

Thermodynamic Behavior of Polyols and Speciation Studies in the Presence of Divalent Metal Cations

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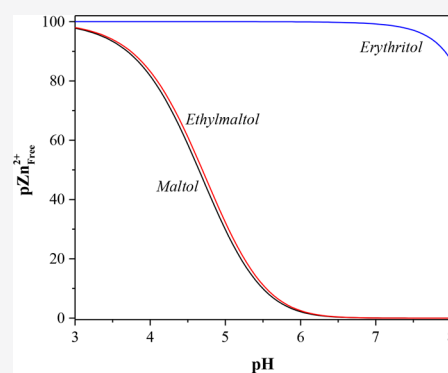
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ABSTRACT: The acid–base properties and complexing ability of some biologically relevant polyols (erythritol, sorbitol, maltol, and ethylmaltol) toward divalent metal cations have been determined by potentiometric measurements with an ISE- H^+ glass electrode in $NaNO_3$ aqueous solutions at $I = 0.151 \text{ mol}\cdot\text{kg}^{-1}$ and $T = 298.15 \text{ K}$. For the erythritol system, the investigations have been carried out in the ionic strength range $0.1 \leq I/\text{mol}\cdot\text{kg}^{-1} \leq 1.0$, and the dependence on the ionic strength of the protonation and stability constants has been modeled by the specific ion interaction theory (SIT). The sequestering ability of the different ligands toward the considered metal cations (Ca^{2+} , Zn^{2+} , and Sn^{2+}) has been evaluated by the $pL_{0.5}$ parameter. For example, for M^{2+}/maltol systems, at $T = 298.15 \text{ K}$ in $NaNO_{3(aq)}$, $I = 0.151 \text{ mol}\cdot\text{kg}^{-1}$, and $pH 7.4$, the sequestering ability toward Zn^{2+} ($pL_{0.5} = 4.60$) is higher than that toward Sn^{2+} ($pL_{0.5} = 3.94$) and Ca^{2+} ($pL_{0.5} = 1.27$).



1. INTRODUCTION

The polyols or polyols are monomers or polymers with more than one hydroxyl functional group available for reactions. They are of great importance in food sciences, since they are used as sweeteners to substitute the sugar. Recently, the interest toward their consumption has increased, due to their potential beneficial effect on health; the principal qualities are non-cariogenicity, a low energy value, a low glycemic and insulin index, they are digested very slowly, and they have osmotic properties (hydration of the colon, with laxative and depurative effect). As regards the last property, the polyols favor the formation of saccharolytic and acidic anaerobic organisms in the colon, purifying it from endotoxic, rotting, and pathological organisms, which explains their importance and clinical relevance. In addition, polyols help to form short-chain fatty acids that are beneficial for colon health.¹ As said above, polyols are employed as food additives, which are substances used in the food industry during the preparation, storage, and marketing of foodstuffs.² The additives are classified according to their function and subdivided into three large groups:

- additives helping to preserve the freshness of food, therefore, preservatives, which slow down the growth of microbes, and antioxidants, which prevent rancidity phenomena
- additives improving the sensory characteristics of foods, such as dyes, thickeners, emulsifiers, sweeteners, and flavor enhancers

- technological additives used to facilitate the processing of food but which do not have a specific function in the final product, for example, anti-foaming and anti-caking agents.

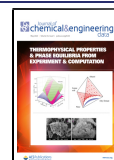
Food additives undergo a safety assessment process before being authorized for food use. In Europe, the evaluation is performed from European Food Safety Authority (EFSA) and by Joint Expert Committee on Food Additives (JECFA), an international scientific expert committee administered jointly by the Food and Agriculture Organization of the United Nations (FAO) and World Health Organization (WHO). The additives authorized at the European level are marked with a numerical code preceded by the letter E.

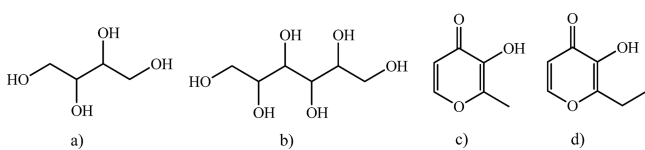
Erythritol (*1,2,3,4-Butanetetrol*, abbreviated to the acronym *Ery*, see [Scheme 1](#)) is a polyol naturally present in fruit and fermented foods,³ industrially obtained from sugary substrates, (for example, starch, glucose, sucrose, etc.), by microbial fermentation by selected osmophilic yeasts (e.g., *Moniliella pollinis*).⁴ The European Commission has included erythritol in the list of polyvalent food additives, with the abbreviation E968. It is used as a sweetener, but it can be employed with different functions, for example, to give body and disguise unwanted

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Scheme 1. Structures of (a) Erythritol, (b) Sorbitol, (c) Maltol, and (d) Ethylmaltol

aftertaste. The metabolic profile of this polyalcohol is unique, due to its small size and therefore its low molecular weight ($122.12 \text{ g mol}^{-1}$); over 90% of ingested erythritol is absorbed in the small intestine through passive diffusion (i.e., without energy consumption by the cell, or osmosis) and is excreted unchanged through the urine. The remaining fraction (<10%) reaches the large intestine where it is only partially metabolized. As a consequence, the total caloric value of erythritol is very low and varies from 0 to a maximum of 0.2 kcal g^{-1} .^{5,6} Furthermore, it is characterized by almost zero value of glycemic index (IG) and insulin index (II) and therefore it represents a valid substitutive ingredient of sucrose to reduce the glycemic impact of the diet, suitable for those at risk or suffering from diabetes.¹ Recent studies have also highlighted the anti-radical activity of erythritol, which has proved to be an excellent scavenger of hydroxyl radicals, with protective properties for cell membranes.⁷ It was certified as a tooth-friendly product, and its acariogenicity is widely demonstrated: erythritol is not converted into acids by the bacteria present in the mouth; therefore, it does not favor dental caries. On the contrary, it seems to have a protective role, similar to that of xylitol, against bacterial plaque.⁸

Sorbitol ((2*S*,3*R*,4*R*,5*R*)-Hexane-1,2,3,4,5,6-hexol abbreviated to *Sorb*, see Scheme 1), a naturally occurring polyol, is widely used as an additive, E420, in the food industry as a sweetener, humectant, and texturizing agent, in toothpastes, shampoo, and soap as a softening ingredient, as an excipient in pharmaceutical formulations, and as a plasticizer in film formulations.^{9,10} Sorbitol may also be used analytically as a marker for assessing liver blood flow.¹¹ Since sorbitol is an alcohol rather than a sugar, it is relatively resistant to fermentation and hampering acid formation caused by micro-organisms found in the mouth. For this reason, it is used for sweetening and bodying of non-cariogenic foods and soft drinks, as said for the erythritol. It was observed that a little amount of sorbitol (0.5–3.0%) in wine is able to chelate low levels of iron and copper and smoothing out bitterness in lower-quality wine.¹² Sorbitol is an isomer of mannitol, and the difference between the two polyols consists of the planar orientation of the OH group on the second carbon atom. Each isomer is characterized by its own individual set of properties; the most important difference is the response toward moisture. Sorbitol is hygroscopic, while mannitol is resistant to moisture sorption, even at high relative humidities. *Sorb* forms water-soluble chelates with many bivalent and trivalent metal cations under strongly acidic and alkaline conditions.

Maltol (3-hydroxy-2-methyl-4*H*-pyran-4-one, abbreviated to *Malt*, see Scheme 1) is naturally present mainly in larch bark and pine needles; in the food industry, it is used as a flavor enhancer (identified with E636) in food, beverage, tobacco, brewing, and cosmetics for its flavor and anti-oxidant properties.¹³ It exhibits interesting anti-neoplastic activities attributed to the formation of reactive oxygen species^{14,15} as well as coordination properties toward metal cations; for this reason, ligands containing maltol

have been developed and exploited as new potential metal-based anti-tumor drugs.^{16,17}

Ethylmaltol (2-Ethyl-3-hydroxy-4*H*-pyran-4-one, abbreviated to *EMalt*, see Scheme 1) differs to maltol for the presence of an ethyl group rather than a methyl one. Also, this polyol is used as a flavor enhancer and is identified with E637. The 3-hydroxy-4-pyranones are employed both for the control of metal levels in the human body and for oral administration in view of diagnostic or therapeutic purposes.¹⁸ Furthermore, they have been suggested for the treatment of anemic patients for introduction of iron or its removal (also in the case of aluminum) from patients suffering of bodily overload as in thalassemia. This family of compounds also has a role in the administration of ⁶⁷Ga or ¹¹¹In for radiopharmaceuticals and of gadolinium for magnetic resonance imaging (MRI).¹⁹ The beneficial therapeutic effects of compounds of zinc have been recognized, and more recently, the isotopes ⁶³Zn and ^{69m}Zn have been employed in radiopharmaceuticals. The absorption of zinc by the human body depends on the form in which it is administered. In fact, it seems that the simple aqua-ion $\text{Zn}^{2+}_{(\text{aq})}$ and its phytate complex are not well absorbed, but the complexes with citrate, histidine, proinate, several EDTA derivatives, and 3-hydroxy-4-pyranones and 3-hydroxy-4-pyridinones are absorbed by the body. In order to increase the bioavailability of zinc, several complexes such as Zn–maltol and Zn–ethylmaltol have been synthesized.²⁰ Following this study, Zn–ethylmaltol complex could be considered as a suitable zinc species for the treatment of metal deficiency in replacement of Zn^{2+} -sulfate. The determination of stability constants of Zn–maltol derivatives may be a new way for the administration of zinc.

The metal cations selected for this study are Ca^{2+} , Zn^{2+} , and Sn^{2+} , and the first two are essential elements for humans, playing a central, if still only dimly understood, role in a number of healing processes, while the main use of tin is for the manufacture of cans and containers, typically as tinfoil.^{21,22} As a consequence, the direct contact of tin with foods may result in migration from the inside wall of cans and other packaging materials to edible contents.

In this paper, the studies, by potentiometric techniques, on the acid–base properties of erythritol and complexing ability of erythritol, sorbitol, maltol, and ethylmaltol toward Ca^{2+} (only for maltol and ethylmaltol), Zn^{2+} , and Sn^{2+} are reported in NaNO_3 aqueous solutions at $I = 0.151 \text{ mol}\cdot\text{kg}^{-1}$ and at $T = 298.15 \text{ K}$. For the erythritol system, the investigations have been performed at different ionic strengths, $0.1 \leq I/\text{mol}\cdot\text{kg}^{-1} \leq 1.0$, and the dependence on I of the protonation and stability constants has been modeled by the Specific Ion Interaction Theory (SIT). The sequestering ability of the different ligands toward the investigated metal cations, Ca^{2+} , Zn^{2+} , and Sn^{2+} , has been analyzed by the empirical $\text{pL}_{0.5}$ parameter.

2. MATERIALS AND METHODS

2.1. Materials. The polyalcohol solutions (erythritol, sorbitol, maltol, and ethylmaltol from Sigma-Aldrich-Merck) were prepared, with analytical grade water ($R = 18 \text{ M}\Omega \text{ cm}^{-1}$) and grade A glassware, from products of high available purity. The hydrochloric acid (HCl) and sodium hydroxide (carbonate free, NaOH) solutions were prepared from dilution of concentrated ampoules (Riedel-deHäen) and standardized against sodium carbonate and potassium hydrogen phthalate, respectively. The NaOH solutions were preserved from atmospheric CO_2 by means of soda lime traps. The solutions of ZnCl_2 and SnCl_2 were prepared, without further purification,

Table 1. Calculated Deprotonation and Formation Constants of Zn²⁺ and Sn²⁺/Ery Species in NaNO_{3(aq)} at Different Ionic Strengths and Ionic Strength Dependence Parameters, eq 3, at T = 298.15 K and p = 0.1 MPa^a

equilibrium	log β ⁰ ^b	z*	Δε ^c	I/mol·kg ⁻¹				
				0.15	0.25	0.50	0.75	1.00
Ery = [Ery(H) ₋₁] ⁻ + H ⁺	-12.54 ± 0.03 ^d	-2	0.35 ± 0.01 ^d	-12.24 ^e	-12.16	-12.01	-11.89	-11.78
Ery = [Ery(H) ₋₂] ²⁻ + 2H ⁺	-24.24 ± 0.04	-6	0.51 ± 0.01	-23.42	-23.24	-22.94	-22.71	-22.51
Zn ²⁺ + Ery = [ZnEry(H) ₋₁] ⁺ + H ⁺	-5.62 ± 0.03 ^d	2	1.37 ± 0.01 ^d	-5.67	-5.57	-5.29	-4.98	-4.66
Model 1								
Sn ²⁺ + Ery = [SnEry] ²⁺	2.82 ± 0.01 ^d	0	-1.44 ± 0.01 ^d	2.61	2.46	2.10	1.74	1.38
Sn ²⁺ + Ery = [SnEry(H) ₋₁] ⁺ + H ⁺	-0.65 ± 0.02	2	0.53 ± 0.01	-0.82	-0.80	-0.73	-0.63	-0.52
Model 2								
Sn ²⁺ + 2Ery = [Sn(Ery) ₂] ²⁺	4.95 ± 0.08	0	-1.31 ± 0.12	4.76	4.62	4.30	3.97	3.64
Sn ²⁺ + Ery = [SnEry(H) ₋₁] ⁺ + H ⁺	-1.01 ± 0.06 ^d	2	0.92 ± 0.08 ^d	-1.12	-1.07	-0.90	-0.70	-0.50

^aStandard uncertainties: $u(T) = 0.1$ K, $u(I) = 0.001$ mol·kg⁻¹. ^bDeprotonation and formation constants at infinite dilution, eq 3. ^cEmpirical parameter of eq 3. ^d±Std. dev. ^eCalculate formation constants according to eq 3.

by weighing the dihydrated pure salt. Their purity was checked by titrations with EDTA standard solutions,²³ and it was in all the cases ≥99.5%.

Particular attention was employed for the preparation of tin solutions, in order to prevent the oxidation of Sn(II) to Sn(IV) and the starting of the hydrolysis process, owing to hamper this, the SnCl₂ solutions were acidified with HCl to reach pH < 2 and a piece of metallic tin was added to the solutions after the preparation. Furthermore, these solutions were bubbled with purified N₂ to exclude O₂.

The ionic medium aqueous solutions, NaNO₃, were prepared by weighing the pure salt (Fluka), previously dried in an oven, at T = 383.15 K, for at least 2 h.

2.2. Potentiometric Technique. The determination of the protonation and complex formation constants of the ligands were carried out by potentiometric ISE-H⁺ measurements. A 25 cm³ portion of the solutions containing the polyalcohol (at different concentrations) and the ionic medium, NaNO₃, at a pre-established ionic strength value was titrated with NaOH standard solutions, in thermostatted cells. In the case of the complex formation studies, an amount of the different metal cations considered and a known aliquot of strong acid (HCl) were added to the investigated solutions. All of the potentiometric titrations were carried out under magnetic stirring and bubbling purified presaturated N_{2(g)} through the solutions, to exclude O_{2(g)} and CO_{2(g)} inside. More details on the procedures for the potentiometric measurements have already been reported in previous papers.²⁴

2.3. Computer Programs. All of the potentiometric parameters such as standard electrode potential (E^0), basic junction coefficient (j_b), analytical concentration of the ligands, ionic product of water ($\log K_w$), and protonation constants were refined using the ESAB2M²⁵ computer program, while the complex formation constants of the different metal–ligand systems were determined by using the BSTAC²⁶ program. The study of the dependence on the ionic strength of the protonation and complex formation constants and the refinement of the corresponding parameters was performed by the least-squares computer program LIANA.²⁷ The ES4ECI²⁸ and HYSS²⁹ computer programs have been used to draw the speciation diagrams and to calculate the species formation percentages. In the case of the second program, it is possible, over considering the protonation, hydrolysis, and formation constants of all of the species present in the speciation model, to take into account also the solubility product of the sparingly soluble species, and

therefore to know the formation percentage of the last one in the distribution diagrams.

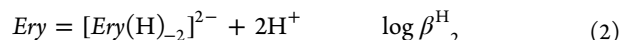
3. RESULTS AND DISCUSSION

3.1. Acid–Base Properties of Polyalcohols. The acid–base properties of erythritol (Ery) have been studied by experimental potentiometric measurements, while, in the case of the sorbitol (Sorb),^{30–32} maltol (Malt), and ethylmaltol (EMalt),³³ literature data have been considered. The hydrolytic constants of the metal cations, Ca²⁺, Zn²⁺, Sn²⁺, and in the last case also the solubility product of the sparingly soluble species Sn(OH)_{2(s)}, have been taken into account in the elaboration of the complex formation constants.^{34,35} The conversion from the molar to the molal concentration scale of the constants was carried out by using the appropriate density values.³⁶

3.2. Acid–Base and Complexing Properties of Erythritol. The acid–base properties and the complexing ability toward Zn²⁺ and Sn²⁺ of Ery have been studied by the potentiometric technique in NaNO₃ aqueous solutions at different ionic strengths ($0.1 \leq I/\text{mol}\cdot\text{kg}^{-1} \leq 1.0$) and at T = 298.15 K. For the determination of the acid–base behavior of this ligand, concentrations in the range $2.0 \leq c_{\text{Ery}}/\text{mmol}\cdot\text{kg}^{-1} \leq 10.0$ were used, in water and a suitable amount of NaNO₃, to obtain the desired ionic strength value. The elaboration of the potentiometric data, in the pH range 7.0–11.5, led us to determine two deprotonation constants, expressed by means of the equilibria



and



The deprotonation constants determined at different ionic strengths have been fitted according to the Specific Ion Interaction Theory (SIT) approach,^{37,38} to obtain the ionic strength dependence parameters

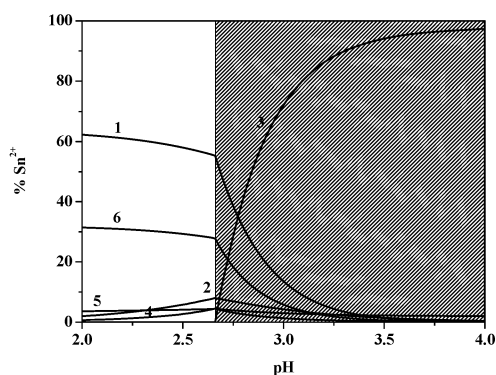
$$\log \beta = \log \beta^0 - z^* \cdot 0.51 \cdot (I^{0.5} / (1 + 1.5 \cdot I^{0.5})) + \Delta \varepsilon \cdot I \quad (3)$$

where $\log \beta^0$ is the equilibrium constant at infinite dilution, z^* is

$$z^* = \sum (\text{charges})_{\text{reag}}^2 - \sum (\text{charges})_{\text{prod}}^2$$

and $\Delta \varepsilon$ is the summation of the specific interaction coefficients of the species involved in the equilibrium and the ions of the background electrolyte.

Model 1



Model 2

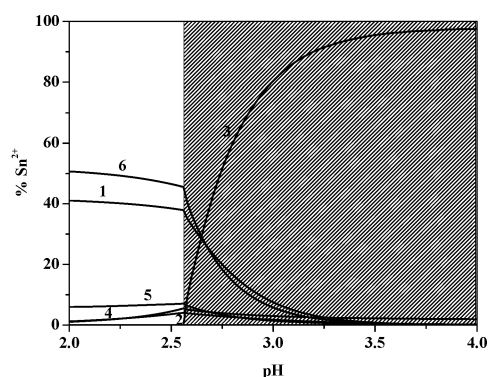


Figure 1. Distribution diagram of the Sn^{2+} /erythritol system: models 1 and 2, in $\text{NaNO}_{3(\text{aq})}$ at $I = 0.151 \text{ mol}\cdot\text{kg}^{-1}$ and at $T = 298.15 \text{ K}$. Experimental conditions: $c_{\text{Sn}^{2+}} = 1.5 \text{ mmol}\cdot\text{kg}^{-1}$ and $c_{\text{Ery}} = 5.0 \text{ mmol}\cdot\text{kg}^{-1}$. Standard uncertainties: $u(\text{pH}) = 0.01$, $u(T) = 0.1 \text{ K}$, $u(I) = 0.001 \text{ mol}\cdot\text{kg}^{-1}$. Legend: **Model 1:** 1. SnEry ; 2. $\text{SnEry}(\text{H}_{-1})$; 3. $\text{Sn}(\text{OH})_{2(\text{s})}$; 4. Sum of the Sn^{2+} hydrolytic species; 5. Sum of the SnCl_n species; 6. Free Sn^{2+} . **Model 2:** 1. SnEry_2 ; 2. $\text{SnEry}(\text{H}_{-1})$; 3. $\text{Sn}(\text{OH})_{2(\text{s})}$; 4. Sum of the Sn^{2+} hydrolytic species; 5. Sum of the SnCl_n species; 6. Free Sn^{2+} . Charges were omitted for simplicity. The shaded zone refers to the pH range where the sparingly soluble species, $\text{Sn}(\text{OH})_{2(\text{s})}$, is present.

This procedure allowed us to calculate the deprotonation constants at different ionic strengths and at infinite dilution, as reported in Table 1.

The knowledge of the acid–base properties of erythritol is important for solutions with $\text{pH} > 10.5$, because the displacement of the proton of the $-\text{OH}$ groups (eqs 1 and 2) occurs at high pH values. As expected, the acidity of the two alcoholic groups is very similar and their values are in agreement with protonation (or deprotonation) data reported in the literature for alcoholic groups (e.g., sorbitol and glycerol). The complexation of Zn^{2+} and Sn^{2+} was investigated preparing solutions at the following experimental conditions: $1.0 \leq c_{\text{Zn}^{2+}}/\text{mmol}\cdot\text{kg}^{-1} \leq 3.0$, $2.0 \leq c_{\text{Ery}}/\text{mmol}\cdot\text{kg}^{-1} \leq 9.0$, and $0.5 \leq c_{\text{Sn}^{2+}}/\text{mmol}\cdot\text{kg}^{-1} \leq 1.5$, $2.0 \leq c_{\text{Ery}}/\text{mmol}\cdot\text{kg}^{-1} \leq 8.2$, with HCl in different amounts and NaNO_3 to adjust the ionic strength values, $0.1 \leq I/\text{mol}\cdot\text{kg}^{-1} \leq 1.0$, at $T = 298.15 \text{ K}$. From the potentiometric investigations of the Zn^{2+} /Ery system, the $\text{ZnEry}(\text{H})_{-1}$ species has been determined. During the measurements, the formation of a sparingly soluble species was observed below $\text{pH} \sim 7.5$, probably due to the formation of a neutral species between Zn^{2+} and erythritol (e.g., $\text{ZnEry}_2(\text{H})_{-2}$), but its formation was not obtained from the calculations. The formation pH of the sparingly soluble species depends on the $m_{\text{Zn}^{2+}}:m_{\text{Ery}}$ molal ratio. The dependence on the ionic strength of the formation constant has been studied by eq 3, and the relative parameters are reported in Table 1, together with the calculated formation constants at different ionic strengths. From the elaboration of the experimental data of the Sn^{2+} /erythritol system, two speciation models have been proposed: model 1 consists of SnEry and $\text{SnEry}(\text{H})_{-1}$ species, while model 2 consists of $\text{Sn}(\text{Ery})_2$ and $\text{SnEry}(\text{H})_{-1}$ species. The formation constant values of the species and their corresponding equilibria are reported in Table 1 together with the $\Delta\varepsilon$ parameter of eq 3. Considering the criteria generally used to select the best speciation model, namely, the simplicity and the likelihood of the proposed species, the formation percentages and the pH range where they form, the consistency of various models under the different conditions, and the values of the variance ratio, both models can be considered reliable, even if the consistency of model 1 under the different conditions is preferable. The formation of the Sn^{2+} /Ery species occurs at acidic pH values and

is poorly stable, leading to the formation of the sparingly soluble hydroxo species at $\text{pH} \sim 2.5$, although the concentration of Sn^{2+} was maintained low, to avoid the precipitation of the $\text{Sn}(\text{OH})_{2(\text{s})}$ species. Figure 1 reports the distribution diagrams of the species at $I = 0.151 \text{ mol}\cdot\text{kg}^{-1}$ and $T = 298.15 \text{ K}$, for the two speciation models. As it can be seen, the formation percentage of the SnEryH_{-1} species is low at ~ 8 and $\sim 2\%$ for models 1 and 2, respectively, while the SnEry and $\text{Sn}(\text{Ery})_2$ species reach about 62 and 40%, respectively. In both cases, the solubility product of the $\text{Sn}(\text{OH})_{2(\text{s})}$ species has been taken into account, and as evidenced in Figure 1, its formation occurs at $\text{pH} \sim 2.7$, for model 1, and at $\text{pH} \sim 2.6$, for model 2.

3.3. Acid–Base and Complexing Properties of Sorbitol. The deprotonation constants of the sorbitol are already known and reported in the literature,^{31,32} where generally a single deprotonation step has been reported. On the contrary, Gaidamauskas et al.³⁰ report two deprotonation steps with constant values very close: $\log K^{\text{H}}_1 = -13.6$ and $\log \beta^{\text{H}}_2 = -27.0$ ($\log K^{\text{H}}_2 = -13.4$, the equilibria are reported in Table 2). The complexing ability of sorbitol toward Sn^{2+} has been investigated by the potentiometric technique, at $I = 0.151 \text{ mol}\cdot\text{kg}^{-1}$ in $\text{NaNO}_{3(\text{aq})}$ and $T = 298.15 \text{ K}$. The analytical concentration ranges used for the measurements are $2.0 \leq c_{\text{Sorb}}/\text{mmol}\cdot\text{kg}^{-1} \leq 4.5$ and $0.5 \leq c_{\text{Sn}^{2+}}/\text{mmol}\cdot\text{kg}^{-1} \leq 1.5$, with HCl in

Table 2. Deprotonation and Formation Constants of Sn^{2+} /Sorb Species in $\text{NaNO}_{3(\text{aq})}$ at $I = 0.151 \text{ mol}\cdot\text{kg}^{-1}$, $T = 298.15 \text{ K}$, and $p = 0.1 \text{ MPa}^a$

equilibrium	$\log \beta$
$\text{Sorb} = [\text{Sorb}(\text{H}_{-1})]^- + \text{H}^+$	-13.6^b
$\text{Sorb} = [\text{Sorb}(\text{H})_{-2}]^{2-} + 2\text{H}^+$	-27.0^b
Model 1	
$\text{Sn}^{2+} + \text{Sorb} = [\text{SnSorb}]^{2+}$	2.63 ± 0.02^c
$\text{Sn}^{2+} + \text{Sorb} = [\text{SnSorb}(\text{H})_{-1}]^+ + \text{H}^+$	-0.84 ± 0.04
Model 2	
$\text{Sn}^{2+} + 2\text{Sorb} = [\text{Sn}(\text{Sorb})_2]^{2+}$	5.13 ± 0.02
$\text{Sn}^{2+} + \text{Sorb} = [\text{SnSorb}(\text{H})_{-1}]^+ + \text{H}^+$	-0.90 ± 0.05

^aStandard uncertainties: $u(T) = 0.1 \text{ K}$, $u(I) = 0.001 \text{ mol}\cdot\text{kg}^{-1}$.

^bCalculated from literature values.^{30–32} ^c \pm Std. dev.

Table 3. Deprotonation and Stability Constants of the $M^{2+}/Malt$ and $M^{2+}/EMalt$ Systems in $NaNO_3(aq)$ at $I = 0.151 \text{ mol}\cdot\text{kg}^{-1}$, $T = 298.15 \text{ K}$, and $p = 0.1 \text{ MPa}^a$

equilibrium	$\log \beta$		
$Malt = [Malt(H_{-1})]^- + H^+$	-8.417 ^b		
$EMalt = [EMalt(H_{-1})]^- + H^+$	-8.504 ^b		
	Ca ²⁺	Zn ²⁺	Sn ²⁺
	Maltol		
$M^{2+} + Malt = [MMalt]^{2+}$	2.33 ± 0.02 ^c	5.598 ± 0.008 ^c	10.66 ± 0.10 ^c
$M^{2+} + 2Malt = [M(Malt)_2]^{2+}$		10.246 ± 0.012	18.26 ± 0.05
$M^{2+} + 3Malt^- = [M(Malt)_3]^{2+}$		11.62 ± 0.15	
	Ethylmaltol		
$M^{2+} + EMalt = [MEMalt]^{2+}$	2.302 ± 0.015 ^c	5.639 ± 0.010 ^c	10.83 ± 0.10 ^c
$M^{2+} + 2EMalt = [M(EMalt)_2]^{2+}$		10.33 ± 0.02	18.61 ± 0.03
$M^{2+} + 3EMalt = [M(EMalt)_3]^{2+}$		12.10 ± 0.10	

^aStandard uncertainties: $u(T) = 0.1 \text{ K}$, $u(I) = 0.001 \text{ mol}\cdot\text{kg}^{-1}$. ^bConstant values from ref 33. ^c±Std. dev.

different amounts and $NaNO_3$ to obtain the desired ionic strength value. The pH range investigated is 2.0–3.5 because, at higher values, the formation of the sparingly soluble species $Sn(OH)_{2(s)}$ occurs. From the elaboration of the experimental data, as for the Sn^{2+}/Ery system, two speciation models have been obtained: model 1, $SnSorb$ and $SnSorb(H)_{-1}$ species; model 2, $Sn(Sorb)_2$ and $SnSorb(H)_{-1}$ species. The formation constant values and the corresponding formation equilibria are reported in Table 2. Applying the criteria of selection already cited, we can consider model 1 as the most reliable with respect to another one. Taking into account the most common databases,^{39,40} where the results of some speciation studies concerning the interaction of glycerol and sorbitol with different metal cations (Ln^{3+} , B^{3+} , As^{3+} , Al^{3+} , Fe^{3+} , Cu^{2+} , etc.) are reported, we can observe that, independent of the temperature, ionic strength, and ionic medium, the formation of ternary hydrolytic metal–ligand species seems to be favored. However, these studies were carried out at a single ionic strength value, generally at $I = 0.1$ or $1.0 \text{ mol}\cdot\text{kg}^{-1}$, and no systematic investigation for the dependence of the stability constants on ionic strength is reported.

3.4. Complexing Properties of Maltol and Ethylmaltol.

The acid–base behavior of maltol and ethylmaltol was already studied and reported in a previous paper.³³ The complexing ability of these two ligands has been studied toward Ca^{2+} , Zn^{2+} , and Sn^{2+} by the potentiometric technique, in $NaNO_3$ aqueous solutions at $I = 0.151 \text{ mol}\cdot\text{kg}^{-1}$ and $T = 298.15 \text{ K}$. The experimental conditions used are ligand $1.3 \leq c_{Malt}$ or $c_{EMalt}/\text{mmol}\cdot\text{kg}^{-1} \leq 22.3$, metal cation $1.0 \leq c_{Ca^{2+}}/\text{mmol}\cdot\text{kg}^{-1} \leq 4.1$ or $1.3 \leq c_{Zn^{2+}}/\text{mmol}\cdot\text{kg}^{-1} \leq 4.3$ or $0.5 \leq c_{Sn^{2+}}/\text{mmol}\cdot\text{kg}^{-1} \leq 2.0$, an amount of strong acid (HCl) and $NaNO_3$. The potentiometric data were collected in the pH ranges 6.0–10.5, 3.0–9.0, and 2.0–9.5 for Ca^{2+} , Zn^{2+} , and Sn^{2+} systems, respectively. The different pH range investigated, for the different systems, is dependent on the different hydrolytic behavior of the considered metal cations and in particular on the formation of the sparingly soluble species during the alkalimetric titrations. The experimental results highlighted that, for a given metal cation (Ca^{2+} , Zn^{2+} , or Sn^{2+}), the same speciation models were obtained independent of the ligand (maltol or ethylmaltol) considered. For Ca^{2+} , only the formation of the CaL species ($L = \text{maltol}$ or ethylmaltol) was observed. Other species were checked, but they were systematically rejected by the BSTAC computer program. In the case of the $Zn^{2+}/Malt$ and $Zn^{2+}/EMalt$, the formation of three complex species was obtained, namely, ZnL , ZnL_2 , and ZnL_3 , while, for the $Sn^{2+}/Malt$ and $Sn^{2+}/EMalt$, the speciation

scheme is represented by two complexes: SnL and SnL_2 . The stability constants of the $M^{2+}/Malt$ and $M^{2+}/EMalt$ species are reported in Table 3. In the case of the Sn^{2+} systems, the experimental measurements were carried out with different $m_{Sn^{2+}}:m_L$ molal ratios but always with a large excess of the ligands. Owing to the high ligand concentrations and $m_{Sn^{2+}}:m_L$ molal ratios used, it has been possible to investigate a wide pH range, 2–9.5, without the formation of the sparingly soluble species $Sn(OH)_{2(s)}$. Concerning maltol, from a comparison of the stability constant values of the ML species, it is possible to note that the stability of the SnL complex is higher than that obtained for ZnL and CaL , i.e., 10.66 ± 0.10 , 5.598 ± 0.008 , and 2.33 ± 0.02 , respectively. There is not a significant difference between the formation constant values of maltol and ethylmaltol species, which indicates the absence of an influence of the methyl and ethyl groups of the lateral chain on the stability of the complexes.

In Figure 2, the distribution diagram of the $Zn^{2+}/maltol$ species shows that the $ZnMalt$ species exists in the pH range 3–7.5 and it achieves 60% of formation even if the main species is the $Zn(Malt)_2$ that at pH ~ 7.5 reaches 96%. The $Zn(Malt)_3$ species forms at pH ~ 7 and achieves 15% of formation. The

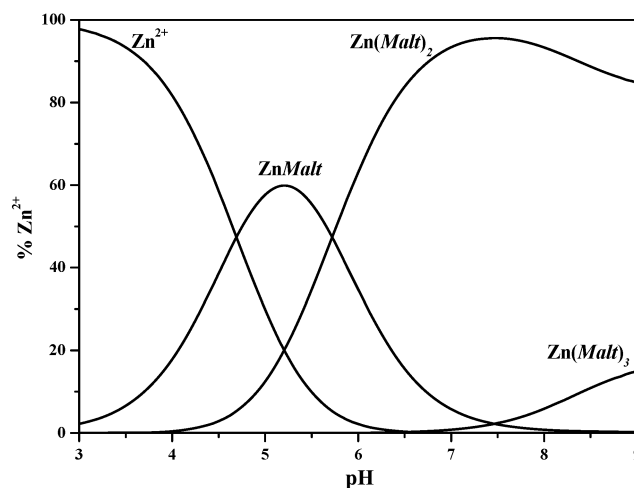


Figure 2. Distribution diagram of the $Zn^{2+}/maltol$ system, in $NaNO_3(aq)$ at $I = 0.151 \text{ mol}\cdot\text{kg}^{-1}$ and at $T = 298.15 \text{ K}$. Experimental conditions: $c_{Zn^{2+}} = 2.6 \text{ mmol}\cdot\text{kg}^{-1}$ and $c_{Malt} = 14.9 \text{ mmol}\cdot\text{kg}^{-1}$. Standard uncertainties: $u(\text{pH}) = 0.01$, $u(T) = 0.1 \text{ K}$, $u(I) = 0.001 \text{ mol}\cdot\text{kg}^{-1}$. Charges were omitted for simplicity.

literature reports some data on the complexation of maltol with different metal cations; for example, for the Zn^{2+} /Malt system, Jakusch et al.⁴¹ report, in the molar concentration scale, at $T = 298.15$ K in KCl aqueous solution and $I = 0.2$ mol·dm⁻³, the formation of three species: ZnL , ZnL_2 , and ZnL_3 with $\log \beta = 5.57 \pm 0.02$, 10.29 ± 0.02 , and 12.71 ± 0.08 , respectively. These data are in good agreement with the results reported in this paper, in the same order, $\log \beta = 5.60$, 10.25 , and 11.62 (see Table 3).

3.5. Sequestering Ability. The sequestering ability of the polyalcohols toward the metal cations has been evaluated by the empirical parameter $\text{pL}_{0.5}$.⁴² It represents the total concentration of ligand required to sequester 50% of a metal cation when present in trace amount (10^{-12} mol·kg⁻¹) in solution. The $\text{pL}_{0.5}$ value depends on the experimental conditions such as pH, ionic strength, ionic medium, and temperature. From a mathematical point of view, this can be expressed by a sigmoidal Boltzmann type equation

$$\chi_M = \frac{1}{1 + 10^{(\text{pL} - \text{pL}_{0.5})}} \quad (4)$$

where χ_M is the mole fraction of metal cation complexed by the ligand, $\text{pL} = -\log c_L$, and $\text{pL}_{0.5} = -\log c_L$, at $\chi_M = 0.5$.

The sequestering ability of a ligand can be graphically represented by a dose–response curve, with asymptotes equal to 1 for $\text{pL} \rightarrow -\infty$ and 0 for $\text{pL} \rightarrow +\infty$, obtained by plotting the mole fraction of metal complexed vs the pL . A high sequestering ability of a ligand toward a metal cation is represented by high $\text{pL}_{0.5}$ values. In the calculation of this empirical parameter, all of the interactions in the system, such as the protonation of the ligand, the hydrolysis of the metal cation, and the interactions with other components, are taken into account in the speciation model.

From the speciation study, it was seen that the acid–base properties and complexing ability of maltol and ethylmaltol appear fairly similar, but analyzing the obtained $\text{pL}_{0.5}$ values, we observe a significantly different behavior between Ca^{2+} , Zn^{2+} , and Sn^{2+} . As examples in Figures 3 and 4, the sequestering

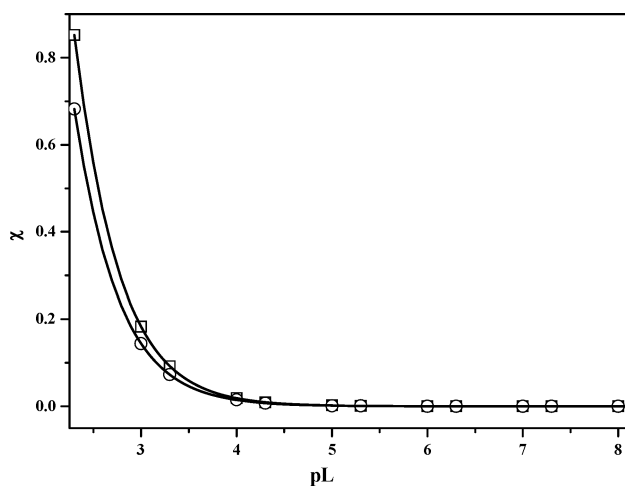


Figure 3. Calcium sequestration diagram by maltol and ethylmaltol. Molar fraction of Ca^{2+} complexed vs the total ligand concentration (pL) at $T = 298.15$ K and $I = 0.151$ mol·kg⁻¹ in $\text{NaNO}_3(\text{aq})$ at pH 7.4. (○) Ca^{2+} /ethylmaltol system, $\text{pL}_{0.5} = 1.16$; (□) Ca^{2+} /maltol system, $\text{pL}_{0.5} = 1.27$. Standard uncertainties: $u(\text{pH}) = 0.01$, $u(T) = 0.1$ K, $u(I) = 0.001$ mol·kg⁻¹.

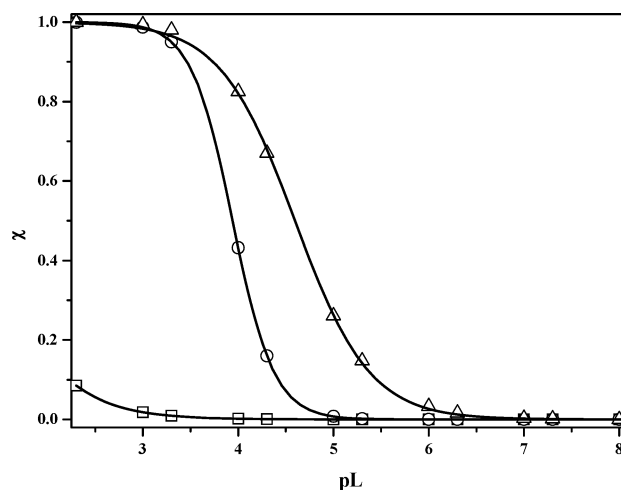


Figure 4. Sequestration diagram of maltol toward Ca^{2+} , Sn^{2+} , and Zn^{2+} cations. Molar fraction of M^{2+} complexed vs the total ligand concentration (pL) at $T = 298.15$ K and $I = 0.151$ mol·kg⁻¹ in $\text{NaNO}_3(\text{aq})$ at pH 7.4. (□) Ca^{2+} /maltol system, $\text{pL}_{0.5} = 1.27$; (○) Sn^{2+} /maltol, $\text{pL}_{0.5} = 3.94$; (△) Zn^{2+} /maltol system, $\text{pL}_{0.5} = 4.60$. Standard uncertainties: $u(\text{pH}) = 0.01$, $u(T) = 0.1$ K, $u(I) = 0.001$ mol·kg⁻¹.

abilities of *Malt* and *EMalt* toward Ca^{2+} and *Malt* toward Ca^{2+} , Sn^{2+} , and Zn^{2+} cations, respectively, are reported. In Figure 3, the sequestration diagram is drawn at pH 7.4, in $\text{NaNO}_3(\text{aq})$ at $I = 0.151$ mol·kg⁻¹ and $T = 298.15$ K. As can be observed, the two ligands show the same sequestering ability toward Ca^{2+} ; in fact, for the Ca^{2+} /ethylmaltol system, the $\text{pL}_{0.5}$ value is 1.16, while, for the Ca^{2+} /maltol, it is 1.27. In Figure 4, the diagram evidences that the sequestering ability of *Malt* is very different toward the various metal cations; the $\text{pL}_{0.5}$ values are 1.27, 3.94, and 4.60 for Ca^{2+} , Sn^{2+} , and Zn^{2+} , respectively. Therefore, the sequestering ability of *Malt* and *EMalt*, under these experimental conditions, follows the trend $\text{Zn}^{2+} > \text{Sn}^{2+} > \text{Ca}^{2+}$.

It is important to note that, in spite of the higher stability of the *SnMalt* and *SnEMalt* species than that of the *ZnMalt* and *ZnEMalt* ones, an opposite trend in terms of sequestering ability is obtained. A comparison of the sequestering ability of maltol, ethylmaltol, and erythritol toward Zn^{2+} is shown in Figure 5. From the calculation of the $\text{pL}_{0.5}$ parameter, it comes out that maltol and ethylmaltol sequester the Zn^{2+} in a more effective way than erythritol, with $\text{pL}_{0.5}$ values of 4.60, 4.56, and 1.72 for the Zn^{2+} /maltol, Zn^{2+} /ethylmaltol, and Zn^{2+} /erythritol systems, respectively. In Figure 6, comparison in terms of the sequestering ability of erythritol and sorbitol toward Sn^{2+} is reported. These two ligands have the same behavior with respect to this metal cation, in $\text{NaNO}_3(\text{aq})$ at $I = 0.151$ mol·kg⁻¹, $T = 298.15$ K, and pH 2.0. The $\text{pL}_{0.5}$ values are 2.61 for Sn^{2+} /erythritol and 2.62 for Sn^{2+} /sorbitol.

CONCLUSIONS

In this paper, the speciation study of four polyalcohols, namely, erythritol, sorbitol, maltol, and ethylmaltol, has been reported in $\text{NaNO}_3(\text{aq})$ at different ionic strengths and $T = 298.15$ K. The results obtained can be reassumed in some points:

- The acid–base properties of the ligands seem to be influenced by their structure; in fact, erythritol and sorbitol, which have the same structure but two $-(\text{CH}_2)-\text{OH}$ groups more in the latter, have the same behavior. Maltol and ethylmaltol, that differ only for an extra methylene group, also have an equal protonation

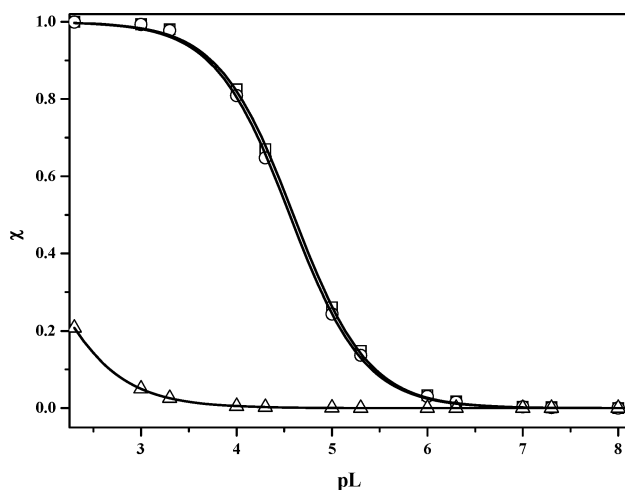


Figure 5. Zinc sequestration diagram by maltol, ethylmaltol, and erythritol. Molar fraction of Zn^{2+} complexed vs the total ligand concentration (pL) at $T = 298.15$ K and $I = 0.151$ mol·kg $^{-1}$ in $\text{NaNO}_3(\text{aq})$ at pH 7.4. (\square) Zn^{2+} /maltol system, $pL_{0.5} = 4.60$; (\circ) Zn^{2+} /ethylmaltol, $pL_{0.5} = 4.56$; (\triangle) Zn^{2+} /erythritol system, $pL_{0.5} = 1.72$. Standard uncertainties: $u(\text{pH}) = 0.01$, $u(T) = 0.1$ K, $u(I) = 0.001$ mol·kg $^{-1}$.

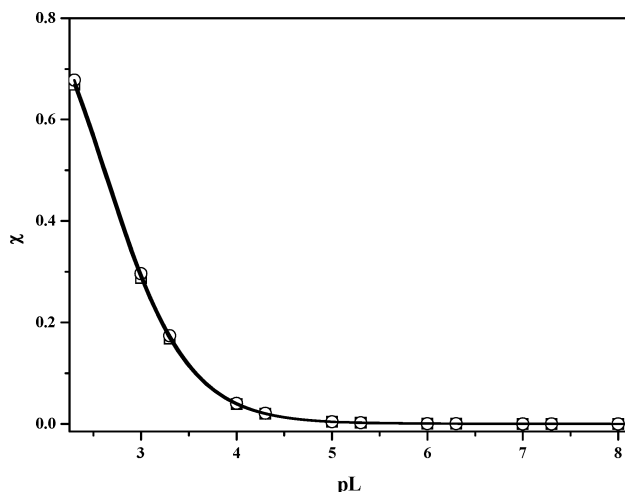


Figure 6. Tin(II) sequestration diagram by erythritol and sorbitol, with respect to model 1. Molar fraction of Sn^{2+} complexed vs the total ligand concentration (pL) at $T = 298.15$ K and $I = 0.151$ mol·kg $^{-1}$ in $\text{NaNO}_3(\text{aq})$ at pH 2.0. (\square) Sn^{2+} /erythritol system, $pL_{0.5} = 2.61$; (\circ) Sn^{2+} /sorbitol, $pL_{0.5} = 2.62$. Standard uncertainties: $u(\text{pH}) = 0.01$, $u(T) = 0.1$ K, $u(I) = 0.001$ mol·kg $^{-1}$.

constant, but the acidity is higher than erythritol and sorbitol, probably because of a greater delocalization of the charge due to aromatoid heterocycle.

- The stability of the complexes of the different systems can be explained considering the ML species; for example, in the case of SnL species, the stability constant for erythritol and sorbitol is the same, $\log K_{\text{SnEry}} = 2.61$ and $\log K_{\text{SnSorb}} = 2.63$, while, for maltol and ethylmaltol, it is higher than the first two ligands; in fact, $\log K_{\text{SnMalt}} = 10.66$ and $\log K_{\text{SnEMalt}} = 10.83$. For all of the ligands, the interaction with the metal cations is through the oxo group, but in the case of the pyranones, the major stability of the complexes probably is due to the electronic interaction with the ring system. The stability of the ML species that maltol forms

with Ca^{2+} , Zn^{2+} , and Sn^{2+} follows the trend $\text{SnMalt} (10.66) > \text{ZnMalt} (5.598) > \text{CaMalt} (2.33)$.

- The sequestering ability of the different ligands has been evaluated by $pL_{0.5}$ parameters: for maltol systems, at $T = 298.15$ K in $\text{NaNO}_3(\text{aq})$, $I = 0.151$ mol·kg $^{-1}$ and pH 7.4, the sequestration trend toward Ca^{2+} , Sn^{2+} , and Zn^{2+} cations is $1.27 < 3.94 < 4.60$, respectively. Under these experimental conditions, comparing the $pL_{0.5}$ values of the Zn^{2+} /maltol, Zn^{2+} /ethylmaltol, and Zn^{2+} /erythritol systems, the zinc sequestration by maltol and ethylmaltol is the same, with $pL_{0.5} = 4.60$ and 4.56 , respectively, while for erythritol this ability is low, $pL_{0.5} = 1.72$.

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Notes

The authors declare no competing financial interest.

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