

COMPLEX FORMATION OF 4,9-DIAZADODECANE-1,12-DIAMINE WITH COPPER(II) AND ZINC(II) IONS IN AQUEOUS SOLUTION

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ABSTRACT

The complex formation of zinc(II) and copper(II) with 4,9-diazadodecane-1,12-diamine (spermine) was studied in aqueous solution by two different techniques: microcalorimetry and spectrophotometry.

The interaction between the complexes formed and the perchlorate ions was also investigated and the equilibrium constants relative to the second sphere of coordination were determined.

INTRODUCTION

The 4,9-diazadodecane-1,12-diamine (4,9NHddd or spermine) is a polyamine of interest in the biochemical field because of its presence in many biological systems. In particular, it is known that this tetramine links with the phosphoric groups of DNA and RNA, stabilizing their helical structures. Moreover, this amino-compound forms complex species with functional groups of some metal-enzymes and seems to inhibit their catalytic activity [1].

Therefore, the complex formation between this ligand and some divalent metal ions [2,3] was investigated. From this viewpoint, the metal ions considered in this paper are copper(II) and zinc(II), which play an important role in the study of the biochemical behaviour of certain enzymes, as they are present in the prostetic group of those enzymes.

The investigation of the coordination compounds formed by Cu(II) and Zn(II) with 4,9NHddd was also extended to their interaction together with some anions, e.g., perchlorate and nitrate. In fact, it is known from the literature [4] that perchlorate interaction with polyamines such as spermine and spermidine affects some biological systems (e.g., tyroidal). From our point of view this particular interaction could be seen as an outer-sphere coordination [5,6].

EXPERIMENTAL

The 4,9NHddd used was Merck "zur synthese" grade. Other chemicals were commercial products of analytical grade. Water (deionized, distilled and CO₂-free) was prepared daily. The spermine packing was stored in a drier under vacuum, because of its low melting point (27–30 °C). The stock solution of the metal perchlorate (5×10^{-2} M) was freshly prepared every week and stored at 4 °C; the ligand stock solution was prepared and used on the same day (5×10^{-2} M).

Spectrophotometric measurements

Visible spectra were recorded on a Perkin-Elmer 559 spectrophotometer at 25 ± 0.1 °C, using quartz cells with a 5.0-cm optical path. The curves $A = f(C_L/C_M)$ were obtained by measuring the absorbances of solutions prepared by adding varying amounts of ligand stock solution to a fixed volume of metal ion stock solution.

Microcalorimetric measurements

The batch microcalorimeter used was an LKB 2107, equipped with two gold vessels of about 7 ml of the total volume, an LKB 2209 multitemp cooling circulator and a potentiometer recorder (LKB 2210).

The calorimetric system was completely housed in a thermostated room and all measurements were carried out at 25 ± 0.5 °C.

The curve $Q = f(C_L/C_M)$ was obtained by filling the measuring vessel (detector 1) with 2 ml of the metal ion stock solution in one side and 2 ml of different solutions of the ligand in the other side of the vessel. The ligand solutions (10^{-3} – 1.5×10^{-2} M) were obtained on dilution of the same stock solution. The final concentration of the metal ion was 10^{-3} M.

RESULTS AND DISCUSSION

The complex species formed by the 4,9NHddd with copper(II) or zinc(II) were investigated by both spectrophotometric and microcalorimetric techniques, in order to obtain useful information on the complex stability, with particular attention to the chemical environment affecting the reactions. Preliminary tests showed that perchlorate ion strongly influences the tetramine complexes. For this reason the complex formation was studied without buffering the ionic strength, whereas the influence of the perchlorate ion upon the species found was investigated separately.

In all calculations the activity coefficients were calculated by the Davies equation [7].

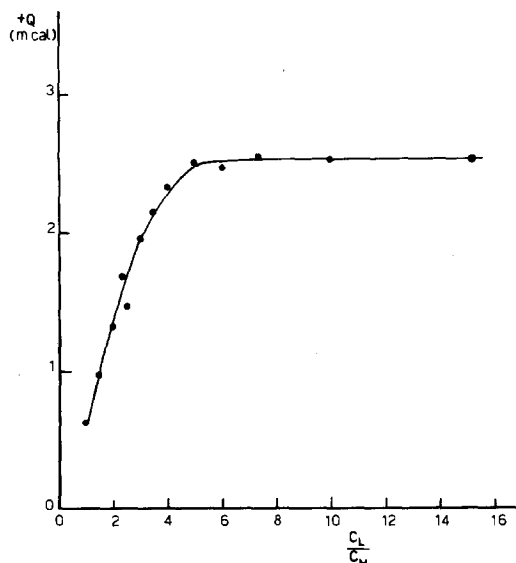


Fig. 1. Variation of the heat response vs. concentration ratio at equilibrium (C_L/C_M) for the system Zn^{2+} - 4,9NHddd at 25°C, pH 6.1, $C_M = 10^{-3}$ M.

The system zinc(II)-4,9 NHddd was investigated by the microcalorimetric technique at pH 6.1 in order to avoid the zinc hydroxide precipitation. The trend of the function $Q = f(C_L/C_M)$ can be seen in Fig. 1. Applying the Asmus method [8] to these Q values, a complexation ratio at equilibrium $C_L/C_M = 2$ was found and the calculated value of the conditional overall constant (β_2) was $1.67 \pm 0.02 \times 10^5 \text{ mol}^{-2} \text{ l}^2$. When complex formation was complete, the enthalpy value (ΔH_{β_2}) was $-10.7 \pm 0.1 \text{ kcal mol}^{-1}$: this value was obtained taking into account the water formation and the ligand deprotonation, on the basis of the protonation constants and the related

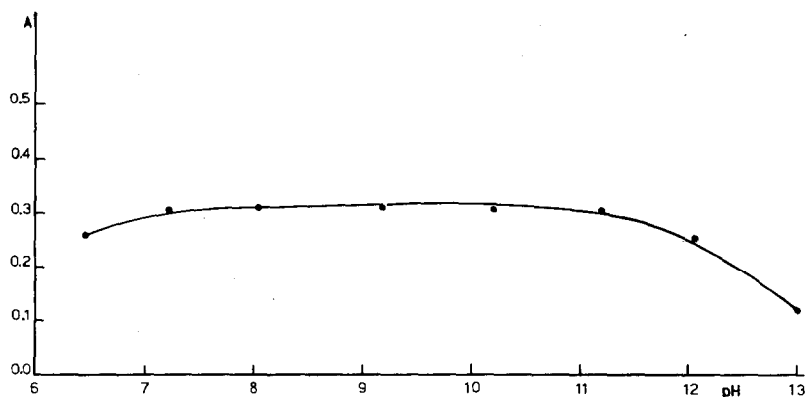


Fig. 2. Variation of the absorbance values vs. pH for the system Cu^{2+} - 4,9NHddd at 25°C, $C_L/C_M = 6 \times 10^{-4}$ M, $\lambda = 558 \text{ nm}$, $b = 5 \text{ cm}$.

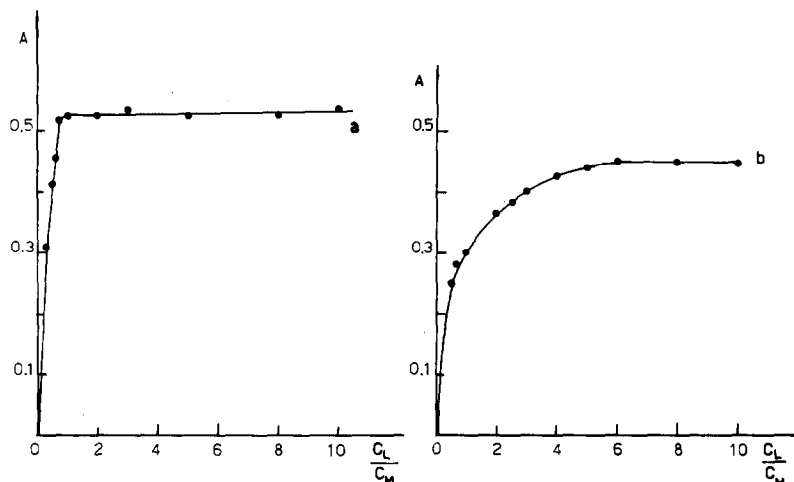


Fig. 3. Absorbance variation vs. concentration ratio at equilibrium (C_L/C_M) for the system Cu^{2+} -4,9NHddd at two different values, $T = 25^\circ\text{C}$, $C_M = 10^{-3}\text{ M}$, $\lambda = 558\text{ nm}$, $b = 5\text{ cm}$: (a) pH 8.0; (b) pH 6.5.

enthalpy values reported by Palmer and Powell [2].

The system copper(II)-4,9NHddd was studied by spectrophotometric measurements at $\lambda = 558\text{ nm}$, which corresponds to the wavelength of the maximum in the visible spectrum. This study was performed at two different pH values (6.5 and 8.0) because they represent two meaningful points in the plot of the function $A = f(\text{pH})$ reported in Fig. 2. The functions $A = f(C_L/C_M)$ at the two pH values mentioned are plotted in Fig. 3. At pH 8.0 a very stable species with a complexation ratio at equilibrium $C_L/C_M = 1$ was found and its molar absorptivity value (ϵ) was $104\text{ mol}^{-1}\text{ cm}^{-1}\text{ l}$. At pH 6.5 a species with a $C_L/C_M = 1$ was found, whose molar absorptivity (ϵ) was $84\text{ mol}^{-1}\text{ cm}^{-1}\text{ l}$ and the calculated conditional constant (K_1) was $1.13 \pm 0.01 \times 10^3\text{ mol}^{-1}\text{ l}$.

Outer-sphere complexes

In order to stress the influence of the ionic strength buffer (NaClO_4) upon the complex equilibria, preliminary measurements were performed using different electrolyte salts (e.g., LiClO_4 , NaClO_4 , NaCl and NaNO_3), in the presence of both copper- and zinc-4,9NHddd systems. From the experimental results it was found that only the anion influences the systems considered. To study the nature of this interaction both spectrophotometric and microcalorimetric measurements were carried out in the presence of perchlorate and nitrate ions; no attempts were made to investigate the sodium chloride interaction, because precipitation occurred under the present experimental conditions.

With respect to the copper(II)-4,9NHddd system, increasing amounts of

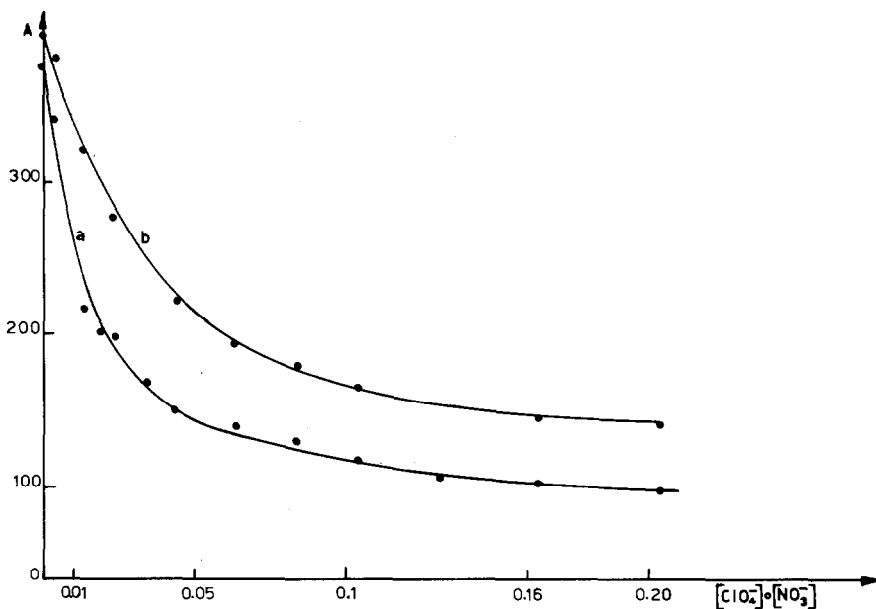
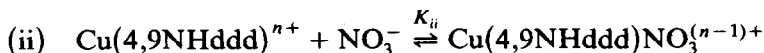
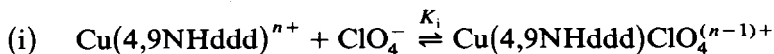


Fig. 4. Absorbance behaviour vs. variable quantities of two different electrolytes for the system Cu^{2+} -4,9NHddd, $T = 25^\circ\text{C}$, pH 6.5, $C_L/C_M = 1$, $C_M = 10^{-3}\text{ M}$, $\lambda = 558\text{ nm}$, $b = 5\text{ cm}$: (a) NaClO_4 ; (b) NaNO_3 .

ClO_4^- and NO_3^- strongly affect the complex equilibria from 0.01 to 0.2 M, while no further variation is detectable for larger concentrations (Fig. 4). The study was carried out at variable ionic strength, whose values have been calculated point by point: the ion activity coefficients were determined by the following equation [7,9]

$$-\log f_i = Bz_i^2(\sqrt{I}/(1 + E\sqrt{I}) - 0.2I) \quad (1)$$

where $B = 0.50$, and $E = 1.5$ (for polyvalent ions) or 1.0 (for monovalent ions). Considering the equilibria



the values of the respective formation constants, on the basis of the elaboration of Gimblett and Monk [9] and of Nyman and Plane [10], were calculated. In particular the equations employed are

$$D = \epsilon_1(a - x) + \epsilon_2x \quad \text{if } \epsilon_2 < \epsilon_1 \quad (2)$$

where D = optical absorptivity values divided by the optical path (A/l), ϵ_1 = molar absorptivity of the complex, ϵ_2 = molar absorptivity of the outer-

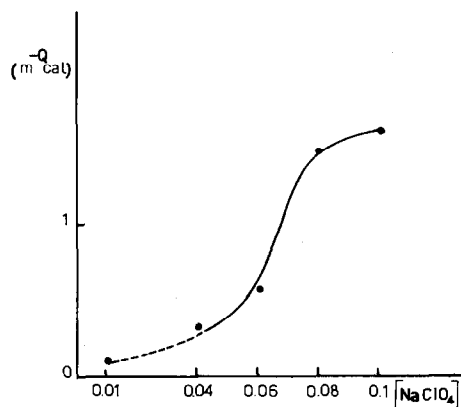


Fig. 5. Variation of heat quantity vs. NaClO_4 concentration at 25°C , for the system Cu^{2+} -4,9NHddd, pH 6.5, $C_L/C_M=1$, $C_M=10^{-3}$ M.

sphere complex, a = initial concentration of the complex, x = concentration at the equilibrium of the outer-sphere complex

$$K = \frac{[\text{Cu}(4,9\text{NHddd})\text{ClO}_4^{(n-1)+}] f_3}{[\text{Cu}(4,9\text{NHddd})^{n+}] f_2 [\text{ClO}_4^-] f_1} = \frac{x f_3}{(a-x) f_2 (b-x) f_1} \quad (3)$$

where: f_1 = activity coefficient of the anion, f_2 = activity coefficient of the complex, f_3 = activity coefficient of the outer-sphere complex and b = initial concentration of the anion. Finding the x value from eqn. (2) and substituting it in eqn. (3), eqn. (4) is obtained

$$\alpha = \frac{1}{\epsilon_1 - \epsilon_2} \beta + \frac{1}{K} \frac{1}{\epsilon_1 - \epsilon_2} \quad (4)$$

where $\alpha = ab/\epsilon_i(a-D)$, $\beta = (a+b)$ and $f_1 = f_3$.

Plotting the function A vs. perchlorate concentration at low values, a linear curve-shape was found and its intercept, at zero perchlorate concentration, was taken as the " $\epsilon_1 a$ " term in eqn. (4).

The two relative formation constants were: $K_i = 1.02 \pm 0.02 \times 10^2 \text{ mol}^{-1} \text{ l}$ and $K_{ii} = 0.63 \pm 0.03 \times 10^2 \text{ mol}^{-1} \text{ l}$ and the values of the molar absorptivities were: $\epsilon_1 = 25 \text{ mol}^{-1} \text{ cm}^{-1} \text{ l}$ and $\epsilon_2 = 28 \text{ mol}^{-1} \text{ cm}^{-1} \text{ l}$.

The microcalorimetric measurements confirmed the interaction between the complex and the perchlorate ion (Fig. 5).

The microcalorimetric investigation of the zinc(II)-4,9NHddd system has shown that some interaction between the complex and the perchlorate ion is still present (Fig. 6), but the shape of the curve is very different on comparison of the previous one. With regard to the zinc complex, in fact, the plot of the heat values vs. increasing perchlorate concentrations results in a

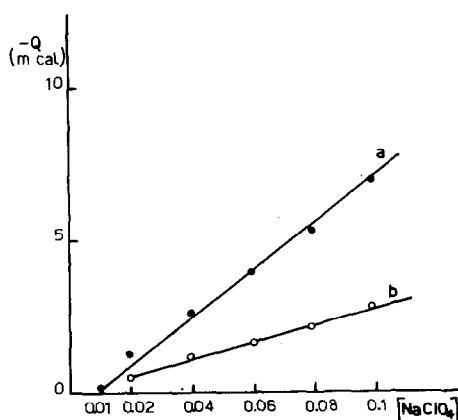


Fig. 6. Variation of heat quantity vs. NaClO_4 concentration at 25°C , pH 6.1, $C_L/C_M = 2$, $C_M = 10^{-3}$ M: (a) for the system Zn^{2+} -4,9NHddd; (b) for the case of 4,9NHddd without metal ion.

straight line, like the interaction between perchlorate ion and the tetramine alone (Fig. 6).

The different behaviour of the 4,9NHddd complexes of zinc(II) and copper(II), with respect to the perchlorate ion, can be explained on the basis of the different structure assumed by the two coordination compounds. In particular, because of its tetrahedral structure, the zinc(II) complex has a less delocalized charge than the copper(II) one. Therefore, interaction with any outside anion would be more likely in the case of the octahedral copper(II) complexes, in order to form some outer-sphere complex.

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