

The solubility of cerium and praseodymium 8-hydroxyquinolates in organic solvents

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The solubility of CeOx_4 and PrOx_3 in nine solvents at 25°C was determined. The solubility of CeOx_4 varies in the range 1.54×10^{-3} – 0.03×10^{-3} kmol m^{-3} and decreases in the following order: chloroform > tetrahydrofuran > dioxan > benzene > chlorobenzene > carbon tetrachloride > acetone > acetonitrile > carbon disulfide. For PrOx_3 the solubility is 8.4×10^{-5} – 1.0×10^{-5} kmol m^{-3} and decreases in the order: chloroform > benzene > tetrahydrofuran > chlorobenzene > carbon tetrachloride > acetone > dioxan > carbon disulfide > acetonitrile. From the determined solubilities in the water-immiscible solvents and from the known solubility products, the two-phase stability constants and the extraction constants of the studied chelates were calculated.

8-Hydroxyquinoline forms compounds with the majority of elements; therefore it became one of the most universal analytical reagents. Rare earth elements form chelates with 8-hydroxyquinoline, utilized in analytical chemistry both for determination of individual lanthanoides and for their chromatographic and extraction separation from mixtures. An important factor here is the solubility of chelate in aqueous media and organic solvents. Though the water solubility of 8-hydroxyquinolates of lanthanum and lanthanoides was rather thoroughly studied [1–3], only qualitative data about their solubility in organic solvents have been as yet published [4, 5].

The subject of our work is to determine the solubility of cerium and praseodymium 8-hydroxyquinolates since these elements are important components of the fission products of uranium and plutonium. Several different liquids, widely used in extraction and chromatographic techniques, were chosen as solvents. The solubilities of chelates in them were determined by a radiometric method using radionuclides ^{144}Ce and ^{143}Pr .

Experimental

Chemicals

Cerium chloride heptahydrate (Merck, FRG), specially pure, free of other rare earth elements; *praseodymium nitrate pentahydrate* 99.5% (Koch-Light, GB); *8-hydroxyquinoline* (Lachema, Brno), anal. grade. Other chemicals and solvents used were anal. grade,

carbon disulfide pure. The acetate buffer solution ($\text{pH} = 5.2$) was prepared by mixing 0.2 M sodium acetate (158 ml) with 0.2 M acetic acid (42 ml). Organic solvents were purified as described in [6].

Radionuclides

^{144}Ce in the radioactive equilibrium with daughter ^{144}Pr , without carrier, as chlorides in 1 M-HCl (ÚVVVR, Prague); the specific activity 250 Ci m^{-3} . Its radioactive purity was checked by the γ -ray spectrometry. ^{143}Pr without carrier, as chloride in 1 M-HCl (ÚVVVR, Prague), the specific activity 182 Ci m^{-3} . Its radioactive purity was checked by measuring the decay curve.

Instruments

The pH of aqueous solutions was measured by standard glass and calomel electrodes, using an OP 201/1 pH-meter (Radelkis, Hungary). A nuclear counter BM 353 (Tesla, Brno) equipped with 30/30 AB Geiger-Müller tube, a mica window (thickness 0.015 kg m^{-2}), was used for the measurements of β -radiation. γ -Radiation of ^{144}Ce — ^{144}Pr was measured by means of a scintillation probe NAB 232 with a well type NaI(Tl) scintillator SKW-1S, connected with a one-channel scintillation γ -spectrometer, type NZG 319-II (Tesla, Liberec). Infrared spectra were recorded on a double-beam UR-20 (Zeiss, Jena) prism spectrometer.

Preparation of chelates

Cerium and praseodymium 8-hydroxyquinolinates were prepared by adding the acetone solution of 8-hydroxyquinoline dropwise into the acetate buffer solution containing the corresponding metal cation [1]. Solution of 3% 8-hydroxyquinoline in acetone (150 ml) was added dropwise under vigorous stirring into aqueous solution of CeCl_3 or $\text{Pr}(\text{NO}_3)_3$ (100 ml) labelled by ^{144}Ce and ^{143}Pr respectively (1 ml of solution contained *ca.* 2 mg of Ce or Pr, their exact concentrations were determined gravimetrically by precipitation as oxalates and igniting to oxides). After six-hour stirring, the brown-violet (Ce) or yellow (Pr) precipitate was filtered off, washed with absolute ethanol and dried at 80°C . The dry precipitate was then placed in a Soxhlet extractor and the chelate extracted into chloroform. The final dry product was obtained after evaporation of chloroform from chelate saturated solution in a stream of nitrogen and then in vacuum. The specific activities of the prepared 8-hydroxyquinolinates were approx. 0.6 Ci kg^{-1} for Ce and 0.31 Ci kg^{-1} for Pr.

Analysis of chelates

Radiometric analysis

Samples (*ca.* 200 mg) of chelate were dissolved in a small amount of concentrated HNO_3 and the solution was made up to 50 ml with distilled water in a graduated flask. Aliquots of the solution were used for activity measurements. Solutions containing ^{144}Ce — ^{144}Pr were measured directly while preparations for activity measurements of ^{143}Pr were prepared by evaporation of its solutions on aluminium planchets. In both cases the found activities were compared with the activities of the starting solutions for the syntheses of chelates or preparations made of them, containing known amounts of Ce or Pr.

Gravimetric analysis

The sample of chelate in a porcelain crucible was covered by a layer of oxalic acid and ignited at 900–1000°C [3], residual CeO₂ or Pr₆O₁₁ was weighed.

Elemental analysis

The content of hydrogen, carbon, nitrogen, and metal in chelates was determined.

Infrared spectra of the studied chelates and 8-hydroxyquinoline were recorded in the region 700–1700 cm⁻¹ in KBr cells with the samples suspended in paraffin oil, the spectrum of which was compensated.

Preparation of the saturated solutions of chelates in organic solvents

In the first series of experiments a mixture of organic solvent (5 ml) with an excess of the corresponding chelate was vigorously shaken for approx. 1 hour in the test tubes closed by ground joints. The mixtures were then cooled with water and stirred for 2 hours at 10°C; then they were allowed to heat slowly and thermostated at 25 ± 0.2°C for 4–6 hours. Such a procedure guaranteed attainment of equilibrium between the solid phase and solution. Two ml of each saturated solution were taken for activity measurements. When the solution was turbid by the fine suspension of the solid phase, it was centrifuged or sucked off through a small sintered glass tempered at 25°C.

The second series of experiments was quite similar but, instead of cooling to 10°C, the solutions were heated up to 45–50°C. Activities of the solutions containing ¹⁴⁴Ce were measured only 3 hours after the sampling.

Results and discussion

Since several authors [7, 8] pointed out that the composition of 8-hydroxyquinolinates of the rare earth elements depends on the method and conditions of their preparation, we paid a special attention to the analysis of the prepared chelates. Their i.r. spectra (Fig. 1) are in good agreement with published data [9, 10]. According to the results of the elemental, radiometric, and gravimetric analysis (Table 1) the prepared cerium and praseodymium 8-hydroxyquinolinates are anhydrous compounds, the metal to ligand ratio being very close to 1 : 4 for cerium and 1 : 3 for praseodymium. Their com-

Table 1

Results of analyses of cerium and praseodymium 8-hydroxyquinolinates

| % | Ce | C | H | N | Pr | C | H | N |
|----------------------|---|-------|------|------|---|-------|------|------|
| Calculated for | Ce(C ₉ H ₆ NO) ₄ | | | | Pr(C ₉ H ₆ NO) ₃ | | | |
| | 19.57 | 60.30 | 3.41 | 7.95 | 24.45 | 56.80 | 3.17 | 5.75 |
| Found by | | | | | | | | |
| Elemental analysis | 19.60 | 60.80 | 3.46 | 7.58 | 24.20 | 56.55 | 3.32 | 5.81 |
| Radiometric analysis | 19.76 | — | — | — | 24.60 | — | — | — |
| [M] : [Ox] | 1 : 3.93 | | | | 1 : 2.96 | | | |
| Gravimetric analysis | 19.35 | — | — | — | 24.78 | — | — | — |
| [M] : [Ox] | 1 : 4.06 | | | | 1 : 2.96 | | | |

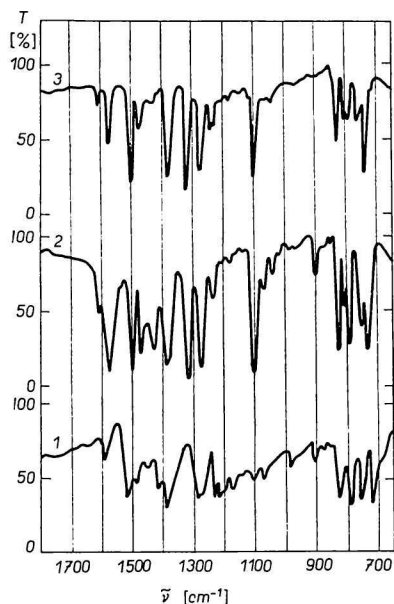


Fig. 1. Infrared spectra (suspension in paraffin oil).

1. HOx; 2. PrOx₃; 3. CeOx₄.

position can be expressed by formulae CeOx₄ and PrOx₃ respectively, where Ox is an anionic ligand of 8-hydroxyquinoline. Formation of CeOx₄ in the reaction of Ce(III) with 8-hydroxyquinoline in the presence of air and without reducing agent was confirmed spectrophotometrically [11] and radiometrically [1].

Umland and Haar [4, 5] pointed to great differences in solubilities of individual 8-hydroxyquinolinates of lanthanoides, particularly in those of cerium and praseodymium in chloroform. The solubility of chelate in various solvents is its important analytical characteristic. The low solubility of lanthanum and lanthanoides 8-hydroxyquinolinates in water is often utilized for their quantitative precipitation from aqueous solutions. Beside the water solubility of chelate, its solubility in the organic phase is of prime importance for its extraction since both the partition constant of chelate between the two phases and the extraction capacity of the organic phase depend on the solubility of chelate in the organic phase. Thus the solubility of chelates is also important for separation of chelates by methods of the paper elution and extraction chromatography.

According to our results, the solubility of CeOx₄ in chloroform at 25°C is as much as twenty times higher than the solubility of PrOx₃ (Table 2). Also in other solvents used the solubility of CeOx₄ largely exceeds that of PrOx₃. After several days of standing certain changes, especially in the colour shade, were observed in some PrOx₃ solutions (in tetrahydrofuran, acetonitrile, carbon disulfide). The equilibrium establishment was characterized by the mutual overlap of the solubility data, irrespective of the method of preparation of solutions.

The solubility of chelate is known to be a complicated function of many factors, including the properties of both the chelate and the solvent. The solubility value characterizes the equilibrium state in the solution, resulting from the series of intermolecular interactions of the donor-acceptor type between the solvent and the solute. The permittivity and donor number of solvent, stability, structure, steric factors of chelate,

Table 2

The solubility of CeOx_4 and PrOx_3 in organic solvents and calculated values of their two-phase stability and extraction constants

| Solvent | Solubility [$\text{kmol m}^{-3} \times 10^5$] | | log $\beta_4 K_D(\text{CeOx}_4)$ | log $\beta_3 K_D(\text{PrOx}_3)$ | -log K_{ex} | |
|----------------------|--|-----------------|-------------------------------------|-------------------------------------|----------------------|-----------------|
| | CeOx_4 | PrOx_3 | | | CeOx_4 | PrOx_3 |
| Chloroform | 154 ± 6 | 8.4 ± 0.2 | 26.71 | 20.47 | 22.57 | 16.49 |
| Benzene | 20.4 ± 1 | 6.1 ± 0.1 | 25.83 | 20.34 | 21.61 | 15.24 |
| Chlorobenzene | 16.2 ± 0.3 | 5.1 ± 0.8 | 25.73 | 20.26 | — | — |
| Carbon tetrachloride | 14.9 ± 1 | 4.0 ± 0.7 | 25.70 | 20.15 | 21.18 | 15.01 |
| Carbon disulfide | 3.4 ± 0.6 | 1.3 ± 0.3 | 25.05 | 19.66 | — | — |
| Tetrahydrofuran | 90.1 ± 6 | 5.8 ± 1.0 | — | — | — | — |
| Dioxan | 54.7 ± 1 | 1.4 ± 0.2 | — | — | — | — |
| Acetone | 13.0 ± 0.1 | 1.6 ± 0.3 | — | — | — | — |
| Acetonitrile | 9.1 ± 1 | 1.0 ± 0.5 | — | — | — | — |

and others are of importance; therefore it is not suitable to correlate the solubility of chelate in the series of solvents only with one of these parameters.

When the solubility product of chelate in water is known, it is possible to calculate from the solubility in the water-immiscible solvent so called two-phase stability constant of this chelate [12]

$$\beta_n K_D(\text{MA}_n) = \frac{[\text{MA}_n]_w}{[\text{M}^{n+}] [\text{A}^-]^n} \frac{[\text{MA}_n]_0}{[\text{MA}_n]_w} = \frac{[\text{MA}_n]_0}{[\text{M}^{n+}] [\text{A}^-]^n} = \frac{S_0}{K_s}, \quad (1)$$

where $\beta_n K_D(\text{MA}_n)$ is the two-phase stability constant of chelate MA_n , $K_D(\text{MA}_n)$ is the partition constant of chelate between the inert solvent and water, β_n the stability constant of chelate in water, S_0 the solubility of chelate in the inert solvent, K_s the solubility product of chelate in water.

The two-phase stability constant and extraction constant [13] of the particular chelate are connected by a formula

$$\log K_{\text{ex}} = \log \beta_n K_D(\text{MA}_n) - n[\text{p}K_a + \log K_D(\text{HA})], \quad (2)$$

where K_{ex} is the extraction constant of chelate, K_a the dissociation constant of the chelating agent, and $K_D(\text{HA})$ the partition constant of this agent.

Values of the two-phase stability constants of CeOx_4 and PrOx_3 calculated from equation (1) for the water-immiscible solvents and the extraction constant calculated from equation (2) for chloroform, benzene, and carbon tetrachloride at ionic strength of the aqueous phase 0.1, temperature 25°C, are listed in Table 2. The numerical value of the CeOx_4 solubility product ($-\log K_s = 29.52$) was taken from [3], that of PrOx_3 ($-\log K_s = 24.55$) from [2], dissociation constant of 8-hydroxyquinoline ($\text{p}K_a = 9.66$) and its partition constant for the chloroform-water system ($\log K_D = 2.66$) were taken from [14], the partition constant for the benzene-water system ($\log K_D = 2.20$) from [15] and for the carbon tetrachloride-water system ($\log K_D = 2.06$) from [16].

The results show that the extraction power of the three solvents increases in the order chloroform < benzene < carbon tetrachloride, with respect to CeOx_4 as well as to PrOx_3 . The extraction constant of PrOx_3 is close to that of lanthanum 8-hydroxyquinolate (in the extraction into chloroform) for which the value -16.37 was found [17]. Better

extraction properties of carbon tetrachloride in comparison with chloroform, expressed by the extraction ratio D (equation (3)), were confirmed for some 8-hydroxyquinolinates by experimental results [18]

$$D = \frac{[\text{MA}_n]_0}{\text{M}^{n+}} = \beta_n K_a^n \frac{K_D(\text{MA}_n)}{K_D^n(\text{HA})} \frac{[\text{HA}]_0^n}{[\text{H}^+]^n} \quad (3)$$

In the series of solvents where values of $K_D(\text{MA}_n)$ change in the same direction as $K_D(\text{HA})$, the lower extraction of chelate MA_n at a given pH into the solvent with the higher value of $K_D(\text{MA}_n)$ can be explained by the greater difference in the values of $K_D^n(\text{HA})$ than in $K_D^n(\text{MA}_n)$ between the two solvents.

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