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REACTION PRODUCTS BETWEEN SODIUM DIPHENYL -AMINE-4-SULFONATE AND HYDRATED $LaCl_3$ Thermogravimetric and spectroscopic study

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Abstract

This paper presents the reactions of synthesis between the ligand sodium diphenylamine-4-sulfonate and the lanthanum(III) chloride hydrated. The compounds $(LaCl_3)_2{\cdot}(C_{12}H_{10}NSO_3Na)_3{\cdot}2(CH_3CH_2OH)$ (A) and $(LaCl_3){\cdot}(C_{12}H_{10}NSO_3Na){\cdot}(CH_3CH_2OH){\cdot}12H_2O$ (B) were obtained using the solvents ethanol and methanol (synthesis A) and ethanol and water (synthesis B). The produced compounds and the ligand were characterized by thermogravimetric and differential thermogravimetric analysis, IR spectroscopy and elemental analysis of sodium, carbon, hydrogen, nitrogen, sulfur, chlorine and lanthanum, whereas the residues from thermal decomposition were investigated by X-ray diffractometry.

Keywords: complexes, lanthanides, sulfonates

Introduction

The sulfonate compounds have important functions in many areas of applied chemistry, being used as additives in the cement and concrete in building material, as organic polymers dopants, in the catalysis fields, as dopants in electrochemical films, as surfactant in light industry and in the chemical separation [1–4]. Nearly all sodium sulfonate products can be used as emulsifier additives, corrosion inhibitor additives, metalworking fluids and cutting [5–7].

Particularly, sodium diphenylamine-4-sulfonate has been investigated on the chemical copolymerization with aniline for the formation of water–soluble conducting copolymers. The chemical polymerization produces the poly(aniline-co-N-(4-sulfophenyl)aniline) (PAPSA), copolymers with high molecular masses presenting electrical conductivities that range between those of the poly(N-(4-sulfophenyl)aniline) homopolymer (0.0035 S cm^{-1}) and of polyaniline (5.2 S cm^{-1}) [8, 9].

This paper reports the synthesis reaction between the sodium diphenylamine-4-sulfonate and lanthanum(III) chloride hydrated employing the solvents ethanol and

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methanol in the route of the synthesis of the compound A and ethanol and water in the route B. Thermogravimetric (TG) and differential thermogravimetric (DTG) analysis were employed associated with infrared (IR) spectroscopy and elemental analysis for the study of the prepared compounds, while X-ray diffractometry (XRD) was used for the structural characterization of the residues from thermal decomposition of the compounds.

Experimental

All the experimental procedures were performed under pure argon atmosphere using vacuum line apparatus. Benzene was purified with sulfuric acid solution, neutralized with sodium bicarbonate solution, then dried with metallic sodium and distilled under O_2-free argon. Ethanol and methanol were distilled several times to eliminate contaminants, followed by a silica gel column and then stored in flasks with calcium sulfate.

The compound A was prepared assembling an ethanol/methanol solution of the ligand diphenylamine-4-sodium sulfonate (0.001423 mols) and an ethanol solution of the lanthanum(III) chloride hydrated (0.000949 mols), in a molar ratio of 1.5:1 moles. The compound B was achieved using lanthanum chloride hydrated (0.001195 mols) in ethanol/water solution of the ligand (0.001794 mols) keeping the same stoichiometry 1.5:1 mols. Both products were crystallized by the addition of benzene. The crystallized products were washed several times with small volumes of heated benzene to remove the solvent and ligand trace. The ligand oxidation products can be avoided by maintaining the reactional solution under vacuum, in the absence of light and under constant agitation.

Elemental analysis of Na was executed on a Spectroflame Plasma Atomic Absorption spectrophotometer, employing the methodology of internal standard. Elemental analysis (CHN) was performed on a Perkin Elmer 2400 microanalytical analyzer instrument. Quantitative elemental analysis of lanthanum(III) was performed by EDTA complexometric titration.

IR spectra were obtained on a Jasco IR-700 and Midac Prospect FTIR instrument (scan number=16, smooth=60% and uncorrected baseline) using nujol mulls and KBr pellets.

TG analysis was conducted using a Shimadzu TGA-50H thermoanalyser. The samples (with nearly the same initial masses) were heated in alumina crucibles under nitrogen flow (30.0 mL min^{-1}) at a heating rate of 2.0°C min^{-1}. The interior of the TG apparatus was vacuum cleaned and filled with nitrogen three times before the start of each measurement. The DTG curves were computationally derived from the TG curves.

XRD powder patterns were recorded with a Rigaku 4053A3 diffractometer equipped with a proportional counter and pulse height discriminator and using CuK_α radiation (λ=1.5418 Å). The patterns were recorded from 2θ=10 up to 100°. An oriented graphite crystal was employed as monochromator and powdered silicon (<200 Mesh) was used as an external reference standard.

Results and discussion

The solid products were obtained in good yield and revealed to be stable with the molecular formulas: $(LaCl_3)_2{\cdot}(C_{12}H_{10}NSO_3Na)_3{\cdot}2(CH_3CH_2OH)$ (A) and $(LaCl_3)(C_{12}H_{10}NSO_3Na)(CH_3CH_2OH){\cdot}12H_2O$ (B), obtained from the elemental analysis results, as shown in Table 1.

Table 1 Elemental analysis results for compounds A and B

	Compound A/%		Compound B/%	
	Theoretical	Experimental	Theoretical	Experimental
C	34.33	33.54	21.59	21.56
H	3.00	2.90	5.14	3.52
N	3.00	3.19	1.80	1.85
Na	4.90	5.00	–	–
S	7.00	6.90	4.11	4.22
Cl	7.60	7.22	13.66	15.08
La	19.87	18.50	17.85	18.19

The ligand sample and the products were analyzed by IR spectroscopy, as shown in Fig. 1. The assignments of the detected IR bands are summarized in Table 2. The IR spectra of the compounds A and B do not reveal any contamination as ligand excess, concerning the examination effected on the sulfonate frequencies. The decrease on intensities of the ligand's frequencies of 748, 841 (bending C–H aromatic), 1513

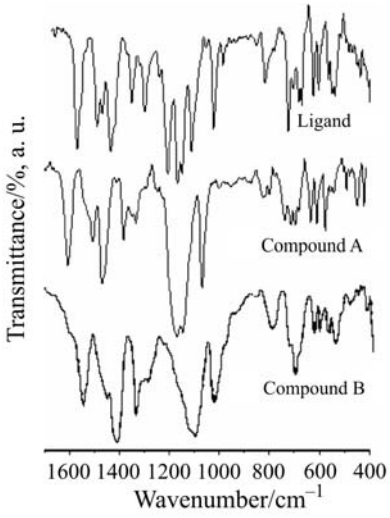


Fig. 1 Infrared spectroscopy analysis of the ligand and compounds A and B, respectively

and 1440 (stretching C=C aromatic) and 1322 (stretching C–N aromatic) cm^{-1} can be associated with the changes on the frequencies of vibrations of the carbon and nitrogen atoms of the aromatic system after the lanthanide ion complexation and to the interaction of the alcohol molecules of the solvent with the ligand molecule. Although the band of frequency 841 cm^{-1} has practically disappeared after the complex formation, the effect noted is also expressive over the 707, 693, 647, 626, 587, 572 and 561 cm^{-1} ligand frequencies.

However, the most remarkable effect of the complex formation is due to displacements of the deformation frequencies of the sulfonic group [10, 11]. The IR data revealed that the frequencies of 1230–1190 and 1050 cm^{-1} of the sulfonic group in the ligand IR spectrum are shifted to values of 1160–1140 and 1070 cm^{-1}, respectively, in the IR spectrum of compound A, corresponding to the most genuine consequence of the interaction between the lanthanide ion and the oxygen of the sulfonic group [11].

Table 2 Infrared data attributions for the ligand and compounds A and B

Attribution	Ligand	Compound A	Compound B
Stretching N–H	3381(s)	3374(s)	3370(s)
Strethching C–H aromatic	3100(w)	3110(w)	3114(w)
Bending N–H	1594(s)	1593(s)	1591(s)
Stretching C=C	1585(sh), 1513(s), 1450(s)	1511(w)	1520(sh), 1452(m)
Stretching C–N aromatic	1322(s)	1328(w)	1327(m)
Stretching M–SO_3	1230(s), 1190(s), 1173(s), 1136(s), 1047(s)	1166(s), 1146(s), 1070(s)	1131(s), 1060(s)
Bending	841(s), 748(s), 730(v)	747(w), 720(v)	844(m), 821(m)
C–H aromatic	707(v), 693(s)	691(w)	740(m), 722(s)

s – strong, w – weak, m – medium, v – variable, sh – shoulder

The TG/DTG curves for the decomposition of compound A are shown in Fig. 2. The mass loss data and the corresponding interpretation are summarized in Table 3 and Scheme 1. The analysis of the XRD pattern of the TG residue of compound A allows its identification as the lanthanum oxide sulfate with the molecular formula $La_2O_2SO_4$, in agreement with the proposed scheme of decomposition. The stability of interaction lanthanide/ligand could be emphasized by the presence of the oxide sulfate as the decomposition residue [12, 13].

Some low intensity peaks observed around 31 and 34°C in this pattern could not be unambiguously identified, being probably associated with minor phases containing Na oxides.

The TG curve of compound B (also shown in Fig. 2) was interpreted as composed of three stages, as presented in Table 3 and Scheme 2. The XRD of this residue

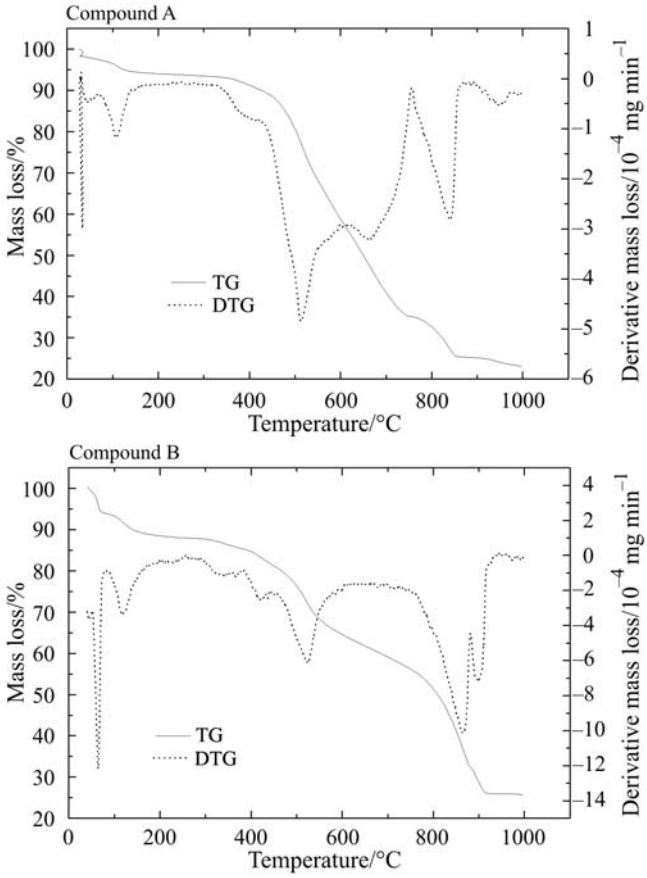
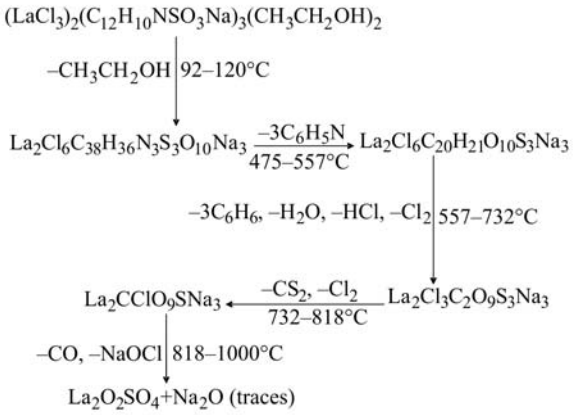
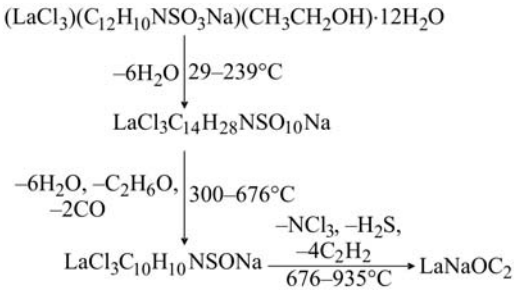


Fig. 2 TG and DTG curves for the ligand and compounds A and B



Scheme 1 Thermal decomposition mechanism for compound A



Scheme 2 Thermal decomposition mechanism for compound B

indicates the occurrence of La_2O_3. The presence of Na compounds is not evident in this XRD pattern, although some low-intensity peaks observed in the XRD pattern of the residue of compound A have been also detected in the XRD pattern corresponding to the residue of compound B. These weak peaks could be assigned to Na carbonates, which would be produced as a consequence of air exposition of the TG residue prior to and during the XRD analysis.

Table 3 Summarized TG data and assignments for compounds A and B

Compound	TG T_{range}/°C	Assignment	Exp. mass loss (theor. mass loss)%
A	92–120	loss of CH_3CH_2OH	3.45 (3.39)
	475–557	loss of $3C_6H_5N$	20.66 (20.15)
	557–732	loss of $3C_6H_6$, H_2O, HCl and Cl_2	26.57 (26.52)
	732–818	loss of CS_2 and Cl_2	11.29 (10.85)
	818–1000	loss of NaOCl and CO	7.93 (7.56)
		leaving the residue $La_2O_2SO_4$ and Na_2O (traces)	69.90 (68.50)
B	29–239	loss of $6H_2O$	13.66 (13.87)
	300–676	loss of $6H_2O$, CH_3CH_2OH and 2CO	26.94 (26.97)
	676–935	loss of NCl_3, H_2S and $4C_2H_2$	33.73 (33.22)
		leaving the residue $LaNaOC_2$	74.33 (74.06)

The poor signal to noise ratio of these XRD spectra, caused by the small amount of powder (residue from TG analysis) employed in the measurement, precludes the accomplishment of a more conclusive analysis on the structure of the compounds found in the residual samples.

Conclusions

The results presented in this paper stimulate the continuous effort on this research field of the diphenylamine-4-sulfonate compounds, once small changes in the reactional conditions allowed the formation of two particular compounds with different stoichiometries (metal to ligand ratios of 1:1 for compound A as compared to 2:3 for the compound B). As already mentioned here, this behavior is unexpected for compounds of lanthanide ions indicating the occurrence of the different level of interaction ligand/solvent.

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