Chemistry of Some Amphoteric Cations (Sn^{2+}; Pb^{2+}; Cr^{3+}) in Hyper-Alkaline Aqueous Solutions

PhD Thesis

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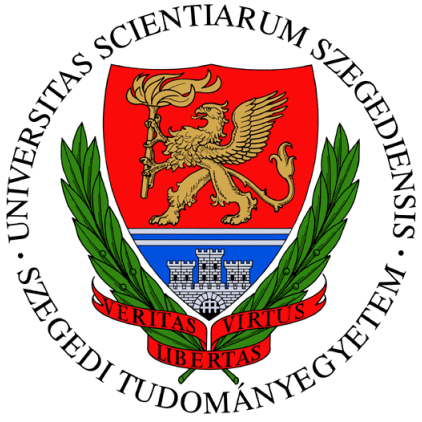

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1. Introduction

The hydrolysis of metal ions is one of the most widely studied fields of inorganic solution chemistry, including the structure, the composition and the thermodynamics of the hydroxido complexes formed. These studies are usually carried out within the pH range of 2 – 13. The speciation and the structure of the hydroxido complexes formed in strongly alkaline aqueous solutions are still mainly unknown. This is due to well-known theoretical and practical difficulties. In concentrated solutions, the ion associations and the effect of the activity coefficients are often inseparable. Technical problems include the effect of impurities, which are readily accumulated because of the high concentrations; therefore, the use of high purity chemicals is inevitable. Another problem is that these highly alkaline solutions are hygroscopic and aggressive, and they tend to corrode/destroy the equipment and instruments during the storage and measurement.

In spite of these hurdles, the number of publications dealing with this particular aspect of solution chemistry steadily increases. For obvious reasons, metal ions with reasonable solubility, like aluminium(III), gallium(III), and thallium(I), are intensely studied. On the contrary, the available literature on the speciation of tin(II), lead(II) and chromium(III) is scarce in strongly alkaline media. Only a few papers deal with them, and they are contradictory, especially about the composition and the structure of the complexes present.

A profound example is Sn(II), for which several textbooks affirm the existence of $[Sn(OH)_4]^{2-}$ in large hydroxide excess, while other references exclude the existence of it, claiming that the last considered hydroxido complex is $[Sn(OH)_3]^-$. The same question arises, when it comes to lead(II); the existence and exclusive formation of $[Pb(OH)_4]^{2-}$ is proposed by some authors in the alkaline end of the pH scale; others disapprove this. Chromium(III) is even more controversial, as not only the speciation is not well established, but also the long-term stability of Cr(III) was scrutinized in a recent publication, and the authors suggested that chromium(III) was spontaneously oxidized to chromate in strongly alkaline media.

Taking the contradictions found in the literature into account, the following aims were set:

- clarifying the composition of the complex(es) of tin(II), lead(II) and chromium(III) forming in concentrated alkaline solutions, as well as revealing whether or not so far unknown hydroxido- or multinuclear complexes are formed in experimentally detectable quantities at pH higher than 13 (even up to 16 M hydroxide concentrations);
- describing the composition and the structural features of the complexes forming with several methods like UV-vis, Raman, X-ray absorption, Mössbauer, and NMR spectroscopies, complemented with quantum chemical calculations;
- giving further experimental proofs for the spontaneous oxidation of chromium(III) to chromium(VI) was also aimed, together with the detailed investigation of the reaction as a function of counter ion, added oxygen, and chromium(III)- and hydroxide concentration.
- As the speciation of chromium(III) in hyper-alkaline conditions in the literature was found to be based on analogies with those in acidic ones, the investigation of it was also intended.

Experimental

2.1 Materials and preparations

Analytical grade NaOH was dissolved in distilled water to obtain carbonate-free ~19 M NaOH stock solution. The exact concentration was calculated from the density of the solution.

The tin(II)-containing stock solutions were prepared in three different ways, depending on the applied experimental method. For the X-ray absorption-, Raman-, and ^{119}Sn Mössbauer spectroscopy measurements, SnO was dissolved in oxygen-free atmosphere in diluted (1 : 1 volume ratio) a.r. grade hydrochloric or perchloric acid. The stock solutions used for the potentiometric measurements were prepared by dissolving metallic tin in a.r. grade diluted hydrochloric acid. The continuously evolving hydrogen gas did secure reducing conditions and the formation of tin(IV) was hampered. The ^{119}Sn enriched stock solution for some of the Mössbauer spectroscopy measurements were prepared by the cementation reaction of Cu(II) perchlorate and metallic tin.

The lead(II) stock solutions were prepared by dissolving a.r. grade $Pb(NO_3)_2$ in a.r. grade nitric acid in order to avoid the hydrolysis of the lead(II) ions when diluted by distilled water.

The alkaline tin(II) and lead(II) samples were prepared by adding the calculated amount of the M(II) (M = Sn, Pb) stock solution dropwise to the NaOH solution. The appropriately diluted NaOH solutions were bubbled by argon gas for at least 15 minutes before the addition of the stock solution containing the metal salt.

Chromium perchlorate stock solutions were prepared by reduction of a.r. grade sodium bichromate with hydrogen peroxide in concentrated perchloric acid.

The sodium perchlorate stock solutions were prepared by adding concentrated NaOH solution to an also concentrated $HClO_4$ solution dropwise under continuous stirring and cooling until the complete neutralization.

Each chromium(III)-containing alkaline sample for the kinetic measurements was prepared by weighting the necessary amount of the stock solutions (with known concentrations and densities). The $Cr(ClO_4)_3$ stock solution was added to the previously diluted, cooled and degassed NaOH solution and the time of the addition was registered. The samples were stored in tightly fitted polypropylene vials with the disclosure of light at room temperature.

During the preparation of the acidic chromium(III)-containing samples, the proper amount of the $Cr(ClO_4)_3$ stock solution was added by volume, while the NaOH and $NaClO_4$ stock solutions were added by weight in a volumetric flask. The ionic strength was kept constant at 1 M, adjusted by sodium perchlorate.

2.2 Instrumentation and calculation methods

The pH potentiometric titrations of the tin(II)-containing solutions were carried out using a Metrohm 888 Titrando instrument equipped with H_2/Pt electrode in order to determine the composition of the forming complex. The full electrochemical cell contained a platinized hydrogen electrode and a Ag|AgCl reference electrode. All the titrations were performed in an

externally thermostated home-made cell, and the temperature was kept at 25.00 ± 0.04°C by circulating water from a Julabo 12 thermostat. The ionic strength was kept constant (I = 4 M) with a.r. grade NaCl.

The Raman spectra of the tin(II)- and lead(II)-containing alkaline solutions were recorded on a BIO-RAD Digilab Division dedicated FT-Raman spectrometer equipped with liquid nitrogen cooled germanium detector and CaF_2 beamsplitter. The spectra were recorded in the range of $3600 - 100\ cm^{-1}$ with $4\ cm^{-1}$ optical resolution. 4096 scans were collected and averaged for each sample. The samples were placed in a 1 cm path length quartz cuvette, and the spectra were recorded at room-temperature. Data were processed by the SpekWin software, and the fitting of the Lorentzian curves were performed with QtiPlot.

The X-ray absorption spectroscopy (XAS) was used to reveal the local structure (i.e., coordination number, geometry and interatomic distances) of the investigated metal ions in their hydroxido complexes. The tin K-edge XAS spectra were collected at the bending magnet beam-line Samba at the Soleil synchrotron facility, Paris, France. The measurements were carried out in transmittance mode. The energy scale of the XAS spectra were calibrated by assigning the first inflection point of the tin K-edge of metallic tin foil to 29200.0 eV.

The lead L_3-edge and the chromium K-edge XAS spectra were collected at the wiggler beam-line I811 at MAX-lab, Lund, Sweden, using the MAX II storage ring. For both metals, the measurements were performed in fluorescence mode at the lead L_3-, and the chromium K-edge, respectively. The energy scales of the X-ray absorption spectra were calibrated by assigning the first inflection point of the lead L_3-, and chromium K-edges of the appropriate metallic foil to 13038.0 eV, and 5989 eV, respectively.

The local structure of tin(II) was also investigated by ^{119}Sn Mössbauer spectroscopy. The measurements were carried out for both quick frozen solutions (78 K) and solutions at room temperature. The latter method is called capillary Mössbauer spectroscopy (CMS) and can be carried out with the help of a certain mesoporous silicate glass, the so called Corning Vycor 'thirsty' glass. The spectra were recorded with a conventional Mössbauer spectrometer (Wissel) in transmission geometry with constant acceleration mode. The spectra were analyzed by least-squares fitting of the Lorentzian lines with the help of the MOSSWINN program. The database of the Mössbauer Effect Data Index was used to interpret the results.

The ^{117}Sn NMR measurements were performed at 178.03 MHz on a 1.75 T Bruker Avance NMR spectrometer (500.13 MHz ^{1}H frequency), in 5 mm Wilmad NMR tubes.

The theoretical Raman spectra and the structure of the possible species were also calculated for the tin(II) and lead(II) complexes. Optimizations and frequency analyses were performed using the GAUSSIAN 09 program with density functional theory (DFT) at the B3LYP level, using SDD basis set for tin and lead atoms and 6-31+G** for oxygens and hydrogens. Solvent effects were systematically modelled by representing H_2O as a polarizable continuum, according to the method implemented in the PCM-SCRF (self-consistent reaction field) procedure in the Gaussian program.

The reactions of the chromium(III)-containing systems (both acidic and alkaline) were followed by UV-vis spectroscopy. The measurements were carried out with either a Specord 200 (Analytic Jena) or a Shimadzu UV-1650 double beam spectrophotometer in the 200 – 800 nm range for the alkaline and in the 200 – 900 nm range for the acidic samples using a 1 cm optical path length quartz cuvette. The analysis of the spectra and their kinetic information were carried out with the PSEQUAD, MRA and ZITA program packages.

The pH measurements during the investigation of the hydrolysis of the slightly acidic chromium(III) solutions were carried out with a JENWAY 3540 pH & conductivity meter equipped with a JENWAY 924 001 combined electrode filled with a 2 M $NaClO_4$, 1 M NaCl solution saturated with AgCl.

2. Novel scientific results

T1. In solutions containing $c_{Sn(II)}$ = 0.05 – 0.2 M and c_{NaOH} = 0.1 - 12 M, the predominant species is $[Sn(OH)_3]^-$ with a distorted trigonal pyramidal structure, in which the Sn – O distance and the Debye-Waller factor are 2.078 Å and 0.0038 $Å^2$, respectively. No other species was necessary to be assumed in the system.

1.1 The composition of the predominant tin(II) complex in hyper-alkaline aqueous solutions was determined by potentiometric pH titrations using an H_2/Pt electrode suitable to use at aqueous hyper-alkaline conditions. The Sn(II) : OH^- ratio in this complex was found to be 1 : 3.

1.2 The structure of the hydroxido complex was determined by Raman spectroscopic measurements complemented with quantum chemical calculations. The observed and calculated Raman peaks were practically identical only for $[Sn(OH)_3]^-$. The measured Raman spectra followed the Beer-Lambert law with the increasing tin(II) concentration, confirming that there was only one kind of species present in such highly alkaline solutions.

1.3 The trigonal pyramidal structure was also confirmed by ^{119}Sn Mössbauer spectroscopy of the quick frozen tin(II)-containing strongly alkaline solutions. The tin K-edge X-ray absorption spectroscopy measurements also confirmed the coordination number of three with an average Sn – O distance of 2.078 Å and Debye-Waller factor of 0.0038 $Å^2$.

T2. For Sn(II)-containing solutions, unlike for Sn(IV)-containing ones, capillary Mössbauer spectroscopic measurements (CMS) cannot be carried out either in acidic or in alkaline solutions: the spectra were found to disappear above ~ 190 K, well below the freezing point of the solutions. This is due to the very steep temperature dependence of the Lamb-Mössbauer factor of tin(II) species.

2.1 CMS experiments were performed both in acidic and in alkaline (0.2 M $HClO_4$ and 4 M NaOH, respectively) solutions containing 0.06 M $Sn(ClO_4)_2$, and only the signal corresponding to tin(IV) was detectable in the solutions. Moreover, in alkaline media, during the collection of the spectrum (several days), the 'thirsty' glass was visibly deteriorated. After a couple of days it started to break into pieces, then, it fully disintegrated and finally, it was completely dissolved.

2.2 The temperature-dependent ^{119}Sn Mössbauer spectrum series of a sample containing 0.2 M $SnCl_2$ in 4 M NaOH were collected from 20 K to 180 K. The normalized area of the spectra decreased with the increasing temperature, and the extrapolation of this trend indicated that the spectrum would disappear well below the melting point of the frozen solution.

T3. The predominant species in Pb(II) containing solutions with $c_{Pb(II)}$ = 0.2 M and c_{NaOH} = 4 - 16 M is $[Pb(OH)_3]^-$ with a distorted trigonal pyramidal structure, in which the Pb – O distance and the Debye-Waller factor are 2.216 Å and 0.0330 $Å^2$, respectively.

3.1 The structure of the hydroxido complex was determined by Raman spectroscopic measurements, complemented with quantum chemical calculations. Similarly to Sn(II), the observed and calculated Raman peaks were found to be superimposable only for $[Pb(OH)_3]^-$.

The measured Raman spectra followed the Beer-Lambert law with the increasing lead(II) concentration, thus, it was confirmed that there was only one kind of species in such highly alkaline solutions.

3.2 The trigonal pyramidal structure was also confirmed by X-ray absorption spectroscopy. The lead L_3-edge XAS measurements are consistent with the coordination number of three with an average $Pb-O$ distance of 2.216 Å and Debye-Waller factor of 0.0330 $Å^2$.

T4. Chromium(III) is spontaneously oxidized by either hydroxide or water in alkaline media, even without any traces of oxygen. Although the reaction is very slow, it is completed stoichiometrically. The proposed mechanism is the following, where the starting point is the reaction taking place between the hydroxide and $[Cr(OH)_4]^-$ ions with the rate constant of $(3.0 \pm 0.2)\cdot 10^{-8}$ $M^{-1}s^{-1}$:

$$\cdot Cr(OH)_4^- + OH^- (+ H_2O) \xrightarrow{k_1} Cr^{IV} + \cdot H (+ 6\, OH^-)$$
$$Cr^{IV} (+ H_2O) \xrightarrow{k_2} \cdot Cr^{V} + \cdot H (+ OH^-)$$
$$\cdot Cr^{V} + \cdot H (+ OH^-) \xrightarrow{k_3} Cr^{IV} (+ H_2O)$$
$$\cdot Cr^{V} (+ 7\, OH^-) \xrightarrow{k_4} CrO_4^{2-} + \cdot H (+ 3\, H_2O)$$
$$\cdot Cr(OH)_4^- + \cdot Cr^{V} + OH^- \xrightarrow{k_5} 2\, Cr^{IV} (+ 5\, OH^-)$$
$$Cr^{IV} + CrO_4^{2-} (+ 4\, H_2O) \xrightarrow{k_6} 2\ \cdot Cr^{V} (+ 8\, OH^-)$$
$$2\ \cdot H \xrightarrow{k_7} H_2$$
$$Cr^{IV} + \cdot H (+ H_2O) \xrightarrow{k_8} \cdot Cr^{V} + H_2 (+ OH^-)$$

4.1 Deoxigenated solutions with varying initial chromium(III) and hydroxide concentrations (0.3 – 43 mM and 3 – 12 M, respectively) were prepared, and their UV-vis spectra were followed over a year. The effect of the oxygen and the ionic strength was also investigated.

4.2 The matrix rank analysis of the collected spectra approved that four colored species were needed to explain all the measured absorbances, thus $[Cr(OH)_4]^-$, CrO_4^{2-}, and one chromium(IV) and one chromium(V) containing intermediates were supposed during the model fitting performed by non-linear parameter estimation.

4.3 The kinetic curves can be divided into three ranges. The first two ones can be formally described by zeroth-order kinetic, but with different slope, while the final stage with a simple exponential curve. The above-proposed mechanism represents all these features of the kinetic curve very well.

4.4 With changing NaOH concentration, the rate of the reaction passes through a maximum (at around 6 – 8 M), which can be explained qualitatively by assuming that the rate determining step is a second order one regarding the hydroxide and the $[Cr(OH)_4]^-$. The apparent rate coefficient can be calculated with taking the extended Debye-Hückel theory (including the Davies correction) into account for interpreting the influence of ionic strength, as well as applying the Stokes-Einstein equation to consider the change of the viscosity.

T5. Contrary to the literature data, where oligo- and polymeric species were claimed to form, only $[Cr(OH)_4]^-$ is present in freshly prepared solutions with 8 M sodium hydroxide. There is no further oligomerization even after significant aging is allowed (~ 1.5 year).

5.1 UV-vis spectra of $Cr(ClO_4)_3$ solutions in 8 M NaOH were recorded after mixing the stock solutions. The number of independent absorbing species was determined by matrix rank analysis, and the calculations showed that the rank is strictly one. Non-linear parameter estimation was also used to find species other than $[Cr(OH)_4]^-$, but the description could not be improved with assuming further species. These calculations proved that only $[Cr(OH)_4]^-$ was present in significant concentration.

5.2 The X-ray absorption spectra of a series of 0.5 M chromium(III) in 8 M NaOH were collected. The solutions were aged for various times up to one month. All the EXAFS spectra were the same within the experimental uncertainty, regardless of the age of the solutions and whether it contained precipitate or not. The spectra could be fitted without assuming any oligomeric species, also indicating that the $[Cr(OH)_4]^-$ was the only dominant one in solution phase.

T6. The widely accepted oligomerization of Cr(III) cannot be confirmed in slightly acidic solutions, where $0 < T(OH^-) / T([Cr(H_2O)_6]^{3+}) < 1$. In such reactive systems, the initial measured pH values can be explained via assuming the formation of $[Cr(OH)]^{2+}$ and $[Cr(OH)_2]^+$. The pH of these solutions monotonously decreases with time until the equilibrium is reached (more than a year). To describe the reaction, a mechanism also was proposed.

$$Crw_6^{3+} \underset{k_{11}^b}{\overset{k_{11}^f}{\rightleftharpoons}} Crw_5OH^{2+} + H^+$$

$$Crw_5OH^{2+} \underset{k_{12}^b}{\overset{k_{12}^f}{\rightleftharpoons}} Crw_4(OH)_2^{+} + H^+$$

$$2\,Crw_5OH^{2+} \underset{\text{too slow}}{\overset{k_{13}}{\rightleftharpoons}} w_5Cr{-}O{-}Crw_5^{4+}$$

$$2\,Crw_4(OH)_2^{+} + H_2O \underset{\text{too slow}}{\overset{k_{14}}{\rightleftharpoons}} w_5Cr{-}O{-}Crw_5^{4+} + 2\,OH^-$$

$$2\,Crw_4(OH)_2^{+} \underset{\text{too slow}}{\overset{k_{15}}{\rightleftharpoons}} w_4Cr{-}O_2{-}Crw_4^{2+}$$

$$w_4Cr{-}O_2{-}H{-}Crw_4^{3+} \underset{k_{16}^b}{\overset{k_{16}^f}{\rightleftharpoons}} w_4Cr{-}O_2{-}Crw_4^{2+} + H^+$$

$$w_5Cr{-}O{-}Crw_5^{4+} \underset{k_{17}^b}{\overset{k_{17}^f}{\rightleftharpoons}} w_4Cr{-}O_2{-}Crw_4^{2+} + 2\,H^+ + H_2O$$

6.1 The stability products of $[Cr(OH)]^{2+}$ and $[Cr(OH)_2]^+$ were found to be $\lg\beta_1 = -4.28 \pm 0.03$ and $\lg\beta_2 = -8.86 \pm 0.03$, respectively, with the value of $pK_w = 13.76$. Any other speciation yielded poor fits, and described our measurements with at least five-fold higher average residual. The $\lg\beta_1$ is practically identical with the ones reported, while our $\lg\beta_2$ results in the less significant presence of $[Cr(OH)_2]^+$ relative to previous reports in the literature.

6.2 The reaction between $[Cr(OH)]^{2+}$ and $[Cr(OH)_2]^+$ is responsible for the kinetic changes. It was experimentally proven that all steps were equilibrium ones, and the final solution contained only dimers, consequently, the presence of more complicated oligomers is not supported by these measurements.

6.3 X-ray absorption spectra of our solutions could be fitted satisfactorily by supposing only one Cr – Cr distance, suggesting that only the dimeric species are present, and higher oligomers are absent.

3. Publications

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