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Thermodynamic investigation on the reactions of formation of the compounds $RE(C_5H_8NS_2)_3(C_{12}H_8N_2)$ ($RE = Eu$, Tb)

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Abstract

The reactions of ammonium pyrrolidinedithiocarbamate (APDC) and 1,10-phenanthroline (*o*-phen · H_2O) by hydrated lanthanide chlorides in the presence of absolute ethanol yield two novel lanthanide derivatives represented with the empirical formula $RE(PDC)_3(phen)$ (RE = Eu, Tb). The resulting compounds were characterized by elemental analysis, TG-DTG and i.r. spectrum. The enthalpy change of the reaction of complex formation from a solution of the reagents, $\Delta_r H_m^\theta(1)$, and the molar heat capacities of the compounds, c_m, were determined at $T = 298.15$ K by using an RD496-III heat conduction microcalorimeter, which were $(-22.21 \pm 0.08)\ kJ \cdot mol^{-1}$ and $(61.68 \pm 0.65)\ J \cdot mol^{-1} \cdot K^{-1}$ for $Eu(PDC)_3(phen)$ and $(-21.04 \pm 0.05)\ kJ \cdot mol^{-1}$ and $(67.74 \pm 0.60)\ J \cdot mol^{-1} \cdot K^{-1}$ for $Tb(PDC)_3(phen)$, respectively. On the basis of the appropriate thermochemical cycles and other auxiliary thermodynamic data, the enthalpy changes of formation of the compounds from the reactions of the regents in solid phase, $\Delta_r H_m^\theta(s)$, were calculated as being $(54.53 \pm 0.31)\ kJ \cdot mol^{-1}$ for $Eu(PDC)_3(phen)$ and $(40.20 \pm 0.36)\ kJ \cdot mol^{-1}$ for $Tb(PDC)_3(phen)$. The thermodynamics of reactions of formation of the compounds were investigated by the reactions in ethanol. Fundamental parameters, the activation enthalpy ($\Delta H_{\neq}^\theta$), the activation entropy ($\Delta S_{\neq}^\theta$), the activation free energy ($\Delta G_{\neq}^\theta$), the apparent reaction rate constant (k), the apparent activation energy (E), the pre-exponential constant (A) and the reaction order (n), were obtained by combination of the thermochemical data of the reaction and kinetic equations with the data of thermokinetic experiments.

Keywords: Hydrated europium chloride; Hydrated terbium chloride; Ammonium pyrrolidinedithiocarbamate; 1,10-Phenanthroline; The enthalpy change of formation of compound; Thermodynamics

1. Introduction

The characterizations of inorganic-organic hybrid complexes reference to rare earth elements dithiocarbamates are of upsurge interest, mainly due, on one hand, to their relevance to the ceramics industry and thin materials [1] and, to the challenge that the binary complexes exhibit high sensitivity to moisture, so these compounds should be synthesized under strongly anhydrous condition [2]. It is noteworthy that the class of these complexes can be used as precursors to generate the lanthanide sulfide nanocrystallites *via* thermo-decomposition conveniently [3–5].

Calorimetry represents a unique technique to gather information about thermodynamics and kinetics when chemical and physical processes are accompanied by heat effects [6]. Reaction calorimetry has a wide application in thermal and kinetic analyses of chemical reactions. Although there have been structural and spectroscopical reports on these complexes [7–10], to our knowledge, experimental data on the thermodynamic behaviors of the compounds are sparse.

As one part of our continual effort in this series of complexes, we herein reported two novel complexes synthesized by the reaction of the corresponding lanthanide salts with ammonium pyrrolidinedithiocarbamate (APDC) and 1,10-phenanthroline (*o*-phen · H_2O) in absolute ethanol, and their detailed characterization by chemical analyses,

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elemental analyses, i.r. spectrum and TG-DTG technique. The enthalpy changes of the reactions in solution above indicated and the molar heat capacities of the resultant solid compounds at $T = 298.15$ K were determined by a microcalorimeter. The enthalpy changes of formation of compounds from the reactions of the regents in solid phase were derived from the rational thermochemical cycles. The thermodynamics of the reactions in ethanol at different temperatures were investigated and the thermochemical parameters, the apparent reaction rate constant (k), the apparent activation energy (E), the pre-exponential constant (A), the reaction order (n), the activation enthalpy ($\Delta H^{\theta}_{\neq}$), the activation entropy ($\Delta S^{\theta}_{\neq}$), the activation free energy ($\Delta G^{\theta}_{\neq}$), and the activation enthalpy ($\Delta_r H^{\theta}_{\neq}$), were obtained on the basis of reaction thermodynamic and kinetic equations.

2. Experimental

2.1. Reagents

$EuCl_3 \cdot 5.96H_2O$ and $TbCl_3 \cdot 3.75H_2O$ were prepared according to reference [11]. Ammonium pyrrolidinedithiocarbamate (abbreviated as APDC, mass fraction higher than 0.9950) and 1,10-phenanthroline (abbreviated as o-phen · H_2O, mass fraction higher than 0.9950) were commercially obtained from Shanghai Regent Factory. They were maintained in desiccators over P_4O_{10} before the calorimetric measurements. Absolute ethanol and dichloromethane are of A.R. grade from Xi'an chemical reagent company. Potassium chloride (mass fraction 0.9999) was purchased from Shanghai No. 1 Regent Factory, Shanghai, China, and dried in a vacuum oven at 500 K for 8 h prior to use. The gamma aluminum oxide are of spectroscopic pure from Shanghai No.1 Regent Factory, which was transformed to α-aluminum oxide in muffle oven at 1473 K prior to use and maintained in desiccator over P_4O_{10}.

The relative atomic masses used were those recommended by IUPAC Commission [12].

2.2. Equipments and analyses methods

The contents of Eu^{3+} and Tb^{3+} were determined volumetrically with EDTA by complexometric titration, the content of Cl^{-1} was determined by $AgNO_3$ titration; C, H, N and S contents were carried out by using a Vario EL III CHNOS elemental analyzer.

The spectra were obtained with samples in KBr matrix for the title compounds and ligands. A BEQ UZNDX-550 series FT-IR spectrophotometer in the $4000\ \mathrm{cm}^{-1}$ to $400\ \mathrm{cm}^{-1}$ region was used. The TG-DTG tests were performed from $T = 303.15$ K to $T = 773.15$ K in a Perkin–Elmer thermobalance and under dynamic atmosphere of high purity N_2 (mass fraction 0.99999) with flow rate of $60\ \mathrm{cm}^3 \cdot \mathrm{min}^{-1}$ and a heating rate of $10\ \mathrm{K} \cdot \mathrm{min}^{-1}$. The ICP-OES spectroscopy was carried out for checking the progress of the reaction occurring in the calorimetric experiments using a Perkin–Elmer ICP Liberty 150 instrument. The phase structure of the solid combustion product was identified by a Rigua D/max-OC X-ray diffractometer using Cu Kα radiation. Calorimetric measurements were performed using an RD496-III type microcalorimeter [13], in which a Mettler AE 240 balance with the precision of 0.00001 g was employed to determine the mass of the sample. The purity of the compound was attested by a HP-1100 type high-performance liquid chromatography analyzer, the solvent was CH_2Cl_2, the rinsing reagent was CH_2Cl_2 and the column was contra-phase carbon-18.

2.3. RD496-III heat conduction calorimeter

All the enthalpies of solutions and that of reaction were measured by an RD496-III micro-calorimeter. The principle and structure of the calorimeter were described in detail elsewhere [13]. The working temperature of the calorimeter lies in the range of 77.15 K to 473.15 K.

The baseline stability was determined at a constant temperature and with a rising temperature at a stated heating rate. Keeping the temperature at $T = 313.15$ K for 50 h, the baseline change was less than ±0.2 μV. While raising the temperature from $T = 313.15$ K to $T = 473.15$ K at the speed of $1\ \mathrm{K} \cdot \mathrm{h}^{-1}$, the stability was $0.4\ \mu\mathrm{V} \cdot \mathrm{K}^{-1}$.

The calorimetric constants at (292.15, 295.15, 298.15, and 301.15) K were determined by the Joule effect before experiment, which were (63.69 ± 0.04), (63.80 ± 0.04), (63.90 ± 0.03), and $(64.00 \pm 0.03)\ \mu\mathrm{V} \cdot \mathrm{mW}^{-1}$ and the uncertainties associated to the calorimetric constants spanned in the range 0.05% to 0.06%. The reliability of the calorimeter was verified by measuring the dissolution enthalpy of KCl (calorimetrically primary standard) in double distilled water at $T = 298.15$ K. According to the molar ratio of KCl to water, $n_{\mathrm{KCl}} : n_{\mathrm{H_2O}} \approx 1 : 500$, a known amount of KCl was dissolved in double distilled water at $T = 298.15$ K. The average enthalpy of dissolution of KCl determined from the 6 tests was, $\Delta_s H^{\theta}_{\mathrm{m,KCl}} = (17.58 \pm 0.04)\ \mathrm{kJ} \cdot \mathrm{mol}^{-1}$, which is in agreement with the published value $(17.584 \pm 0.007)\ \mathrm{kJ} \cdot \mathrm{mol}^{-1}$ [14].

2.4. Syntheses of the compounds

A mixture of $RECl_3 \cdot nH_2O$ (RE = Eu, $n = 5.96$; RE = Tb, $n = 3.75$), o-phen · H_2O, and APDC in a molar relation salt/phen/APDC of 1/1/3, were dissolved independently in a minimal amount of absolute ethanol. To the mixed ethanolic solution of o-phen · H_2O and APDC, the ethanolic solution of salt was slowly drop-wise under electromagnetically stirring. The reaction mixture was allowed to stand for 30 min resulting in the formation of a solid which was filtered, washed with three small portions of absolute ethanol and recrystallized with CH_2Cl_2. The resulting crystals were dried in vacuum and stored in a desiccator over P_4O_{10} ready to be used.