YTTRIUM-90 SEPARATION IN CARBONATE MEDIA BY SOLVENT EXTRACTION

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Abstract. The possibilities of 90Y/90Sr separation from carbonate media are investigated as a green alternative method. Solvent extraction of yttrium and strontium from carbonate solution is studied using several extractants in different organic diluents. 8-hydroxyquinoline and 2,3-dihydroxynaphthalene possess a promising Y/Sr separation. Yttrium and strontium distribution ratios D and separation factors SF are evaluated. pH interval 13 - 13.5 is regarded as the optimum for separation. Yttrium is extracted much better in 2-nitrotoluene (DY = 3.9), maximum separation is observed in 2-nitrotoluene SF = 195 at pH 13.5.

Key words: Yttrium-90, Strontium-90, separation, carbonate media, solvent extraction

1. INTRODUCTION

Yttrium-90 (T1/2 = 64 h, Eβmax = 2.28 MeV) is beta-emitting radionuclide, it exists in equilibrium with his maternal radionuclide 90Sr (T1/2 = 28.8 yrs) [1]-[3]. Yttrium-90 is of great interest to monitor strontium-90 in natural samples. It is also a therapeutic radioisotope due to its pure β−-particle emission, its decay produces a stable daughter nuclide (90Zr) (Fig. 1), thus yttrium extraction and separation demand is more urgent [1], [4].

Strontium-90 is one of the fission products. It is considered as one of the major heat generators in nuclear waste [1], [5]. The annual world production of 90Sr in nuclear reactors reaches several hundred MCi. Currently, the spent nuclear fuel is processed in a small number of countries, and these countries have capability to develop chemical process for large scale separation of 90Sr from spent nuclear fuel [1]-[4], [6], [7].

It is crucial to separate 90Y from 90Sr both for radioecology (90Sr determination) and medicine (90Sr/90Y generators). Various extractants have been developed for 90Y extraction and separation from 90Sr in acidic media. Peppard et al. in 1957 used diocylphosphoric acid as the extractant in separation of carrier free 90Y from 90Sr [8]. Then, Mirza in 1968 succeeded to separate 90Y from 90Sr by β-diketone (1-phenyl-3-methyl-4-caprylypyrazolene-5) [9]. Also di-(2-ethyl hexyl)-phosphoric acid (D2EHPA) has been extensively studied, and presented high 90Y separation from 90Sr. Wike et al. reported about extraction of multicurie levels of 90Y from the 90Sr solution using D2EHPA [10]-[12]. Crown ethers also have been extensively studied [13], but their main drawback is radio-chemical instability, high cost and third-phase formation tendency [14].

Figure 1. Decay scheme for 90Sr/90Y

In this work we examined a novel method of 90Y/90Sr separation in alkaline carbonate media. The main advantage of 90Y/90Sr separation in carbonate solution is avoiding handling difficulties and hazards of classical nitric acid extraction products. In addition, in this case, the analysis time is significantly reduced, since there is no need to wait for the 90Y/90Sr equilibrium to be reached. This method gives opportunity to use a selective solvent extraction agent for 90Y and or 90Sr.

Carbonate media already became interesting in recent years for 90Y and 90Sr recovery: for example, functionalized p-alkylcalix[8]arenes in perchloroethylene were examined as potential extractants of these radionuclides [15].
2. MATERIALS AND METHODS

2.1. Reagents

8-HQ, PAN, PAR, chromotropic acid and toluene were purchased from “Vekton” (Russia), 98.5%-99.5% 2,3-DHN was from SCHUHARDT MUNCHEB (Germany).

Butyl acetate and SrCO₃ (analytical grade) were purchased from Lancaster (England), all organic diluents are analytical grade and used without any further purification.

Yttrium oxide was prepared by Y(NO₃)₃ decomposition at 800 °C for 1.5 h at muffle furnace.

Yttrium carbonate stock solution was prepared by Y(NO₃)₃ dissolution in alkaline carbonate solutions (Na₂CO₃, K₂CO₃ and (NH₄)₂CO₃). All these salts were of analytical grade. For yttrium spectrophotometric determination Arsenazo III of analytical grade was used.

Radioactive isotopes ⁹⁰Sr and ⁹⁰Y were received from JSC Khlopin Radium Institute (Russia). Liquid scintillation cocktail Optiphase HiSafe 3 was purchased from PerkinElmer (USA).

2.2. Apparatus and analysis

The pH of aqueous phase was measured by pH-meter Expert (±0.5 °C, pX (pH) ±0.005, mV ±0.2).

Stable yttrium isotope concentration was determined with Arsenazo III by standard spectrophotometric method (l = 10 nm, л = 650 nm) using UV-2600 SHIMADZU UV-VIS spectrophotometer and double checked by emission spectrometer ICPE-9000 SHIMADZU, stable strontium isotope concentration was determined by emission spectrometer ICPE-90000 SHIMADZU.

Radioactive isotopes ⁹⁰Sr and ⁹⁰Y were determined by liquid scintillation counting and Cherenkov counting standard methods using low level liquid scintillation spectrometer Quantulus 1220 (PerkinElmer).

2.3. Procedure

The dissolution rate was calculated using two-point standard method according to eq. 1 and eq. 2. To study yttrium dissolution rate we prepared a disk with a constant surface area: 0.073 g of Y₂O₃ transformed into the disk (6 mm - diameter and 0.4 mm – thickness) with the surface (S), expressed by eq. 3:

\[ \Delta c / \Delta t = V / g / s \]  
\[ V / S = V g / s m^2 \]  
\[ S = 2 \pi r + 2 \pi h = 2 \pi (r + h) \]

The kinetics experiments were conducted in 25 mL penicillin bottle for 120 min and 20 mL of each alkaline carbonate solutions.

The distribution ratios (D) were determined as follows; 1 mL of each (aqueous and organic phase) was placed into the 4 mL centrifugal polypropylene tube, the two phase systems were shaken at 21 ± 1 °C for 10 min (sufficient for a complete equilibrium, confirmed in our preliminary experiments).

In the stripping experiments, 0.8 mL of organic phase contacted with 0.8 mL of HNO₃ solution (shaken at 21 ± 1 °C for 10 min), then centrifuged at 3000 rpm for 10 min. The distribution ratios (D) were expressed by eq.4

\[ D_Y = [Y]_{org} / [Y]_{aq} \]

For stable yttrium extraction experiments the following system was chosen: “0.01 mol/L of L (8-HQ/2,3-DHN) in organic phase (BuAc/2-nitrotoluene) - 0.001 mol/L of yttrium in 0.5 mol/L K₂CO₃ aqueous solution”, for ⁹⁰Y/⁹⁰Sr separation the following system was chosen: “0.001 mol/L of L (8-HQ/2,3-DHN) in organic phase (BuAc/2-nitrotoluene) - 4·10⁻⁵ mol/L of yttrium and 1·10⁻⁴ mol/L of strontium in 0.5 mol/L K₂CO₃ aqueous solution”.

3. RESULTS AND DISCUSSION

3.1. Y₂O₃ solubility and dissolution kinetics study

The dissolution kinetics of Y₂O₃ solubility was studied using different alkaline carbonates agents (Tab. 1). Carbonates have stabilly increased in dissolution kinetics in following order: 2 mol/L (NH₄)₂CO₃ >> 2 mol/L K₂CO₃ > 2 mol/L Na₂CO₃ >> 1 mol/L (NH₄)₂CO₃ > 1 mol/L K₂CO₃ > 1 mol/L Na₂CO₃.

Table 1 depicts yttrium solubility and dissolution kinetics, 1 mol/L Na₂CO₃, K₂CO₃ and (NH₄)₂CO₃ possessed yttrium solubility 1.7, 0.9, 2.8 g/L with dissolution rate of 0.21, 0.26, 0.24 g/m²/s, respectively, 2 mol/L Na₂CO₃, K₂CO₃ and (NH₄)₂CO₃ - 4.9, 1.4, 8.2 g/L and dissolution rate of 0.43, 0.46, 0.62 g/m²/s, respectively.
Table 1. Yttrium solubility and dissolution kinetic studies in different alkaline agents

<table>
<thead>
<tr>
<th>Alkaline agent</th>
<th>Solubility, g/L</th>
<th>Dissolution rate $V, g/s \cdot m^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 mol/L Na$_2$CO$_3$</td>
<td>1.7 ± 0.017</td>
<td>0.213 ± 0.025</td>
</tr>
<tr>
<td>2 mol/L Na$_2$CO$_3$</td>
<td>4.9 ± 0.096</td>
<td>0.430 ± 0.013</td>
</tr>
<tr>
<td>1 mol/L K$_2$CO$_3$</td>
<td>0.9 ± 0.031</td>
<td>0.262 ± 0.021</td>
</tr>
<tr>
<td>2 mol/L K$_2$CO$_3$</td>
<td>1.4 ± 0.029</td>
<td>0.458 ± 0.010</td>
</tr>
<tr>
<td>1 mol/L (NH$_4$)$_2$CO$_3$</td>
<td>2.8 ± 0.182</td>
<td>0.243 ± 0.026</td>
</tr>
<tr>
<td>2 mol/L (NH$_4$)$_2$CO$_3$</td>
<td>8.2 ± 1.01</td>
<td>0.622 ± 0.018</td>
</tr>
</tbody>
</table>

3.2. Yttrium extraction and Y/Sr separation in alkaline carbonate media

Based on yttrium oxide solubility, we extracted yttrium from Na$_2$CO$_3$, K$_2$CO$_3$ and (NH$_4$)$_2$CO$_3$ using extractants in different organic diluents.

Despite the fact that (NH$_4$)$_2$CO$_3$ showed the highest yttrium oxide solubility and dissolution rate, it demonstrated a poor yttrium extraction and distribution ratio ($D$) (with the third phase formation). K$_2$CO$_3$ showed the lowest yttrium oxide solubility, but it had the highest yttrium distribution ratio ($D$) with 8-HQ (in butyl acetate and 2-nitrotoluene), followed by Na$_2$CO$_3$. Therefore, K$_2$CO$_3$ was chosen for further extraction and separation studies. Only 8-HQ and 2,3-DHN demonstrated sufficient values of yttrium distribution ratios (Fig. 3).

3.3.1. Yttrium extraction

8-HQ demonstrates that the value of yttrium distribution ratio depends on initial pH of the aqueous phase, pH gradually increases from 10 to 13.5 in 2-nitrotoluene and BuAc (Fig. 4).

$$D_Y \text{gradually increases after pH 10 (8-HQ $pK_a$: 9.9),}$$

in 2-nitrotoluene pH 13 has maximum ($D_Y$) while in butyl acetate - pH 13.5. The $D_Y$ decreases after pH 13 in 2-nitrotoluene might be due to hydroxide precipitation and/or 8-HQ dissolution into aqueous phase. The $\log D_Y$ was 2.60 and 2.03 for 2-nitrotoluene and butyl acetate, respectively.

$$\log D_Y$$

Figure 4. Effect of initial pH on yttrium extraction by 8-HQ

Organic phase saturation shows the limit ratio [L]:[M] ~ 4, which one can interpret as solvate composition ML$_4$ (Fig. 5).

Figure 5. Correlation between yttrium concentrations in aqueous and organic phases in different diluents

Figure 6. Effect of initial pH on yttrium extraction by 2,3-DHN
Extraction with 2,3-DHN demonstrates that the value of yttrium distribution ratio $D$ depends on initial pH of the aqueous phase, gradually increasing from pH 12 to pH 13.5 in BuAc and to pH 13 in 2-nitrotoluene (Fig. 6).

2,3-DHN showed acceptable $D_Y$ in BuAc, whereas $D_Y$ in 2-nitrotoluene is very low. This might be due to the 2,3-DHN solubility in aqueous phase.

3.3.2. Yttrium extraction and separation with 8HQ

Extraction and separation of stable Y and Sr $^{0.001 \text{ mol/L}}$ of 8-HQ - $4\times10^{-5}$ mol/L of yttrium and $1\times10^{-6}$ mol/L of strontium in 0.5 mol/L K$_2$CO$_3$ aqueous solution were carried out (Fig. 7, 8).

Figs. 7-8 demonstrate the values of SF in BuAc and 2-nitrotoluene. It is seen that for stable yttrium and strontium isotopes SF increases with pH and reaches its maximum values at pH 13.5 in both BuAc and 2-nitrotoluene. Yttrium is better extracted ($D_{Y,\text{max}} = 3.89$) in 2-nitrotoluene. Maximum separation is observed in 2-nitrotoluene: SF = 195.

Extraction and separation experiments, carried out for radioactive $^{90}\text{Y}$ and $^{90}\text{Sr}$ confirmed the principal possibility of Y/Sr pair separation by solvent extraction with some features for trace amounts of radioactive isotopes (Fig. 9, 10).

The trend of SF dependence on pH is the same: it reaches maximum values at pH = 13.5 both for BuAc and 2-nitrotoluene. In contrast with the stable Y and Sr, $^{90}\text{Y}$ is extracted much better ($D_{Y,\text{max}} > 65$) in BuAc. Maximum separation is observed in BuAc: SF ~ 200. The main results comparing two methods are presented in Tab. 2.

Table 2. Yttrium extraction and separation in different extraction systems (* - measured radiometrically)

<table>
<thead>
<tr>
<th>Diluent</th>
<th>$D_Y$</th>
<th>$D_{Sr}$</th>
<th>SF$_{Y/Sr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>8-HQ pH = 13.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BuAc</td>
<td>$0.177$</td>
<td>$0.177$</td>
<td>$1$</td>
</tr>
<tr>
<td></td>
<td>$65.7^*$</td>
<td>$0.33^*$</td>
<td>$200^*$</td>
</tr>
<tr>
<td>2-nitrotoluene</td>
<td>$3.89^*$</td>
<td>$0.02$</td>
<td>$195$</td>
</tr>
<tr>
<td></td>
<td>$9.59^*$</td>
<td>$0.1^*$</td>
<td>$96^*$</td>
</tr>
</tbody>
</table>

The similarity of extraction and separation data, obtained for stable and radioactive isotopes with 8-HQ, is evident for 2-nitrotoluene. Taking into account the different experimental methods, the values are very close. This confirms the principal possibility of Y/Sr separation in carbonate media. The opposite situation for BuAc requires further investigation.
The same experiments were carried out for 2,3-DHN, but the system with 2-nitrotoluene formed third phase, whereas for the system, based on BuAc, there were neither sufficient yttrium extraction, nor Y/Sr separation.

4. CONCLUSION

Y/Sr extraction and separation in carbonate media with several ligands showed, that only 8-HQ and 2,3-DHN can be regarded as perspective compounds for further studies.

The data obtained for stable and radioactive isotopes separation with 8-HQ revealed differences in the behavior of the extracted elements, which can be explained by differences in their concentrations (trace amounts for $^{90}$Y and $^{90}$Sr with the background of stable Y).

2,3-DHN demonstrated high solubility in aqueous phase with low values of distribution ratios, but it is still regarded as perspective after addition of modifier, preventing its transfer into aqueous phase.

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