

Article

**Equilibrium Studies of Ternary Complexes Formed by Bromide, Sulfate, Selenite and Selenate Ions with  $Zn^{2+}$ ,  $Mg^{2+}$  and 1, 4, 7, 13, 16, 19-Hexaaza- 10, 22- Dioxacyclotetracosane (Obisdien)<sup>†</sup>**

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Brometo, sulfato, selenito e selenato foram encontrados formando pontes na cavidade dos complexos mononucleares e binucleares de Obisdien:Zn(II) e Obisdien:Mg(II) em solução aquosa a 25 °C e  $\mu = 0,100$  M (KCl). Medidas de equilíbrio potenciométrico foram realizadas para determinar as constantes de formação das espécies formadas nestes sistemas na faixa de p[H] de 2 a 12. Para os complexos do Obisdien:Zn(II): ânions, foram detectadas quatro espécies com o íon brometo, cinco espécies com o íon sulfato, seis espécies com o íon selenito e quatro espécies com o íon selenato. Os complexos binucleares hidróxidos predominam sobre todas as outras espécies e a constante de associação diminui na seqüência:  $SeO_4^{2-} > SeO_3^{2-} > SO_4^{2-} > Br^-$ . O sistema envolvendo os complexos de Obisdien:Mg(II) apresenta três espécies com o íon brometo, quatro espécies com o íon sulfato, cinco espécies com o íon selenito e cinco com o íon selenato. A variação da constante de associação para este sistema é o mesmo observado no sistema anterior:  $SeO_4^{2-} > SeO_3^{2-} > SO_4^{2-} > Br^-$ .

Cálculos de mecânica molecular mostram que os complexos de Obisdien dizinc(II) e dimagnésio(II) adotam várias conformações de baixa energia com diferentes separações Zn-Zn e Mg-Mg permitindo a coordenação dos ânions  $SeO_4^{2-}$ ,  $SeO_3^{2-}$ ,  $SO_4^{2-}$ ,  $Br^-$  e  $OH^-$ .

Bromide, sulfate, selenite and selenate were found to form bridges in the cavity of mononuclear and binuclear Obisdien:Zn(II) and Obisdien:Mg(II) complexes in aqueous solution at 25.0 °C and  $\mu = 0.100$  M (KCl). Potentiometric equilibrium measurements were used to determine the formation constants of the species formed in these systems in the p[H] range 2-12. For the Obisdien:Zn<sup>2+</sup>:anions complexes, we have established the existence of four species for bromide ion, five species for sulfate ion, six species for selenite ion and four species for selenate ion. We found that the hydroxo binuclear complexes predominate over the others species, and the binding strength decreases in the sequence:  $SeO_4^{2-} > SeO_3^{2-} > SO_4^{2-} > Br^-$ . The Obisdien:Mg(II) system presents three species in case of binding with bromide ion, four with sulfate ion, five with selenite ion and five with selenate ion. Variation of the binding strength in the Obisdien:Mg(II) complexes is the same as in the Obisdien:Zn(II) complexes:  $SeO_4^{2-} > SeO_3^{2-} > SO_4^{2-} > Br^-$ .

Molecular mechanics calculations show that the dizinc(II)- and dimagnesium(II)-Obisdien complexes adopt several low energy conformations differing in their Zn to Zn and Mg to Mg separations that allow the coordination of  $SeO_4^{2-}$ ,  $SeO_3^{2-}$ ,  $SO_4^{2-}$ ,  $Br^-$  and  $OH^-$  anions.

**Keywords:** *selenite, selenate, sulfate, Obisdien complexes*

<sup>†</sup>Abstracted in part from a dissertation submitted by Marcos Rivail da Silva to the faculty of the Universidade Federal de Santa Catarina in partial fulfillment of the requirements for the degree of Doctor of Chemistry.

## Introduction

The complexation of organic and inorganic anions which results from the association of two or more species through noncovalent bonds yields what has been termed supramolecular chemistry. Although great amount of researches involve the development of ligands for metal ions, the inorganic and organic anions that play important roles in the environment and biological systems are scarcely studied<sup>1</sup>. Several reasons may be invoked to explain the unequal treatment between anions and cations complexes chemistry. While the cations have usually a spherical shape, the anions exist under various geometries. The anions are more strongly solvated than cations of comparable size and the anions are bulkier than cations<sup>2</sup>. Great interest has been devoted to macrocyclic receptors containing in their framework both oxygen and nitrogen donor atoms<sup>3,4</sup>. Firstly synthesized by Lehn<sup>5,6</sup> and co-workers, the macrocyclic Obisdien has been studied as a ligand that form stable complexes with metal ions and anions<sup>7,8</sup>. Their capacity to form stable binuclear complexes with metal ions is remarkable. Several equilibrium constants of metal complexes were determined and due to the fact that this ligand can be hexaprotonated, the potentiometric titration has been the technique of choice for equilibrium constants determinations<sup>9</sup>.

Studies involving the equilibrium determination with anions as  $\text{Br}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{AsO}_2^-$ ,  $\text{PO}_4^{3-}$ , malonic acid, glycine and others<sup>8,10</sup>, and more recently involving  $\text{SeO}_3^{2-}$ ,  $\text{SeO}_4^{2-}$ ,<sup>11</sup> indicates that this ligand is very important for the selective molecular recognition of these anions. Organic anions also bridges binuclear metal complexes<sup>12</sup>. In these systems, the mono- and binuclear complexes of metal ions can set themselves as host, and the bridging anions are the guests.

The imidazolate-, oxalate- and acetate-bridged binuclear metal ion-Obisdien complexes with  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Zn}^{2+}$  ions have been characterized also by X-ray crystallography<sup>13-16</sup>. Although the equilibrium constants for some anions are known for Cu(II) and Co(II)-Obisdien complexes<sup>4</sup>, these metal ions are not so abundant as Mg(II) and Zn(II) in the environment. The purpose of the present work is to determine the association constants of Mg(II) and Zn(II)-Obisdien with bromide, sulfate, selenite and selenate ions.

The bromide ion is present in great amount<sup>17</sup> in the environment and a previous work<sup>10</sup> has shown that this anion forms complexes with Obisdien: $\text{Cu}^{2+}$ . The sulfate ion is also present in the environment in great amount and its property are similar to that of selenate ions<sup>18</sup>. Selenite and selenate ions are present in the environment generally in trace amount and can be essential or toxic when in excess<sup>19-21</sup>. On the other hand, metal ions as  $\text{Zn}^{2+}$  and  $\text{Mg}^{2+}$  are present in the environment in appreciable amount<sup>18,22</sup>,

and only a few complexes involving selenite and selenate ions and metal ions with some ligands have been synthesized and characterized<sup>23-27</sup>.

## Experimental

### Materials

KCl (MERCK) used as a supporting electrolyte in all potentiometric measurements was used without further purification. The macrocyclic Obisdien used was synthesized by a modification of the method previously described<sup>5,6</sup>. Zinc (II) nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), magnesium(II) nitrate hexahydrate ( $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), HCl, sodium sulfate, sodium selenite and sodium selenate, were reagents grade materials. Carbonate free solutions of about 0.100M KOH were prepared from Dilut-it ampoules (J.T. BAKER) and were standardized by titration with potassium acid phthalate. The stocks solutions of zinc(II) and magnesium(II) were standardized by titration with EDTA using murexide as the indicator<sup>28</sup>.

### Potentiometric equilibrium measurements

It has been shown<sup>29,30</sup> that in calculating unknown equilibrium constants by the least-squares technique from pH (or potentiometric) titration data, errors in the chemical model (initial volume, reactant concentrations, carbonate or other impurities,  $\text{pK}_w$  and other known equilibrium constants) and measurement errors (electrode calibration, drifts in ionic strength, non-ideal titrant mixing or temperature control) can strongly influence the results. To minimize possible errors, at the least three titrations were performed with the ligand alone, and at least one for each anion added. All the potentiometric studies of Obisdien.6HBr in the presence of zinc(II), magnesium(II) with bromide, sulfate, selenite, and selenate ions were carried out with a Digimed model DMPH3 research pH-meter fitted with blue-glass and Ag/AgCl reference electrodes calibrated with standard HCl  $10^{-2}$  M ( $\mu = 0.100\text{M}$  (KCl)) and  $\text{CO}_2$  - free KOH solutions to read  $-\text{Log} [\text{H}^+]$  directly. All systems were studied under anaerobic conditions, by using a stream of purified nitrogen. The temperature was maintained at  $25.00 \pm 0.03$  °C and the ionic strength ( $\mu$ ) was adjusted to 0.100 M by the addition of KCl. Samples of about 0.10 mmol of Obisdien.6HBr (*ca.* 5% excess) in presence and absence of 0.10 mmol of the anions, (sulfate, selenite or selenate) accurately weighted and about 0.20 mmoles of Zn(II) or Mg(II) were diluted with 50 mL of doubly distilled water ( $\text{KMnO}_4$ ) in a sealed thermostated weasel in the conditions described above. All the solutions were titrated with 0.100 M standard  $\text{CO}_2$  - free KOH. The p[H] range was from 2.8 to 11.2. The p[H] reproducibility are  $< 0.002$  p[H] in buffer regions and absolute p[H] accuracy are  $< 0.002$  p[H] at low p[H] and  $< 0.015$  p[H] at high p[H]. The brackets in p[H] is used to emphasize the deter-

mination of  $-\text{Log}_{10}[\text{H}^+]$ . Under these conditions, it appeared that equilibrium was attained within about few minutes (stable  $\text{p}[\text{H}]$  readings were obtained).

### Computations

The equilibrium constants for Obisdien: $\text{Br}^-$ , Obisdien: $\text{SO}_4^{2-}$ , Obisdien: $\text{SeO}_3^{2-}$ , Obisdien: $\text{SeO}_4^{2-}$  and Obisdien: $\text{Zn}(\text{II})$  systems have been reported earlier<sup>9,11</sup>. The proton association constants of sulfate, selenite and selenate ions were taken from the literature<sup>31</sup> and the hydrolysis constants of  $\text{Zn}^{2+}$  and  $\text{Mg}^{2+}$  ions were reported by Baes and Mesmer<sup>32</sup>. The dissociation constant of water ( $\text{pK}_w$ ) at 25,00 °C and  $\mu = 0.100 \text{ M}$  used was 13.78. All these constants were kept fixed during refinement.

In the present work some of the constants taken from the literature were determined in background electrolytes different from the one we used. But this is of minor importance as the literature shows that equilibrium constants obtained in different background electrolytes with Obisdien as ligand, are in good agreement with each other<sup>8</sup>.

The species considered are those which are the most likely to be formed according to the present knowledge in coordination chemistry in solutions and care has been taken to avoid highly improbable unrealistic species.

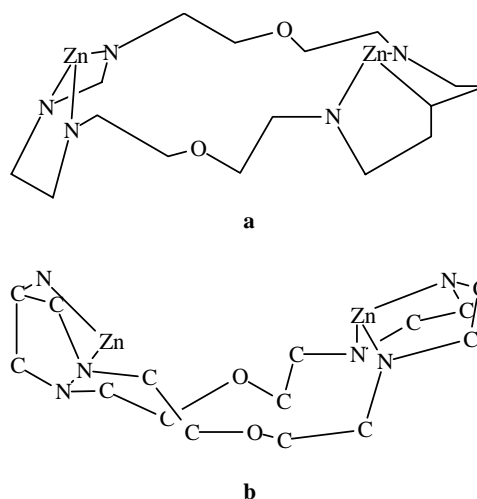
All the equilibrium constants determined in this work were calculated with the aid of the interactive computer program BEST and the species distribution were calculated with the aid of the SPECIES program that used as input the output of BEST program<sup>33,34</sup>. The input of BEST program consists of millimoles of each component, the initial estimates of the equilibrium constants of each species thought to be formed from the solution components and the experimentally determined profiles of  $\text{p}[\text{H}]$  vs. base added<sup>33</sup>. At each increment of base added the program sets mass balance equations for all species present and solves for the concentration of hydrogen ions which is compared to the experimental value. The sequence of the calculation begins with the set of known and unknown (estimated) overall stability constants and compute  $[\text{H}^+]$  at the equilibrium for each quantity of added base. For each equilibrium points the fitting process consists in the minimization of the differences between the observed and the calculated  $\text{p}[\text{H}]$  values by using a weighted least squared method. The iterative process is repeated until no further minimization can be obtained for these differences. Further details about the method of calculation are described elsewhere<sup>33</sup>.

Molecular mechanic calculations were performed using the program PC Model running on a IBM compatible PC computer. The molecular mechanics force field presents in the program was used in all molecular mechanics calculations.

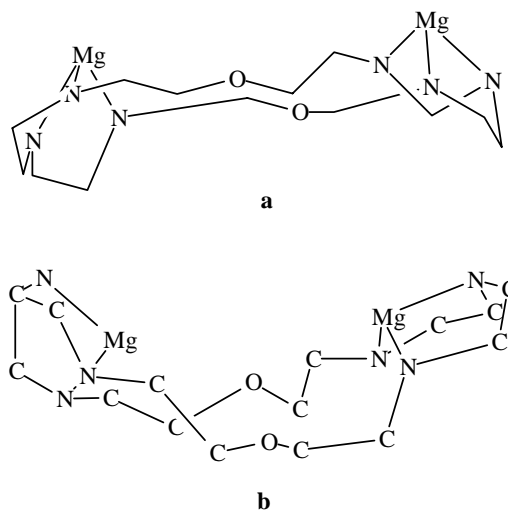
## Results and Discussion

### Molecular mechanics calculations

Molecular mechanic calculations showed that dizinc(II) - and dimagnesium (II) - Obisdien complexes are able to exist under several low energy conformers, two of them being the most important: the extended and the bowl-shaped conformers (Fig. 1 and 2). The distance between Zn atoms in the extended conformer is 7.32 Å and the Mg - Mg distance is 7.35 Å. The Zn - Zn separation in the bowl shaped conformer is 4.85 Å while the Mg - Mg distance is 4.95 Å for the same conformer. Previous molecular mechanic calculations on dicopper (II)-Obisdien complex have revealed the existence of similar types of conformers<sup>35</sup>. In all cases such conformers allow the coordination of bridging ligands of differing size as selenate, selenite, sulfate, bromide and hydroxide ions.



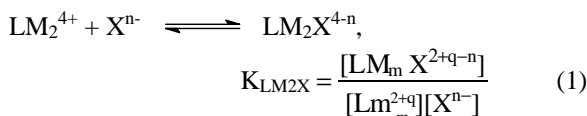
**Figure 1.** (a) Extended conformer, Zn to Zn separation is 7.32 Å. (b) Bowl-shaped conformer, Zn to Zn separation is 4.85 Å.



**Figure 2.** (a) Extended conformer, Mg to Mg separation is 7.35 Å. (b) Bowl-shaped conformer, Mg to Mg separation is 4.95 Å.

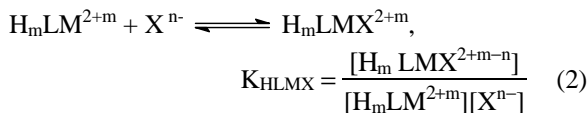
### The Obisdien: Metal: Anions complex systems

The stability constants of normal (deprotonated) complex having 1:2 molar ratios of Obisdien:Zn<sup>2+</sup> and Obisdien:Mg<sup>2+</sup> to ligands in the 1:2:6 of Br<sup>-</sup>, and 1:2:1 of SO<sub>4</sub><sup>2-</sup>, SeO<sub>3</sub><sup>2-</sup>, and SeO<sub>4</sub><sup>2-</sup> ions are defined by general Eq. 1. The constants represent the association of X<sup>n-</sup> with the binuclear receptor complex LM<sub>2</sub><sup>4+</sup>.

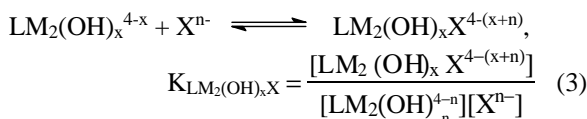


where X<sup>n-</sup> is the anion, LM<sub>2</sub>X<sup>4-n</sup> represents the unprotonated, unhydrolysed binuclear chelates.

The equilibrium constants for the mononuclear chelates are defined by Eq. 2, where H<sub>m</sub>LMX<sup>2+m-n</sup> are the unhydrolyzed mononuclear chelates and H<sub>m</sub>LM<sup>2+m</sup> are the mononuclear receptor complexes. The association constants of the

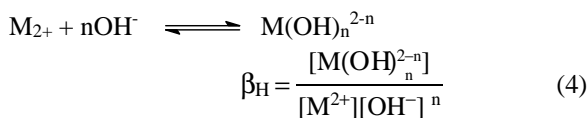


anions with the hydroxo binuclear receptor complexes are defined by Eq. 3.



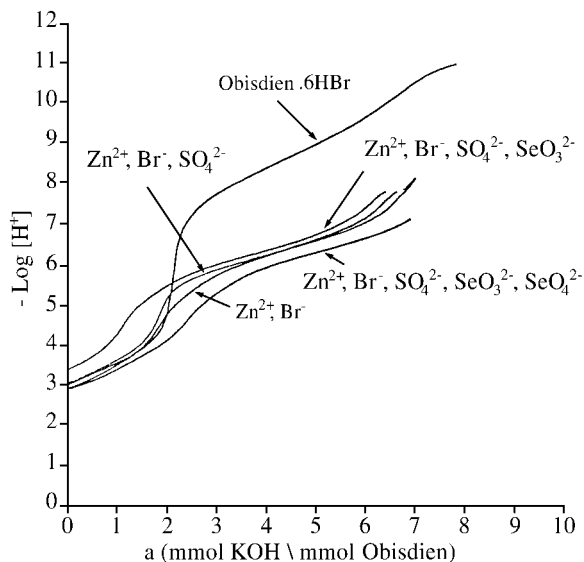
where LM<sub>2</sub>(OH)<sub>x</sub>X<sup>4-(x+n)</sup> represents the binuclear hydroxo chelates and LM<sub>2</sub>(OH)<sub>x</sub><sup>4-x</sup> represents the binuclear hydroxo receptor complexes.

The hydrolysis of metal ions were considered in the calculations, and are expressed by Eq. 4. The appropriate hydrolysis constants were obtained from the literature<sup>32</sup> and we considered the following hydrolytic species: Zn(OH)<sup>+</sup>, Zn(OH)<sub>2</sub>, Zn(OH)<sub>3</sub><sup>-</sup>, and Zn(OH)<sub>4</sub><sup>2-</sup> for the Obisdien:Zn(II):X systems and MgOH<sup>+</sup>, and Mg<sub>4</sub>(OH)<sub>4</sub><sup>4+</sup> for the Obisdien:Mg(II):X systems.



### Obisdien-Zinc(II)-Bromide complexes

Potentiometric equilibrium curves of Obisdien.6HBr in the presence and in the absence of Zn<sup>2+</sup> ions under nitrogen in 1:2:6 molar ratio of Obisdien:Zn(II):Br<sup>-</sup> system were determined and they are shown in the Fig. 3. The bromide species is present because the Obisdien sample was crystallized with six molecules of HBr. Due to the great amount of chloride in solution (supporting electrolyte), we checked for the possible competition of this ion with bromide and



**Figure 3.** Potentiometric p[H] profiles for solutions containing: a) Obisdien.6HBr 1.00 x 10<sup>-3</sup> M; b) Obisdien.6HBr 1.00 x 10<sup>-3</sup> M and Zn<sup>2+</sup> 2.00 x 10<sup>-3</sup> M; c) Obisdien.6HBr 1.00 x 10<sup>-3</sup> M, Zn<sup>2+</sup> 2.00 x 10<sup>-3</sup> M and SO<sub>4</sub><sup>2-</sup> 1.00 x 10<sup>-3</sup> M; d) Obisdien.6HBr 1.00 x 10<sup>-3</sup> M, Zn<sup>2+</sup> 2.00 x 10<sup>-3</sup> M, and SeO<sub>3</sub><sup>2-</sup> 1.00 x 10<sup>-3</sup> M; e) Obisdien.6HBr 1.00 x 10<sup>-3</sup> M, Zn<sup>2+</sup> 2.00 x 10<sup>-3</sup> M, SeO<sub>3</sub><sup>2-</sup> 1.00 x 10<sup>-3</sup> M and SeO<sub>4</sub><sup>2-</sup> 1.00 x 10<sup>-3</sup> M. (a = moles of base added per mole of Obisdien (t = 25.0 °C; μ = 0.100 M (KCl)).

no complexes were detected. Similarly, minor species involving bromo or chloroselenites or selenates complexes were not considered in this work<sup>36</sup>. In this system, we observed the formation of a precipitate at about p[H] 8.0. This precipitate is probably the zinc dihydroxo species Zn(OH)<sub>2</sub> which can be formed in this p[H] range. The precipitate remains until p[H] 11.5. The p[H] data mentioned in this range were not considered in the calculations.

The equilibrium for formation of normal and protonated complexes are indicated by Eqs. 1, 2, and 3. The stability constants determined are presented in Table 1. The curve starts at about p[H] 3.0, and until p[H] 4.0 where a = 2 it has the same profile as that for Obisdien.6HBr without Zn(II) ions. This indicates no formation of complex in this p[H] range until the first two protons of the ligand have been neutralized. Above p[H] 4.0 the curve of Obisdien:Zn(II):Br<sup>-</sup> is lower than the Obisdien:Br<sup>-</sup> curve indicating a displacement of protons. The data values were analyzed considering the formation of both mono- and binuclear species. The formation constants for Obisdien:Zn(II):Br<sup>-</sup> species were estimated and refined by the BEST program while leaving fixed the equilibrium constants for the others species<sup>34</sup>.

The species distribution curves as shown in the Fig. 4, were calculated with the aid of the computer program SPECIES and plotted with SPEPLOT program<sup>34</sup>. The mononuclear diprotonated species (H<sub>2</sub>LZnBr<sup>3+</sup>) reaches a maximum at p[H] 6.4 where it is 38.6% formed, and the mononuclear triprotonated species (H<sub>3</sub>LZnBr<sup>4+</sup>) reaches a

**Table 1.** Log of equilibrium constants of Obsidien-Zn<sup>2+</sup>- bromide, Obsidien-Zn<sup>2+</sup>- sulfate, Obsidien-Zn<sup>2+</sup>- selenite, and Obsidien-Zn<sup>2+</sup>- selenate complexes (t = 25.0 °C; μ = 0.100M (KCl)).

	$\frac{[\text{LZnX}]}{[\text{LZn}][\text{X}]}$	$\frac{[\text{HLZnX}]}{[\text{HLZn}][\text{X}]}$	$\frac{[\text{H}_2\text{LZnX}]}{[\text{H}_2\text{LZn}][\text{X}]}$	$\frac{[\text{LZn}_2\text{X}]}{[\text{LZn}_2][\text{X}]}$
Br <sup>-</sup>			3.57	1.91
SO <sub>4</sub> <sup>2-</sup>		4.40	5.03	4.12
SeO <sub>3</sub> <sup>2-</sup>				5.37
HSeO <sub>3</sub> <sup>-</sup>	5.40	4.82	4.69	
SeO <sub>4</sub> <sup>2-</sup>			6.67	5.58

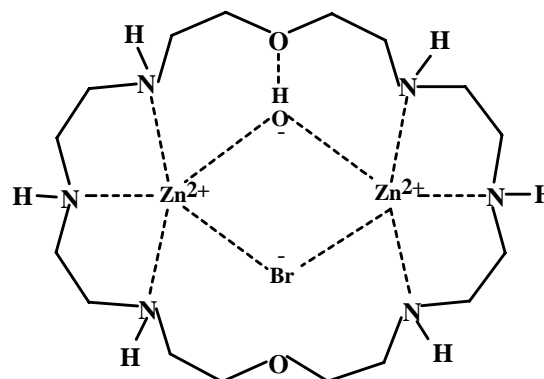
Br<sup>-</sup> σ-fit = 0.010304; SO<sub>4</sub><sup>2-</sup> σ-fit = 0.013551; SeO<sub>3</sub><sup>2-</sup> σ-fit = 0.009018; SeO<sub>4</sub><sup>2-</sup> σ-fit = 0.013718. σ-fit is the standard deviation computed from calculated p[H] values relative to those observed experimentally<sup>33</sup>.

Overall stability constants: H<sub>3</sub>LZnBr<sup>4+</sup> = 33.36; LZn<sub>2</sub>OHR<sup>2+</sup> = 9.29; LZn<sub>2</sub>OHSO<sub>4</sub><sup>+</sup> = 11.20; LZn<sub>2</sub>(OH)<sub>2</sub>SO<sub>4</sub> = 4.29; H<sub>3</sub>LZnHSeO<sub>3</sub><sup>4+</sup> = 42.96; LZn<sub>2</sub>(OH)<sub>2</sub>SeO<sub>3</sub> = 4.66; H<sub>3</sub>LZnSeO<sub>4</sub><sup>3+</sup> = 36.42; LZn<sub>2</sub>(OH)<sub>2</sub>SeO<sub>4</sub> = 5.92.

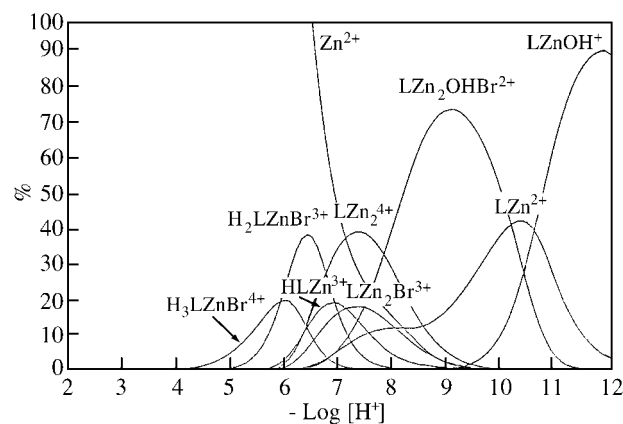
maximum at p[H] 6.0 where it is 20.0% formed. The binuclear species (LZn<sub>2</sub>Br<sup>3+</sup>) reaches a maximum at p[H] 7.3 where it is 18.0% formed. The species LZn<sub>2</sub><sup>4+</sup> competes with this species. The major species is the binuclear monohydroxo complex (LZn<sub>2</sub>OHR<sup>2+</sup>) that reaches a maximum at p[H] 9.0 where it is 74.3% formed. This is the major species for Obsidien:Zn(II):Br<sup>-</sup> system. It predominates in the p[H] range 7.8 to 10.0. Above p[H] 10.0 the monohydroxo mononuclear species LZnOH<sup>+</sup> and hydrolyzed products takes place (not shown on Fig. 4).

The crystal structure of bridging hydroxide ion in the cavity of binuclear macrocyclic and macrobicyclic complexes has been already characterized<sup>37, 38</sup> and a suggested structure for LZn<sub>2</sub>OHR<sup>2+</sup> is schematized in 1, where two Zn(II) ions are coordinated in the two pockets of Obsidien

while the bromide and hydroxide ions are bridging the two metal centers.



1, (μ-Bromide)(μ-Hydroxo) binuclear Zn(II)-Obsidien



**Figure 4.** Species distribution curves for a supersaturated solution containing Obsidien 1.00 x 10<sup>-3</sup> M and Zn<sup>2+</sup> ion 2.0 x 10<sup>-3</sup> M, in presence of 6.00 x 10<sup>-3</sup> M of bromide. H<sub>2</sub>LZnBr<sup>3+</sup>, H<sub>3</sub>LZnBr<sup>4+</sup>, and LZn<sub>2</sub>Br<sup>3+</sup> represent the di- and triprotonated mononuclear, and binuclear deprotonated Obsidien:Zn<sup>2+</sup>:Br<sup>-</sup> species respectively. LZn<sub>2</sub>OHR<sup>2+</sup> is the binuclear hydroxo Obsidien:Zn<sup>2+</sup>:Br<sup>-</sup> species. HLZn<sup>3+</sup> and LZn<sup>2+</sup> are the monoprotonated and complete deprotonated Obsidien: Zn(II) species and LZnOH<sup>+</sup> is the hydroxo one. LZn<sub>2</sub><sup>4+</sup> is the binuclear receptor complex. All no metallic species and the hydrolysis product of Zn(II) ion are not represented. Zn<sup>2+</sup> is the free (aquo) zinc(II) ion.

#### Obsidien-Zinc(II)-Sulfate complexes

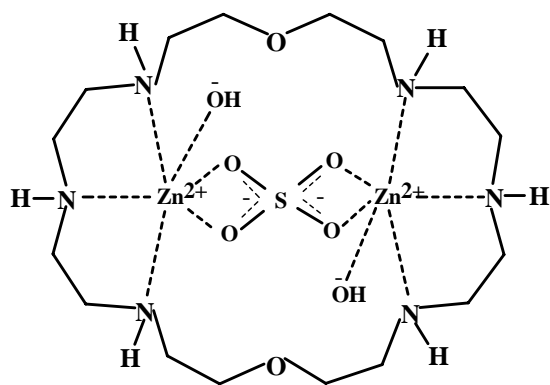
Potentiometric equilibrium curves of Obsidien.6HBr in the presence and in the absence of Zn<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> under nitrogen in 1:2:1 molar ratio of Obsidien.6HBr:Zn(II):SO<sub>4</sub><sup>2-</sup> system were carried out and the results are shown in the Fig. 3. It was also observed a precipitate at about p[H] 8.0. The curve shows that until about p[H] 5.0 the profile is about the same as that of the Obsidien.6HBr curve. This is a indication that non complexes of Zn(II) is formed in this p[H] range, but above p[H] 4.0 the curve is below that of the Obsidien.6HBr system, indicating that complexation reaction takes place.

The equilibrium constants for all Obsidien:Zn(II):SO<sub>4</sub><sup>2-</sup> probable complexes are defined by general Eqs. 1, 2 and 3, and the stability constants are presented in Table 1. The difference in the profile of the Obsidien:Zn(II):SO<sub>4</sub><sup>2-</sup> and Obsidien.6HBr:Zn(II) systems in the p[H] range 5.0 to 6.0 (a equal 2 to 4) is due to the fact that the mononuclear diprotonated species (H<sub>2</sub>LZnSO<sub>4</sub><sup>2+</sup>) compete with the

$\text{H}_4\text{LSO}_4^{2+}$  species (not shown on Fig. 5) and the formation of the last one is more probable, *i.e.*, the equilibrium favor the non metallic species which retains two more protons than the bromide species. The species distribution curves are presented in the Fig. 5.

$\text{Zn}^{2+}$  ion does not complex at  $\text{p}[\text{H}]$  values below 5, and the Obisdien: $\text{SO}_4$  species predominate in this region. The major species formed in this system is the (dihydroxo) ( $\mu$ -sulfate) binuclear zinc(II)-Obisdien species, 2, which predominates at  $\text{p}[\text{H}]$  values above 7.3. The sulfate group is believed to bridge and coordinate the two metal ions in the way suggested by formula 2.

The mononuclear monoprotonated species,  $\text{HLZnSO}_4^+$ , reaches a maximum at  $\text{p}[\text{H}]$  6.9 where it is 24.3% formed, while the mononuclear diprotonated  $\text{H}_2\text{LZnSO}_4^{2+}$  species reaches a maximum at  $\text{p}[\text{H}]$  6.3 where it is only 12.7% formed. The binuclear completely deprotonated species  $\text{LZn}_2\text{SO}_4^{2+}$  was found in the neutral  $\text{p}[\text{H}]$  values. It reaches a maximum at  $\text{p}[\text{H}]$  7.0 where it is 31.1% formed.

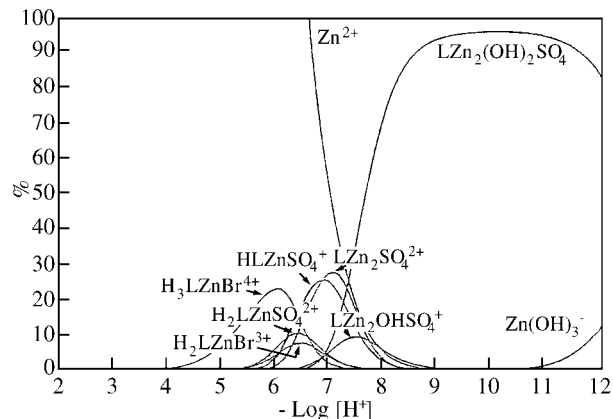


2, Sulfate adduct of dihydroxo binuclear Zn(II)-Obisdien complex.

#### Obisdien-Zinc(II)-Selenite complexes

Potentiometric equilibrium curves of Obisdien.6HBr in the presence of  $\text{Zn}^{2+}$  and selenite ions under nitrogen are illustrated in Fig. 3. The curve with selenite shows that the  $\text{SeO}_3^{2-}$  ion retain one proton for its protonation by forming  $\text{HSeO}_3^-$  ion. While 2 mmoles of KOH are necessary for the observed sharp inflection at  $\text{a} = 2$  in the Obisdien.6HBr curve, the presence of  $\text{SeO}_3^{2-}$  in the  $\text{Zn}^{2+}$ ,  $\text{Br}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{SeO}_3^{2-}$  curve only about 1 mmol of base is sufficient.

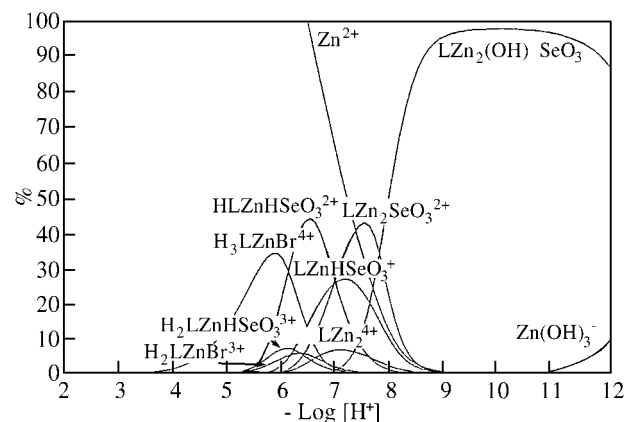
The equilibrium constants for all Obisdien: $\text{Zn}(\text{II})$ : $\text{SeO}_3^{2-}$  probable complexes are defined by Eqs. 1, 2, and 3 and the stability constants are shown in Table 1. At  $\text{p}[\text{H}]$  values below 8, selenite ion is monoprotonated ( $\text{Log } K = 8$ ), thus the formation constants of zinc(II)-Obisdien complexes with this anion defined by Eqs. 1, and 2 represents the association of zinc(II)-Obisdien complexes with  $\text{HSeO}_3^-$  ion. Most of the equilibrium constants necessary for the calculations were taken from literature. For some



**Figure 5.** Species distribution curves for a supersaturated solution containing Obisdien  $1.00 \times 10^{-3}$  M,  $\text{Zn}^{2+}$  ion  $2.0 \times 10^{-3}$  M and  $1.00 \times 10^{-3}$  M of  $\text{SO}_4^{2-}$  ion in presence of  $6.00 \times 10^{-3}$  M of bromide.  $\text{HLZnSO}_4^+$ ,  $\text{H}_2\text{LZnSO}_4^{2+}$ , and  $\text{LZn}_2\text{SO}_4^{2+}$  are the mono- and diprotonated mononuclear species, and the deprotonated binuclear Obisdien: $\text{Zn}^{2+}$ : $\text{SO}_4^{2-}$  species respectively.  $\text{LZn}_2\text{OHSO}_4^+$  and  $\text{LZn}_2(\text{OH})_2\text{SO}_4$  are the binuclear hydroxo Obisdien: $\text{Zn}^{2+}$ : $\text{SO}_4^{2-}$  species.  $\text{H}_2\text{LZnBr}^{3+}$  and  $\text{H}_3\text{LZnBr}^{4+}$  are the di- and triprotonated OBISDIEN: $\text{Zn}(\text{II})$ : $\text{Br}^-$  species.  $\text{Zn}^{2+}$  is the free (aquo) zinc(II) ion, and  $\text{Zn}(\text{OH})_3^-$  is a hydrolyzed product of zinc(II) ion. Non metallic species are not represented as well as the species formed less than 2% for clarity.

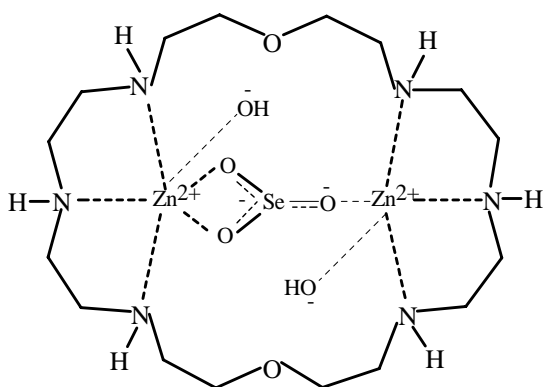
species, because of the lack of data of the equilibrium constants in the absence of anions, only the overall stability constants of their complexes with anions were determined. These overall stability constants are given in the caption of Table 1. Minors species (less than 2% ) are not computed in these system.

The species distribution curves of the Obisdien: $\text{Zn}(\text{II})$ : $\text{SeO}_3^{2-}$  system are showed in Fig. 6. Zinc(II) ion begins to



**Figure 6.** Species distribution curves for a supersaturated solution containing Obisdien  $1.00 \times 10^{-3}$  M,  $\text{Zn}^{2+}$  ion  $2.00 \times 10^{-3}$  M and  $\text{SeO}_3^{2-}$  ion  $1.00 \times 10^{-3}$  M in presence of bromide  $6.00 \times 10^{-3}$  M.  $\text{LZn}_2\text{SeO}_3^{2+}$ , and  $\text{LZn}_2(\text{OH})_2\text{SeO}_3$  are the complete deprotonated and dihydroxo binuclear Obisdien: $\text{Zn}^{2+}$ : $\text{SeO}_3^{2-}$  species.  $\text{LZnHSeO}_3^+$ ,  $\text{HLZnHSeO}_3^{2+}$  and  $\text{H}_2\text{LZnHSeO}_3^{3+}$  are the mononuclear species and,  $\text{H}_2\text{LZnBr}^{3+}$  and  $\text{H}_3\text{LZnBr}^{4+}$  are the di- and triprotonated Obisdien: $\text{Zn}(\text{II})$ : $\text{Br}^-$  species.  $\text{LZn}_2^{4+}$  is the binuclear Obisdien: $\text{Zn}^{2+}$  species,  $\text{Zn}^{2+}$  is the free (aquo) zinc(II) ion, and  $\text{Zn}(\text{OH})_3^-$  is a hydrolyzed product of zinc(II) ion. Non metallic species are not represented as well as the species formed less than 2% for clarity.

complex above  $p[H]$  4.0 forming protonated species of mononuclear zinc(II)-Obisdien complexes. The protonated mononuclear species,  $H_2LZnHSeO_3^{3+}$ ,  $HLZnHSeO_3^{2+}$  and  $LZnHSeO_3^+$  are at their maximum at  $p[H]$  values 6.1, 6.5 and 7.2 where they are 7.2, 44.3 and 27.6% formed respectively. The binuclear species  $LZn_2SeO_3^{2+}$  reaches a maximum at  $p[H]$  7.5 where it is 43.2% formed, and the dihydroxo species  $LZn(OH)_2SeO_3$  is the major species above  $p[H]$  8.0, reaching a maximum of 97.5% at  $p[H]$  9.7. The selenite group is believed to bridge and coordinate the two zinc(II) ions as suggested by formula 3, in the same way as it was suggested for the sulfate ion in formula 2.

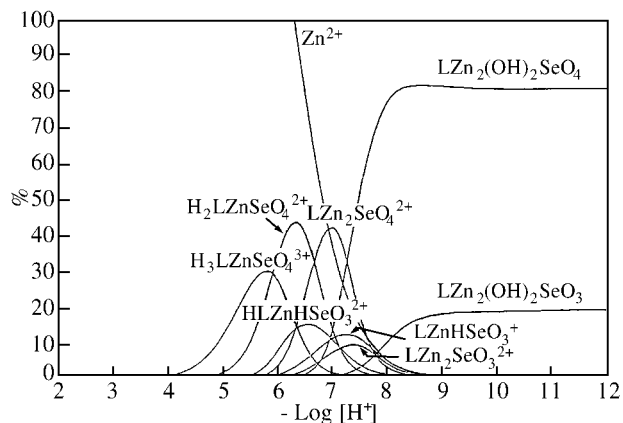


3, Selenite adduct of dihydroxo binuclear Zn(II)-Obisdien complex

#### Obisdien-Zinc(II)-Selenate complexes

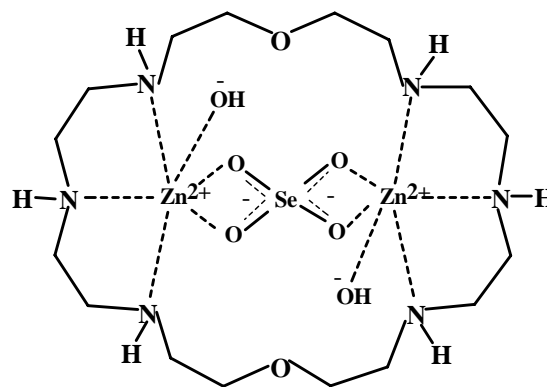
Potentiometric equilibrium curves of Obisdien.6HBr in the presence and in the absence of  $Zn^{2+}$ , selenite and selenate ions under nitrogen were determined by the method described in the experimental section and the result is shown in the Fig. 3. The curve were interrupted at  $p[H]$  8.0 due to formation of a precipitate. The curve shows that in the presence of  $SeO_4^{2-}$  ion, the buffer regions extend to almost  $a = 6$  indicating possible formation of hydroxo complexes and binuclear deprotonated complexes.

The equilibrium constants for all probable species are defined by Eqs. 1, 2, and 3 and the stability constants are shown in the Table 1. The species distribution curves of Obisdien.6HBr: $Zn(II)$ :  $SeO_3^{2-}$ :  $SeO_4^{2-}$  system are showed in the Fig. 7. Formation of metal complexes occurs at  $p[H]$  values above 4.0. The zinc(II)-Obisdien complexes are coordinated with  $SeO_3^{2-}$  and  $SeO_4^{2-}$  ions. The mononuclear triprotonated complex ( $H_3LZnSeO_4^{3+}$ ) reaches a maximum at  $p[H]$  5.8 where it is 27.6% formed and the diprotonated complex ( $H_2LZnSeO_4^{2+}$ ) reaches a maximum at  $p[H]$  6.3 where it is 42.0% formed. The major species formed at neutral  $p[H]$  is the binuclear species  $LZn_2SeO_4^{2+}$  and it is 42% formed. The binuclear



**Figure 7.** Species distribution curves for a supersaturated solution containing Obisdien  $1.00 \times 10^{-3}$  M,  $Zn^{2+}$  ion  $2.00 \times 10^{-3}$  M,  $SeO_3^{2-}$  ion  $1.00 \times 10^{-3}$  M and  $SeO_4^{2-}$  ion  $1.00 \times 10^{-3}$  M in presence of bromide  $6.00 \times 10^{-3}$  M.  $LZn_2(OH)_2SeO_4$  and  $LZn_2SeO_4^{2+}$  are the dihydroxo and complete deprotonated binuclear Obisdien: $Zn^{2+}$ : $SeO_4^{2-}$  species and  $H_2LZnSeO_4^{2+}$  and  $H_3LZnSeO_4^{3+}$  are the mononuclear ones.  $LZn_2(OH)_2SeO_3$  is the dihydroxo binuclear Obisdien: $Zn^{2+}$ : $SeO_3^{2-}$  species and the  $LZn_2SeO_3^{2+}$  is the complete deprotonated binuclear species.  $LZnHSeO_3^+$  and  $HLZnHSeO_3^{2+}$ , are the mononuclear species.  $Zn^{2+}$  is the free aquo zinc(II) ion and non metallic species are not represented as well as species formed less than 2% for clarity.

dihydroxospecies  $LZn_2(OH)_2SeO_4$  predominates at  $p[H]$  values above 7.3. The suggested structure of (dihydroxo)(-selenate) binuclear zinc(II)-Obisdien complex (4) is showed below.



4, Selenate adduct of dihydroxo binuclear Zn(II)-Obisdien complex

#### Obisdien-Magnesium(II)-Bromide complexes

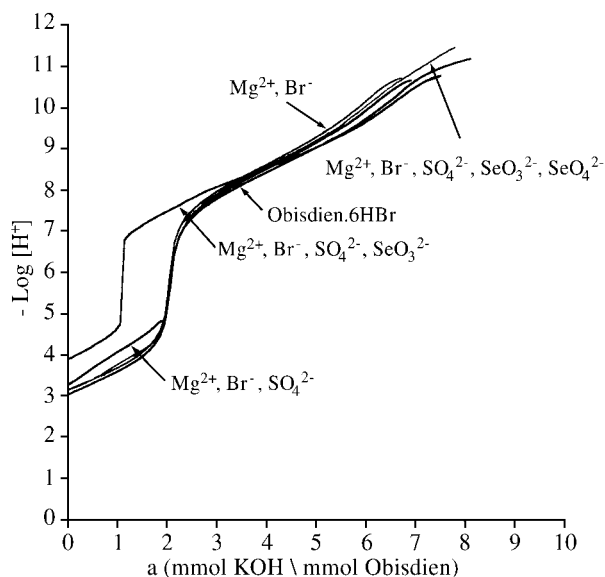
Potentiometric equilibrium curves of Obisdien.6HBr in the presence and in the absence of  $Mg^{2+}$  ions under nitrogen in 1:2:6 molar ratio of Obisdien: $Mg(II)$ : $Br^-$  system were determined. They are illustrated in Fig. 8.

This figure shows that until about  $p[H]$  6.5 the profile of the potentiometric titration curve is identical to the profile recorded for the Obisdien.6HBr system. This indicates that no complex formation with  $Mg(II)$  ion in this  $p[H]$  range takes place until the first two protons of the

ligand have been neutralized. Above this p[H], the difference of the profiles for the two curves is small indicating the formation of weak complexes.

The equilibrium constants for the Obsidien:Mg(II):Br<sup>-</sup> complexes defined by Eqs. 1, 2, and 3 were determined and they are reported on Table 2. The stability constants for the receptor Obsidien:Mg<sup>2+</sup> complexes were also determined and they are shown in the caption of Table 2.

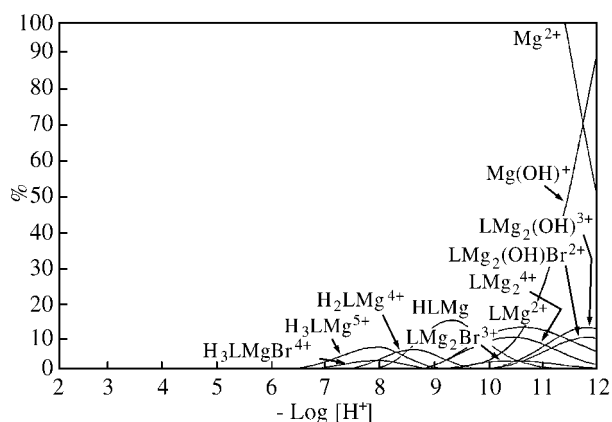
The species distribution curves are shown in Fig. 9. Most of the metal species are formed in small amount. The Obsidien:Mg(II) species formed are: the binuclear LMg<sub>2</sub><sup>4+</sup>



**Figure 8.** Potentiometric p[H] profiles for solutions containing: a) Obsidien.6HBr  $1.00 \times 10^{-3}$  M; b) Obsidien.6HBr  $1.00 \times 10^{-3}$  M and  $Mg^{2+}$   $2.00 \times 10^{-3}$  M; c) Obsidien.6HBr  $1.00 \times 10^{-3}$  M,  $Mg^{2+}$   $2.00 \times 10^{-3}$  M and  $SO_4^{2-}$   $1.00 \times 10^{-3}$  M; d) Obsidien.6HBr  $1.00 \times 10^{-3}$  M,  $Mg^{2+}$   $2.00 \times 10^{-3}$  M,  $SO_4^{2-}$   $1.00 \times 10^{-3}$  M and  $SeO_3^{2-}$   $1.00 \times 10^{-3}$  M; e) Obsidien.6HBr  $1.00 \times 10^{-3}$  M,  $Mg^{2+}$   $2.00 \times 10^{-3}$  M,  $SO_4^{2-}$   $1.00 \times 10^{-3}$  M,  $SeO_3^{2-}$   $1.00 \times 10^{-3}$  M and  $SeO_4^{2-}$   $1.00 \times 10^{-3}$  M. (a = moles of base added per mole of Obsidien ( $t = 25.0$  °C;  $\mu = 0.100$  M (KCl)).

which is 9.4% formed at p[H] 10.3, the hydroxo species  $LMg_2OH^{3+}$  which is 12.4% formed at p[H] 11.8 and the mononuclear  $LMg^{2+}$ ,  $HLMg^{3+}$ ,  $H_2LMg^{4+}$  and  $H_3LMg^{5+}$  which are 12.3%, 14.5%, 6.2% and 7% formed at p[H] values 10.5, 9.3, 8.6 and 7.9 respectively. Very careful work were done to evaluate the constants of species which are less than 5% formed and their constants has been determined with the largest errors. Species which are less than 3% formed were not mentioned in Fig. 9.

The Obsidien:Mg(II):Br<sup>-</sup> species are formed even in less amount. The hydroxo binuclear  $LMg_2OHBr^{2+}$  is 9.4% formed at p[H] 11.8, the binuclear  $LMg_2Br^{3+}$  is only 3% formed at p[H] 10.2 and the triprotonated mononuclear  $H_3LMgBr^{4+}$  is 3.1% formed at p[H] 7.9.



**Figure 9.** Species distribution curves for a supersaturated solution containing Obsidien  $1.00 \times 10^{-3}$  M and  $Mg^{2+}$  ion  $2.00 \times 10^{-3}$  M in presence of bromide  $6.00 \times 10^{-3}$  M.  $H_3LMgBr^{4+}$  and  $LMg_2Br^{3+}$  are the triprotonated and binuclear deprotonated Obsidien: $Mg^{2+}$ :Br<sup>-</sup> species respectively and  $LMg_2OHBr^{2+}$  is the binuclear hydroxo Obsidien: $Mg^{2+}$ :Br<sup>-</sup> species.  $LMg^{2+}$ ,  $HLMg^{3+}$ ,  $H_2LMg^{4+}$ ,  $H_3LMg^{5+}$  and  $LMgOH^+$  are the mononuclear Obsidien: $Mg^{2+}$  species and  $LMg_2^{4+}$  and  $LMg_2OH^{3+}$  are the binuclear species.  $Mg^{2+}$  is the free aquo magnesium(II) ion and  $MgOH^+$  is a hydrolysis product. Non metallic species are not represented as well as species formed less than 2% for clarity.

**Table 2.** Log of equilibrium constants of Obsidien- $Mg^{2+}$ -bromide, Obsidien- $Mg^{2+}$ -sulfate, Obsidien- $Mg^{2+}$ -selenite, and Obsidien- $Mg^{2+}$ -selenate complexes ( $t = 25.0$  °C;  $\mu = 0.100$  M (KCl)).

	$\frac{[LMgX]}{[LMg][X]}$	$\frac{[HLMgX]}{[HLMg][X]}$	$\frac{[H_2LMgX]}{[H_2LMg][X]}$	$\frac{[H_3LMgX]}{[H_3LMg][X]}$	$\frac{[LMg_2X]}{[LMg_2][X]}$	$\frac{[LMg_2(OH)X]}{[LMg_2OH][X]}$
Br <sup>-</sup>				1.90	1.70	2.10
$SO_4^{2-}$		3.00	3.45		3.34	3.67
$SeO_3^{2-}$					4.59	5.37
$HSeO_3^-$	5.62	4.74	4.38			
$SeO_4^{2-}$		5.66	6.00	6.58	6.98	7.94

Br<sup>-</sup>  $\sigma$ -fit = 0.010974;  $SO_4^{2-}$   $\sigma$ -fit = 0.013052;  $SeO_3^{2-}$   $\sigma$ -fit = 0.009753;  $SeO_4^{2-}$   $\sigma$ -fit = 0.020969.  $\sigma$ -fit is the standard deviation computed from calculated p[H] values relative to those observed experimentally<sup>33</sup>.

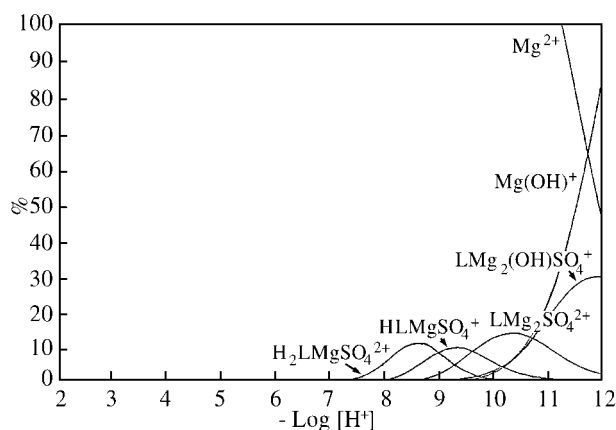
Overall stability constants for Obsidien: $Mg^{2+}$  systems:  $LMg^{2+} = 2.17$ ;  $HLMg^{3+} = 12.04$ ;  $H_2LMg^{4+} = 20.58$ ;  $H_3LMg^{5+} = 28.88$ ;  $LMg_2^{4+} = 4.90$ ;  $LMg_2OH^+ = -6.14$  (This work).



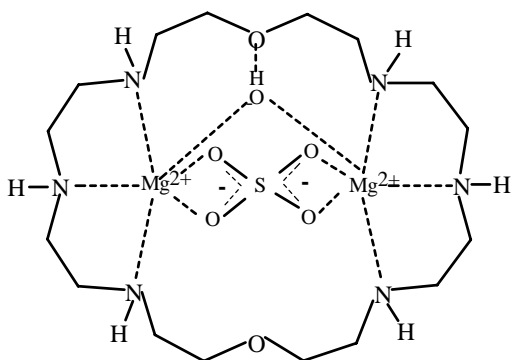
### Obsidien-Magnesium(II)-Sulfate complexes

Potentiometric equilibrium curves of Obsidien.6HBr in the presence and in the absence of  $Mg^{2+}$ , and  $SO_4^{2-}$  ions under nitrogen in 1:2:1 molar ratio of Obsidien.6HBr:Mg(II): $SO_4^{2-}$  system were determined and they are shown in the Figure 8. The equilibrium constants for all Obsidien:Mg(II): $SO_4^{2-}$  complexes detected are defined by Eqs. 1, 2, and 3 and the equilibrium constants are presented in Table 2.

The species distribution curves are presented in the Fig. 10. The binuclear species are formed at p[H] values above 8.5 and the mononuclear species are formed in the p[H] range 7.3-10.0. There are no metal complexes at p[H] values lower than 7.3. The  $Mg^{2+}$  complexes are formed only in basic region, as it was also observed in the Obsidien:Mg(II): $Br^-$  system. The monoprotonated mononuclear species  $HLMgSO_4^+$  reaches a maximum at p[H] 9.3 where



**Figure 10.** Species distribution curves for a supersaturated solution containing Obsidien  $1.00 \times 10^{-3}$  M,  $Mg^{2+}$  ion  $2.00 \times 10^{-3}$  M and  $SO_4^{2-}$  ion  $1.00 \times 10^{-3}$  M in presence of bromide  $6.00 \times 10^{-3}$  M.  $HLMgSO_4^+$ ,  $H_2LMgSO_4^{2+}$  and  $LMg_3SO_4^{2+}$  are the mononuclear, and binuclear Obsidien: $Mg^{2+}$ : $SO_4^{2-}$  species and  $LMg_2OHSO_4^+$  is the binuclear hydroxo species.  $Mg^{2+}$  is the free aquo magnesium(II) ion and  $MgOH^+$  is a hydrolysis product. Non metallic species are not represented as well as species formed less than 2% for clarity.



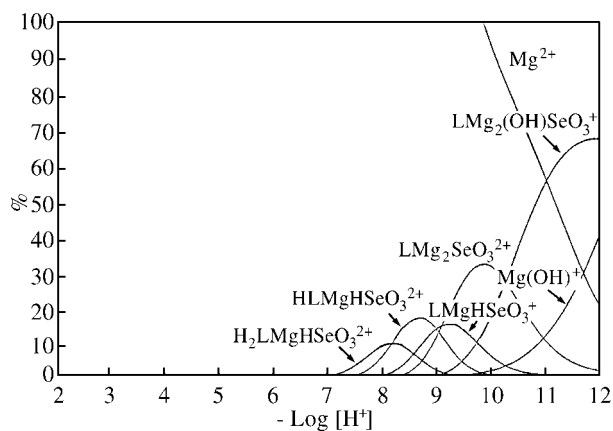
5, Sulfate adduct of hydroxo-bridged binuclear Mg(II)-Obsidien complex

it is 8.4% formed, and the diprotonated mononuclear  $H_2LMgSO_4^{2+}$  is 9.0% formed at p[H] 8.6. The binuclear species are formed at p[H] values above 8.5. They are formed in larger than the mononuclear ones. The deprotonated binuclear species  $LMg_2SO_4^{2+}$  reaches a maximum at p[H] 10.3 where it is 10.6% formed and the monohydroxo binuclear species  $LMg_2OHSO_4^+$  is 23.1% formed at p[H] 11.8. The structure suggested for the  $LMg_2OHSO_4^+$  complex (5) is shown below.

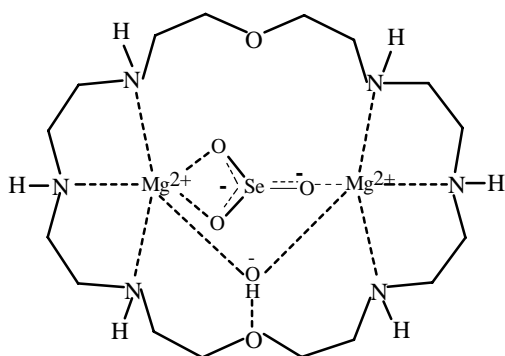
### Obsidien-Magnesium(II)-Selenite complexes

Potentiometric equilibrium curves of Obsidien.6HBr in the presence of  $Mg^{2+}$ , sulfate and selenite ions under nitrogen are illustrated in Fig. 8. The profile of this system, shown that one proton is retained for formation of  $HSeO_3^-$  ion. The equilibrium constants for all Obsidien:Mg(II): $SeO_3^{2-}$  complexes are defined by Eqs. 1, 2, and 3, and the stability constants of the species detected are shown in Table 2.

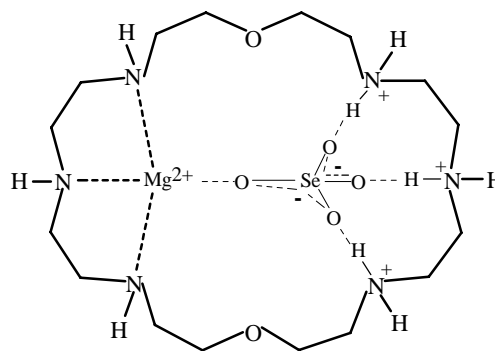
The species distribution curves of the Obsidien.6HBr:Mg(II): $SO_4^{2-}$ : $SeO_3^{2-}$  system are shown in Fig. 11. The major species in this system are the binuclear species:  $LMg_2SeO_3^{2+}$  and  $LMg_2OHSeO_3^+$ . The binuclear species  $LMg_2SeO_3^{2+}$  reaches a maximum at p[H] 9.9 where it is 32.6% formed and the hydroxo species  $LMg_2OHSeO_3^+$  is 67.8% formed at p[H] 12.0. As in formula 3 it is suggested that the selenite group bridges and coordinate the two metal ions as in 6. The mononuclear species appears at the p[H] range 7-10 and they are less than 20% formed (Fig. 9).



**Figure 11.** Species distribution curves for a supersaturated solution containing Obsidien  $1.00 \times 10^{-3}$  M,  $Mg^{2+}$  ion  $2.00 \times 10^{-3}$  M,  $SO_4^{2-}$  ion  $1.00 \times 10^{-3}$  M and  $SeO_3^{2-}$  ion  $1.00 \times 10^{-3}$  M in presence of bromide  $6.00 \times 10^{-3}$  M.  $LMgHSeO_3^+$ ,  $HLMgHSeO_3^{2+}$ ,  $H_2LMgHSeO_3^{3+}$ , and  $H_3LMgHSeO_3^{4+}$ , are the mono-, di-, tri-, and tetraprotonated forms of mononuclear Obsidien: $Mg^{2+}$ : $SeO_3^{2-}$  species respectively.  $LMg_2SeO_3^{2+}$ , and  $LMg_2OHSeO_3^+$  are the complete deprotonated and hydroxo Obsidien: $Mg^{2+}$ : $SeO_3^{2-}$  binuclear species.  $Mg^{2+}$  is the free aquo magnesium(II) ion and  $MgOH^+$  is a hydrolysis product. Non metallic species are not represented as well as species formed less than 2% for clarity.



6, Selenite adduct of hydroxo-bridged binuclear Mg(II)-Obsdien complex

7, Selenate adduct of mononuclear Mg(II) triprotonated Obsdien complex,  $\text{H}_3\text{LMgSeO}_4^{3+}$ 

### Obsdien-Magnesium(II) -Selenate complexes

Potentiometric equilibrium curve of Obsdien.6HBr in the presence of Mg(II), sulfate, selenite, and selenate ions under nitrogen is shown in Fig. 8. The shape of the curve is about the same as the one in presence of selenite without selenate (previous system), but its buffer region above p[H] 7.0 is lower, indicating complex formation with selenate in this p[H] range is stronger. The equilibrium constants for all detected species are defined by Eqs. 1, 2, and 3 and the stability constants determined are shown in Table 2. Minor species (less than 3%) are not considered in this system.

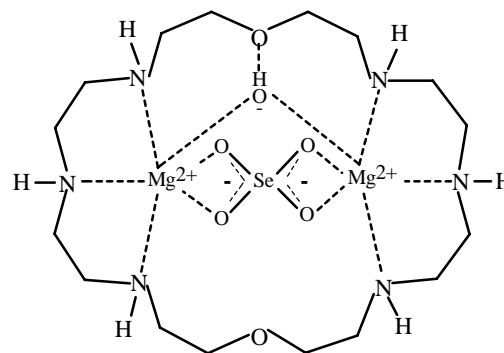
The species distribution curves of metal complexes of  $\text{SeO}_4^{2-}$  in presence of  $\text{Br}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{SeO}_3^{2-}$  ions are shown in the Fig. 12. All metal complex species are  $\text{SeO}_4^{2-}$  adducts. One binuclear and three mononuclear species were detected. The hydroxo binuclear species  $\text{LMg}_2\text{OHSeO}_4^+$  is 91% formed at p[H] 12.0 and the species  $\text{LMg}_2\text{SeO}_4^{2+}$  reaches a maximum at p[H] 9.5 where it is 50.5% formed.

The mononuclear species predominate at lower p[H] values and the triprotonated species is the major species at neutral and moderately basic region. It is 55% at p[H] 7.6 and the di- and the monoprotonated species are maximum formed at p[H] values 8.4 and 9.0 where they are 44% and 37% formed respectively. The selenate adducts of these Obsdien complexes are bound by coordinate bonds, and in the case of mononuclear complexes  $\text{H}_3\text{LMgSeO}_4^{3+}$ ,  $\text{H}_2\text{LMgSeO}_4^{2+}$  and  $\text{HLMgSeO}_4^+$ , both the coordination bonds and hydrogen bonds are involved (formula 7 for  $\text{H}_3\text{LMgSeO}_4^{3+}$ )

In the binuclear complexes, the selenate group is believed to bridge and coordinate the two Mg(II) ions in the manner suggested by formula 8.

### Conclusion

Equilibrium constant determination and species distribution curves in the p[H] 2 - 12 range for the Obsdien: $\text{Zn}^{2+}$  and Obsdien: $\text{Mg}^{2+}$  systems in the presence of  $\text{Br}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{SeO}_3^{2-}$ , and  $\text{SeO}_4^{2-}$  ions has been carried on by potentiomet-



8, Selenate adduct of hydroxo-bridged binuclear Mg(II)-Obsdien complex

ric studies. For both systems, the strength of binding increases in the order  $\text{Br}^- < \text{SO}_4^{2-} < \text{SeO}_3^{2-} < \text{SeO}_4^{2-}$ . Studies of a model macrocycle which has the capacity of forming binuclear metal complexes as Obsdien, provide useful results for understanding the behavior of anions and metals involved in complex formation in solution. In all cases metal complex species appears above [H] 6.0. While the mononuclear species predominates at neutral and moderately basic p[H] for Mg(II) systems, for the zinc(II) system, the binuclear species are the major species. At more basic p[H] values, the binuclear species predominate in both metal systems, however the dihydroxo binuclear species are not formed in the magnesium(II) system while it is the major species in the zinc(II) system. Zinc(II) ion has a strong tendency to form hydroxo complexes and the results is consistent with the behavior of zinc(II) in aqueous solution.

The monohydroxo species is the major species in the magnesium(II) systems. The species formed in the magnesium(II) systems are less stable than the ones formed in the zinc(II) systems. Nevertheless, Mg(II) ion are much more abundant in the oceans than Zn(II) ion. Thus, it is expected to play important roles in the complexation of naturally

occurring anions as selenite and selenate anions in the presence of ligands.

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