equation obeys a first order law with respect to each reagent, cation or ligand, it can be assumed that the formation of the species $M(HL)^+$ is the rate determining step. Therefore the following sequence of reactions can be proposed, being $r_2 >> r_1$:

Consequently, the equation rate can be written as

$$r = k_B \times [A] \tag{1}$$

where A is the species with variable concentration and B is the species with constant concentration, and where

$$k_B = k_1 \times [B] \tag{2}$$

For the experiments with the PAR concentration constant, the plot (r *versus* $[M^{2+}]$) is a straight line whose angular coefficient corresponds to

$$k_{PAR} = k'_1 \times [HL^-] \tag{3}$$

For the experiments with metal cation concentration constant, the plot (r *versus* $[HL^-]$) is a straight line whose angular coefficient corresponds to

$$k_{metal} = k''_1 \times [M^{2+}] \tag{4}$$

From the above discussion, the reaction rate law is shown in Equation 5, where $k_1 = k'_1 = k''_1$.

$$r = k_1 \times [HL^-] \times [M^{2+}] \tag{5}$$

Calculations for all sets of experimental data to give rate constant k_1 are described in Table 8. It can be observed that the anions do not affect the values of the rate constant. Also, it is clear that the rate constants for the Cu^{2+} solutions ($CuSO_4$ or $CuCl_2$) are higher ($k_{1Cu} = 1.66 \times 10^4$ L mol^{-1} s^{-1}) than for Zn^{2+} solutions ($ZnSO_4$ or $ZnCl_2$) ($k_{1Zn} = 0.94 \times 10^4$ L mol^{-1} s^{-1}). For the solutions containing Zn^{2+}+ Cu^{2+} equimolar mixtures $k_{1mixture} = 1.54 \times 10^4$ L mol^{-1} s^{-1}. If the rate constant observed for the mixture of the cations was only an average of the independent reaction processes of each cation, a value close to 1.30×10^4 L mol^{-1} s^{-1} (the mathematical mean value of the rate constants) should be observed. However, the higher value observed is closer to the rate constant of the copper solutions. This fact suggests that the reaction of the mixture is more influenced by Cu^{2+} than by Zn^{2+}. The electronic spectrum of the complex of the Zn^{2+}+Cu^{2+} equimolar mixtures in solution also resembles that of Cu^{2+}, as can be seen in Figure 1. These two observations indicate that Zn^{2+} and Cu^{2+}, when mixed in solution, assume properties as if they were an unique species. This behavior had already been observed in the study of the reaction of Cu^{2+} and Zn^{2+} with ZINCON [9].

Reagent solution	$[HL^-]_{constant}$ k' (10^4 L mol^{-1} s^{-1})	$[metal]_{constant}$ k''$_1$ (10^4 L mol^{-1} s^{-1})	mean k_1 (10^4 L mol^{-1} s^{-1})	$k_{1\,metal} \pm \sigma^a$ (10^4 L mol^{-1} s^{-1})
$CuCl_2$	1.78	1.56	1.67	1.66 ± 0.13
$CuSO_4$	1.79	1.54	1.66	
$ZnCl_2$	1.01	0.89	0.95	0.94 ± 0.05
$ZnSO_4$	0.94	0.90	0.92	
$CuCl_2$ 1:1 $ZnCl_2$	1.52	1.54	1.53	1.54 ± 0.06
$CuSO_4$ 1:1 $ZnCl_2$	1.52	1.63	1.58	
$CuCl_2$ 1:1 $ZnSO_4$	1.52	1.59	1.56	
$CuSO_4$ 1:1 $ZnSO_4$	1.43	1.55	1.49	

[a] σ is the estimated standard deviation

Table 8: Reaction rate constants for aqueous Zn^{2+} and Cu^{2+} (chlorides, sulfates and mixtures) solutions with aqueous monoprotonated PAR, HL^-,solutions, at 25.0 ± 0.1 °C, in borate buffer, pH = 8.5.

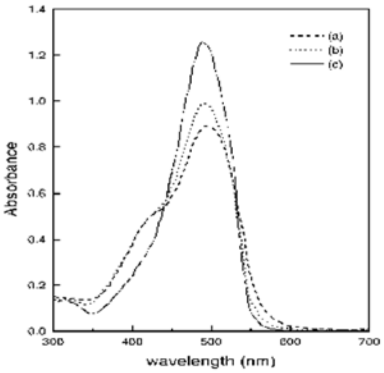


Figure 1. Electronic spectra of aqueous solutions of (a) $[Cu(HL)_2]$ 2.96 10^{-5} mol L^{-1}; (b) mixture $[(Zn+Cu)(HL)_2]$ $(1.50+1.50) \times 10^{-5}$ mol L^{-1}; (c) $[Zn(HL)_2]$ 3.03×10^{-5} mol L^{-1}. Distilled water was used as reference.

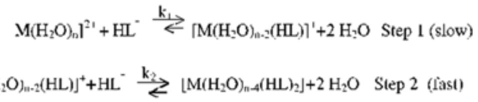
According to Eigen [3], the release of water molecules from the central metal species is rate-determining and controls the formation of the first metal-ligand bond. Usually the chelate ring closure is very rapid, compared with the rate of this first coordination [5].

The experimental observations done in this work and Eigen's proposition, summarized above, can be understood in terms of the water solvation shells of the cations. Initially it must be supposed that the ions are homogeneously distributed through the solvent. The solvated cations can be assumed to form clusters that could contain more than one cation. The solution could be understood as an assembly of these clusters that interact among themselves through hydrogen bonding. Despite the fact that the interactions that form the clusters are weak, it seems that they determine the complexation reaction. Mixed clusters can be imagined in solutions such as a mixture of Zn^{2+}+ Cu^{2+}. Therefore, the final product, in solution, after the reaction of complexation can be a polynuclear hydrated species containing Zn^{2+} and Cu^{2+}, for instance, $[(Zn+Cu)(H_2O)_n\,(HL)_2]x$. This supposition is reinforced by the spectral and kinetical observations obtained in this work. Despite the fact that, from the experimental data obtained in this work, the polynuclear species are only evident in the mixed solution, certainly, this character must be considered for the solutions containing only one kind of cation, such as Zn^{2+} or Cu^{2+}.

According to Eigen [3], the characteristic rate constants for H_2O substitution in the inner coordination sphere of Cu^{2+} is about 3×108 s^{-1} and of Zn^{2+} is about 3×107 s^{-1}. The observed rate constant for the reaction of Cu^{2+} with HL^- is higher than that for Zn^{2+}, as can be seen in Table 8, following the order found by Eigen. It suggests that the entrance of the ligand is strongly dependent on the leaving of water molecules from the cation.

Conclusion

On the basis of the kinetic results obtained in this work, a plausible mechanism of this reaction can be proposed. The following representations are used: k_i = rate constants; **$[M(H_2O)n]^{2+}$** represents the metal cation and its solvation sphere; **HL^--** is the ligand in the monoprotonoated form (reacting species at the working pH = 8.5, according to PAR pKa values(1,2)); **$[M(H_2O)_n\text{-}4(HL)_2]$** is the formed complex, *i.e.,* the spectroscopically monitored species. **$[M(H_2O)_n]^{2+}$** and **$[M(H_2O)_{n-4}(HL)_2]$** can be polynuclear species and therefore the representations used are simplifications.



$$M(H_2O)_n]^{2+} + HL^- \underset{}{\overset{k_1}{\rightleftarrows}} [M(H_2O)_{n-2}(HL)]^+ + 2\,H_2O \quad \text{Step 1 (slow)}$$

$$[M(H_2O)_{n-2}(HL)]^+ + HL^- \overset{k_2}{\rightleftarrows} [M(H_2O)_{n-4}(HL)_2] + 2\,H_2O \quad \text{Step 2 (fast)}$$

In the proposed mechanism, the first ligand site coordination is supposed to be the slow step. The second ligand site coordination is faster. Both steps involve the exchange of water solvation molecules and the solution is assumed as homogeneous distribution of groups of cations and water solvation molecules. The following scheme illustrates a simplified model for this proposal.

The experimental deviations of the kinetic measurements are quite satisfactory for stopped-flow experiments. All the individual solution behaviors are coherent with this model and the rate constant depends only on the cation. The effect of the anion does not significantly affect the reaction.

As was already pointed out, it seems that the equimolar mixtures react like an unique species with a rate constant closer to that of copper. The complex formed in the solution containing both cations closely resembles that of copper alone than that of zinc. This kind of behavior may be surprising but it becomes easier to understand if interactions of water molecules of the solution and the metallic cations are considered to form an assembly. This kind of interaction, briefly commented above is hard to visualize due to the difficulty in providing a structural description which accounts for the ability of water molecules to form structures of a collective character. So, in most cases the effects of these interactions are neglected. Earlier infrared studies of aqueous ionic solutions [7] and kinetic studies of ZINCON complexes [9] indicate that the solvation water molecules, and the "structure" of the aqueous solution, must be considered in reaction mechanism studies. Although these kinds of interactions are weak, they probably affect the complexation. It can be supposed that in aqueous solution there are solvated cations clusters linked by H-bondings. In solutions of Zn^{2+}+ Cu^{2+} mixtures, these assemblies probably contain both cations. The reaction of complex formation would occur through these solvated cations clusters, whose properties are not necessarily the average of Zn^{2+} and Cu^{2+} individual clusters. In this way, the proposed mechanism could be described in more detail by considering the solvated cations clusters. Under such conditions the kinetics of the mixtures could be understood.

Polynuclear aquo-hydroxo copper and zinc complexes have been reported in the literature [2, 6, 4]. In complexation reactions of ZINCON with Zn^{2+} and Cu^{2+}, such aquo-hydroxo complexes are assumed to play an important role [9].

The formation of hydroxo and/or borate aquo complexes of Zn^{2+} and of Cu^{2+} cannot be actually ignored as borate buffer was used. For instance, borate could be supposed to be bonded to cations complexed with PAR, substituting water molecules or OH^-, acting, or not, as bridges. However the borate buffer was chosen among others as less troubling and the eventual participation of borate may be neglected in the general mechanism proposed above.

The results obtained in this study indicate that in kinetic studies, and therefore in the development of quantitative kinetic methods of analysis, the results obtained in mixtures are not necessarily the mathematical mean of those of the individual species. Also, for analytical determinations in equilibrium systems, it must be taken into account that the spectra of the complexes formed in solutions containing more than one kind of cation that is being complexed, are not necessarily the sum of the individual spectra.

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ROSSI, A. V.; TUBINO, M. Sobre a cinética e o mecanismo das reações de 4-2(piridilazo)-resorcinol como Zn^{2+}, Cu^{2+} e com misturas equimolares de Zn^{2+} + Cu^{2+}, em solução aquosa.

Resumo

A cinética e o mecanismo das reações entre 4-(2-piridilazo)-resorcinol e Zn^{2+}, Cu^{2+} e misturas equimolares de Zn^{2+}+Cu^{2+} foram estudados. As reações foram realizadas em solução aquosa (pH = 8.5, tampão borato) e monitoradas espectrofotometricamente em 500 nm com a técnica de fluxo interrompido. Os dados espectrais e cinéticos indicam que a mistura equimolar Zn^{2+}+Cu^{2+} comporta-se como uma única espécie, sendo que isto pode ser atribuído a interações dos íons Zn^{2+} e Cu^{2+} com moléculas de água na solução aquosa. Apresenta-se uma proposta de mecanismo e as constantes de velocidade são calculadas.

Palavras-chave: PAR, zinco, cobre, cinética, mecanismo.

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