

# Zinc(II) complexes with hydroxocarboxylates and mixed metal species with tin(II) in different salts aqueous solutions at different ionic strengths: formation, stability, and weak interactions with supporting electrolytes

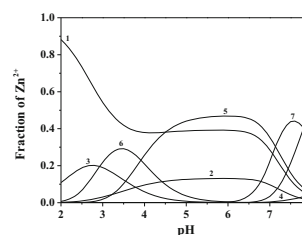
Rosalia Maria Cigala · Francesco Crea · Concetta De Stefano ·  
Claudia Foti · Demetrio Milea · Silvio Sammartano

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**Abstract** This paper reports the results of an investigation carried out on the interaction between Zn(II) and some hydroxocarboxylic ligands (L), namely: malate (Mala<sup>2-</sup>), tartrate (Tar<sup>2-</sup>) and citrate (Cit<sup>3-</sup>). The stability constants of the mono- and polynuclear  $Zn_iH_jL_k^{(2i+j-kz)}$  species were determined by potentiometric measurements at  $T = 298.15$  K in different ionic media, NaCl<sub>(aq)</sub> and NaNO<sub>3(aq)</sub>, at different ionic strengths:  $I = 0.15$  mol dm<sup>-3</sup> (NaCl<sub>(aq)</sub>) and 1.00 mol dm<sup>-3</sup> (NaCl<sub>(aq)</sub> and NaNO<sub>3(aq)</sub>). As a further contribution to the study of the formation of mixed species, that are of particular importance in fluids that hyperaccumulated metal ions, the ternary interactions between two different metals and a ligand (Zn<sup>2+</sup>/Sn<sup>2+</sup>/hydroxocarboxylic ligands) were also investigated. The formation of the hetero-metal complexes produces an enhancement of the stability of the complexes with respect to the same homo-metal ones, shifting significantly the pH of precipitation of the sparingly soluble species and increasing the mobility and bioavailability of the species. From the analysis of experimental data at  $I = 1.00$  mol dm<sup>-3</sup> in NaCl<sub>(aq)</sub> and NaNO<sub>3(aq)</sub>, it results that the stability constants in NaCl<sub>(aq)</sub> are significantly higher than the ones in NaNO<sub>3(aq)</sub>. The higher stability of the species in NaCl<sub>(aq)</sub> can be explained in terms of ion pairs formation with chloride ion. As an example, for the hetero-metals/Mala/chloride system, the following stability constants, on the basis of the general

reaction: mixed-complex + Cl<sup>-</sup> = mixed-complex/Cl (quaternary species), we obtained:  $\log K_{1111} = 0.48$ ,  $\log K_{1121} = 0.36$ ,  $\log K_{112-11} = 0.82$  for ZnSnMalaCl, ZnSn(Mala)<sub>2</sub>Cl, and ZnSn(Mala)<sub>2</sub>OHCl, respectively. The sequestering ability of the three ligands toward Zn<sup>2+</sup> was evaluated, at different experimental conditions, by means of the empirical parameter, pL<sub>0.5</sub>. The effect of the chloride anion on the stability of various species and on the sequestration of the metal was also evaluated.

*Graphical abstract*



**Keywords** Hydroxocarboxylic acids · Stability constants · Mixed Sn<sup>2+</sup>/Zn<sup>2+</sup> species · Speciation · Sequestration

## Introduction

The largest natural emission of zinc(II) is due to erosion of the rocks, whilst the main anthropogenic sources are corrosion of galvanized structures, waste disposal, fertilizer, and pesticides [1]. This metal is widely used in several fields, as a protective coating of other metals, in dye casting and in many industrial fields. The Zn(II)/inorganic-ligand complexes have various applications, for automotive equipment, storage, dry cell

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R. M. Cigala · F. Crea (✉) · C. De Stefano · C. Foti ·  
D. Milea · S. Sammartano  
Dipartimento di Scienze Chimiche, Università di Messina, Viale  
F. Stagno d'Alcontres, 31, 98166 Messina (Vill. S. Agata), Italy  
e-mail: fcrea@unime.it

batteries, dental treatment, medical and householding applications. The Zn(II)/organo-ligand complexes are used as fungicides, topical antibiotics, and lubricants [1].

The transport and distribution of zinc in water, sediment and soil are dependent on the species of zinc present and on the characteristic of the environment [1]. Zinc may also forms stable complexes with several high molecular weight organic ligands; for example, with humic and fulvic acid. The formation of such complexes contributes to increase the mobility and/or solubility of the metal in the environment [2–5].

In this light, it is interesting to study the interaction of zinc with naturally occurring organic ligands or with molecules able to mime the behavior of the organic matter. In this order, the interaction of the Zn(II) with some hydroxocarboxylate ligands (L), as malate ( $\text{Mala}^{2-}$ ), tartrate ( $\text{Tar}^{2-}$ ), and citrate ( $\text{Cit}^{3-}$ ), that are involved in many physiological processes, were studied.

The literature reports many data on the interaction of Zn(II) with this kind of ligands, but generally the thermodynamic data are given at a single ionic strength and no systematic investigations on their dependence on ionic strength, medium, temperature, etc., were found [6–10].

When metal ions are solubilised in a multicomponent solution, like a natural fluid, the contemporary presence of other cations and several organic and inorganic ligands can lead to the formation of mixed metal or mixed ligand species [11–15]. This aspect has been until now not frequently investigated owing to the difficulty to correctly study the speciation of such systems. In fact, this kind of studies require first of all the knowledge of the speciation and of the thermodynamic aqueous parameters in the same experimental conditions of the binary metal-ligand complexes and successively the investigations of the ternary interactions that lead to the formation of the mixed metal<sub>1</sub>-metal<sub>2</sub>-ligand species. The difficulty increases progressively when the supporting electrolyte solution includes ion(s) able(s) to interact with the metal(s) or with the ligand(s); in this case, the formation of quaternary complexes, stabilized by the interaction with such ion(s) can be observed. In many cases, the formation percentages of these species depend on the concentration of the ions of the ionic medium.

Keeping in mind that in natural waters and biological fluids, the organic and inorganic components can be present in a wide range of concentrations and of molar ratios, it follows that the formation of mixed species cannot be neglect in a correct speciation study. Performing this kind of investigation, different ways can be chosen to study the speciation of the system. One way consists of studying and simply determining the conditional stability constants, without taking into account the influence of the supporting electrolyte on the speciation and neglecting all the possible interactions of the binary or mixed species with the ions of the supporting electrolytes. The second more complete way,

equivalent to the previous one in terms of results, consists of studying the system in two different ionic media. The first ionic medium contains ion(s) that form ternary and quaternary species with the metal-ligand species, whilst the second medium must be not interacting. From the difference of the stability constants in the two ionic media, it is possible to estimate the stability constants of the formed metal(s)-ligand(s)/supporting electrolyte ion species [16]. This second procedure to study the speciation of the same system in two differently interacting ionic media is more accurate with respect to the first procedure where only the conditional stability constants were determined; in fact, this second way allows, by means of the difference of the stability constants, to estimate the stability constants of the species formed by the interaction of the metal/ligand species with the ion(s) of the supporting electrolyte.

In the past, our group has been already involved in this kind of investigation, studying the formation of both mixed ligand [16] and mixed metal [17–25] complexes of metals and ligands of biological and environmental importance. In recent years, we observed that when two metals, even if with fairly different acid–base properties, are present in the same solution, they tend to form mixed hydrolytic species of high stability also in absence of organic ligands. These studies [17–25] revealed important aspects: the first one is that the mixed species have an higher stability with respect to the corresponding binary species, and the second that the formation of the mixed species, thermodynamically favored, contribute to enhance the solubility and then the mobility of the metal ions in the environment.

Recently, we also studied the interaction of Sn(II) with the hydroxocarboxylic ligands here investigated, in  $\text{NaCl}_{(\text{aq})}$  and  $\text{NaNO}_{3(\text{aq})}$  [16]. From the analysis of the results obtained in those experimental conditions resulted that in different ionic media ( $\text{NaCl}_{(\text{aq})}$  and  $\text{NaNO}_{3(\text{aq})}$ ), at different ionic strengths and temperatures, the metal ion can form both binary  $\text{Sn}_1\text{L}_k^{(21-kz)}$  and binary protonated/hydrolytic  $\text{Sn}_1\text{L}_k(\text{H}/\text{OH})_j^{(21+j-kz)}$  species of high stability. In  $\text{NaCl}$  aqueous solution, owing to the high tendency of the metal (i.e. Sn(II)) to form stable complexes with  $\text{Cl}^-$ , the formation of ternary  $\text{Sn}_1\text{L}_k(\text{H}/\text{OH})_j\text{Cl}_m^{(21+j-kz-m)}$  species was found. From a comparison with the stability constants of the same species obtained in  $\text{NaNO}_{3(\text{aq})}$ , resulted that they are stabilized by chloride; this information is of fundamental importance, since  $\text{Cl}^-$  is the main inorganic anion component of the biological fluids and natural waters.

Therefore, we decided to update the information on the speciation of Zn(II) with the same hydroxocarboxylic ligands and in the same experimental conditions used in the previous work, both in the presence and absence of Sn(II), but taking into account that: (1) Sn(II) forms generally stronger complexes than Zn(II), and (2) Sn(II) forms stable  $\text{SnCl}_m$  species also at low chloride concentrations.

The sequestering ability of the three investigated ligands toward Zn(II) was then evaluated in different conditions (pH, ionic strength, ionic medium) by means of the  $pL_{0.5}$ , a semiempirical parameter already proposed in many papers for an objective quantification of this ability (see, e.g., refs. [26, 27]). Moreover, the importance of the stabilizing effect of the chloride ion toward the complex species was also evaluated. A comparison between the data here reported and literature findings is reported too.

## Results and discussion

### Formation constants of tartrate complexes of $Zn^{2+}$

The analysis of the potentiometric data was performed following the procedures and the criteria used in several previous papers [16, 27–30], to select the best speciation model for each investigated system.

**Table 1** Recalculated hydrolytic constants of Zn(II) [9, 10, 31] at different ionic strengths and in different ionic media at  $T = 298.15$  K

Species	$I = 0.15 \text{ mol dm}^{-3a}$	$I = 1.00 \text{ mol dm}^{-3b}$
Zn(OH)	−9.16	−8.64
Zn(OH) <sub>2</sub>	−17.22	−16.68
Zn(OH) <sub>3</sub>	−28.47	−28.30
Zn <sub>2</sub> (OH)	−8.89	−10.11
Zn <sub>2</sub> (OH) <sub>6</sub>	−57.32	−57.31

Zn<sub>p</sub>(OH)<sub>q</sub><sup>(2p−q)</sup> hydrolytic constants were recalculated from literature data that were selected as reliable and by means least squares calculation (overall solution minimizes the sum of the squares of the errors made in the results of an equation)

<sup>a</sup> NaCl<sub>(aq)</sub>

<sup>b</sup> NaNO<sub>3(aq)</sub>

For a correct definition of the best speciation model, it is necessary also to take into account the hydrolysis of Zn(II) and the protonation constants of the ligands in all the investigated conditions; the hydrolysis constants of this metal ion were recalculated from literature data that were selected as reliable [9, 10, 31] and are reported in Table 1.

The protonation constants of the ligands were taken from a previous paper [16] and are reported in Table 1S of the Supplementary material.

The use of the Zn(II) and Sn(II) chloride salts also in the investigation in nitrate medium did not influence significantly the speciation, owing to the low chloride concentration (two times the metal concentration) respect to nitrate (supporting electrolyte). In any cases when the potentiometric data were processed with the BSTAC computer program (see here after), the formation of the  $M^{2+}$ -Cl<sup>−</sup> complexes was taken into account, especially in the case of the SnCl<sub>i</sub><sup>2−i</sup> species. In the case of Zn(II), the very weak ZnCl<sub>i</sub><sup>2−i</sup> complexes can be neglected.

For Zn(II)/Tar system, the best results were obtained by taking into account the formation of ZnTar, ZnHTar, ZnTar(OH)<sub>2</sub>, Zn(Tar)<sub>2</sub>, Zn<sub>2</sub>H(Tar)<sub>2</sub>, Zn<sub>2</sub>(Tar)<sub>2</sub>(OH)<sub>2</sub> and Zn<sub>2</sub>(Tar)<sub>2</sub>(OH)<sub>3</sub> (charges omitted for simplicity) species. The experimental conditions (NaCl<sub>(aq)</sub>:  $I = 0.15 \text{ mol dm}^{-3}$  and NaNO<sub>3(aq)</sub>:  $I = 1.00 \text{ mol dm}^{-3}$ ) were chosen to compare the stability constants in quite different experimental conditions of ionic strength and ionic media.

Table 2 reports the stability constants, both in NaCl<sub>(aq)</sub> and NaNO<sub>3(aq)</sub> at  $I = 0.15 \text{ mol dm}^{-3}$  and  $1.00 \text{ mol dm}^{-3}$ , respectively. The first possible comparison allow us to observe that the speciation of the systems is similar, except for the Zn<sub>2</sub>H(Tar)<sub>2</sub> species, formed only in NaNO<sub>3(aq)</sub> at  $I = 1.00 \text{ mol dm}^{-3}$ , for each ionic strength and the ionic medium; this is a confirmation that the chloride ion, at

**Table 2** Stability constants of the Zn(II)/Tar system in different ionic media and ionic strengths at  $T = 298.15$  K

Species	Reaction	log $K_{ijk}$		log $\beta_{ijk}^a$	
		$I = 0.15 \text{ mol dm}^{-3b}$	$I = 1.00 \text{ mol dm}^{-3c}$	$I = 0.15 \text{ mol dm}^{-3b}$	$I = 1.00 \text{ mol dm}^{-3c}$
ZnTar	$Zn^{2+} + Tar^{2-} = ZnTar$	2.85	2.26	$2.85 \pm 0.01^d$	$2.26 \pm 0.12^d$
ZnTarH	$Zn^{2+} + HTar^- = ZnHTar^+$	2.41	2.28	$6.30 \pm 0.02$	$6.05 \pm 0.07$
ZnTar(OH) <sub>2</sub>	$ZnTar = ZnTar(OH)_2^{2-} + 2 H^+$	−17.09	−15.41	$−14.24 \pm 0.08$	$−13.15 \pm 0.04$
Zn(Tar) <sub>2</sub>	$ZnTar + Tar^{2-} = Zn(Tar)_2^{2-}$	2.34	3.29	$5.19 \pm 0.02$	$5.55 \pm 0.03$
(Zn) <sub>2</sub> (Tar) <sub>2</sub> H	$ZnTar + ZnHTar^+ = (Zn)_2H(Tar)_2^+$		3.97	–	$12.28 \pm 0.04$
(Zn) <sub>2</sub> (Tar) <sub>2</sub> (OH) <sub>2</sub>	$2 ZnTar = (Zn)_2(Tar)_2(OH)_2^{2-} + 2 H^+$	−11.52	−10.23	$−5.82 \pm 0.02$	$−5.71 \pm 0.05$
(Zn) <sub>2</sub> (Tar) <sub>2</sub> (OH) <sub>3</sub>	$(Zn)_2(Tar)_2(OH)_2 = (Zn)_2(Tar)_2(OH)_3^{3-} + H^+$	−13.56	−12.33	$−13.68 \pm 0.03$	$−13.52 \pm 0.04$

<sup>a</sup> According to equilibrium (5)

<sup>b</sup> NaCl<sub>(aq)</sub>

<sup>c</sup> NaNO<sub>3(aq)</sub>

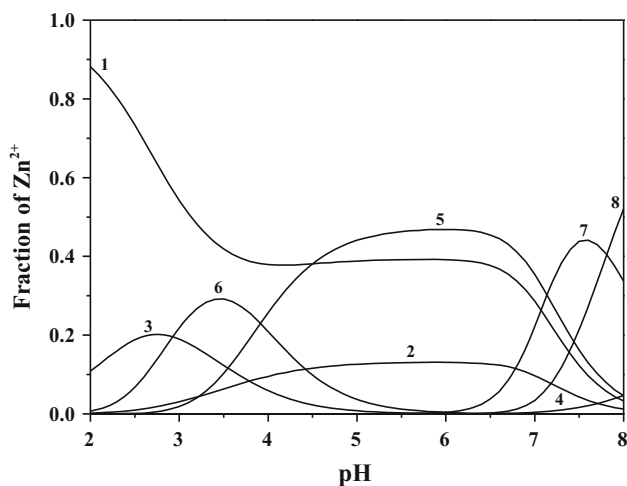
<sup>d</sup> ± std. dev

$I = 0.15 \text{ mol dm}^{-3}$ , does not influence the speciation of the system (with respect to that formed in  $\text{NO}_3^-$ ).

Figure 1 shows the distribution diagram of the species in  $\text{NaNO}_3$  at  $I = 1.00 \text{ mol dm}^{-3}$ . All the species proposed in the speciation model reach significant formation percentages in different pH ranges; in the acidic region, the ternary protonated species are formed in significant amounts. At pH values 3.5–6.5, the  $\text{ZnTar}$  and especially  $\text{Zn}(\text{Tar})_2$  species are the main species, whilst for pH values higher than 6.5,  $\text{ZnTar}(\text{OH})_2$ ,  $\text{Zn}_2(\text{Tar})_2(\text{OH})_2$ , and  $\text{Zn}_2(\text{Tar})_2(\text{OH})_3$  species are predominant with a yield of  $\sim 50\%$ .

#### Formation constants of citrate complexes of $\text{Zn}^{2+}$

The  $\text{Zn}(\text{II})/\text{Cit}$  system was investigated in the same experimental conditions of the  $\text{Zn}(\text{II})/\text{Tar}$  one; the



**Fig. 1** Distribution diagram of  $\text{Zn}(\text{II})/\text{Tar}$  species in  $\text{NaNO}_3(\text{aq})$  at  $I = 1.00 \text{ mol dm}^{-3}$  and at  $T = 298.15 \text{ K}$ . Experimental conditions:  $c_{\text{Zn}} = 2.0 \text{ mmol dm}^{-3}$ ,  $c_{\text{Tar}} = 4.0 \text{ mmol dm}^{-3}$ . Curves: 1 Free  $\text{Zn}^{2+}$ , 2  $\text{ZnTar}$ , 3  $\text{ZnHTar}$ , 4  $\text{ZnTar}(\text{OH})_2$ , 5  $\text{Zn}(\text{Tar})_2$ , 6  $\text{Zn}_2\text{H}(\text{Tar})_2$ , 7  $\text{Zn}_2(\text{Tar})_2(\text{OH})_2$ , 8  $\text{Zn}_2(\text{Tar})_2(\text{OH})_3$  (charge omitted for simplicity)

proposed speciation scheme, includes the following species:  $\text{ZnCit}$ ,  $\text{ZnHCit}$ ,  $\text{ZnCitOH}$ ,  $\text{Zn}(\text{Cit})_2$ , and  $(\text{Zn})_2(\text{Cit})_2(\text{OH})_2$  (charges omitted for simplicity), whose stability constants are reported in Table 3.

This speciation model is more simple with respect to the previous one for the  $\text{Zn}(\text{II})/\text{Tar}$  system, and the speciation scheme is identical for the two ionic strengths. The stability of the species in  $\text{NaNO}_3(\text{aq})$  appears significantly lower with respect to the same species in  $\text{NaCl}(\text{aq})$  at  $I = 0.15 \text{ mol dm}^{-3}$ . For example, for the  $\text{ZnCit}(\text{OH})$ , there is a difference of about 2 log units, and for the  $\text{Zn}(\text{Cit})_2$  about 3 log units.

Figure 2 reports the distribution diagram of the  $\text{Zn}(\text{II})/\text{Cit}$  species in  $\text{NaCl}(\text{aq})$  at  $I = 0.15 \text{ mol dm}^{-3}$  and  $T = 298.15 \text{ K}$ ; the  $\text{Zn}(\text{Cit})_2$  is the predominant species at  $\text{pH} > 5$ , with a yield of  $\sim 80\%$ ; in the same pH range,  $\text{ZnHCit}$  and the  $\text{ZnCit}$  species show  $\sim 30$  and  $\sim 40\%$  of formation, respectively. The ternary hydrolytic species  $(\text{Zn})_2(\text{Cit})_2(\text{OH})_2$  and  $\text{ZnCitOH}$  result to be important at  $\text{pH} > 7.0$ .

The comparison between the speciation models of these two  $\text{Zn}(\text{II})$ -ligand systems shows that the  $\text{Zn}(\text{II})/\text{Cit}$  species are significantly more stable with respect to the  $\text{Zn}(\text{II})/\text{Tar}$  ones, due probably to the well-known ability of citrate to bind strongly the metal ions [8–10].

#### Formation constants of malate complexes of $\text{Zn}^{2+}$

In the case of the  $\text{Zn}(\text{II})/\text{Mala}$  system, the proposed speciation model includes the species:  $\text{ZnMala}$ ,  $\text{ZnHMala}$ ,  $\text{ZnMalaOH}$ ,  $\text{Zn}(\text{Mala})_2$ , and  $\text{Zn}_2(\text{Mala})_2(\text{OH})_2$  (charges omitted for simplicity). This speciation model and the stability constants can be considered reliable in the pH range 2.0–7.5, since at higher pH values, the formation of the sparingly soluble species was observed, for all the ligand/metal concentrations investigated.

The stability constants of the  $\text{Zn}(\text{II})/\text{Mala}$  system in  $\text{NaCl}(\text{aq})$  and  $\text{NaNO}_3(\text{aq})$  at  $I = 0.15 \text{ mol dm}^{-3}$  and  $1.00 \text{ mol dm}^{-3}$ , respectively, are reported in Table 4.

**Table 3** Stability constants of the  $\text{Zn}(\text{II})/\text{Cit}$  system in different ionic media and ionic strengths at  $T = 298.15 \text{ K}$

Species	Reaction	$\log K_{ijk}$		$\log \beta_{ijk}^a$	
		$I = 0.15 \text{ mol dm}^{-3b}$	$I = 1.00 \text{ mol dm}^{-3c}$	$I = 0.15 \text{ mol dm}^{-3b}$	$I = 1.00 \text{ mol dm}^{-3c}$
$\text{ZnCit}$	$\text{Zn}^{2+} + \text{Cit}^{3-} = \text{ZnCit}^-$	4.71	4.024	$4.71 \pm 0.01^d$	$4.024 \pm 0.006^d$
$\text{ZnCitH}$	$\text{Zn}^{2+} + \text{HCit}^{2-} = \text{ZnHCit}$	3.04	2.35	$8.68 \pm 0.02$	$7.57 \pm 0.02$
$\text{ZnCitOH}$	$\text{ZnCit}^- = \text{ZnCitOH}^{2-} + \text{H}^+$	-6.94	-9.15	$-2.99 \pm 0.05$	$-5.13 \pm 0.03$
$\text{Zn}(\text{Cit})_2$	$\text{ZnCit}^- + \text{Cit}^{3-} = \text{Zn}(\text{Cit})_2^{4-}$	4.19	2.06	$8.90 \pm 0.02$	$6.08 \pm 0.05$
$(\text{Zn})_2(\text{Cit})_2(\text{OH})_2$	$2\text{ZnCit}^- = (\text{Zn})_2(\text{Cit})_2(\text{OH})_2^{4-} + 2\text{H}^+$	-11.65	-11.38	$-2.23 \pm 0.03$	$-3.35 \pm 0.03$

<sup>a</sup> According to equilibrium (5)

<sup>b</sup>  $\text{NaCl}(\text{aq})$

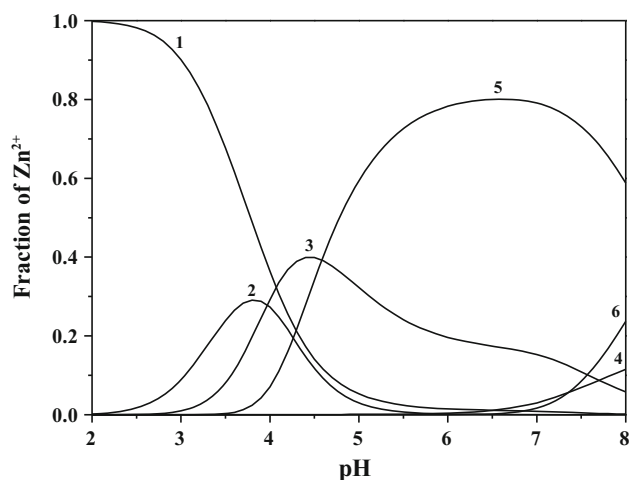
<sup>c</sup>  $\text{NaNO}_3(\text{aq})$

<sup>d</sup>  $\pm$  std. dev

In Fig. 3 the distribution diagram of the Zn(II)/Mala species in  $\text{NaCl}_{(\text{aq})}$  at  $I = 0.15 \text{ mol dm}^{-3}$  and  $T = 298.15 \text{ K}$  is plotted; there are two predominant species in the whole pH range investigated, the first species is the ZnMala that reaches at pH  $\sim 5.5$ , 60 % of formation, whilst the second is the ZnHMala that reaches 20 % at pH  $\sim 3.5$  (where the ligand is partially protonated).

The other species, ZnMalaOH and  $\text{Zn}_2\text{Mala}_2(\text{OH})_2$ , are significant at pH  $\sim 7.0$ . The  $\text{Zn}(\text{Mala})_2$  species is also very important in the speciation of this system, since its presence in the speciation scheme gave a significant improvement of the statistical parameters, even if is formed in low amount.

From the analysis of the formation constants reported in the Tables 2, 3, 4 seems that the trend of stability is: Cit > Mala > Tar.



**Fig. 2** Distribution diagram of Zn(II)/Cit species in  $\text{NaCl}_{(\text{aq})}$  at  $I = 0.15 \text{ mol dm}^{-3}$  and at  $T = 298.15 \text{ K}$ . Experimental conditions:  $c_{\text{Zn}} = 1.6 \text{ mmol dm}^{-3}$ ,  $c_{\text{Cit}} = 3.2 \text{ mmol dm}^{-3}$ . Curves: 1 Free  $\text{Zn}^{2+}$ , 2  $\text{ZnHCit}$ , 3  $\text{ZnCit}$ , 4  $\text{ZnCitOH}$ ; 5  $\text{Zn}(\text{Cit})_2$ ; 6  $(\text{Zn})_2(\text{Cit})_2(\text{OH})_2$  (charge omitted for simplicity)

This trend does not give sufficient tools to compare in a rigorous way the sequestering ability of the ligands toward the  $\text{Zn}^{2+}$ , owing to the different speciation models in the three systems. This goal can be obtained only by using the  $\text{pL}_{0.5}$  parameter reported in the section “Sequestration”.

#### Formation constants of ternary $\text{Zn}_i\text{Sn}_j\text{H}_j\text{L}_k$ complexes

In the past, our group has been involved in studies regarding the formation of mixed metals or mixed ligands species in aqueous solutions [16–25, 29, 32]. Recently a similar investigation has been carried out on Sn(II)/hydroxocarboxylate complexes in different ionic media, ionic strengths and temperatures [16].

In another previous investigation [33], the thermodynamic parameters of the inorganic speciation (hydrolytic and chloride species) of Sn(II) in  $\text{NaCl}$  aqueous solution were determined; these data are reported in Table 1S of the Supplementary material section, whilst the speciation models and the stability constants of the Sn(II)/hydroxocarboxylate species are reported as a comparison in Tables 2S–4S.

The results obtained in those investigations [16] revealed the formation of both binary and ternary species stabilized in chloride medium with respect to the analogous ones in nitrate; this is due to the formation, at high  $\text{Cl}^-$  concentration, of  $\text{Sn}_i\text{H}_j\text{L}_k\text{Cl}_m$  complexes. The formation of these species was justified by the ability of Sn(II) to form stable complexes with chloride [29, 33].

In this order, we decided to perform similar investigation for the Zn(II), taking into account that: (1) it does not form stable complexes with chloride; (2) the formation of both binary metal-hydroxocarboxylic ligands and heterometal complexes between Zn(II)-Sn(II) and the hydroxocarboxylic ligands may occur.

Measurements were carried out at  $I = 0.15 \text{ mol dm}^{-3}$  (and  $I = 1.00 \text{ mol dm}^{-3}$  only for malate) in  $\text{NaCl}_{(\text{aq})}$  and

**Table 4** Stability constants of the Zn(II)/Mala system in different ionic media and ionic strengths at  $T = 298.15 \text{ K}$

Species	Reaction	$\log K_{ijk}$		$\log \beta_{ijk}^a$	
		$I = 0.15 \text{ mol dm}^{-3b}$	$I = 1.00 \text{ mol dm}^{-3c}$	$I = 0.15 \text{ mol dm}^{-3b}$	$I = 1.00 \text{ mol dm}^{-3c}$
ZnMala	$\text{Zn}^{2+} + \text{Mala}^{2-} = \text{ZnMala}$	3.12	2.66	$3.12 \pm 0.03^d$	$2.66 \pm 0.04^d$
ZnMalaH	$\text{Zn}^{2+} + \text{HMala}^- = \text{ZnHMala}^+$	2.51	2.27	$7.14 \pm 0.05$	$6.72 \pm 0.06$
ZnMala(OH)	$\text{ZnMala} = \text{ZnMalaOH}^- + \text{H}^+$	-7.30	-7.85	$-4.18 \pm 0.05$	$-5.19 \pm 0.06$
$\text{Zn}(\text{Mala})_2$	$\text{ZnMala} + \text{Mala}^{2-} = \text{Zn}(\text{Mala})_2^{2-}$	1.43	1.31	$4.55 \pm 0.10$	$3.97 \pm 0.12$
$\text{Zn}_2(\text{Mala})_2(\text{OH})_2$	$2\text{ZnMala} = (\text{Zn})_2(\text{Mala})_2(\text{OH})_2^{2-} + 2\text{H}^+$	-10.77	-11.50	$-4.53 \pm 0.15$	$-6.18 \pm 0.18$

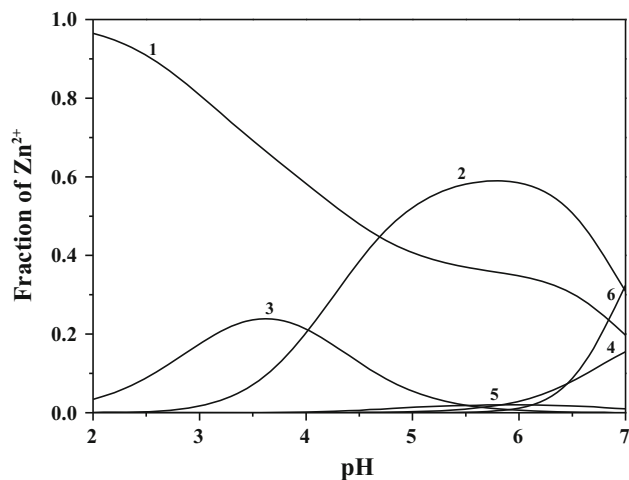
<sup>a</sup> According to equilibrium (5)

<sup>b</sup>  $\text{NaCl}_{(\text{aq})}$

<sup>c</sup>  $\text{NaNO}_{3(\text{aq})}$

<sup>d</sup>  $\pm \text{std. dev}$

$I = 1.00 \text{ mol dm}^{-3}$  in  $\text{NaNO}_{3(\text{aq})}$ ; also in this case, like for the  $\text{Zn(II)/hydrocarboxylate}$  systems, the speciation schemes are identical for each ligand, ionic strength, and ionic medium, even if the stability constants at  $I = 0.15 \text{ mol dm}^{-3}$  in  $\text{NaCl}$  are higher with respect to the analogous ones formed at  $I = 1.00 \text{ mol dm}^{-3}$ . This can be explained taking into account both the lowering of the stability constants increasing the ionic strength and the different interacting nature of the ions of the supporting electrolyte.

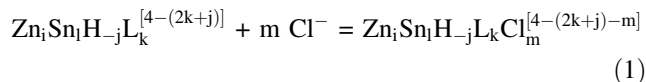


**Fig. 3** Distribution diagram of  $\text{Zn(II)/Mala}$  species in  $\text{NaCl}_{(\text{aq})}$  at  $I = 0.15 \text{ mol dm}^{-3}$  and at  $T = 298.15 \text{ K}$ . Experimental conditions:  $c_{\text{Zn}} = 1.0 \text{ mmol dm}^{-3}$ ,  $c_{\text{Mala}} = 2.0 \text{ mmol dm}^{-3}$ . Curves: 1 Free  $\text{Zn}^{2+}$ , 2  $\text{ZnMala}$ , 3  $\text{ZnHMala}$ ; 4  $\text{ZnMalaOH}$ , 5  $\text{Zn(Mala)}_2$ ; 6  $(\text{Zn})_2(\text{Mala})_2(\text{OH})_2$  (charge omitted for simplicity)

The stability constants of the hetero-metals species obtained in those experimental conditions are reported in Table 5. The presence of the second metal,  $\text{Sn(II)}$  in our case, gives a significant stabilizing effect on the complexes with respect to the ones (same stoichiometric coefficients) formed by only  $\text{Zn(II)}$ . This can be simply explained taking into account that  $\text{Sn(II)}$  forms more stable complexes with these ligands with respect to  $\text{Zn(II)}$  (see as an example the stability constants of the  $\text{Zn}_2(\text{Mala})_2(\text{OH})_2$  and  $\text{ZnSn(Mala)}_2(\text{OH})_2$  species).

To verify the effect of chloride on the formation of the species, the same measurements were also performed for malate, at  $I = 1.00 \text{ mol dm}^{-3}$  in  $\text{NaCl}_{(\text{aq})}$ . The conditional stability constants in  $\text{NaCl}_{(\text{aq})}$  reported in Table 5 are systematically higher with respect to those in  $\text{NaNO}_{3(\text{aq})}$  at the same ionic strength, due to the fact that chloride tends to favor and to stabilize the mixed metals-ligand/chloride species with respect to the same homo-metal species. This aspect has been already discussed in a previous paper on the formation of the  $\text{Sn}^{2+}$ -hydrocarboxylate complexes [16].

The stabilizing effect of chloride on the formation of the  $\text{Zn}_i\text{Sn}_j\text{H}_j\text{Mala}_k\text{Cl}_m$  species can be estimated calculating the corresponding stability constants on the basis of the equilibrium (7). The overall formation constants of the  $\text{Zn}_i\text{Sn}_j\text{H}_j\text{Mala}_k\text{Cl}_m$  complexes are reported in Table 6; according to the equilibrium:



**Table 5** Stability constants of the  $\text{Zn(II)/Sn(II)/ligand}$  species in different ionic media and ionic strengths at  $T = 298.15 \text{ K}$

Species	$\log \beta_{ijk}^a$		
	$I = 0.15 \text{ mol dm}^{-3b}$	$I = 1.00 \text{ mol dm}^{-3c}$	$I = 1.00 \text{ mol dm}^{-3b}$
$\text{ZnSnHTar}$	$12.60 \pm 0.04^d$	$11.86 \pm 0.07^d$	
$\text{ZnSnTar}$	$10.17 \pm 0.04$	$7.64 \pm 0.10$	
$\text{ZnSnTarOH}$	$7.89 \pm 0.05$	$4.60 \pm 0.10$	
$\text{ZnSnTar(OH)}_2$	$3.63 \pm 0.05$	$1.76 \pm 0.06$	
$\text{ZnSn(Tar)}_2\text{OH}$	$11.03 \pm 0.04$	$8.56 \pm 0.10$	
$\text{ZnSnCitOH}$	$7.80 \pm 0.03^d$	$6.99 \pm 0.03^d$	
$\text{ZnSnCit(OH)}_2$	$3.15 \pm 0.03$	$1.86 \pm 0.06$	
$\text{ZnSnH}_2(\text{Cit})_2$	$25.03 \pm 0.01$	$22.21 \pm 0.03$	
$\text{ZnSnH(Cit)}_2$	$21.52 \pm 0.02$	$19.20 \pm 0.03$	
$\text{ZnSn(Cit)}_2$	$17.61 \pm 0.02$	$15.32 \pm 0.08$	
$\text{ZnSn(Cit)}_2\text{OH}$	$13.23 \pm 0.02$	$11.29 \pm 0.03$	
$\text{ZnSnMala}$	$10.36 \pm 0.08^d$	$8.53 \pm 0.02^d$	$9.29 \pm 0.10^d$
$\text{ZnSnMalaOH}$	$7.78 \pm 0.06$	$5.11 \pm 0.04$	$6.65 \pm 0.02$
$\text{ZnSnMala(OH)}_2$	$4.08 \pm 0.03$	$1.91 \pm 0.04$	$2.48 \pm 0.04$
$\text{ZnSn(Mala)}_2$	$14.47 \pm 0.09$	$12.59 \pm 0.01$	$12.82 \pm 0.07$
$\text{ZnSn(Mala)}_2\text{OH}$	$11.03 \pm 0.04$	$9.13 \pm 0.01$	$10.00 \pm 0.09$
$\text{ZnSn(Mala)}_2(\text{OH})_2$	$6.18 \pm 0.09$	$4.13 \pm 0.02$	$3.66 \pm 0.12$

<sup>a</sup> According to equilibrium (6) or (8)

<sup>b</sup>  $\text{NaCl}_{(\text{aq})}$

<sup>c</sup>  $\text{NaNO}_{3(\text{aq})}$

<sup>d</sup>  $\pm \text{std. dev}$

**Table 6** Stability constants of the Zn(II)/Sn(II)/Mala/Cl system in NaCl<sub>(aq)</sub> at  $I = 1.00 \text{ mol dm}^{-3}$  and  $T = 298.15 \text{ K}$ 

Species	$\log \beta_{ijklm}^a$	$\log K_{ijklm}^b$
ZnSnMalaCl	$9.77 \pm 0.02^c$	0.48
ZnSn(Mala) <sub>2</sub> Cl	$13.18 \pm 0.02$	0.36
ZnSn(Mala) <sub>2</sub> OHCl	$9.18 \pm 0.04$	0.82

<sup>a</sup> According to equilibrium (7)

<sup>b</sup> According to the equilibrium  $\text{Zn}_i\text{Sn}_j\text{H}_k\text{L}_m^{[4-(2k+j)]} + m \text{Cl}^- = \text{Zn}_i\text{Sn}_j\text{H}_k\text{L}_m\text{Cl}_m^{[4-(2k+j)-m]}$

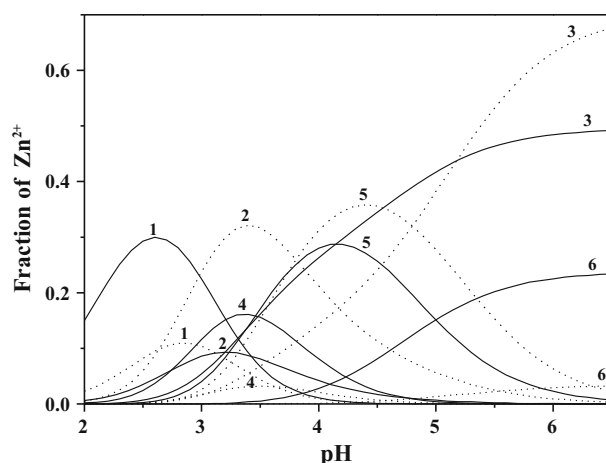
<sup>c</sup>  $\pm$  st. dev

the stepwise stability constants of the mixed  $\text{Zn}_i\text{Sn}_j\text{H}_k\text{Mala}_l\text{Cl}_m$  species at  $I = 1.00 \text{ mol dm}^{-3}$  in NaCl<sub>(aq)</sub> were also calculated (see 2<sup>nd</sup> column). The stability and the strength of these species can be compared to the stability of the  $\text{Sn}_i\text{H}_j\text{Mala}_k\text{Cl}_m$  species reported in our previous paper [16] (see also Table 3S of the Supplementary material); for the  $\log K_{ijklm}$  species of Sn(II), the following values were obtained:  $\log K_{1111} = 0.01$ ,  $\log K_{1101} = -0.05$ ,  $\log K_{1201} = -0.03$ , and  $\log K_{22-21} = 0.15$ . The comparison between the stability constants of the SnMalaCl species and of the mixed  $\text{Zn}_i\text{Sn}_j\text{H}_k\text{Mala}_l\text{Cl}_m$  species indicates that the formation of the mixed hetero-metal-ligand/chloride species is favored with respect to the homo-metalMala/chloride ones.

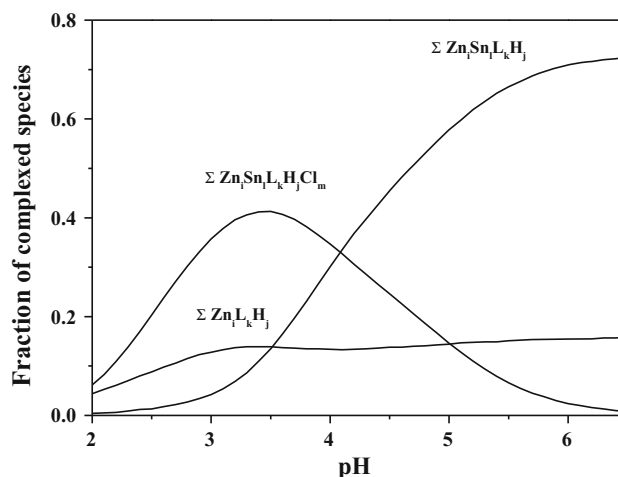
In previous works [16–25], the formation of mixed complexes were already reported, and resulted that the formation of mixed metal or ligand species contributes in many cases to increase the solubility and bioavailability of metal ions in the natural fluids, since the formation of possible sparingly soluble species can be shifted in term of pH or avoided.

To clearly define the contribution of Cl<sup>-</sup> to the stabilization of the mixed species, Fig. 4 reports as a comparison the distribution of the mixed metal species formed by malate both in NaCl<sub>(aq)</sub> and NaNO<sub>3(aq)</sub> at  $I = 1.00 \text{ mol dm}^{-3}$ . The main aspect that can be observed is that some of the mixed species formed in chloride medium reach significant higher formation percentages than the same species in nitrate.

The importance of the mixed chloride species in the speciation of the system can be highlighted from an analysis of Fig. 5, where the sum of the formation percentages of the binary Zn(II)/Mala species, of the mixed Zn(II)/Sn(II)/Mala species and of the mixed Zn(II)/Sn(II)/Mala/chloride species were reported as a function of the pH in NaCl<sub>(aq)</sub> at  $I = 1.00 \text{ mol dm}^{-3}$ . By observing this figure, some aspects can be evidenced: (1) the presence of the second metal, Sn(II) in our case, contributes to the formation of different mixed species; (2) the formation of the mixed metal species lowers significantly the formation



**Fig. 4** Distribution diagram of Zn(II)/Sn(II)/Mala species in NaCl<sub>(aq)</sub> and NaNO<sub>3(aq)</sub> at  $I = 1.00 \text{ mol dm}^{-3}$  and at  $T = 298.15 \text{ K}$ . Experimental conditions:  $c_{\text{Zn}} = 1.5 \text{ mmol dm}^{-3}$ ;  $c_{\text{Sn}} = 1.1 \text{ mmol dm}^{-3}$ ;  $c_{\text{Mala}} = 4.6 \text{ mmol dm}^{-3}$ . Curves: 1 ZnSnMala, 2 ZnSnMalaOH, 3 ZnSnMala(OH)<sub>2</sub>, 4 ZnSnMala<sub>2</sub>, 5 ZnSnMala<sub>2</sub>OH, 6 ZnSnMala<sub>2</sub>(OH)<sub>2</sub> (charge omitted for simplicity). Straight line: NaNO<sub>3(aq)</sub>, Dot line: NaCl<sub>(aq)</sub>



**Fig. 5** Sum of the binary Zn(II)/Mala, mixed Zn(II)/Sn(II)/Mala, and Zn(II)/Sn(II)/Mala/Cl species in NaCl<sub>(aq)</sub> at  $I = 1.00 \text{ mol dm}^{-3}$  and at  $T = 298.15 \text{ K}$

percentages of the Zn(II)/Mala species, with respect to those observed in Fig. 3; (3) moreover, the presence of chloride favors the formation of the quaternary species that reach a sum of molar fraction of 0.4 and are formed in a wide pH range.

Despite the complexity of all the mixed metals investigated systems, due to the high number of secondary equilibria (metals hydrolysis, ligand protonation constants, interaction of the components with the ions of the supporting electrolyte, binary interaction of the metals with the ligand) that must be taken into account to obtain an accurate speciation model, the results here reported can be considered very satisfactory, owing to the low standard

deviation in the fit and the low error values associated at each stability constant.

As an example, Table 5S of the Supplementary material reports an abstract of the output file of the Zn(II)Sn(II)/Cit system studied in NaCl<sub>(aq)</sub> at  $I = 0.15 \text{ mol dm}^{-3}$  and  $T = 298.15 \text{ K}$ . This output contains in the first part the input data (stability constants of the secondary equilibria [9, 10, 16, 31, 33], the  $z^*$  and  $p^*$  [34], the analytical molar concentrations of all the components in the vessel, titrand and the number of experimental points collected for each measurement). The second part contains the stability constants of the refined mixed metals/Cit species, the statistical parameters (standard deviation in the fit and the error values associated with the stability constants). The third part contains the tables with the formation percentages (expressed in this case with respect to Zn(II)) of all the species present in the speciation model. Owing to the very high number of experimental points collected ( $\sim 2,000$ ), we report for simplicity, the formation percentages of only four measurements, but in the supplementary material, all the experimental points collected from the potentiometric data are reported.

During these investigations, to check the robustness of the system and the validity of the thermodynamic data obtained for the binary metal-ligand systems, the stability constants of the ZnL ( $L = \text{Mala, Cit, Tar}$ ) species were alternatively refined together with the mixed metals-ligand ones. As an example, Table 6S reports the output file of the Zn(II)Sn(II)/Cit system, where the ZnCit and ZnHCit

species were also refined. As it can be seen, the stability constants of these binary species are in very good agreement with respect to the  $\log \beta_{ijk}$  values reported for the same experimental conditions in Table 3, and the values of the mixed species are, within the experimental errors, unchanged.

#### Empirical correlation

In previous papers, we observed that the stability constants of the complexes follow regular trends and depend on some factors, such as: the coordination number and number of chelate rings; the complex charge; the number of  $-\text{OH}$  groups present in the molecule; the interaction of negatively charged complex species with the cation of the supporting electrolyte (medium stabilization), etc. On the basis of these evidences, we tried to find some simple rules to explain the stability of Zn-hydroxocarboxylate complexes.

Taking into account the overall formation constants of the complexes reported in Tables 2, 3, 4, the stepwise formation constants reported in Table 7 were calculated taking into account the ligands fully deprotonated and the contribution of the alcoholic group(s) to the stability. As an example, in the case of the species ZnTar(OH)<sub>2</sub> at  $I = 0.15 \text{ mol dm}^{-3}$  in NaNO<sub>3(aq)</sub>, we can consider the equilibrium:  $\text{Zn}^{2+} + \text{TarH}_2^{2-} = \text{ZnTarH}_2^{2-} + 2 \text{H}^+$  or  $\text{Zn}^{2+} + \text{TarH}_2^{2-} = \text{ZnTarH}_2^{2-}$ ; these two equilibria are equivalent if the deprotonation of alcoholic groups is taken

**Table 7** Equilibrium constants of Zn<sup>2+</sup> complexes calculated according to the reported reactions

Species	Equilibrium <sup>c</sup>	$\log K_{ijk}$		$n_{\text{Zn}}^{2+}$	$n_{\text{COO}}^-$	$n_{\text{OH}}$
ZnTar(OH) <sub>2</sub>	$\text{Zn}^{2+} + \text{Tar}^{2-} = \text{ZnTarH}_2^{2-} + 2\text{H}^+$	12.8 <sup>a</sup>	13.5 <sup>b</sup>	1	2	2
(Zn) <sub>2</sub> (Tar) <sub>2</sub> (OH) <sub>2</sub>	$2 \text{Zn}^{2+} + 2 \text{Tar}^{2-} = \text{Zn}_2\text{Tar}_2\text{H}_2^{2-} + 2\text{H}^+$	21.18	21.29	2	4	2
(Zn) <sub>2</sub> (Tar) <sub>2</sub> (OH) <sub>3</sub>	$2 \text{Zn}^{2+} + 2 \text{Tar}^{2-} = \text{Zn}_2\text{Tar}_2\text{H}_3^{3-} + 3\text{H}^+$	26.81	26.98	2	4	3
ZnCitOH	$\text{Zn}^{2+} + \text{Cit}^{3-} = \text{ZnCitH}_1^{2-} + \text{H}^+$	10.51	8.37	1	3	1
(Zn) <sub>2</sub> (Cit) <sub>2</sub> (OH) <sub>2</sub>	$2 \text{Zn}^{2+} + 2 \text{Cit}^{3-} = \text{Zn}_2\text{Cit}_2\text{H}_2^{4-} + 2\text{H}^+$	24.77	23.65	2	6	2
ZnMala(OH)	$\text{Zn}^{2+} + \text{Mala}^{2-} = \text{ZnMalaH}_1^- + \text{H}^+$	9.32	8.31	1	2	1
Zn <sub>2</sub> (Mala) <sub>2</sub> (OH) <sub>2</sub>	$2 \text{Zn}^{2+} + 2 \text{Mala}^{2-} = \text{Zn}_2\text{Mala}_2\text{H}_2^{2-} + 2\text{H}^+$	22.47	20.82	2	4	2
ZnTar	$\text{Zn}^{2+} + \text{Tar}^{2-} = \text{ZnTar}$	2.85	2.26	1	2	0
ZnTarH	$\text{Zn}^{2+} + \text{HTar}^- = \text{ZnHTar}^+$	2.41	2.28	1	1	0
Zn(Tar) <sub>2</sub>	$\text{Zn}^{2+} + 2 \text{Tar}^{2-} = \text{ZnTar}_2^{2-}$	5.19	5.55	1	4	0
ZnCit	$\text{Zn}^{2+} + \text{Cit}^{3-} = \text{ZnCit}^-$	4.71	4.024	1	3	0
ZnCitH	$\text{Zn}^{2+} + \text{HCit}^{2-} = \text{ZnHCit}$	3.04	2.35	1	2	0
Zn(Cit) <sub>2</sub>	$\text{Zn}^{2+} + 2 \text{Cit}^{3-} = \text{ZnCit}_2^{4-}$	8.9	6.08	1	6	0
ZnMala	$\text{Zn}^{2+} + \text{Mala}^{2-} = \text{ZnMala}$	3.12	2.66	1	2	0
ZnMalaH	$\text{Zn}^{2+} + \text{HMala}^- = \text{ZnHMala}^+$	2.51	2.27	1	1	0
Zn(Mala) <sub>2</sub>	$\text{Zn}^{2+} + 2 \text{Mala}^{2-} = \text{ZnMala}_2^{2-}$	4.5	3.97	1	4	0

<sup>a</sup>  $I = 0.15 \text{ mol dm}^{-3}$  (NaCl<sub>(aq)</sub>)

<sup>b</sup>  $I = 1.00 \text{ mol dm}^{-3}$  (NaNO<sub>3(aq)</sub>)

<sup>c</sup>  $\text{L}^z \equiv \text{LH}_j^z$  ( $\text{L}^z = \text{Tar}^{2-}; \text{Cit}^{3-}, \text{Mala}^{2-}; \text{H}_j = \text{number of alcoholic groups not deprotonated}$ )



into account. Analyzing the literature [8–10, 35–37], we found for the deprotonation of an alcoholic group, the rough value  $pK^{\text{OH}} = 13.5 \pm 0.5$ .

The stepwise stability constants of the  $\text{ZnTarH}_2^{2-}$  can be calculated as:  $\log K_{ijk} = \log \beta - 2 \cdot pK^{\text{OH}} = -14.2 + 2 \cdot 13.5 = 12.8$ . Following the same procedures, we calculate the  $\log K$  values for all the species of the three systems at  $I = 0.15$  and  $1.00 \text{ mol dm}^{-3}$ . These stability constants were fitted with the equation:

$$\log K_{ijk} = n_{\text{COO}^-} \cdot (p_1 + p_2 \cdot n_{\text{Zn}^{2+}}) + n_{\text{OH}} \cdot (p_3 + p_4 \cdot n_{\text{COO}^-}) \quad (2)$$

where  $n_{\text{COO}^-}$  is the number of carboxylic units in the ligand and free to interact with the metal;  $n_{\text{Zn}^{2+}}$  is the stoichiometric coefficient of the metal involved in the formation of the complexes;  $n_{\text{OH}}$  is the number of alcoholic groups involved in the formation of the complexes. In the case of formation of protonated complexes such as  $\text{ZnCitH}$ , we have that the number of carboxylic groups potentially available for the interaction with the metal will be  $(3 \cdot n_{\text{COO}^-}) - 1$ . By using a least square computer program, the empirical parameters of the Eq. (2) were calculated fitting the data at each ionic strength. Table 8 reports the calculated  $p_i$  ( $1 < i < 4$ ) values at each ionic strength; the estimated precision of  $\log K \pm 0.6$  and  $\log K \pm 0.4$  were obtained at  $I = 0.15 \text{ mol dm}^{-3}$  and  $I = 1.00 \text{ mol dm}^{-3}$ , respectively.

The estimated precision may appear quite high, but it can be considered reasonable if we take into account the origin of these relationships and the scope of their formulation. Moreover, these equations can be used as a predictive tool to calculate rough formation constants of species in particular conditions.

### Sequestration

In our previous papers, we focused our discussion on the importance to provide a simple tool that allows to select the best ligand able to sequester, in many cases selectively, a given cation, in different experimental conditions and to compare the different sequestering ability of two or more ligands [16, 26–29, 38].

In the past, other methods were proposed to evaluate the efficacy of a chelant; among them, the free metal

concentration in solution at equilibrium, expressed as  $pM$ , is one of the most used parameters to assess the binding ability of various chelants toward a given metal, even if its use results sometimes problematic [39].

Since 2006, our group started to use a semiempirical parameter ( $pL_{0.5}$  or  $pL_{50}$  in some cases); this parameter represents the total ligand concentration necessary to sequester 50 % of a given metal ion.  $pL_{0.5}$  can be calculated from the sum of the percentage of all the metal-ligand species formed in a given experimental condition (pH, temperature, ionic strength, ionic media, etc.) when the metal is present in trace (usually  $c_M \ll 10^{-12} \text{ mol dm}^{-3}$ ). It is rapidly calculated in a very simple way by the most common programs used to plot the speciation diagrams, once the speciation model is given. The resulting graph is a sort of sigmoidal, dose–response curve represented by the Boltzmann type equation with asymptotes of 1 for  $pL \rightarrow -\infty$  and 0 for  $pL \rightarrow +\infty$ :

$$x = \frac{1}{1 + 10^{pL - pL_{0.5}}}, \quad (3)$$

where  $x$  represents the fraction of metal sequestered by the ligand at a specific condition of pH, ionic strength, temperature;  $pL_{0.5}$  is obtained graphically, or by fitting plotted data to Eq. (3).

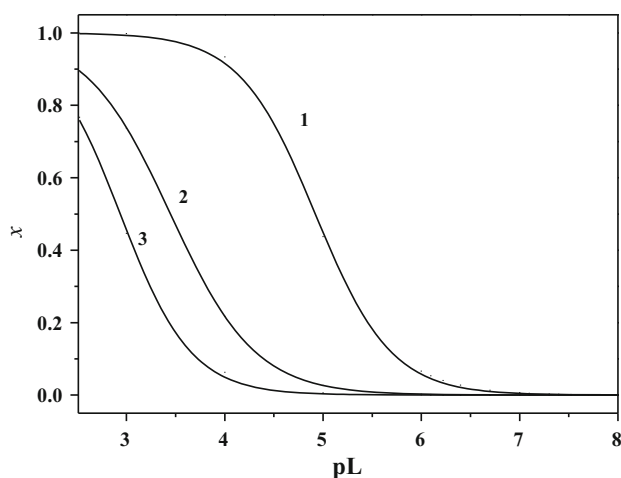
It is important to point out that performing an evaluation and/or comparison of the sequestering ability of a ligand, all the competitive reactions occurring in the system (metal hydrolysis, ligand protonation, interactions with other components) must be taken into account, but they are not taken into account in the calculation of  $pL_{0.5}$ . This is necessary because the sequestering power of a ligand must be “cleaned” from all the interferences, giving a more reliable picture of the real behavior of the chelant.

Figure 6 reports, as an example, the sequestration diagrams of the three hydroxocarboxylic ligands investigated toward Zn(II) at  $I = 0.15 \text{ mol dm}^{-3}$  in  $\text{NaCl}_{(\text{aq})}$ . Taking into account the speciation models and the stability constants reported in Tables 2, 3, 4, we obtained at  $\text{pH} = 7.4$ , the following values;  $pL_{0.5}$ : Cit (4.92)  $\gg$  Mala (3.45)  $>$  Tar (2.94). This trend is not unusual, since it reflects the trend of the chelating ability of the different ligands toward the metal ion.

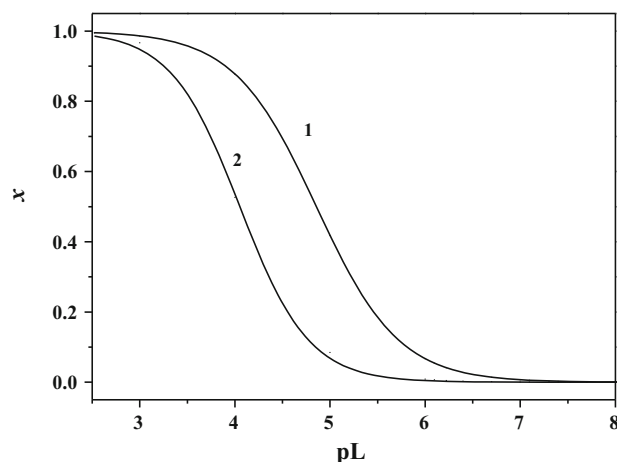
Significant is also the diagram reported in Fig. 7, where the different sequestering ability of citrate towards Sn(II) and Zn(II) is compared; these diagrams were obtained in the same experimental conditions, namely in  $\text{NaCl}_{(\text{aq})}$  at  $I = 0.15 \text{ mol dm}^{-3}$  and  $\text{pH} = 5.0$ , at the same component concentrations. Taking into account the formation constants of each system and the higher stability of the Sn(II) species with respect to the Zn(II) ones, we should obtain a significant higher  $pL_{0.5}$  value in favor of the first metal. From the experimental evidences we instead observed that

**Table 8** Empirical parameters of Eq. (2)

Parameters	0.15 mol dm <sup>-3</sup>	1.00 mol dm <sup>-3</sup>
$p_1$	0.82	0.57
$p_2$	0.65	0.58
$p_3$	4.44	4.39
$p_4$	0.92	1.20



**Fig. 6** Sequestration diagram of Zn(II) toward citrate, malate, and tartrate at pH = 7.4 in NaCl<sub>(aq)</sub> at  $I = 0.15 \text{ mol dm}^{-3}$  and  $T = 298.15 \text{ K}$ . 1 Citrate ( $pL_{0.5} = 4.92$ ), 2 Malate ( $pL_{0.5} = 3.44$ ), 3 Tartrate ( $pL_{0.5} = 2.94$ )



**Fig. 7** Sequestration diagram of Zn(II) and Sn(II) toward citrate, at pH = 5.0 in NaCl<sub>(aq)</sub> at  $I = 0.15 \text{ mol dm}^{-3}$  and  $T = 298.15 \text{ K}$ . 1 Sn(II) ( $pL_{0.5} = 4.86$ ), 2 Zn(II) ( $pL_{0.5} = 4.05$ )

in those conditions, the difference is not so high, and this can be explained taking into account that part of Sn(II) is also sequestered by chloride, creating a sort of competition between the two ligands, namely citrate and chloride.

As regards the hetero-metals/ligand species, a simple way to illustrate the importance and the influence of these species on the speciation of a given system and on the distribution of the species is to calculate the apparent or conditional stability constants as introduced by Schwarzenbach [40]:

$$\log K_{app} = \frac{[\text{Metal}]_{\text{Tot}} \text{ bound to the ligand}}{[\text{Metal}]_{\text{Tot}} \text{ not bound to the ligand} \cdot [\text{Ligand}]_{\text{Tot}} \text{ not bound to metal}} \quad (4)$$

These calculations were carried out at  $I = 0.15 \text{ mol dm}^{-3}$  in NaCl<sub>(aq)</sub>; in particular, Fig. 8 reports a comparison for

the variation of the  $\log K_{app}$  for the ZnCit, SnCit, and ZnSnCit species respect to the pH. These diagrams are important since they allow to highlight how the formation of the mixed hetero-metal species is favored with respect to the binary ones.

In Fig. 8a, the  $\log K_{app}$  were calculated with respect to Zn(II) both for the binary ZnCit and the ZnSnCit-mixed species. The first indication that can be derived is that for the whole pH range, the  $\log K_{app}$  values of the hetero-metal species (ZnSnCit) is always higher with respect to the ZnCit species. This is an evident indication that the formation of the mixed species is favored, as already observed in other studies [16, 20–25, 29, 41, 42]. The higher differences are observed at low pH values (<4.5), since probably at these pHs even if the ligand is partially protonated, it can be easily complexed by Sn(II) than Zn(II) to form the mixed species. In fact, whilst in these conditions and up to pH  $\sim 4.5$ , we have that about 50 % of Zn(II) is free, in similar conditions Sn(II) is present only in  $\sim 15$  % as free metal ion [16].

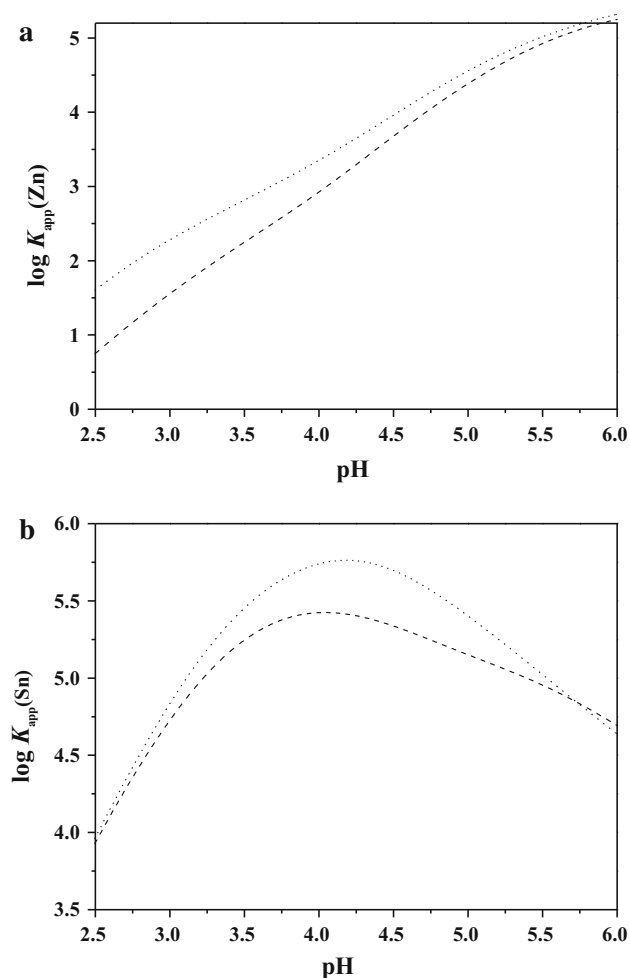
Figure 8b reports the trend of the  $\log K_{app}$  vs. pH for the SnCit species and still for the mixed ZnSnCit one; in this case, the calculation was performed with respect to the Sn(II). This explains the different profile of the curve of the  $\log K_{app}$  of the mixed species with respect to the same curve reported in Fig. 8a.

In fact, in Fig. 8b we observe that independent of the system considered, the  $\log K_{app}$  reaches a maximum at pH  $\sim 4.0$ – $4.2$ , decreasing successively. This is probably due to the hydrolysis of Sn(II) that becomes significant from this point. Also in this case, the formation of the hetero-metal species is favored with respect to the binary SnCit, indicating that these complexes cannot be neglected for a correct speciation study in multicomponent systems.

#### Literature comparison

The literature reports many data on the interaction of Zn(II) toward several classes of organic ligands [6–10]. These studies regard not only the formation of simple binary species formed by the interaction with a single ligand, but also in many cases with two different ligands of biological interest. As an example, only in the last decade, we can find in the literature interesting papers on the formation of binary and ternary species with vitamins, drugs, amino acid derivatives, etc. [3–5, 14, 43–53]. Whilst data on the formation of zinc-mixed ligand species are abundant, the literature data concerning the formation of zinc(II) hetero-metal species were reported in few papers.

In the past our research group has been already involved in the studies regarding the formation of hetero-metal complexes between different kinds of metals, since as well known, mixed metal complexes may play a role in in vivo



**Fig. 8** Log  $K_{app}$  of **a**: ZnCit and ZnSnCit; **b**: SnCit and SnZnCit complexes vs. pH in  $\text{NaCl}_{(aq)}$  at  $I = 0.15 \text{ mol dm}^{-3}$  and  $T = 298.15 \text{ K}$ . *Dash line*: homo-metal/ligand species, *Dot line*: hetero-metal/ligand species. Concentrations:  $c_{\text{Zn}} = 1.6 \text{ mmol dm}^{-3}$ ,  $c_{\text{Sn}} = 1.0 \text{ mmol dm}^{-3}$ , and  $c_{\text{Cit}} = 3.2 \text{ mmol dm}^{-3}$

metal–metal stimulation phenomena. From literature data regarding the speciation of metals and ligands in quite different experimental conditions, it is possible to observe that the speciation of such systems depend on a high number of variables, such as pH, temperature, metal/ligand molar ratio, concentration of components, ionic medium, ionic strength, etc.

This aspect highlights the importance and utility of such investigation, since hetero-metal complexes can be useful as models for natural systems, where excessive concentration of ions can produce undesired effects. In our previous works [16, 18–25, 29], we reported that the formation of these hetero-metal complexes cannot be neglected, since this can produce an unrealistic species distribution, both in particular environments and particularly in fluids that hyperaccumulated metal ions [17].

As regards Zn(II), the literature reports several data on binary systems with hydroxocarboxylic ligands, among

them citrate, malate and tartrate, in different ionic media and at different ionic strengths [6–10]. From a rough comparison of the stability constants here proposed and those reported in the literature, it is possible to observe that independent of the experimental conditions and of the different speciation models proposed, the stability constants of the species with same stoichiometric coefficients can be considered in fairly good agreement, also with the values proposed in the past for citrate from this group in  $\text{KNO}_3$  at  $I = 0.1 \text{ mol dm}^{-3}$  [18]. Similar observation can be also made for malate and tartrate with the literature values reported in refs. [6–10].

Concerning the mixed metal complexes, Table 9 reports some literature data for the citrate mixed complexes with different cations. The difference in the stability of the species can be explained in terms of stabilizing/destabilizing effect of the metals on the formation of the species.

The high stability of the  $\text{Zn}_i\text{Sn}_j\text{Cit}_k(\text{OH})_l$  species can be explained in term of stabilizing effect of Sn(II) on the complexes, owing also to the strength of the binary Sn(II)/Cit complexes; similar consideration can be made for the malate and tartrate ones.

The bridging hydroxo groups play a role in forming the polynuclear and mixed metal complexes. Moreover, the stability of the mixed complexes increases as the effective basicity of the acid anions increases: Tar < Mala < Cit.

From a simple comparison of the stability constants of Sn(II)/hydroxocarboxylate species (see Table 1S of Supplementary Material) and the same formed by Zn(II), it is possible to observe a significant difference in  $\log \beta_{ijk}$  values, in some case of many log units in favor of the Sn(II) complexes. As an example at  $I = 0.15 \text{ mol dm}^{-3}$  in  $\text{NaCl}_{(aq)}$ ,  $\log \beta_{\text{SnCit}} = 8.39$  and  $\log \beta_{\text{ZnCit}} = 4.71$ , or  $\log \beta_{\text{Sn}_2\text{Cit}_2(\text{OH})_2} = 10.81$  and  $\log \beta_{\text{Zn}_2\text{Cit}_2(\text{OH})_2} = -2.23$ . Similar comparison can be made with the Sn(II)/Tar and Sn(II)/Mala complexes, obtaining similar evidences.

Concerning the mixed metal citrate complexes, owing to the different speciation model proposed in this paper, the only comparison with literature data can be done only with the  $\text{ZnCdCit}_2\text{OH}$  species reported in a previous work [19]. Authors proposed for this species, an overall stability constant value of 4.12 in  $\text{KNO}_3$  at  $I = 0.1 \text{ mol dm}^{-3}$ ; this value is significantly lower with respect to the same constant of the  $\text{ZnSnCit}_2\text{OH}$  complexes at  $I = 0.15 \text{ mol dm}^{-3}$  ( $\log \beta_{112-1} = 13.23$ ).

From the data reported in our previous works on the formation of mixed metal citrate species with different cations, it can be observed that the formation of the hetero-metal complexes is entropically stabilized.

In our knowledge, the only literature data for the mixed metal species formed by Sn(II) is reported by Binder [54], who studied the mixed metal system Sn(II)/Fe(III) with citrate; also in this case, the author observed an high stability of

**Table 9** Literature data of mixed metal citrate complexes

Species	$\log \beta_{112-2}^a$	$\log \beta_{112-1}^a$	$T/K$	Medium	$I/\text{mol dm}^{-3}$	$\Delta G^b$	$\Delta H^b$	$\Delta S^c$	Ref.
CuNiCit <sub>k</sub> (OH) <sub>j</sub>	1.2		283.15	KNO <sub>3</sub>	0.1				[24]
	1.58		298.15	KNO <sub>3</sub>	0.1	9.04	39	160	
	1.80		308.15	KNO <sub>3</sub>	0.1				
	2.10		318.15	KNO <sub>3</sub>	0.1				
CuZnCit <sub>k</sub> (OH) <sub>j</sub>	0.84		283.15	KNO <sub>3</sub>	0.1				[24]
	1.59		298.15	KNO <sub>3</sub>	0.1	9.1	64	245	
	1.77		308.15	KNO <sub>3</sub>	0.1				
	2.22		318.15	KNO <sub>3</sub>	0.1				
CuCdCit <sub>k</sub> (OH) <sub>j</sub>	-0.16		283.15	KNO <sub>3</sub>	0.1				[24]
	0.33		298.15	KNO <sub>3</sub>	0.1	1.9	52	180	
	0.57		308.15	KNO <sub>3</sub>	0.1				
	0.97		318.15	KNO <sub>3</sub>	0.1				
CuNiCit <sub>k</sub> (OH) <sub>j</sub>	1.55		298.15	KNO <sub>3</sub>	0.1				[18]
CuZnCit <sub>k</sub> (OH) <sub>j</sub>	1.51		298.15	KNO <sub>3</sub>	0.1				
NiZnCit <sub>k</sub> (OH) <sub>j</sub>	-2.94		298.15	KNO <sub>3</sub>	0.1				
CdMnCit <sub>k</sub> (OH) <sub>j</sub>	-5.75		298.15	KNO <sub>3</sub>	0.1				[19]
CdNiCit <sub>k</sub> (OH) <sub>j</sub>	-4.22	3.65	298.15	KNO <sub>3</sub>	0.1				
CdZnCit <sub>k</sub> (OH) <sub>j</sub>	-3.30	4.12	298.15	KNO <sub>3</sub>	0.1				
FeSnH <sub>2</sub> (Cit) <sub>3</sub> <sup>d</sup>	24.8		298.15	NaClO <sub>4</sub>	0.6				[54]

<sup>a</sup>  $\log \beta$  refers to the general equation:  $M^{2+} + M^{2+} + k L^{2-} = MM'L_k(OH)_j^{(4-kz-j)} + j H^+$  ( $L = \text{Citrate}$ )

<sup>b</sup>  $\text{kJ mol}^{-1}$

<sup>c</sup>  $\text{J mol}^{-1} \text{K}^{-1}$

<sup>d</sup> citrate was considered as a  $L^{4-}$  ligand:  $\log \beta$  refers to the general equation:  $Fe^{3+} + Sn^{2+} + 3 HL^{3-} = FeSnH_2L_3^{5-}$

the mixed SnFeCit<sub>3</sub>H<sub>2</sub> species, in NaClO<sub>4</sub> at  $I = 0.6 \text{ mol dm}^{-3}$ ; in that work, author considered citrate as a  $L^{4-}$  ligand, and for this reason an attempt of comparison with the mixed complexes here reported is quite difficult.

## Experimental

Stock solutions of L(+)-tartrate (Tar<sup>2-</sup>), L(-)-malate (Mala<sup>2-</sup>), and citrate (Cit<sup>3-</sup>) were prepared by weighing the corresponding acids (Fluka), and the concentration of the ligands was checked potentiometrically by alkalimetric titrations, resulting always  $\geq 99\%$ . Zn(II) and Sn(II) were used in the form of chloride salts without further purification. Their solutions were standardized against EDTA standard solutions and the purity was always  $\geq 99\%$ . Nitric and hydrochloric acids and sodium hydroxide solutions were prepared by diluting concentrated ampoules (Riedel-deHaën); the solutions were standardized against sodium carbonate and potassium hydrogen phthalate, respectively. NaNO<sub>3</sub> and NaCl aqueous solutions were prepared by weighing pure salts (Fluka) dried in an oven at  $T = 383.15 \text{ K}$ . To preserve Sn(II) solutions from oxidation to Sn(IV), the precaution already used in previous works

were adopted [16, 28, 29, 33]. All solutions were prepared with analytical grade water ( $R = 18 \text{ M}\Omega \text{ cm}^{-1}$ ) using grade A glassware.

## Potentiometric apparatus

Potentiometric measurements were carried out, in thermostated cells at  $T = 298.15 \pm 0.15 \text{ K}$ , using an apparatus consisting of a Model 713 Metrohm potentiometer, equipped with a half cell glass electrode (Ross type 8101, from Orion) and a double junction reference electrode (type 900200, from Orion), containing a filling solution of the same ionic medium (NaCl or NaNO<sub>3</sub>) and at the same ionic strength of the investigated one. The titrant was delivered in the vessel by means of a Model 765 Metrohm motorized burette. Estimated precision was  $\pm 0.15 \text{ mV}$  and  $\pm 0.003 \text{ cm}^3$  for e.m.f. and titrant volume readings, respectively. The apparatus was connected to a PC, and automatic titrations were performed using a suitable computer program to control titrant delivery, data acquisition and to check for emf stability. Some measurements were also carried out using a Metrohm model 809 Titrand apparatus controlled by Metrohm TiAMO 1.0 software for the automatic data acquisition.

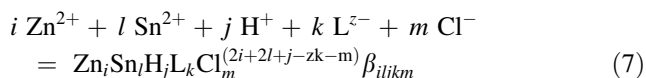
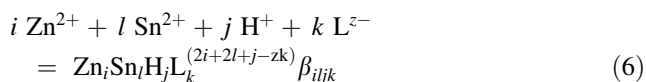
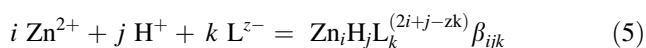
The measurements were performed by titrating 25 cm<sup>3</sup> of the investigated solutions, containing different amounts of the ligands ( $1.5 \leq c_L \text{ mmol dm}^{-3} \leq 5.0$ ), Zn<sup>2+</sup> or in the case of the mixed metal solutions, Zn<sup>2+</sup> and Sn<sup>2+</sup> (total cations concentration:  $0.5 \leq c_M \leq 5.0 \text{ mmol dm}^{-3}$ , in different Zn<sup>2+</sup>:Sn<sup>2+</sup> ratios) and the supporting electrolyte to obtain the desired ionic strength values, at  $I = 0.15 \text{ mol dm}^{-3}$  in NaCl<sub>(aq)</sub> and at  $I = 1.00 \text{ mol dm}^{-3}$  in NaNO<sub>3(aq)</sub>; only for the hetero-metals/Mala system, measurements at  $I = 1.00 \text{ mol dm}^{-3}$  were also carried out in NaCl<sub>(aq)</sub>. These solutions were titrated with standard NaOH solutions up to pH  $\sim 7.5$ – $8.0$  or up to the formation of sparingly soluble species. Solutions were magnetically stirred and a constant flow of purified presaturated N<sub>2</sub> was bubbled through the solution to exclude O<sub>2</sub> and CO<sub>2</sub> inside.

For each experiment, independent titrations of strong acid solution with standard base were carried out under the same medium and ionic strength condition as the system to be investigated, with the aim of determining electrode potential ( $E^0$ ) and the acidic junction potential ( $E_j = j_a [\text{H}^+]$ ). In this way, the pH scale used was  $\text{pH} \equiv -\log [\text{H}^+]$ , where  $[\text{H}^+]$  is the free proton concentration. For each titration, 80–100 data points were collected.

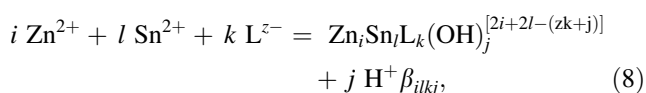
### Calculations

The BSTAC and STACO [34] computer programs were used in the calculation of complex formation constants. Both programs can deal with measurements at different ionic strengths. The ES4ECI [34] and/or HySS [55] programs were used to draw the speciation and sequestration diagrams and to calculate species formation percentages.

Homo- and hetero-metal complex formation constants are given according to the equilibria:



When the formation of homo or hetero-metals/ligand hydrolysis species was observed, the following general equilibrium can be written:



where  $\text{OH} \equiv \text{H}_{-j}$ .

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