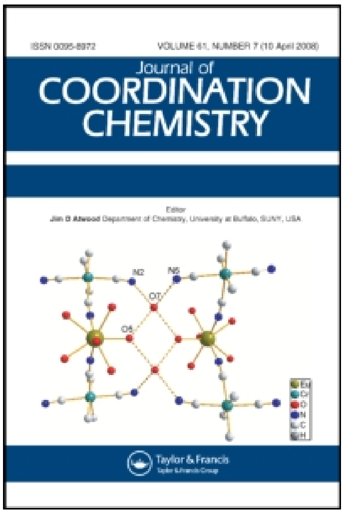

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EQUILIBRIA IN AQUEOUS SOLUTION BETWEEN BERYLLIUM(II) AND ORTHO-PHENYLENE-DIAMINE-*N,N,N',N'*-TETRAACETIC, 3,4-TOLUENE-DIAMINE-*N,N,N',N'*-TETRAACETIC AND 4-CHLORO-1,2-PHENYLENEDIAMINE-*N,N,N',N'*-TETRAACETIC ACIDS

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The complex species formed in aqueous solution between Be(II) and *ortho*-phenylenediamine-*N,N,N',N'*-tetraacetic acid (*o*-PDTA), 3,4-toluenediamine-*N,N,N',N'*-tetraacetic acid (3,4-TDTA) and 4-chloro-1,2-phenylenediamine-*N,N,N',N'*-tetraacetic acid (4-Cl-*o*-PDTA) were studied at 25° and ionic strength 0.5 M in $NaClO_4$. The application of the program LETAGROP to the experimental potentiometric data, taking into account hydrolysis of the ion Be(II), indicates that, upon varying the ligand/metal relationships, only the complexes $BeHC^-$ and BeC^{2-} (ligands, H_4C) are formed in significant amounts for the three systems studied, in an analogous manner to EDTA, the nitrogen atom conformation of which is similar.

INTRODUCTION

The greater proximity of the nitrogen atoms in tetraacids derived from aromatic diamines in the *ortho* position (Figure 1) with respect to their isomers in *meta* and *para* positions, permits the simultaneous coordination of both to one and the same metallic cation.[1] Moreover, the proximity of the four methylcarboxylate groups allows the formation of a greater number of chelate rings. Both effects considerably increase the stability constants of the complexes formed in aqueous solution, to the extent that for some cations the coordinating capacity of these acids is close to that of EDTA.[2] This is only to be expected, since despite the lesser basicity of aromatic amines by comparison with aliphatic ones, the conformation of the nitrogen atoms is similar in both cases. Such acids are therefore excellent complexing agents.

In the case of the ion Be(II), hydrolysis of which must be borne in mind if the results obtained are to be reliable,[3,4] its coordination index of four is totally fulfilled by the three potentially hexacoordinated ligands studied, so the existence of complex species

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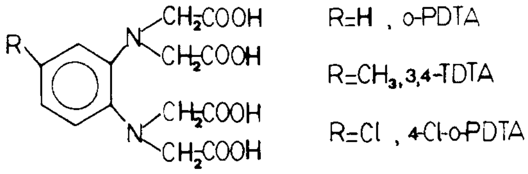

FIGURE 1 Structural formulae of *o*-PDTA, 3,4-TDTA and 4-Cl-*o*-PDTA acids.

with excess ligand is not expected. Since, moreover, the conformation of the ligands does not favour the probable existence of species with excess metal, complex species will presumably be formed only in the ratio 1/1 for the three systems studied. These predictions are confirmed in the present work, contrary to observations in the system Be(II)-*m*-PDTA (*m*-PDTA = *meta*-phylenediamine-*N,N,N',N'*-tetraacetic acid), whose nitrogen atom conformation hinders the simultaneous coordination of both nitrogens to the same metallic cation, but permits the coordination of nitrogen atoms of different ligands, giving rise to the formation of species with a ligand/metal ratio of 2/1.[5]

EXPERIMENTAL

o-PDTA acid was obtained following a modification of the method developed by McCandlish *et al.*[6] with a significant increase in the yield of this synthesis.[7] Adopting a similar technique, the monopotassic salt of 3,4-TDTA acid[7] and the monosodic salt of 4-Cl-*o*-PDTA acid[8] were prepared for the first time and used as a base product in the titrations, since the acids did not precipitate from their respective aqueous solutions when the pH decreased. The solution of $Be(ClO_4)_2$ was prepared by reacting metallic Be with an excess of $HClO_4$, its free acidity[9] being determined, as well the concentration of Be(II) in aqueous solution which was evaluated gravimetrically.[10,11]

The potentiometric titrations were carried out in an inert atmosphere, at 25 ± 0.05, ionic strength 0.5 M in $NaClO_4$, with CO_2-free NaOH as titration agent, using a Radiometer Type PHM-64 potentiometer, a Radiometer G 202 B glass electrode and a NaCl-saturated K401 calomel electrode. Measurements were taken of the ligands only, at an approximate concentration of 1 mM, and of the ligands in the presence of Be(II) at the ratios 1/1, 2/1 and 1/2, using concentrations of Be(II) of 0.8, 1.2 and 1.6 mM for the *o*-PDTA acid, of 0.8, 1.6 and 2.0 mM for the monopotassic salt of 3,4-TDTA acid and of 1.0, 1.5 and 2.0 mM for the monosodic salt of the 4-Cl-*o*-PDTA acid.

The experimental potentiometric data were analysed by means of the NERNST/LETA/GRAFICA version[12] of the LETAGROP program,[13] based on a generalised form of the least-squares method, that establishes the best model and best values of the β_{pqr} constants, minimizing the function $U = \Sigma(Z_{exp} - Z_{calc})^2$, Z being the average number of dissociated protons for the total concentration of ligand (Z_C) or for the total concentration of metal (Z_B). Hydrolysis of Be(II) was previously studied under the same experimental conditions.[4]

RESULTS AND DISCUSSION

The values obtained for the overall ionization constants, β_{-p1}, that correspond to the equilibrium (*1*)

$$-p\,H^+ + H_4C \rightleftharpoons H_{4-p}C^{p-} \qquad (1)$$

TABLE I

Ionization Constants of *o*-PDTA, 3,4-TDTA, 4-Cl-*o*-PDTA and EDTA acids (25°; $\mu = 0.5$ M in $NaClO_4$)

p	$-\log \beta_{pq}$		p	$-\log \beta_{pq}$		Equilibrium	pK_i			
	o-PDTA	EDTA		3,4-TDTA	4-Cl-*o*-PDTA		*o*-PDTA	EDTA	3,4-TDTA	4-Cl-*o*-PDTA
-1	2.916 ± 0.014	1.676 ± 0.018	1	-2.922 ± 0.062	-3.208 ± 0.092	H_4C/H_3C^-	2.92	1.68	2.92	3.21
-2	6.419 ± 0.013	4.160 ± 0.011	-1	3.512 ± 0.028	3.692 ± 0.085	H_3C^-/H_2C^{2-}	3.50	2.48	3.51	3.69
-3	10.990 ± 0.024	10.207 ± 0.008	-2	8.128 ± 0.019	8.386 ± 0.070	H_2C^{2-}/HC^{3-}	4.58	6.05	4.62	4.69
-4	17.415 ± 0.036	19.106 ± 0.012	-3	14.908 ± 0.023	14.207 ± 0.107	HC^{3-}/C^{4-}	6.42	8.90	6.78	5.82

Dispersion, $\sigma(Z) = 0.008$ (*o*-PDTA), $\sigma(Z) = 0.009$ (EDTA), $\sigma(Z) = 0.007$(3,4-TDTA), $\sigma(Z) = 0.026$(4-Cl-*o*-PDTA).

(The use of the monopotassic salt of 3,4-TDTA acid and the monosodic salt of 4-Cl-*o*-PDTA acid led to the calculated real values of p of 1, -1, -2 and -3, respectively).

TABLE II

Stability Constants of *o*-PDTA, 3,4-TDTA, 4-Cl-*o*-PDTA and EDTA Acids with Be(II) (25°C; $\mu = 0.5$ M in $NaClO_4$).

pqr	$-\log \beta_{pqr}$		pqr	$-\log \beta_{pqr}$						
	o-PDTA	EDTA		3,4-TDTA	4-Cl-*o*-PDTA		*o*-PDTA	EDTA[5]	3,4-TDTA	4-Cl-*o*-PDTA
						log K′	3.37	3.48	3.74	3.59
-311	7.624 ± 0.056	6.727 ± 0.190	-211	4.391 ± 0.042	4.799 ± 0.037	log K	6.51	8.06	6.88	5.79
-411	10.902 ± 0.013	11.051 ± 0.040	-311	8.024 ± 0.026	8.421 ± 0.022	pK_H	3.28	4.32	3.64	3.62

Dispersion, $\sigma(Z) = 0.019$ (*o*-PDTA), $\sigma(Z) = 0.048$ (EDTA), $\sigma(Z) = 0.024$ (3,4-TDTA), $\sigma(Z) = 0.021$ (4-Cl-*o*-PDTA). $K' = [BeHC^-]/[Be^{2+}][HC^{3-}]$; $K = [BeC^{2-}]/[Be^{2+}][C^{4-}]$; $K_H = [BeC^{2-}][H^+]/[BeHC^-]$

(The use of the monopotassic salt of 3,4-TDTA acid and the monosodic salt of 4-Cl-*o*-PDTA acid led to real values of pqr of -211 and -311, respectively).

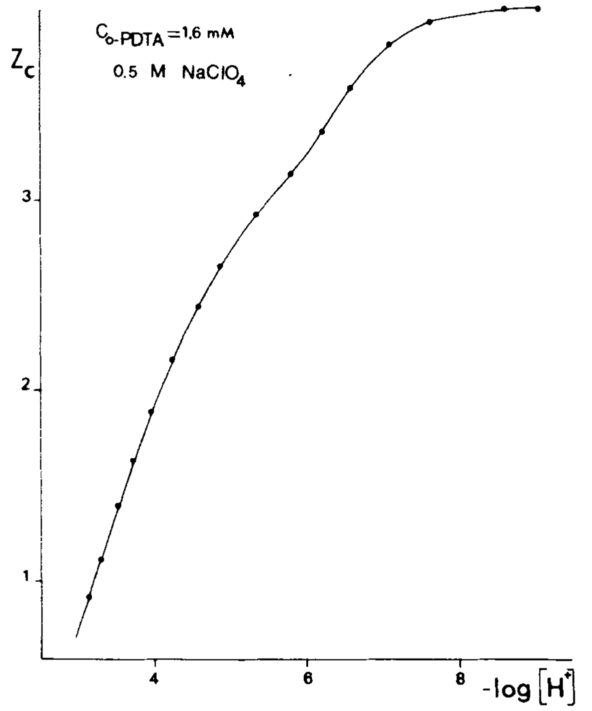

FIGURE 2 $Z_C(-\log[H^+])$ curve corresponding to *o*-PDTA acid.

can readily be related with the corresponding values of pK_i presented in Table I, where the values obtained for EDTA[5] under the same conditions of temperature and ionic strength are also included for comparative purposes.

The validity of the values found is proven by the perfect concordance between the curves $Z_{exp}(-\log[H^+])$ (dotted curve) and $Z_{calc}(-\log[H^+])$ (continuous line), as can be observed in Figure 2 for *o*-PDTA acid and that can be applied to the other two ligands studied. Moreover, these results are in perfect agreement with those found by us[7,8] at 25° and ionic strength 0.1 M in KCl for the three acids and with the results obtained by Grimes *et al.*[14] for *o*-PDTA acid at 30° and identical ionic strength.

The values given in Table I indicate that while pk_1 and pK_2 correspond to protons situated fundamentally over carboxylic groups, pK_3 and pK_4 correspond to protons situated mainly over the nitrogen atoms.[7,15] As expected, the values of pK_3 and pK_4 are higher for EDTA than for *o*-PDTA, 3,4-TDTA and 4-Cl-*o*-PDTA acids, due to the greater basicity of the aliphatic diamines with respect to the aromatic ones. When the three aromatic ligands studied are compared, it is observed that the nitrogen atoms of 3,4-TDTA acid are slightly more basic than those of *o*-PDTA acid, which must be attributed to the electrodonor nature of the methyl radical situated as a substituent on the aromatic ring. As for 4-Cl-*o*-PDTA acid, the presence of a chlorine atom in the *meta* position with regard to one of the nitrogen atoms, and in a *para* position with regard to the other, draws electronic density from the former due to its negative inductive effect (responsible for the smaller value of pK_4, with respect to *o*-PDTA and 3,4-TDTA acids), while due to the effect of resoanance, the basicity of the *para* nitrogen atom increases (which would explain the slightly higher value of pK_3 with respect to the other two acids). The values of pK_1 and pK_2 for 4-Cl-*o*-PDTA acid indicate slightly more basic protons than those corresponding to carboxylic protons of *o*-PDTA and 3,4-TDTA acids, which can be attributed to some type of interaction of the above-mentioned protons with the non-bonding pairs of electrons of the chlorine atom. Summing up, the values of pK_4 indicate that the basic strength of these acids follows the order: EDTA > 3,4-TDTA > *o*-PDTA > 4-Cl-*o*-PDTA.

The analysis of the experimental data of the ligand-Be(II) systems studied by the NERNST/LETA/GRAFICA version[12] of the LETAGROP program[13] shows that the best fit is achieved assuming the existence of the model "FONDO + $BeHC^-$ + BeC^{2-}", where FONDO includes the species proceeding from the successive ionizations of the ligands (H_3C^-, H_2C^{2-}, HC^{3-} and C^{4-}) as well as the hydrolithic species of Be(II) existing in the area of calculus, *i.e.*, $Be_2(OH)^{3+}$ and $Be_3(OH)_3{}^{3+}$, whose formation constants, at this temperature and ionic strength, have been calculated by us in a previous work.[4] Although models were tested that included the possible presence of the

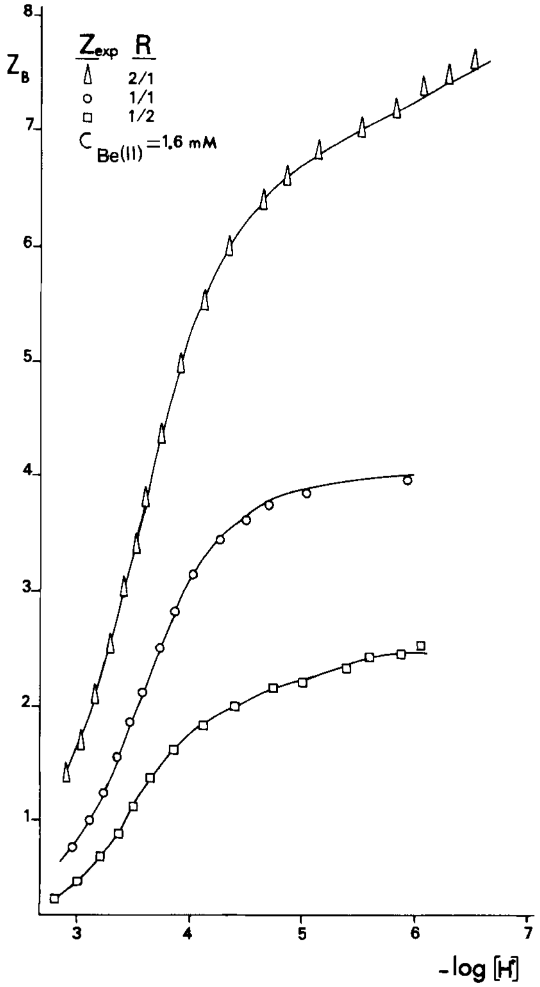

FIGURE 3 Z_B(-log [H^+]) curves of the system *o*-PDTA-Be(II). Dotted line, experimental curves. Full line, calculated curves.

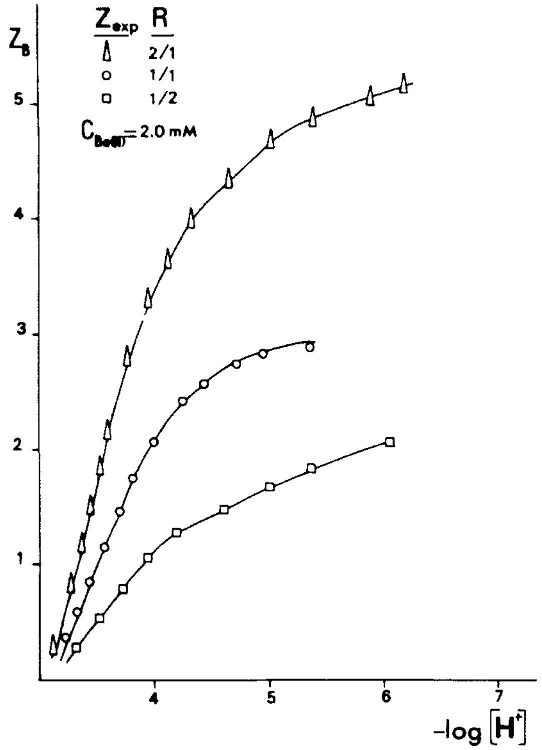

FIGURE 4 $Z_B(-\log[H^+])$ curves of the system 3,4-TDTA-Be(II). Dotted line, experimental curves. Full line, calculated curves.

diacid species, BeH_2C, hydroxocomplex, $Be(OH)C^{3-}$, and complex species with excess of ligand and excess of metal, the results indicate that they are not present in significant amounts. The validity of this analysis can be checked in Figures 3, 4 and 5, where an excellent fit can be observed between the experimental and calculated values of Z.

The results are given in Table II, where they are expressed as formation constants, readily obtained from the LETAGROP constants, β_{pqr}, defined as:

$$p\ H^+ + q\ Be^{2+} + r\ H_4C \rightleftharpoons H_pBe_q(H_4C)_r^{p+2q} \qquad (2)$$

The different values found for the complexes $BeHC^-$ and BeC^{2-} are explained by the fact that a protonated nitrogen atom is to be found in the acid complex, whereas in the non-protonated complex both nitrogen atoms are coordinated to the same atom of Be (Figure 6). These structures are analogous to those proposed for EDTA.[5] Upon comparing the values of pK_H (Table II) with those of pK_3 (Table I), it is found that for all the ligands $pK_3 > pK_H$, proving that the betainic proton of the species $BeHC^-$ is repelled by the coordinated beryllium in view of the strong tendency of the beryllium to coordinate with the two atoms of nitrogen to form the species BeC^{2-}.

The values of log K, which follows the order EDTA > 3,4-TDTA > *o*-PDTA > 4-Cl-*o*-PDTA, can be explained considering the basicity found for the atoms of nitrogen of the ligands studied (*vide supra*). The formation of the same type of complex

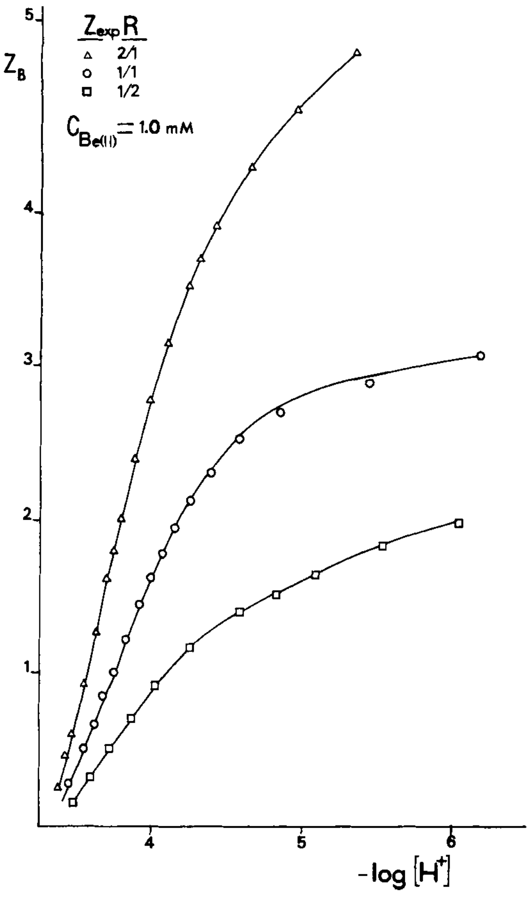

FIGURE 5 $Z_B(-\log [H^+])$ curves of the system 4-Cl-*o*-PDTA-Be(II). Dotted line, experimental curves. Full line, calculated curves.

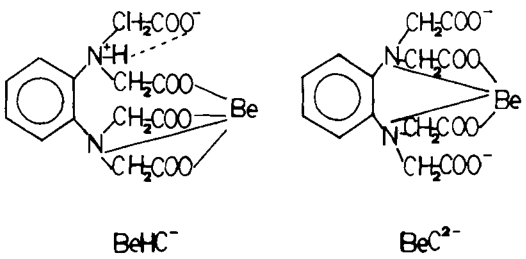

FIGURE 6 Structural formulae proposed for the complexes $BeHC^-$ and BeC^{2-}.

species by EDTA and by the three diaminepolycarboxylic ligands derived from aromatic diamines in an *ortho* position is due to the fact that they all present a comparable conformation with respect to the nitrogen atoms. On the contrary, the fact that the nitrogen atoms of the tetraacid isomers in *meta* and *para* positions are more distant permits only one nitrogen to be coordinated to one atom of beryllium, an increase taking place in the number of complex species in aqueous solution, as found by us in the system *m*-PDTA-Be(II)[5].

EDTA, *o*-PDTA, 3,4-TDTA and 4-Cl-*o*-PDTA acids are appropriate ligands for the coordination of the alkaline earth cations to be classed in the so-called "irregular" sequence,[16] *i.e.*, Be(II) $<$ Ca(II) $>$ Mg(II) $>$ Sr(II) $>$ Ba(II), explaining the greater stability of the CaC^{2-} complexes[2] with respect to BeC^{2-}, since these ligands are potentially hexadentates and totally fulfil the coordination needs of the hexacoordinated and larger cation Ca^{2+}, forming two new five-membered chelate rings.

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