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THERMAL BEHAVIOUR OF TIN(II) COMPLEX WITH 8-HYDROXYQUINOLINATE IN THE SOLID STATE

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Abstract

Tin(II) complexes with 8-hydroxyquinolinate in solid state have been obtained by adding aqueous ammonium to a solution containing stannous chloride and 8-hydroxiquinoline in medium of HCl and acetone up to pH 5 and 9, respectively. The products obtained show the same composition, $Sn(C_9H_6ON)_2$; however there are some differences regarding both the thermal behaviour in an oxidant atmosphere and morphology. These products were characterised by elemental and complexometric analysis, TG and DTA curves, infrared and X-ray diffractometry. TG curves show, above 448 K, the partial oxidation on air atmosphere of Sn(II) complexes to Sn(IV) complexes, $SnO(C_9H_6ON)_2$. This behaviour does not depend only on pH in which the compounds were obtained but also on the heating rate in TG curves. Sn(II) complexes volatilise almost completely on nitrogen atmosphere and partially on air atmosphere depending on the oxidation degree of the compound.

Keywords: 8-hydroxyquinoline, oxidation, thermal behaviour, tin(II) complexes, volatilisation

Introduction

Tin(IV) complex with 8-hydroxyquinoline, $Sn(C_9H_6ON)_4$, was reported in 1950 by Centry and Sherrington [1]; nevertheless, its precipitation was incomplete and the compound shows high proportion of hydroxide.

In 1965 Ramaniah and Martin [2] reported the production of tetrakis(8-hydroxyquinolinate)tin(IV) by heating, at 573 K, of a mixture of phenylbis(8-hydroxyquinolinate)tin(IV) and 8-hydroxyquinoline. The compound obtained had its melting point around 673 K and C_6H_6 liberated was removed by distillation.

Bis(8-hydroxyquinolinate)tin(II) was prepared by Doskey and Curren [3] in 1969, in oxygen-free water medium under nitrogen atmosphere. 8-Hydroxyquinoline was dissolved in a stoichiometric amount of sodium hydroxide solution and the calculated quantity of $SnCl_2$ was added during constant stirring. The product was studied by infrared and Mössbauer spectra.

The adduct $SnCl_4 \cdot n$OxH, where n=1 or 2, was reported by Frazer and Goffer [4] in 1966, by mixing 8-hydroxyquinoline (OxH) and the appropriate tetrahalides in the medium of $CHCl_2$. It was suggested, in these adducts, that the ligand 8-hydroxyquinoline was probably unidentate.

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Akiyama *et al.* [5] in 1966, reported the preparation of Sn(II) complexes with 8-hydroxyquinoline and Sn(IV) complexes with 8-hydroxyquinoline and 5,7-dichloro derivative by adding $SnCl_2$ or $SnCl_4$, respectively, to a solution of ligand in the medium of HCl. The compounds obtained were $Sn(C_9H_6ON)_2$, $Sn(C_9H_6NO)_2Cl_2$ and $Sn(C_9H_4NOCl_2)_2Cl_2$.

Tin(II) complexes with 8-hydroxyquinoline and 5,7-dichloro, 5,7-dibromo, 5,7-diiodo derivatives were prepared by Bhide *et al.* [6] in 1977, and the products characterised by their elemental analysis, infrared and UV-visible spectra data. Tin(IV) chelates were obtained by the reaction of these complexes with biphenyl disulphide, dibenzoylperoxide, iodine and others.

In this work, Sn(II) complexes with 8-hydroxyquinoline have been prepared by precipitation medium of acetone and HCl by adding aqueous ammonium up to pH 5 and 9. The compounds obtained were characterised by thermogravimetric and DSC curves on several heating rates and oxidant and inert atmospheres, elemental and gravimetric analysis, infrared spectra and X-ray diffractograms data.

Experimental

4.2 mmol of metallic tin was dissolved in a minimum quantity of hot concentrated chloridric acid to obtain $SnCl_2$ in the medium of HCl, in which volume was filled with water up to 200 mL. This solution was added, during constant stirring, to an excess of 8-hydroxyquinoline dissolved in acetone, and the precipitates were obtained by raising pH to 5 (A) and 9 (B), respectively. The precipitates were washed first with distilled water up to the total elimination of chloride and after with 10% acetone solution, to eliminate the excess of 8-hydroxyquinoline. They were then dried at 333 K.

The compounds, after wet digestion with a mixture of concentrated sulphuric acid and 30% hydrogen peroxide, were characterised gravimetrically as SnO_2 concerning the metal.

8-Hydroxyquinoline content was determined by elemental analysis (C, N, H).

TG-DTG and DSC curves were obtained using a Mettler TA-4000 thermoanalyser system on synthetic air and nitrogen atmospheres with flux of 150 mL min^{-1}, on different heating rates, sample mass around 7 mg, alumina crucible to TG/DTG curves and aluminium crucible to DSC curves.

X-Ray powder diffraction patterns were performed on a HZG 4/B horizontal diffractometer in a Bragg-Bretano arrangement and CoK_α radiation (λ=1.7889 Å), with proportional counter and pulse-height discriminator.

Infrared absorption spectra were obtained over the range of 4000–200 cm^{-1} by Bomem-Hartmann and Braun Infrared Spectrophotometer with 4 cm^{-1} of resolution.

Results and discussion

Through analytical and thermal analytical methods it has been verified that the compounds present the same composition, $Sn(C_9H_6ON)_2$, Table 1.

Table 1 Sn, C, H and N data from gravimetric, elemental analysis and TG curves

Compounds		Theoretical and experimental contents/%			
		theor.	exp.	grav.	TG
$Sn(C_9H_6ON)_2$ (A) pH 5	Sn	29.18	–	28.89	29.14
	C	53.10	51.03	–	–
	H	2.98	2.88	–	–
	N	6.88	6.76	–	–
$Sn(C_9H_6ON)_2$ (B) pH 9	Sn	29.18		29.02	–
	C	53.10	53.08	–	–
	H	2.98	3.03	–	–
	N	6.88	6.84	–	–

IR spectra of the compounds, Figs 1a–b, show a very strong main band in 1104 cm^{-1} attributed to the electron distribution charge around C–O group due to Sn–O bond, characteristic bands due to Sn–O–Sn bond in 733 cm^{-1}, S–N stretching frequency in 381 cm^{-1} and Sn–O mode in 514 and 572 cm^{-1} [7–9]. It suggests the occurrence of metal bond through both the nitrogen and oxygen atoms from the ligand.

Through X-ray diffractograms, Figs 2a–b, it is verified the 2θ changes and intensity of the peaks between compounds A and B, which may be related to distinct morphologies depending on the pH in which these compounds were obtained. The X-ray of compound B suggests more than one crystalline phase, in which, one of them might be from A.

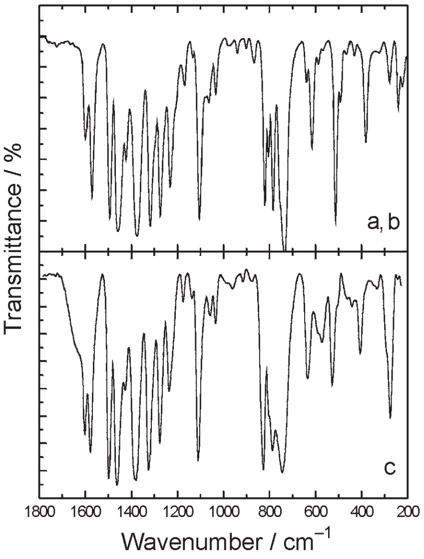

Fig. 1 IV spectra (1a–b) representative to compounds A and B, (1c) compound B heated up to 503 K

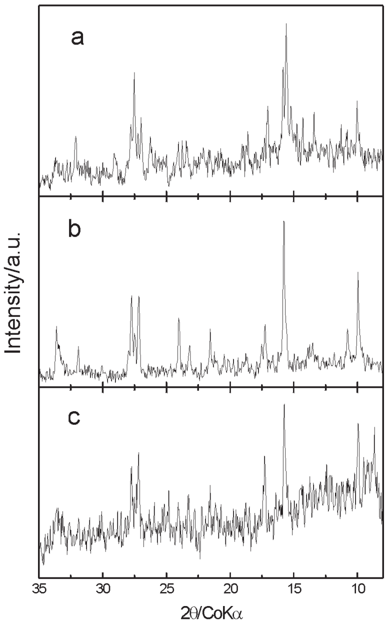

Fig. 2 X-ray diffractograms to compound A (2a), compound B (2b) and compound B (2c) heated up to 503 K

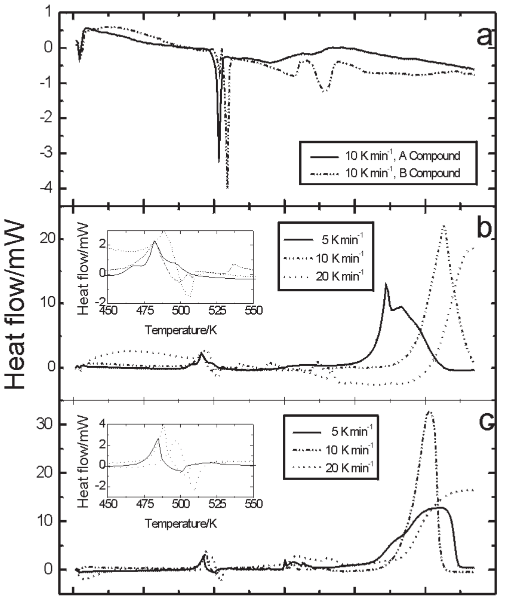

Fig. 3 DSC curves on nitrogen (3a) to compounds A and B, on synthetic air (3b) to compound A and on synthetic air atmosphere (3c) to compound B

DSC curve, Fig. 3a, in N_2 atmosphere and 10 K min^{-1}, shows the endothermic peak, at 507 K, due to the fusion to compound A while two consecutive endothermic peaks were observed to compound B. The first small intense one at 507 K, like in compound A, and a second very intense at 519 K indicate more than one morphology to compound B as mentioned through X-ray data.

Above 523 K the volatilisation of both compounds through two wide peaks at 581 and 637 K and through 613 and 658 K of compounds A and B is observed.

TG curves of compounds A and B, Figs 4b–d, on nitrogen atmosphere and 5, 10 and 20 K min^{-1} show the beginning mass loss above 448 K with almost complete volatilisation up to 748 K and the formation of a residue as oxide and carbonaceous compounds which does not decompose totally up to 1173 K.

TG curves on oxidant atmosphere, Figs 4a–c, show different behaviour regarding the oxidation process of Sn(II) to Sn(IV) compound with a mass gain depending on the heating rate, Table 2.

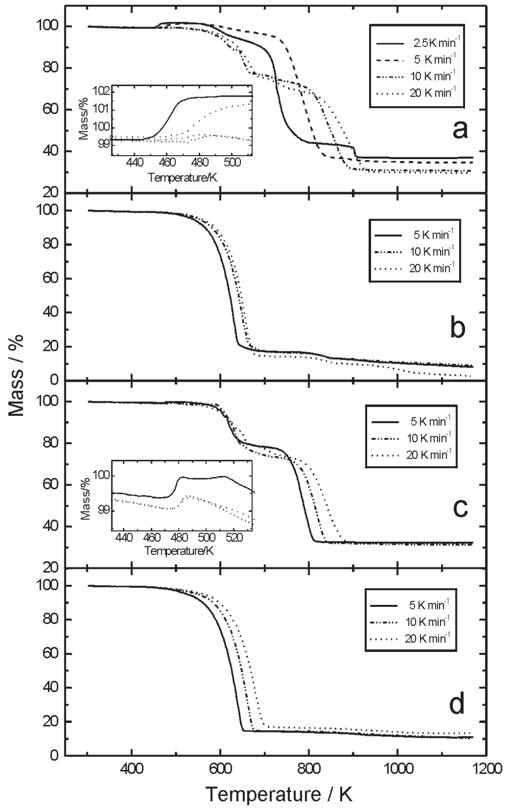

Fig. 4 TG curves to compound A in synthetic air (4a), nitrogen (4b) and compound B in synthetic air (4c) and nitrogen (4c) atmosphere

Table 2 Oxidation (%) from $Sn(C_9H_6ON)_2$ to $SnO(C_9H_6ON)_2$, amount of SnO_2 residues (%) and volatilised tin(II) complex (%) obtained through TG curves on synthetic air

$Sn(C_9H_6ON)_2$		Oxidation/%	Residue SnO_2/%		Volatilised complex/%
pH	heating rate	Sn(II)→Sn(IV)	obtained	expected	
5	2.5	62.89	37.09	100	0
	5	49.37	34.87	94.19	5.82
	10	9.16	31.04	83.82	16.18
	20	7.32	29.96	80.92	19.08
9	5	13.99	32.34	87.32	12.68
	10	9.38	31.52	85.12	14.88
	20	7.72	32.13	86.76	13.24

For compound A an increase in the oxidation from Sn(II) to Sn(IV) compound with the decrease in the heating rate, which reaches up to around 63% of oxidation to 2.5 K min^{-1} is verified. On the other hand, the volatilised material decreases with the lowest heating rate, suggesting that it is due to Sn(II) compound.

For compound B, either the oxidation and consequently the volatilisation process presented low and not too much significant changes according to the heating rate as observed to compound A. However, the behaviour observed for both compounds are relatively similar to the heating rate equal or higher than 10 K min^{-1}.

Neither compounds A or B present proportionality between the amount of oxidised/volatilised compounds suggesting that the oxidised compound causes the thermal decomposition of Sn(II) compound.

DSC curves on synthetic air atmosphere, Figs 3b–c, show exothermic peaks above 448 K attributed to the oxidation of Sn(II) in the compounds, followed by an endothermic peak to 10 K min^{-1} or higher due to the remaining Sn(II) compound. After this, the observed endothermic peaks are probably due to the partial volatilisation of Sn(II) compound along with the exothermic peaks attributed to the oxidation of remaining Sn(II) compound and thermal decomposition the Sn(IV) compound.

IR spectrum, Fig. 1c, obtained for both of the compounds heated up to 503 K in 2.5 K min^{-1}, when the maximum oxidation occurs, does not show the presence of an intense band between 1000 and 900 cm^{-1} referring to Sn=O, suggesting the formation of Sn–O–Sn through bridge bond. The X-ray diffractogram of the heated materials up to 503 K, Fig. 2c, shows that compound B still presents the crystalline Sn(II) compound.

Conclusions

In spite of the same composition, pH, in which the complexes are precipitated, may result in the formation of compounds with different structures and thermal behaviour.

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