Journal of Alloys and Compounds 275–277 (1998) 863–867

Preparation of lanthanide (III) neutral compound ligands in the $Ln(CH_3COO)_3$–HDEHP–decane system and study of their solubility in HDEHP–decane solutions

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Abstract

Investigations have resulted in the development of synthesis procedures and the synthesis of solid compounds of Pr, Nd, Sm, Eu, Gd, Tb, Ho, Er, Yb and Lu in $Ln(CH_3COO)_3$–HDEHP–decane systems. Based on the results of chemical analysis and IR spectroscopy data it was concluded that the compounds are neutral mixed ligand complexes, the composition of which corresponds to the formula $LnA_n(CH_3COO)_y$ (where $y = 3 - n$). Di-(2-ethylhexyl)phosphatoacetates are of polymeric structure. The lanthanides of solid compounds are assumed to have coordination number 6. A scheme for the molecular structure of these compounds is proposed. The solubility of di-(2-ethylhexyl)phosphatoacetates in HDEHP–decane solutions has been studied and the composition of the extracted complexes was specified by the solubility method.

Keywords: Di-(2-ethylhexyl)phosphate; Extracted complexes; IR spectra; Lanthanide; Solubility

1. Introduction

Di-(2-ethylhexyl)phosphorus acid (HA) and its solutions in organic solvents are widely used in analytical chemistry and technology for separation of lanthanides by extraction and extraction-chromatography methods [1]. Lanthanide (III) extraction is usually carried out under conditions of excess extractant when the ($MeA_3 \cdot xHA$) extractable complex is solvated with HA molecules as much as possible and is very soluble in the organic phase. However, if the concentration of the extracted metal is sufficient for complete extractant saturation then the composition of the saturated organic phase is close to the MeA_3 salt-type stoichiometric compound. In this case the third phase is released as a gel or solid precipitate [2–5]. The formation of a gelatinous third phase was also observed in the separation of lanthanides using the extraction-chromatographic method [5]. Therefore, when the mechanism of the extraction process is considered with the use of HDEHP, it is necessary to obtain information on the formation of solid di-(2-ethylhexyl)phosphate complexes, their chemical composition, structure and state in organic media, along with equilibrium and kinetic relationships of the Ln distribution among the phases under conditions of excess extractant.

A number of methods dealing with the preparation of solid lanthanide di-(2-ethylhexyl)phosphates are described in the literature. These methods involve an exchange reaction between NaA and $Ln(NO_3)_3$ in acetone solution [6], organic extract neutralization with gaseous ammonia [7], and lanthanide extraction with HDEHP alcohol solution from applied nitrate solutions of $0.1\,mol\,l^{-1}$ HNO_3 [8].

Lanthanide di-(2-ethylhexyl)phosphates take the form of a paraffin powder which is slightly soluble in saturated hydrocarbons, acetone, alcohol, alkyl phosphate and acetonitrile. LnA_3 compounds are anhydrous coordination polymers unable to hydrate [9]. The crystal structure of reported LnA_3 compounds has been determined by X-ray analysis [3].

In spite of the low coordination number of 6, the lanthanide ions in di-(2-ethylhexyl)phosphates do not add to neutral electron-excess ligands (ROH, TBP, hexamethylphosphortriamide, etc.). This is a peculiarity of LnA_3 compounds [10]. The polymeric nature of LnA_3 is displayed by its swelling in some (CCl_4, C_6H_6) solutions [9].

Under specific conditions lanthanide di-(2-ethylhexyl)phosphates can form neutral compound ligands; in this

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0925-8388/98/$19.00
PII: S0925-8388(98)00473-3

case some alkyl phosphate anions of LnA_3 are replaced with acidoligands. Lanthanide neutral compound ligands may be prepared as solid compounds of chemical composition $LnA(NO_3)_2 \cdot 2H_2O$ [11]. The coordination number of Ln in these compounds is 8 [11].

Due to the great similarity between the mixed ligand coordination sphere and protons there are acid (protonated) analogues along with neutral compound ligands [12,13]. The lanthanide ion of di-(2-ethylhexyl)phosphatonitrates has a coordination number of 8, but in $LnA_2(ClHA)$ it is 6 [12].

The present report incorporates information on the synthesis of lanthanide (III) di-(2-ethylhexyl)phosphates in the $Ln(CH_3COO)_3$–HDEHP–decane system, a study of their chemical composition and structure, and the determination of the extracted lanthanide complexes in the HDEHP–decane system using the prepared compounds.

2. Experimental

Di-(2-ethylhexyl)phosphoric acid of 99.2% purity refined according to the procedure of Ref. [5] was used. Other reagents were of appropriate chemical purity.

To prepare neutral di-(2-ethylhexyl)phosphates in the $La(CH_3COO)_3$–HDEHP–decane system we developed an original method of synthesis, and solid di-(2-ethylhexyl)phosphates of Pr, Nd, Sm, Eu, Gd, Tb, Ho, Er, Yb and Lu were prepared.

The chemical composition of the synthesized di-(2-ethylhexyl)phosphates was specified as follows. A sample of compound (0.2 g) was agitated with 2 ml decane and shaken with an equal volume of 4–6 mol l^{-1} HNO_3 in a plugged test tube. The organic phase was separated and rinsed with water followed by a sample aliquot, the addition of ethanol and determination of the HDEHP content by potentiometric titration with aqueous NaOH solution. Lanthanide was determined by compleximetric titration [14]. The IR spectra were recorded using samples prepared as a suspension in vaseline oil and as KBr pellets. The spectra were recorded using an IRS-29 spectrometer. A comparative identification of the absorption bands was performed using the IR spectra of HDEHP solutions in decane, the pure extractant and the $Yb(CH_3COO)_3 \cdot 4H_2O$ spectrum.

The solubility of the lanthanide di-(2-ethylhexyl)phosphates prepared in the $La(CH_3COO)_3$–HDEHP–decane system was studied in HDEHP–decane solutions at extractant concentrations from 0.001 to 2 mol l^{-1} and pure diluent.

3. Results and discussion

Along the lanthanide series the [A]/[Ln] ratios according to the composition of the prepared di-(2-ethylhexyl)phosphates are different (Fig. 1). Dependence of the change in chemical composition on the atomic number of the lanthanide is characteristic of the change in composition of complex compounds along the lanthanide series [15]. It should be noted that the value of n ($n = [A]/[Ln]$) differs from that reported in Refs. [7,9,16,17], where the chemical composition of di-(2-ethylhexyl)phosphates corresponds to LnA_3, i.e. $n = 3$. The deviation of the [A]/[Ln] ratio from the stoichiometric ratio is probably caused by the formation of ligand compounds (with participation of acetate ions) of lanthanide di-(2-ethylhexyl)phosphates in the $Ln(CH_3COO)_3$–HDEHP–decane system.

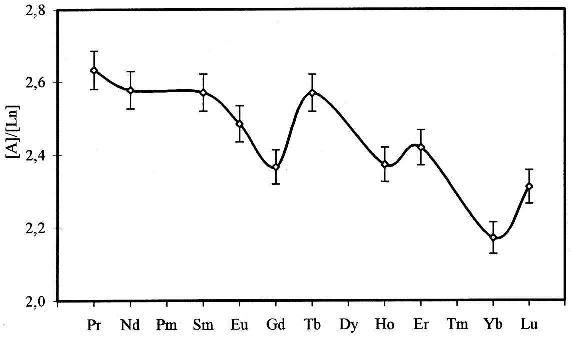

Fig. 1. Change in the [A]/[Ln] ratio of the chemical composition of lanthanide solid compounds prepared in the $Ln(CH_3COO)_3$–HDEHP–decane system.

The IR absorption bands of the lanthanide di-(2-ethylhexyl)phosphate spectra have maxima at 615, 730, 770, 885, 930, 980–1080, 1100, 1170, 1185, 1380, 1470, 1575–1580 (an indistinct and weak band for Pr, Nd, Sm, Eu, Gd and Tb) and 2850–2970 cm^{-1} (Fig. 2).

No essential changes were observed in the absorption bands at frequencies 730, 770, 930, 1380, 1470 and 2850–2970 cm^{-1} attributed to the deformation of alkyl radicals [18,19,8] in the HDEHP–lanthanide interaction.

The IR spectra of lanthanide compounds compared with the spectra for HDEHP solutions do not contain absorption bands in the ranges 2330–2340 and 1675–1685 cm^{-1} attributable to the deformation of the (P)–O–H group in accordance with Ref. [18]. The absence of these bands in the spectra suggests that hydrogen in the hydroxyl groups

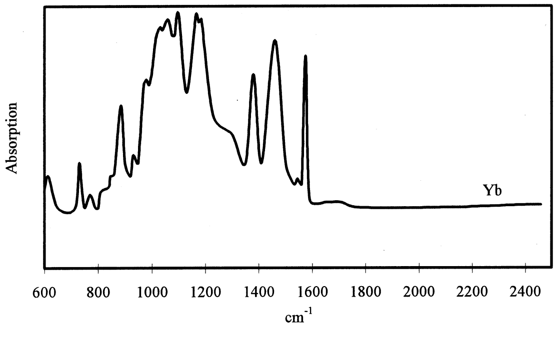

Fig. 2. IR spectra of Yb solid compound with HDEHP prepared in the $Ln(CH_3COO)_3$–HDEHP–decane system.

of di-(2-ethylhexyl)phosphoric acid is replaced by metal. Therefore, the compounds are free from HDEHP as HA. In addition, the IR spectra do not contain absorption bands attributable to either crystalline or coordinately linked water.

It is impossible to interpret exactly the absorption band in the range 885 cm^{-1}. However, taking into consideration that its intensity increases in the di-(2-ethylhexyl)phosphate spectra, in comparison with the extractant spectra, on the one hand, and the absence of absorption bands in the IR spectra in the ranges 2330–2340 and 1675–1685 cm^{-1}, on the other, one can suggest that the band at 885 cm^{-1} observed in the IR spectra of lanthanide di-(2-ethylhexyl)phosphates corresponds to the deformation of the (P)–O–Ln group.

All spectra of lanthanide di-(2-ethylhexyl)phosphates, compared with the spectra of HDEHP solutions, have an intense absorption band at a frequency of 1100 cm^{-1} corresponding to symmetric valent variation of –O–(PR_2)–O– bridge groups [12]. The absorption band at 1230 cm^{-1} observed in the IR spectra of HDEHP solutions is attributable to asymmetrical variations of the P=O group with hydrogen bonding [18]. In the spectra of lanthanide di-(2-ethylhexyl)phosphates there is a longwave shift of this band and its splitting into two components at 1170 and 1185 cm^{-1}. The absorption bands visible at 1170 and 1100 cm^{-1} suggest a polymeric structure for solid lanthanide–HDEHP compounds [12,17].

The wide intensive absorption band in the range 980–1080 cm^{-1} is a complex structure due to the superposition of variation bands of (P)–O–Ln, P–O–(Ln) and (C)–O–P bonds, symmetrical valent variations of bridge phosphoryl groups (1100 cm^{-1}) and deformation variations of the alkyl radical.

The IR absorption band of di-(2-ethylhexyl)phosphates with a maximum in the range 1575–1580 cm^{-1} is assumed to be attributable to the acetate group which is confirmed by a comparative analysis of the IR spectra typical of di-(2-ethylhexyl)phosphate and ytterbium acetate.

Chemical analysis of the di-(2-ethylhexyl)phosphates allows us to report the presence of acetate ions in the investigated compound. Thus the IR spectrum absorption band of solid lanthanide–HDEHP compounds in the range 1575–1580 cm^{-1} (absorption band of the acetate group) is caused by valent oscillations of the bridge carbonyl group of the acetate ion symmetrically coordinated to two adjacent metal atoms [19].

Hence, the lanthanide compounds prepared in $Ln(CH_3COO)_3$–HDEHP–decane are the neutral compound ligand di(2-ethylhexyl)phosphatoacetates, the composition of which corresponds to the formula $LnA_n(CH_3COO)_y$ (where $y = 3 - n$). Taking into account the polymeric structure the overall formula of the compounds may be presented as $(LnA_n(CH_3COO)_y)_m$.

Based on the results of the chemical analysis of the compounds and their IR spectra, lanthanides in di-(2-ethylhexyl)phosphatoacetates are expected to have a coordination number of 6 and, consequently, an octahedral coordination sphere [20,16]. As is the case with LnA_3, $(LnA_n(CH_3COO)_y)_m$ compounds are expected to be linear rigid-chain polymers where the faces of adjacent coordination octahedra are bonded to one another by bridge alkylphosphate (Ln–O–P–O–Ln) and carbonyl (Ln–O–C–O–Ln) groups. A proposed model of the di-(2-ethylhexyl)phosphatoacetate polymeric molecule is shown in Fig. 3.

Di-(2-ethylhexyl)phosphatoacetates as LnA_3 dissolve in HDEHP solutions due to solvation of the compounds with extractant molecules to form an acid ligand compound [12]. However, the solution process of di-(2-ethylhexyl)phosphateacetates is more complex and likely includes a number of stages which can be described by the following reaction equations:

$$LnA_n(CH_3COO)_y + yHA \Leftrightarrow LnA_n(CH_3COO)_y \cdot yHA \quad (1)$$

$$LnA_n(CH_3COO)_y + xHA \Leftrightarrow LnA_n(CH_3COO)_y \cdot xHA \quad (2)$$

$$LnA_n(CH_3COO)_y \cdot yHA \Leftrightarrow LnA_3 + yCH_3COOH \quad (3)$$

$$LnA_n(CH_3COO)_y \cdot xHA \Leftrightarrow LnA_n \cdot (x-y)HA + yCH_3COOH \quad (4)$$

$$LnA_n \cdot (x-y)HA + yHA \Leftrightarrow LnA_3 \cdot xHA \quad (5)$$

$$LnA_3 + xHA \Leftrightarrow LnA_3 \cdot xHA \quad (6)$$

where $y = 3 - n$.

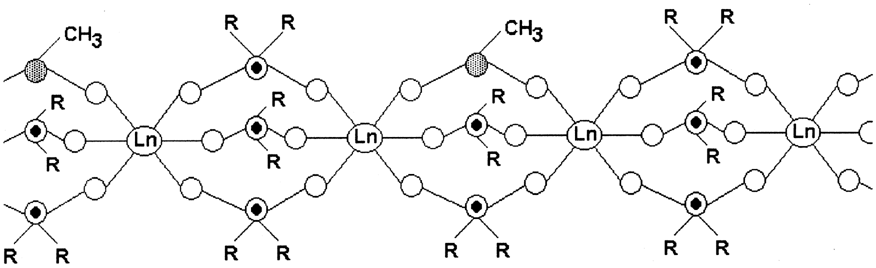

Fig. 3. Model of the $(LnA_n(CH_3COO)_y)_m$ polymeric molecule (where $y = 3 - n$): R = 2-ethylhexyl radical; (●) carbon atom; (○) oxygen atom; (♦) phosphorus atom.

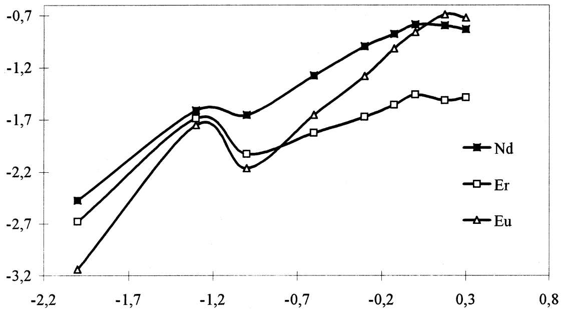

Fig. 4. Solubility of Nd, Eu and Er di-(2-ethylhexyl)phosphatoacetates in the HDEHP–decane system.

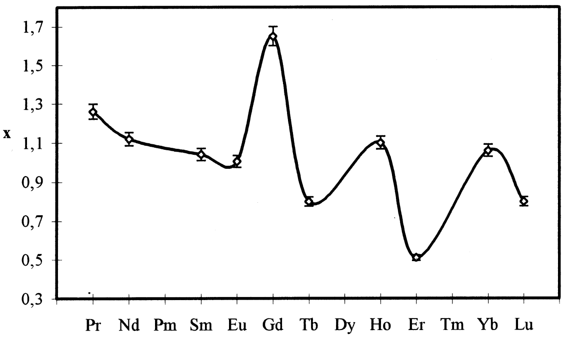

Fig. 6. Change in HA molecule number in the external coordination sphere of $LnA_3 \cdot x HA$ complex along the lanthanide series.

The possibility of reactions (1) and (2) is demonstrated by the formation of a mixed complex with the participation of acetate ions in the extraction of lanthanide acetates by HDEHP solutions from acetic acid solution (separated in the solid form and identified). Due to the curvature of the lanthanide di-(2-ethylhexyl)phosphatoacetate solubility curves at low HDEHP concentration (0.05–0.1 mol l^{-1}) it may be expected that, in this region, there is damage to acid ligand compounds formed in $LnA_n(CH_3COO)_y$ solution by reaction (2) and a decrease of lanthanide content in the organic phase due to the formation of slightly soluble LnA_3 by reaction (3).

Taking into consideration that HDEHP at concentrations above 1 mol l^{-1} is in the form of a dimer in most organic solvents, it should be noted that the solubility of the solid compounds in solutions of high extractant concentration will be decreased at the expense of the decreased equilibrium concentration of the HA monomer. This assumption is demonstrated by the experimental data. At concentrations of HDEHP >1.5 mol l^{-1} the solubility of lanthanide di-(2-ethylhexyl)phosphatoacetates is observed to be reduced (Fig. 4).

The change in the solubility of the di-(2-ethylhexyl)phosphatoacetate along the lanthanide series is of complex character (Fig. 5). At low concentration of extractant (0.1 mol l^{-1}) the solubility of these compounds depends on their initial composition. At high DHEHP concentration in decane (≥ 1 mol l^{-1}) the solubility of di-(2-ethylhexyl)phosphatoacetate for lanthanides from Pr to Tb practically does not change. A decrease in compound solubility was observed with increasing atomic number.

The composition of the extracted complexes, i.e. the number of HDEHP molecules in the external coordination sphere of the alkylphosphate complexes, was determined by the slope of the linear section of the lanthanide di-(2-ethylhexyl)phosphatoacetate solubility curve (Fig. 4) [21]. From Pr to Eu and from Gd to Lu there was a decrease in HDEHP solvent molecules from 1.2 to 1.0 and from 1.7 to 0.85, respectively (Fig. 6).

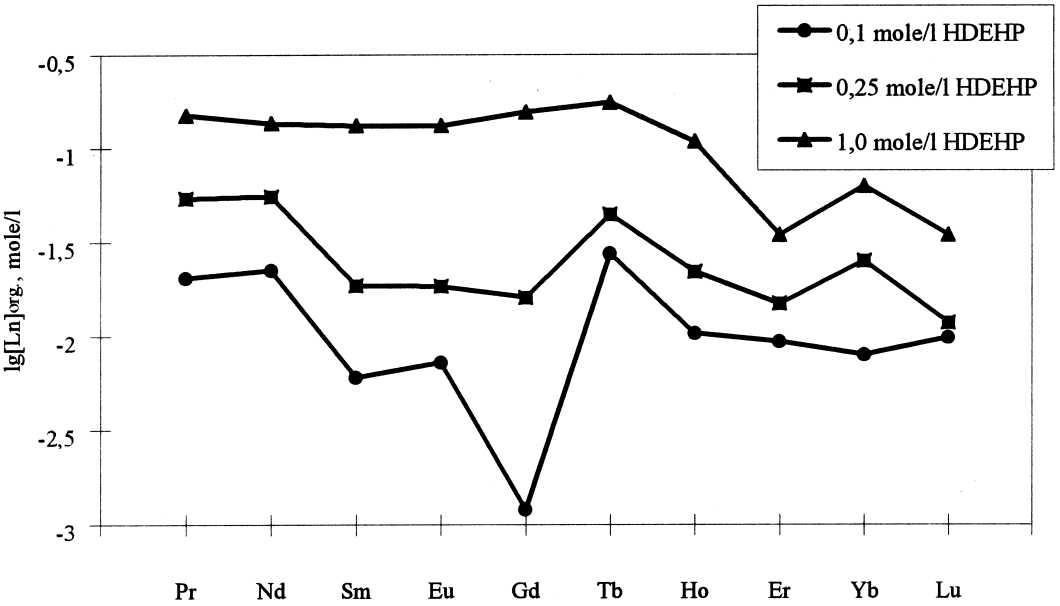

Fig. 5. Solubility of di-(2-ethylhexyl)phosphatoacetates in HDEHP–decane solution along the lanthanide series.

Both curves display the number of external coordinated HA molecules of the extracted complexes (Fig. 6) and the curves of the composition change of solid di-(2-ethylhexyl)phosphatoacetates (Fig. 1) are typical for the composition change of complex compounds along the lanthanide series. The course of the curves shown in Figs. 1 and 6 is well correlated with the energy change of f-electron interconfiguration transitions in trivalent ions along the lanthanide series [15]. The reasons for the periodical deviations of the composition of f-element complex compounds from stoichiometry are under investigation [15].

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