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THE THERMAL DECOMPOSITION OF THE COMPLEXES OF ZIRCONIUM(IV) EXTRACTED FROM HYDROCHLORIC ACID SOLUTIONS WITH TRI-*n*-OCTYLAMINE AND TRICAPRYLMETHYLAMMONIUM CHLORIDE

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ABSTRACT

The complexes of zirconium(IV) prepared by drying in vacuo the organic solutions from the extraction of aqueous zirconium chloride solution with tri-*n*-octylamine (TOA) and tricaprylmethylammonium chloride (Aliquat-336) have been investigated by thermogravimetry and differential thermal analysis, and the complexes and their thermally decomposed products by IR spectrophotometry. The structures are proposed for the complexes with TOA and Aliquat-336 on the basis of the results obtained.

INTRODUCTION

In order to elucidate further the composition of the metal complexes formed in the solvent extraction system, the thermal decomposition of sulphato and nitrato complexes of uranium(VI)[1] and of the chloro complexes of copper(II)[2], vanadium(IV)[3] and uranium(VI)[4] with long-chain aliphatic amines have been investigated previously. Furthermore, the present authors have studied the extraction of zirconium(IV) from hydrochloric acid solutions by tri-*n*-octylamine (R_3N, TOA)[5] and tricaprylmethylammonium chloride ($R_3R'NCl$, Aliquat-336)[6]; therefore, this paper extends the work to the thermal decomposition of chloro complexes of zirconium(IV) with TOA and Aliquat-336.

EXPERIMENTAL

Chemicals

Tri-*n*-octylamine (Kao Soap Co. Ltd.), used without purification, and tricaprylmethylammonium chloride (General Mills), purified by washing several times with aqueous sodium chloride solution and *n*-hexane, were diluted with benzene. The solution of zirconium(IV) was prepared by dissolving zirconium chloride in hydrochloric acid solution of selected concentration. Other chemicals were of analytical reagent grade.

Preparation and analysis of complexes

On the basis of the distribution results[5, 6], the organic solutions saturated with zirconium were prepared as follows: 0.05 M TOA and 0.082 M Aliquat-336 in benzene were shaken for 10 min with the aqueous solution containing zirconium chloride of 0.02 M in hydrochloric acid of 10 and 8 M, respectively, at 20 °C; the organic phases were separated from the aqueous phase by centrifugation and again equilibrated with a fresh aqueous solution; this procedure was repeated 10 times. The organic solutions thus obtained were heated in vacuo at 50–60 °C to remove benzene. For chemical analysis, the resulting materials were dissolved in benzene, and the chloride and water in portions of the solution were determined by Volhard's and Karl-Fischer titrations. The benzene solutions were then washed with 1 M nitric acid, and zirconium in the acidic layers was determined by EDTA titration with xylenol orange as indicator[6, 7].

The complexes obtained were examined by thermogravimetry and differential thermal analysis (TG and DTA), and the complexes and their thermally decomposed products by IR spectroscopy. TG and DTA were carried out on an automatic recording thermobalance and DTA apparatus by using platinum–platinum/rhodium thermocouples, at a heating rate of 5 °C min^{-1} under atmosphere. The thermally decomposed products were prepared by heating the samples at the stated temperature for 1 h after heating to the temperature at a rate of 5 °C min^{-1}, on the basis of the results of thermal analysis. The IR spectra were determined on a Japan Spectroscopic Co. Ltd. Model IR-S, equipped with potassium chloride prisms, and Model IR-Al grating IR spectrophotometer for measurement at 4000–650 cm^{-1}, and Model IR-F, a grating model for measurement at 700–200 cm^{-1}, using a capillary film between thallium halide or polyethylene plates.

RESULTS AND DISCUSSION

The DTA curves for the zirconium(IV) complexes (Fig. 1) exhibit three endothermic reactions at 275, 340 and 385 °C with TOA, and at 205, 320 and 380 °C with Aliquat-336. These endothermic reactions occur at points near the change of shape in the TG curves (Fig. 2).

The IR spectrum of the complex of zirconium(IV) with TOA shows the following absorption bands: the NH^+ stretching vibration[8-10] at 2600 cm^{-1}; C–N asymmetric and symmetric stretching bands at 1060 and 760 cm^{-1}, respectively; C–H symmetrical and asymmetrical stretching vibration at 2920 and 2860 cm^{-1}; the CH_3 degenerate (and CH_2 scissoring) and symmetrical bending modes at 1465 and 1375 cm^{-1}, respectively; CH_2 wagging and rocking frequencies at 1300 and 720 cm^{-1}, respectively; the Zr–Cl stretching frequency at 295 cm^{-1}. The spectrum is little affected when the complex is heated at 200 °C. On heating at 300 °C, the absorption bands due to the presence of TOA decrease in intensity, and the NH^+ stretching vibration shifts to a lower frequency. With further heating above 400 °C, these bands disappear and the broad band of ZrO_2[11-14] appears at around 450 cm^{-1}. On the

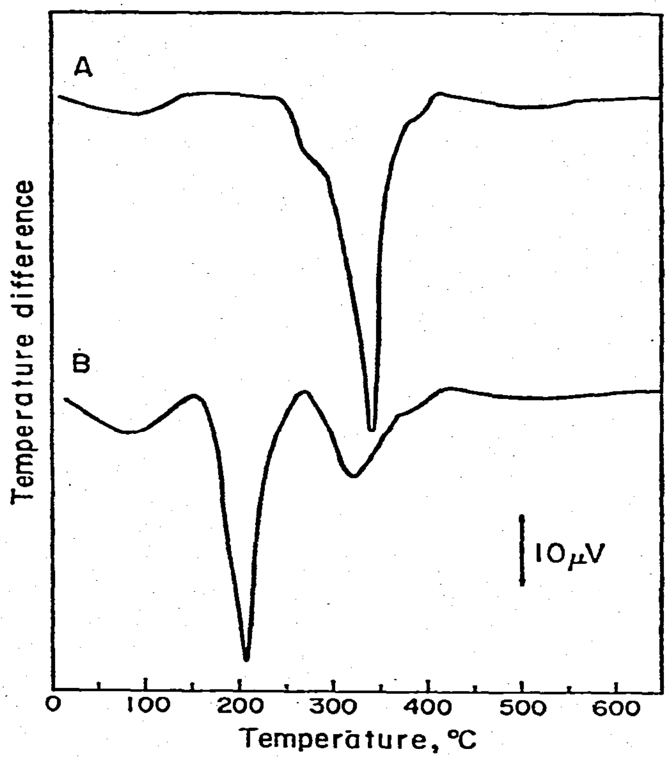


Fig. 1. DTA curves for the complexes of zirconium(IV) with TOA and Aliquat-336 (A, TOA; B, Aliquat-336).

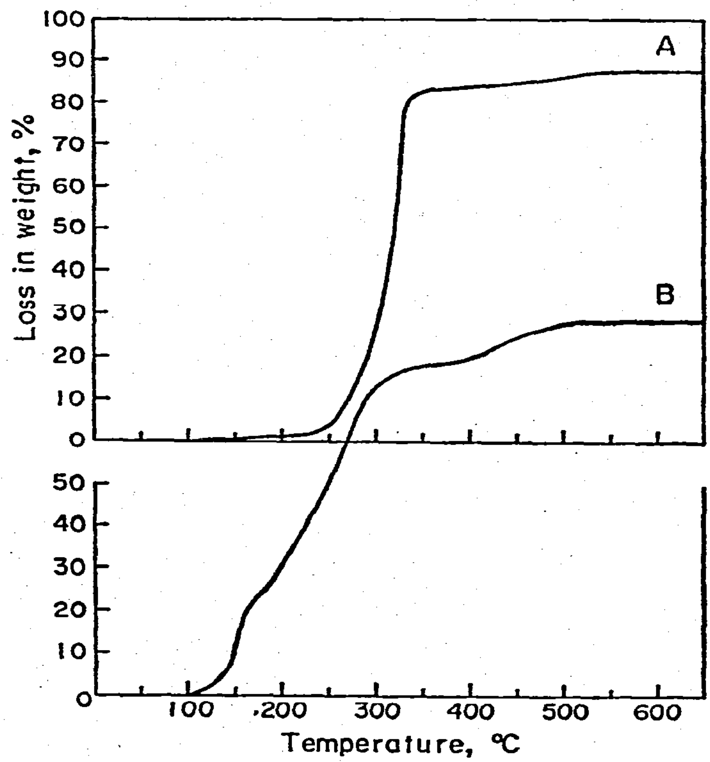


Fig. 2. TG curves for the complexes of zirconium(IV) with TOA and Aliquat-336 (A, TOA; B, Aliquat-336).

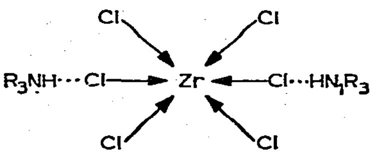
one hand, the complex of zirconium(IV) with Aliquat-336 gives an IR spectrum similar to the complex with TOA: C–H symmetrical and asymmetrical stretching vibrations at 2920 and 2860 cm^{-1}; the CH_3 degenerate (and CH_2 scissoring) and symmetrical bending modes at 1465 and 1375 cm^{-1}, respectively; CH_2 rocking frequency at 720 cm^{-1}; the Zr–Cl stretching band at 300–280 cm^{-1}. Additionally, the changes in the spectra of the thermally decomposed products from the complex with Aliquat-336 are almost the same in those from the complex with TOA, except the fact that the absorptions due to Aliquat-336 disappear at 300 °C, while the broad band due to the formation of ZrO_2 appears at around 475 cm^{-1}.

The DTA curve for TOA[2] exhibits endothermic peaks at 275 and 380 °C, which arise from the formation of hydrocarbon by the cracking of the amine and the carbonization of its product, respectively, and the curve for TOA hydrochloride[2] shows peaks at 285 and 335 °C, which are due to the thermal decomposition of TOA hydrochloride and the carbonization of its products, respectively. In addition, the TG and DTA curves for the complex of zirconium(IV) resemble those for the chloro complex of copper(II) with TOA[2]. In connection with the data for the chlorine content in the thermally decomposed products of the complex, these results allow the interpretation of the DTA curve for the complex of zirconium(IV) with TOA as follows: at 275 °C, part of the coordinated chlorine is removed and the derived amine is coordinated immediately to zirconium through hydrogen bonding; at 340 °C, more chlorine is removed, and simultaneously the derived amine is thermally decomposed and the resulting hydrocarbon is then carbonized; at 385 °C, the remaining chlorine is removed.

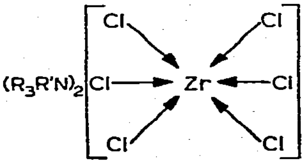
In contrast, the DTA curve for Aliquat-336 reveals the endothermic reactions at 195, 260 and 370 °C, which result from the thermal decomposition of Aliquat-336, the cracking of the derived amine and the carbonization of its products. Accordingly, the following explanation may be given for the three endothermic reactions in the DTA curve for the complex of zirconium(IV) with Aliquat-336; the first reaction at 205 °C is due to the thermal decomposition of Aliquat-336; the second reaction at 320 °C is attributed to the release of part of the coordinated chlorine and at the same time to the cracking of the derived amine followed by carbonization; the final reaction at 380 °C is ascribed to the removal of the remaining chlorine. It is thus expected that the complex with TOA is more thermally stable than that with Aliquat-336, corresponding to the TG curves.

The complex with TOA or Aliquat-336 gave the components zirconium:chlorine:TOA or Aliquat-336 in the molar ratio 1:6:2 (exactly 1:5.86:2.15 for TOA and 1:6.10:2.02 for Aliquat-336), indicating the composition $(R_3NH)_2ZrCl_6$ or $(R_3R'N)_2ZrCl_6$. The IR spectra of the complexes showed no absorption caused by the OH groups, indicating that the complexes contain no coordinated water, and this was confirmed by Karl-Fischer titration. In addition, the IR spectra of the zirconium complexes with TOA and Aliquat-336 exhibit the absorption bands at 295 and 300–280 cm^{-1}, respectively, assigned to the Zr–Cl stretching frequency, corresponding to the result[15] that the ν_3 frequency for the anionic hexahalides $ZrCl_6^{2-}$

appears at 297–276 cm^{-1}, but for the compound $ZrCl_4$ at 423–421 cm^{-1}. Hence the following structures displaying a coordination number of six for zirconium (a point group O_h symmetry) may be proposed for the complexes



(I)
ToA complex



(II)
Alignat-336 complex

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