

Complex formation equilibria in the binary Zn^{2+} -oxalate and In^{3+} -oxalate systems †

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Received 20th March 2003, Accepted 21st May 2003

First published as an Advance Article on the web 5th June 2003

The complex formation equilibria between oxalate and Zn^{2+} as well as between oxalate and In^{3+} have been investigated through a potentiometric methodology at 25 °C in 1, 2 and 3 M $NaClO_4$, by using both glass and metal amalgam electrodes. Owing to the low solubility of the $Zn(II)$ and $In(III)$ oxalates, the analytical concentration of the metal ions was forced to be kept below the 5 mM level: constant current coulometry has been used in order to prepare solutions containing the metal ion at very low but accurately known total concentration. At each ionic strength, the formation constants of the complexes $ZnC_2O_4(aq)$, $Zn(C_2O_4)_2^{2-}$, $InC_2O_4^+$, $In(C_2O_4)_2^-$ and $In(C_2O_4)_3^{3-}$ have been determined. By using the specific ion interaction theory the constants have been extrapolated at zero ionic strength. Thus relevant *interaction coefficients* have been obtained, which appear in the mathematical development of the theory. Solutions, containing $InC_2O_4^+$ or $In(C_2O_4)_2^-$ as the prevailing metal-containing species, were prepared on the basis of the thermodynamic parameters determined, and were analysed through electrospray mass spectrometry. The fragmentation of the $In(C_2O_4)(H_2O)_2^+$ and $In(C_2O_4)_2^-$ complexes detected produced respectively the InH_2O^+ and $InC_2O_4^-$ species of $In(I)$.

Introduction

Modelling the migration of metal ions in the environment or in a biological system is complicated by the large number of chemical equilibria and thermodynamic parameters to be dealt with simultaneously. The problem is usually faced by dividing the overall system into smaller metal–ligand sub-systems, whose complexity increases with increasing reliability of thermodynamic information (mainly ΔG and ΔH) in the database.¹ When organic molecules of high molecular weight are considered as the ligands, oxalate is often used to simulate the effect of two adjacent carboxylic residues able to strongly bind metal ions through the formation of five-atom rings. Actually oxalate is very frequent in natural systems, being one of the final fragments in the degradation of natural organic matter (NOM) as well as the simplest dicarboxylic acid involved in metabolic pathways; moreover, it has widespread industrial uses: such a small molecule may thus be considered to be at the borderline within natural, biological and industrial worlds.

On the other hand the zinc and indium oxalates have fundamental,^{2–4} environmental,^{5,6} biological⁷ and industrial^{8–10} relevance, both with respect to their solid state compounds and to their solution chemistry.

In the present work the complex formation equilibria in the binary Zn^{2+} - $C_2O_4^{2-}$ and In^{3+} - $C_2O_4^{2-}$ systems have been studied in order to determine the ionic strength dependence of the formation constants: the Zn^{2+} and In^{3+} are d^{10} -ions, which are known¹¹ to form with oxalate the complexes $ZnC_2O_4(aq)$, $Zn(C_2O_4)_2^{2-}$, $InC_2O_4^+$, $In(C_2O_4)_2^-$ and $In(C_2O_4)_3^{3-}$, having electrical charge spanning from +1 to –3. Concerning these species, though enough data are available to define the dependence of their formation constants from the temperature,¹¹ there is however a lack of information about the influence of the

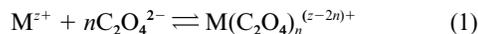
ionic strength. The extrapolation at infinite dilution of the equilibrium constants determined was a prerequisite to define the best experimental conditions for using electrospray mass spectrometry to identify at least some of the complexes found having different electrical charge.

Since its first appearance,^{12,13} electrospray mass spectrometry (ESMS) has been applied in several research areas, playing a pivotal role mainly in the structural characterisation of biological/organic molecules.^{14,15} Nevertheless, a parallel interest for the development of applications in the inorganic field has led to a growing number of publications related to the identification of metal complexes in solution.¹⁶ The success of such applications relies on the soft ionisation mode occurring in the electrospray sources. Two main steps have to be considered in the ionisation process, which eventually allows to transfer ionic analytes from a solution into the gas phase: the generation of charged droplets and the gaseous ion formation. Proposed models concerning the putative mechanisms taking place in the electrospray source, such as the single ion droplet theory¹⁷ (SIDT) or the ion evaporation theory^{18,19} (IET), cannot explain the complexity of the process alone. The extended charged residue model²⁰ (CRM) has recently been proposed, which describes a concerted mechanism combining SIDT and IET. Actually many other “parameters” have been suggested²¹ to affect the mass spectra: aqueous solution chemistry, kinetics of ion desorption, efficiency of gas phase ion formation, ion transmission into the vacuum, desolvation and declustering, and electrostatic optics/quadrupole mass filter transmission efficiencies. Charles and coworkers²² have showed that relative abundance, charge state and intensity distribution of potassium bromate salt clusters depended on both the nature and the amount of the organic solvent in solution. Apart from these considerations, experimental observations indicate that the ion abundance profile shown in a mass spectrum retains the aqueous solution pattern. Such a finding, along with the tolerance of ESMS to complex matrices, has allowed the development of elemental speciation studies, with a special interest in the environmental scenario.²³

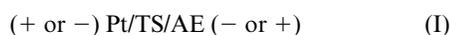
† Electronic supplementary information (ESI) available: primary data and the analytical concentrations (Tables S1 and S2), distribution diagrams (Figs. S1 and S2), of the extrapolation procedure results (Fig. S3) and MS/MS spectra (Figs. S4 and S5). See <http://www.rsc.org/suppdata/dt/b3/b303202g/>

Notation. M^{z+} : metal ion of electrical charge $z = +2$ ($M = \text{Zn}$) or $+3$ ($M = \text{In}$). H = analytical proton excess with respect to the zero level constituted by H_2O , M^{z+} and $\text{C}_2\text{O}_4^{2-}$. B = analytical concentration of the metal ion. A = analytical concentration of oxalate. $h = [\text{H}_3\text{O}^+]$, $b = [M^{z+}]$, $a = [\text{C}_2\text{O}_4^{2-}]$. Concentrations are expressed in mol dm^{-3} .

The determination of the equilibrium constant β_n of the reaction (1)



has been performed at 25 °C through a potentiometric methodology, in solutions containing, besides the reacting species, also about a thousand fold concentration of NaClO_4 as the ionic medium, in order to keep at a minimum the variation of the activity coefficients of the species involved in the equilibria. The measurements were carried out in the form of potentiometric titrations. Each experiment started by placing into a titration vessel, thermostatted at (25.00 ± 0.02) °C, an accurately known volume, V_0 , of solution of the ionic medium, S_0 : H_0 M HClO_4 , $(C - H_0)$ M NaClO_4 , purged with a continuous stream of highly pure nitrogen. The total concentration of strong acid in S_0 was then regulated stepwise to a prefixed value through coulometry, by using the electrolysis circuit (I)



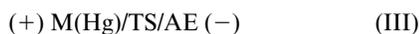
in which Pt was a platinum foil, TS was the test solution, and AE was C M $\text{NaClO}_4/0.050$ M $\text{Hg}_2(\text{ClO}_4)_2$, $(C - 0.100)$ M NaClO_4 ; Pt and AE were connected through a DC power supply. After each coulometric addition the emf of the galvanic cell (II)



was monitored until it attained a value constant within ± 0.02 mV. In the cell (II), RE indicates an Ag/AgCl reference electrode, external to the cell but in electrical contact with it through a salt bridge, while GE was a glass membrane electrode, sensitive to the activity of hydrogen ions. In the experimental conditions chosen, the Nernst equation for the cell (II) at 25 °C may be written as in eqn. (2)

$$E_h = E_h^0 + 59.16 \log h + E_j \quad (2)$$

in terms of the equilibrium H_3O^+ concentration, h , instead of its activity, owing to the constancy of the activity coefficients in the presence of large concentrations of the medium ions. Eqns. (2) and (3) contain the constant terms E_h^0 and E_b^0 that include both, among other quantities, the activity coefficients term. The liquid junction potential E_j arises at the interface between TS and the solution of the salt bridge as a consequence of the substitution of the Na^+ with the H_3O^+ ions.²⁴ Both the activity coefficients variations and the liquid junction term are negligible because the composition of the test solutions differs, but very little, from the composition of the ionic medium. The primary data collected at this stage of the experiment were elaborated by using the Gran's method,²⁵ in order to accurately determine the trace amounts of strong acid in the ionic medium, H_0 , and the constant term E_h^0 appearing in eqn. (2). Accurately known amounts of the metal ions were than stepwise produced in the test solution, TS, through the electrolysis circuit (III)



and after each addition the emf, E_b , of the cell was monitored (IV)



Table 1 Survey of the dissociation constants (pK_a) of oxalic acid in NaClO_4 at 25 °C used in the emf data processing

[NaClO ₄]/M	pK_{a_1}	pK_{a_2}	Ref.
1	1.00	3.57	28
2	1.14	3.64	^a
3	1.26	3.80	29

^a Estimated through the specific interaction theory.³⁰

In both electrolysis and galvanic cells (III) and (IV), $M(\text{Hg})$ was a diluted (about 0.1% w/w) amalgam of the metal in mercury. While the acidity of the solutions was regulated to be high enough to suppress the formation of hydrolytic species, the analytical and the equilibrium concentrations of the metal ion, B and b respectively, coincided. Hence, the data thus collected allowed the determination, through a Gran plot, of the constant quantity E_b^0 appearing in the Nernst equation (3), for cell (IV), at 25 °C

$$E_b = E_b^0 + (59.16/z) \log b + E_j \quad (7)$$

and to attain a prefixed value of B . Once the test solution had reached the desired composition, TS: B_x M M^{z+} , H_x M H_3O^+ , $(C - H_x - zB_x)$ M Na^+ , C M ClO_4^- , the experiment was completed by titrating TS with known volumes, V_T , of the solution T: A_T M $\text{C}_2\text{O}_4^{2-}$, H_T M H_3O^+ , $(C + 2A_T - H_T)$ M Na^+ , C M ClO_4^- , until the incipient formation of a solid phase. After each addition the emfs of the cells (II) and (IV), which were monitored around the clock, required about 10 min to attain a stable value, within ± 0.05 mV, for several hours. This was assumed as a criterion for equilibrium. The analytical concentrations of protons (H), metal ion (B) and oxalate (A) were varied in the largest possible interval, compatibly with the very low solubility of the metal oxalates. Experiments were performed at $C = 1, 2$ and 3 M.

Calculations and results

The primary (V_T , E_h , E_b) data and the analytical concentrations H , B and A (which are available as ESI Tables S1 and S2†) were the basis for the determination of the constants of the reaction (1) at each ionic strength, and were processed through the least-squares programs Letagrop-Etitr²⁶ and Hyperquad.²⁷ The dissociation constants of oxalic acid used in the calculations are reported in Table 1. The literature values do not differ appreciably from the most recent and accurate determinations obtained by the use of a second type $\text{Hg}_2\text{Hg}_2\text{C}_2\text{O}_4$ oxalate electrode described in ref. 33. At each ionic medium concentration the formation constants of the binary $\text{ZnC}_2\text{O}_4(\text{aq})$, $\text{Zn}(\text{C}_2\text{O}_4)_2^{2-}$, and $\text{In}(\text{C}_2\text{O}_4)_2^+$, $\text{In}(\text{C}_2\text{O}_4)_2^-$, $\text{In}(\text{C}_2\text{O}_4)_3^{3-}$ complexes of Zn(II) and In(III), reported in Table 2 and Table 3 respectively were determined.

The speciation in the two binary Zn^{2+} -oxalate and In^{3+} -oxalate systems for a 1 mM total metal concentration at $\text{pH} = 2$ and from 0 to 10 mM total oxalate in 3 M NaClO_4 is presented through distribution diagrams available as ESI Figs. S1 and S2. †

The equilibrium constants determined at different perchlorate concentrations were extrapolated to the infinite dilution activity scale by using the specific interaction theory³⁰ (SIT), from which it follows the general equation (5)

$$f_n(M) = \log^0 \beta_n + (\Delta \varepsilon_n)m \quad (5)$$

In eqn. (5)

$$f_n(M) = \log \beta_n - n \log \delta + [z^2 + 4n - (z - 2n)^2]D \quad (6)$$

depends on the equilibrium constant β_n of reaction (1) at the ionic strength I (in molality), the ratio $\delta = \text{molality/molarity}$, and the Debye term

Table 2 Survey of the constants of the binary $\text{Zn}^{2+}\text{-C}_2\text{O}_4^{2-}$ system determined at 25 °C and different NaClO_4 concentrations, expressed as $\log\beta_n$. The errors are reported in parenthesis and correspond to three times the standard deviation on the value of the constant

Data processing program	$\log\beta_1$			$\log\beta_2$		
	1 M	2 M	3 M	1 M	2 M	3 M
Letagrop	3.61(4)	3.65(3)	3.79(2)	6.15(4)	6.33(3)	6.67(5)
Hyperquad	3.58(4)	3.59(4)	3.77(4)	6.15(3)	6.36(2)	6.68(4)
Proposed value	3.60(5)	3.62(7)	3.77(4)	6.15(4)	6.34(4)	6.67(5)

Table 3 Survey of the constants of the binary $\text{In}^{3+}\text{-C}_2\text{O}_4^{2-}$ system determined at 25 °C and different NaClO_4 concentrations, expressed as $\log\beta_n$. The errors are reported in parentheses and correspond to three times the standard deviation of the value of the constant

Data processing program	$\log\beta_1$			$\log\beta_2$			$\log\beta_3$		
	1 M	2 M	3 M	1 M	2 M	3 M	1 M	2 M	3 M
Letagrop	5.74(4)	5.65(4)	5.79(3)	10.83(2)	10.95(2)	11.36(3)	13.81(4)	14.37(8)	15.10(8)
Hyperquad	5.73(5)	5.65(3)	5.78(4)	10.80(3)	10.94(2)	11.35(2)	13.79(6)	14.37(8)	15.09(9)
Proposed value	5.73(5)	5.65(4)	5.78(4)	10.81(4)	10.95(3)	11.36(3)	13.79(6)	14.37(8)	15.09(9)

Table 4 Survey of the results of the extrapolation procedure of the equilibrium constants β_n through the SIT

	$\text{Zn}(\text{C}_2\text{O}_4)_n^{(2-2n)+}$		$\text{In}(\text{C}_2\text{O}_4)_n^{(3-2n)+}$		
	$n = 1$	$n = 2$	$n = 1$	$n = 2$	$n = 3$
Correlation coefficient	0.99998	0.9999995	0.99993	0.999992	0.9993
$\log^0\beta_n \pm 3\sigma$	5.03 ± 0.01	7.426 ± 0.002	7.95 ± 0.02	13.57 ± 0.01	15.5 ± 0.2
$\Delta\epsilon_n \pm 3\sigma/\text{kg H}_2\text{O mol}^{-1}$	0.196 ± 0.004	0.318 ± 0.001	0.220 ± 0.008	0.477 ± 0.006	0.69 ± 0.08

$$D = 0.5107I^{1/2}/(1 + 1.5I^{1/2}) \quad (7)$$

while

$$\Delta\epsilon_n = \epsilon(\text{M}^{z+}, \text{ClO}_4^-) + n\epsilon(\text{Na}^+, \text{C}_2\text{O}_4^{2-}) - \epsilon(\text{M}(\text{C}_2\text{O}_4)_n^{(z-2n)+}, \text{Na}^+ \text{ or } \text{ClO}_4^-) \quad (8)$$

is a linear combination of the *interaction coefficients* of the reacting species, which appears in the mathematical development of the SIT. The last term on the second member of eqn. (8) depends on the stoichiometry of the species considered: thus it must be intended as $\epsilon(\text{ZnC}_2\text{O}_4(\text{aq}), \text{NaClO}_4)$ (analogous to a “salting coefficient”) and $\epsilon(\text{Zn}(\text{C}_2\text{O}_4)_2^{2-}, \text{Na}^+)$ in the case of the Zn^{2+} complexes, or as $\epsilon(\text{InC}_2\text{O}_4^+, \text{ClO}_4^-)$, $\epsilon(\text{In}(\text{C}_2\text{O}_4)_2^-, \text{Na}^+)$ and $\epsilon(\text{In}(\text{C}_2\text{O}_4)_3^{3-}, \text{Na}^+)$, in the case of the In^{3+} complexes. Thus from eqn. (5) it follows that the function $f_n(\text{M})$ should be a linear variable of the medium ions concentration m , expressed in molal units: from the intercept and the slope of the $f_n(\text{M})$ vs. m graph the constants $^0\beta_n$ at infinite dilution and the $\Delta\epsilon_n$ terms may be obtained. In Table 4 the results of the extrapolation procedure are summarised (see also ESI Fig S3 †).

Electrospray mass spectrometry measurements

Solutions containing known ratios of the binary $\text{In}(\text{C}_2\text{O}_4)_n^{(3-2n)+}$ complexes were prepared on the basis of the formation constants extrapolated at zero ionic strength through the SIT. They were analysed through ESMS, both in positive and in negative ion mode. This was done with the aim to establish the capacity of the technique to identify the well known complexes InC_2O_4^+ and $\text{In}(\text{C}_2\text{O}_4)_2^-$, the main metal containing species in the prepared solutions.

Fig. 1 displays a portion of the positive ESMS spectrum of an equimolar solution of $\text{In}(\text{ClO}_4)_3$ and $\text{Na}_2\text{C}_2\text{O}_4$; no significant signals were detected out of the mass/charge (m/z) range. The most intense signals found in the m/z 200–300 range were interpreted as In-containing species; a complete list is reported in Table 5. At this regard, it is interesting to note the occurrence of the species $\text{In}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_y^+$ with $y = 0, 1$ or 2 . Fig. 2 shows the equivalent negative ESMS spectrum. Also in this case no

Table 5 Identification of some of the charged fragments appearing in the electrospray mass spectra of a solution containing 0.5 mmol dm^{-3} $\text{In}(\text{ClO}_4)_3$ and 0.5 mmol dm^{-3} $\text{Na}_2\text{C}_2\text{O}_4$, presented in Figs. 1 and 2. Data are reported in the form [species] (mass/charge)

Positive fragments
$[\text{InC}_2\text{O}_4^+] (203)$; $[\text{In}(\text{H}_2\text{O})_5^+] (205)$; $[\text{In}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})^+] (221)$; $[\text{In}(\text{H}_2\text{O})_6^+] (223)$; $[\text{In}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_2^+] (239)$; $[\text{In}(\text{Na}_2\text{C}_2\text{O}_4)^+] (249)$; $[\text{In}(\text{Na}_2\text{C}_2\text{O}_4)(\text{H}_2\text{O})^+] (267)$; $[\text{In}(\text{Na}_2\text{C}_2\text{O}_4)(\text{H}_2\text{O})_2^+] (285)$.
Negative fragments
$[\text{H}(\text{ClO}_4)_2^-] (199)$; $[\text{Na}(\text{ClO}_4)_2^-] (221)$; $[\text{In}(\text{C}_2\text{O}_4)_2^-] (291)$.

significant signals were recorded out of the range displayed. In the negative ion mode only one signal at m/z 291 was attributed to In-containing compound, as reported in Table 5.

In order to confirm such attributions, tandem mass spectrometry (MS/MS) measurements were performed on the most interesting species detected (spectra available as ESI Figs. 4 and 5 †). The MS/MS analysis on the positive signal at m/z 239 (assigned to $\text{In}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_2^+$) led to three main fragments: 221, 149 and 143, attributed to the species $\text{In}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})^+$, $\text{InO}(\text{H}_2\text{O})^+$ and $\text{In}(\text{H}_2\text{O})^+$, respectively. By selecting the negative signal at m/z 291 for the MS/MS analysis, a unique main signal at m/z 203 was recorded and interpreted as $\text{In}(\text{C}_2\text{O}_4)^-$.

Experimental

Reagents and analysis

Twice distilled water was used throughout to prepare the solutions. Perchloric acid stock solutions were prepared by diluting the 65% R.P.E. Carlo Erba product without any further purification, since it showed not to contain significant levels of redox impurities. The analysis, carried out by the classical acid-base titration procedures, using KHCO_3 and methyl red, agreed within $\pm 0.05\%$. Sodium perchlorate stock solutions were synthesised from 65 % HClO_4 and Na_2CO_3 (R.P.E. Carlo Erba), and analysed as described elsewhere.³¹

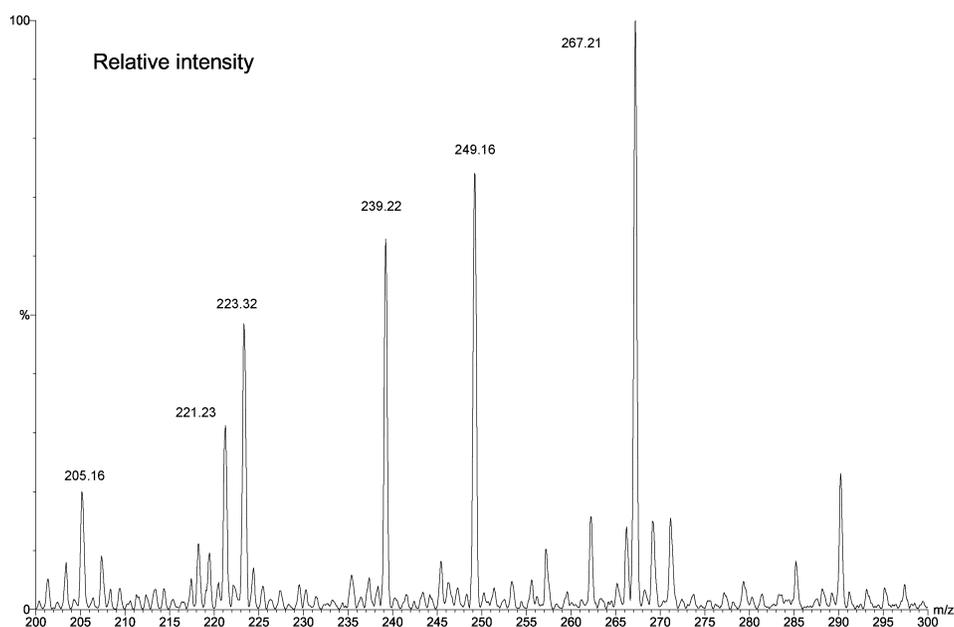


Fig. 1 Positive ESMS of a solution containing $0.5 \text{ mmol dm}^{-3} \text{ In}(\text{ClO}_4)_3$ and $0.5 \text{ mmol dm}^{-3} \text{ Na}_2\text{C}_2\text{O}_4$.

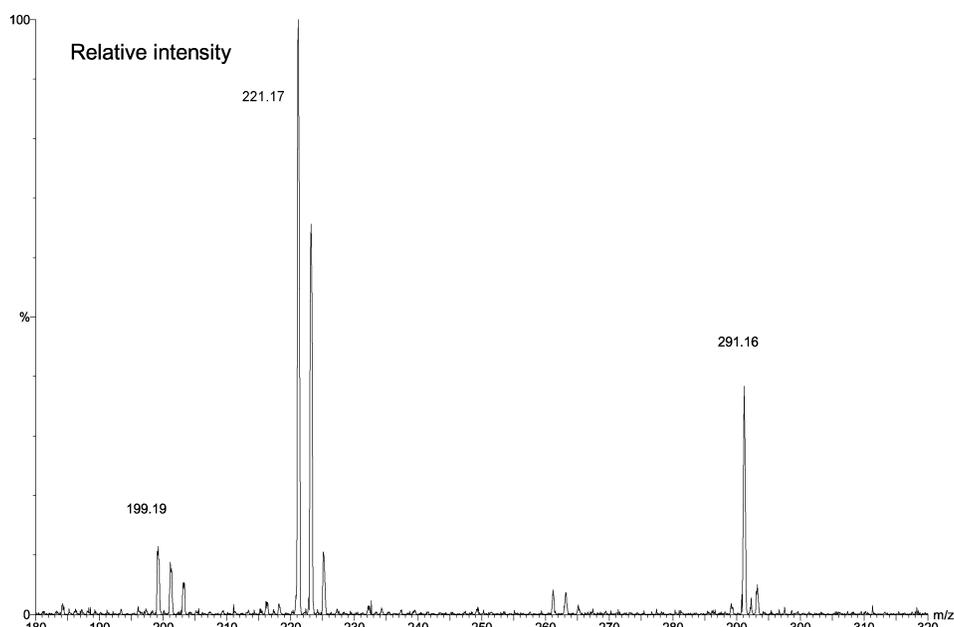


Fig. 2 Negative ESMS of a solution containing $0.5 \text{ mmol dm}^{-3} \text{ In}(\text{ClO}_4)_3$ and $0.5 \text{ mmol dm}^{-3} \text{ Na}_2\text{C}_2\text{O}_4$.

Stock solutions of mercury(II) perchlorate were obtained by mixing $\text{HgO}(\text{s})$ (R.P.E. Carlo Erba) and $\text{Hg}(\text{l})$, 5 N, furnished by Fluka, in a slight excess of HClO_4 . The stocks were titrated potentiometrically, varying the Hg_2^{2+} concentration by coulometric reduction at a mercury cathode. Sodium oxalate (pro analysis), metallic indium (5 N) and zinc (5 N) were Sigma-Aldrich Chemical Co products. All the solutions were deoxygenated by purging them with a vigorous nitrogen stream. The gas (99.98%), from cylinders, bubbled through a series of washing bottles containing a Cr(II) reducing solution consisting of an acidic (HCl) solution of $\text{K}_2\text{Cr}_2\text{O}_7$ and Zn amalgam, 10% NaOH , 1 M H_2SO_4 , twice distilled water and CM NaClO_4 so as to saturate it at the same water vapour pressure as TS.

Materials and equipment

All the potentiometric experiments were carried out into an air box thermostat, capable of keeping the temperature of the solutions at $(25.00 \pm 0.02) ^\circ\text{C}$. The high impedance glass electrodes were supplied by Metrohm; highly precise ($\pm 0.01 \text{ mV}$) emf measurements could be made by using home-made

impedance adapters. Ag/AgCl electrodes were prepared according to Brown.³² A fully automated data acquisition system based on Hewlett-Packard components, combined with the software TITPOTTM, produced by InLab Software House, was allowed to control the experiments around the clock. The automatic burettes employed were Dosimat 715s from Metrohm, having a precision of $\pm 0.004 \text{ cm}^3$. The coulometry was carried out using a Hewlett-Packard DC Power Supply mod. E3612A.

Mass spectra were acquired on the triple quadrupole QUATTRO μ electrospray mass spectrometer equipped with a Z-spray source (Micromass, Manchester, UK). Aqueous solutions of the sample under investigation were infused into the ion source at $10 \mu\text{l min}^{-1}$ by means of the syringe infusion pump present in the instrument apparatus. A nitrogen flow of $200 \text{ dm}^3 \text{ h}^{-1}$ was applied. Spectra were acquired in positive and negative ion mode over a mass range of 50–2000 m/z , at 6 s scan^{-1} with an acquisition time of 1–3 min. The resolution of the instrument was set in order to allow the observation of the isotopic mass distribution. The settings were as follows: capillary at 3.2 kV (positive mode) and 2.8 kV (negative mode),

Table 6 Survey of the interaction coefficients (in kg H₂O mol⁻¹) between Na⁺ or ClO₄⁻ and the binary M(C₂O₄)_n⁽²⁻²ⁿ⁾⁺ complexes

$\varepsilon(\text{InC}_2\text{O}_4^+, \text{ClO}_4^-)$	$\varepsilon(\text{ZnC}_2\text{O}_4, \text{NaClO}_4)$	$\varepsilon(\text{Na}^+, \text{In}(\text{C}_2\text{O}_4)_2^-)$	$\varepsilon(\text{Na}^+, \text{Zn}(\text{C}_2\text{O}_4)_2^{2-})$	$\varepsilon(\text{Na}^+, \text{In}(\text{C}_2\text{O}_4)_3^{3-})$
0.33 ± 0.08	0.18 ± 0.05	0.1 ± 0.1	0.11 ± 0.07	0 ± 0.2

Table 7 Survey of the results of the extrapolation at zero ionic strength of the overall formation constants of the binary Zn²⁺-oxalate and In³⁺-oxalate complexes

T/°C	Medium	Method	logβ ₁	logβ ₂	logβ ₃	log ⁰ β ₁	log ⁰ β ₂	log ⁰ β ₃	Ref.
Zn²⁺-C₂O₄²⁻									
25	0	Solubility	5.00	7.36	—	—	—	—	34
25	0.10 M NaCl	Ionic exchange	3.88	6.40	—	4.76	7.27	—	35
20	0.10 M NaClO ₄	Distribution	—	7.59	—	—	8.49	—	36
25	2.00 M KCl	Potentiometry	3.48	5.48	—	5.32	7.29	—	37
25	1.00 M NaClO ₄	Distribution	3.42	6.16	—	5.25	8.10	—	38
37	0.15 M NaClO ₄	Potentiometry	4.05	—	—	5.08	—	—	39
23	1.00 M NaClO ₄	Distribution	3.26	6.63	—	5.09	8.57	—	40
30	0.10 M NaClO ₄	Potentiometry	3.87	6.08	—	4.76	6.98	—	41
25	0.5 M NaCl	Potentiometry	3.46	6.03	—	4.86	7.43	—	42
25	0.68 M NaCl	Distribution	3.58	—	—	5.08	—	—	43
In³⁺-C₂O₄²⁻									
20	0.10 M NaClO ₄	Distribution	—	—	14.7	—	—	16.1	36
25	1.00 M NaClO ₄	Distribution	5.30	10.52	—	8.0	14.3	—	44
20	0.10 M NaClO ₄	Potentiometry	7.78	—	—	9.1	—	—	45

cone 20 V, source temperature 120 °C, desolvation temperature 120 °C.

For MS/MS measurements, fragmentation of selected species was performed with argon at pressure 2 × 10⁻³ mbar. Spectra were acquired at different collision energies.

Discussion

On the basis of the values $\varepsilon(\text{Zn}^{2+}, \text{ClO}_4^-) = (0.33 \pm 0.03)$ kg H₂O mol⁻¹,³⁰ $\varepsilon(\text{Na}^+, \text{C}_2\text{O}_4^{2-}) = (0.05 \pm 0.02)$ kg H₂O mol⁻¹,³³ and assuming $\varepsilon(\text{In}^{3+}, \text{ClO}_4^-) = (0.50 \pm 0.05)$ kg H₂O mol⁻¹, as it is for most of the metal ions of charge +3, the interaction coefficients reported in Table 6 could be estimated from the experimental $\Delta\varepsilon_n$ data.

Concerning the values of the interaction coefficients, epsilon, obtained, it is hard to explain their trend, if not through the consideration of the charge and the dimensions of the interactive species. For the epsilon of Zn(C₂O₄)₂²⁻ with Na⁺, the comparison with -2 charged ions in literature suggests an average value around zero, which is not far from the value (0.11 ± 0.07) kg H₂O mol⁻¹ found by us. Referring to the neutral complex ZnC₂O₄, the value of epsilon found in this study, (0.18 ± 0.05) kg H₂O mol⁻¹, compares very well with the value of (0.19 ± 0.05) kg H₂O mol⁻¹ estimated according to the empirical equation given by Ciavatta.³⁰

The specific interaction theory was used to extrapolate the literature values of the constants at zero ionic strength, using the $\Delta\varepsilon_n$ values determined in sodium perchlorate in the present work and assuming $\Delta\varepsilon_n = 0$ for the other ionic media. In Table 7 the data set used and the results of the extrapolation procedure are reported.

In the case of the Zn²⁺ complexes the data set spans over a significantly wide ionic media and concentrations interval, at temperatures varying between 20 and 37 °C. This allowed to obtain the averaged log⁰β₁ = 5.0 ± 0.3 and log⁰β₂ = 7.7 ± 0.9 values, which are in fair agreement with the values determined through solubility measurements³⁴ and with the ones extrapolated from the potentiometric data of the present work. On the other hand the available data concerning the In³⁺ complexes were too scarce to produce an evaluation safely comparable with the results of the present work.

The ESMS spectra recorded showed the presence of oxalate complexes of In(I) as fragments probably formed through the

electrospray process. Actually, while the existence of In(I) in solid compounds is firmly established,⁴⁶ it may be easily demonstrated, on the basis of the well known standard potentials of the In(III)/In(I) and In(I)/In(0) couples,⁴⁷ that the concentration of In(I) in the solutions investigated is negligible.

The possible existence of some correlation between the β₁ value of the metal-oxalate complexes and the charge/ionic radius ratio of the metal ion was examined by analysing the literature data^{11,48} for a series of di- and trivalent metal ions. Owing to the relative abundance of data at 25 °C and 1 M NaClO₄, those conditions were chosen as the reference, and the values determined in other media were reported to these activity scales through the SIT. The results of the evaluation are presented in Fig. 3. In the case of the transition metal ions a good correlation could be obtained by assuming a co-ordination number (CN) of vi for Mn, Fe, Co, Ni, and iv for Cu; both of the co-ordination numbers v and vi were instead considered in the case of Zn. Besides the expected regular variation of β₁ vs. charge/ionic ratio of the lanthanides,

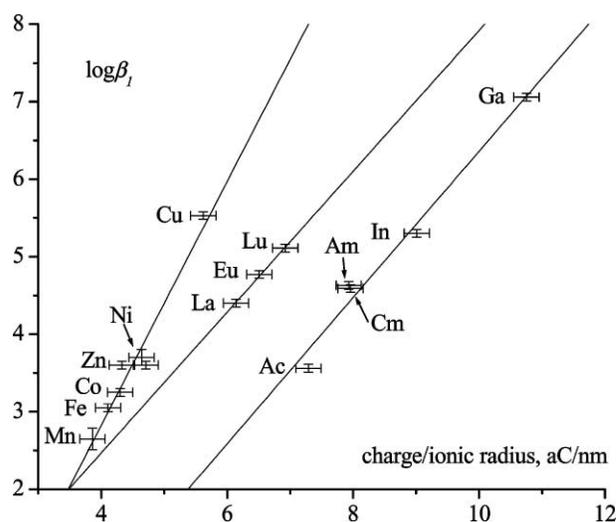


Fig. 3 Correlation diagram between logβ₁ and the charge/ionic radius ratio for some di- and trivalent metal ions. For the sake of clarity the abscissas of the lanthanides are shifted two units and those of the others trivalent ions are increased by three units. The error bars represent three times the standard deviation on the data.

of some interest may be the correlation between the data referring to Ga³⁺ and In³⁺ with those of some actinides, such as Ac³⁺, Am³⁺ and Cm³⁺, which are of great relevance in nuclear waste management.

Acknowledgements

The financial contribution to the present work by the Italian Ministero per l'Istruzione, l'Università e la Ricerca is gratefully acknowledged.

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