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Novel 90Sr-90Y generator system based on a cross-flow hollow fiber supported liquid membrane contactor

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Novel ^{90}Sr - ^{90}Y generator system based on a cross-flow hollow fiber supported liquid membrane contactor

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ABSTRACT

Separation of yttrium(III) from strontium(II) with 15% (v/v) di(2-ethylhexyl)phosphoric acid (DEHPA) in dodecane was carried out in a hollow fiber supported liquid membrane (SLM) extraction system operated under closed-loop recirculation of the donor and acceptor phase. The donor phase was a mixture of 5.7 mmol dm^{-3} of Sr(II) and $0.23 \text{ mmol dm}^{-3}$ of Y(III) in 0.1 mol dm^{-3} HCl, the acceptor solution was 3 mol dm^{-3} HCl, and the donor to acceptor phase volume ratio was 6.2. At the donor flow rate of $4.7 \text{ cm}^3 \text{ min}^{-1}$ and the acceptor flow rate of $0.8 \text{ cm}^3 \text{ min}^{-1}$, the yield of Y(III) in the acceptor phase reached 60% after 360 min with a molar ratio of Y(III) to Sr(II) in the acceptor of 250:1, as compared to 1:25 in the donor phase. The yield of Y(III) was 72% at the acceptor flow rate to $1.9 \text{ cm}^3 \text{ min}^{-1}$, but a breakthrough of Sr(II) through liquid membrane increased from 0.02 to 0.2%.

Keywords: Strontium, Yttrium, Supported liquid membrane extraction, DEHPA, ^{90}Sr - ^{90}Y generator

1. Introduction

Radionuclide ^{90}Y possesses suitable radiophysical and chemical characteristics for application in radionuclide therapy. The decay of ^{90}Y is not accompanied with gamma-ray radiation and the emitted beta particles have a maximum energy of 2.3 MeV and an effective path length of 5.3 mm, meaning that 90% of their energy is adsorbed within a sphere with a radius of 5.3 mm. This path length corresponds to 100-200 cell diameters, which means that antibodies labeled with ^{90}Y can kill not only the cancer cells to which they adsorb, but also adjacent tumor cells. A half-life of 64.1 h is consistent with the rate of antibody accumulation in tumor and the antibodies can be labeled with ^{90}Y using various chelating agents. ^{90}Y can be obtained in a carrier-free form by the separation from its long-lived parent, radionuclide ^{90}Sr ($T_{1/2} = 28 \text{ y}$) in a ^{90}Sr - ^{90}Y generator system [1-5]. The use of in-house generators can significantly reduce the production cost of ^{90}Y and provide activity on demand. The basic requirements

for ^{90}Sr - ^{90}Y separation are (i) a high yield of the daughter radionuclide, ^{90}Y , and (ii) low breakthrough of the parent, ^{90}Sr , which is a bone seeker. Various separation methods such as precipitation [6], liquid-liquid extraction (LLE) [7-9], ion exchange [10] and extraction chromatography [11,12] have been investigated for the $^{90}\text{Sr}/^{90}\text{Y}$ separation, but they are usually labour intensive and require multi-stage processing.

Membrane-assisted LLE has been used as an alternative to conventional LLE to achieve separation of a wide range of solutes including biological molecules [13,14], metal ions [15,16], organic pollutants [17,18] and radionuclides, such as ^{177}Lu and ^{137}Cs [19-21]. Supported liquid membrane (SLM) extraction is based on a three-phase system (pertraction) with an organic phase (liquid membrane) placed between two aqueous phases. The organic phase (extractant) is immobilized by capillary forces in the pores of hydrophobic membrane, while the feed (donor) and the stripping (acceptor) solutions are placed on opposite sides of the membrane. Mass transfer in SLM extraction comprises diffusion of the solute of interest from the bulk of the donor phase to the donor/(organic phase) interface, partitioning of the solute between the donor phase and the organic phase, diffusion of the solute through the organic phase to the (organic phase)/acceptor interface and its re-extraction into the acceptor phase. The main advantages of SLM extraction over conventional LLE are in simultaneous extraction and re-extraction, low amount of organic phase needed in the system, high interfacial area per unit volume, no phase separation problems, high concentration factors, low capital and operating costs, and good opportunity for process automation [22,23]. However, due to insufficient membrane stability caused by the loss of the organic phase from the membrane pores over prolonged period of time, there have been very few large scale applications of SLM extraction. Recent developments in forming stable SLM include formation of barrier layers on the membrane surface, either by physical deposition, interfacial polymerization or plasma polymerization [22].

SLM extraction can be performed in continuous-contact mass transfer devices - membrane contactors using flat sheet (FS) or hollow fiber (HF) hydrophobic membranes. In membrane contactors, the aqueous phases flow along opposite sides of the SLM without forming dispersion of one phase into

another. Mass transfer occurs only by diffusion across the SLM, and its direction depends on the concentration driving force maintained across the SLM [24]. The mass transfer rate is significantly affected by the membrane porosity and the wall thickness. The membrane porosity should be high in order to obtain high fluxes, while the flux across the membrane is inversely proportional to the membrane thickness [25]. The membrane is typically made of polymers such as polypropylene (PP), polyethylene (PE), polytetrafluoroethylene (PTFE), poly(tetrafluoroethylene-*co*-perfluorovinylether) (PFA) or polyvinylidene fluoride (PVDF) [24]. HF membrane contactors are commercially available and offer much higher surface area per unit of module compared to FS membrane units.

The aim of this study was to develop a novel method for separation of yttrium from strontium with DEHPA using a SLM extraction. The optimal separation conditions in terms of the donor pH and the concentration of DEHPA in the organic phase were determined by batch LLE. The SLM extraction was then performed under these optimal conditions in a cross-flow HF contactor operated in a recirculation mode. The influence of the donor and acceptor flow rates and recirculation time on the mass transfer rate of Y(III) and the separation effects in the applied system has been investigated.

2. Experimental section

2.1. Chemicals and materials

SrCl₂·6H₂O, YCl₃·6H₂O, DEHPA and dodecane were purchased from Sigma-Aldrich (St. Louis, MO, USA). Hydrochloric acid and hexane were purchased from Lach Ner (Brno, Czech Republic). All the chemicals were of analytical-reagent grade. Deionised water was supplied from a Milli-Q water purification system (Millipore, Bedford, MA, USA). The microporous polypropylene hollow fiber membranes, Accurel PP 50/280, were supplied from Membrana GmbH (Wuppertal, Germany).

The standard stock solutions containing 1000 mg dm⁻³ (11 mmol dm⁻³) of Sr(II) and 100 mg dm⁻³ (1.1 mmol dm⁻³) of Y(III) were prepared for each metal separately by dissolving an adequate amount of salt in 0.1 mol dm⁻³ HCl. Working donor solutions were prepared shortly before each experiment by

appropriate dilution of the stock solutions with HCl. The organic phase was prepared by dissolving DEHPA in hexane or dodecane, and the acceptor (stripping) phase was prepared by diluting HCl with water.

2.2. Batch LLE experiments

The donor solution was the mixture of 502 mg dm⁻³ (5.7 mmol dm⁻³) of Sr(II) and 20.8 mg dm⁻³ (0.23 mmol dm⁻³) of Y(III) in aqueous phase of varying acidity (0.1-2 mol dm⁻³ HCl). The concentration of Sr(II) was significantly higher than that of Y(III), because in a typical ⁹⁰Sr-⁹⁰Y generator system a ratio of Sr(II) to Y(III) concentration is very high. The content of DEHPA in the organic phase was varied from 0.16 to 1.28 mol dm⁻³ (5 to 40% (v/v)).

Experiments were performed in glass test tubes with polyethylene stoppers by mixing equal volumes (4 cm³) of the donor and organic phase for 60 min at room temperature (24 ± 1°C). Preliminary experiments revealed that this time was sufficient for attaining the equilibrium. The mixture was then centrifuged for 60 min to allow a complete phase separation. Then, the concentrations of strontium and yttrium remaining in the aqueous phase after extraction were determined by inductively coupled plasma optical emission spectrometry (ICP–OES) using a Spectroflame model B spectrometer (Spectro Inc., MA, USA).

The partition coefficient of strontium (m_{Sr}) and yttrium (m_Y) between organic and aqueous phases, and the Y/Sr separation factors (α) were calculated according to the following equations:

$$m_M = \frac{C_{M,org}}{C_{M,aq}} \quad (1)$$

$$\alpha = \frac{m_Y}{m_{Sr}} \quad (2)$$

where $C_{M,org}$ and $C_{M,aq}$ are the concentrations of metal ion in the organic and aqueous phase, respectively.

2.3. Experimental setup of a recirculating SLM extraction system and procedure

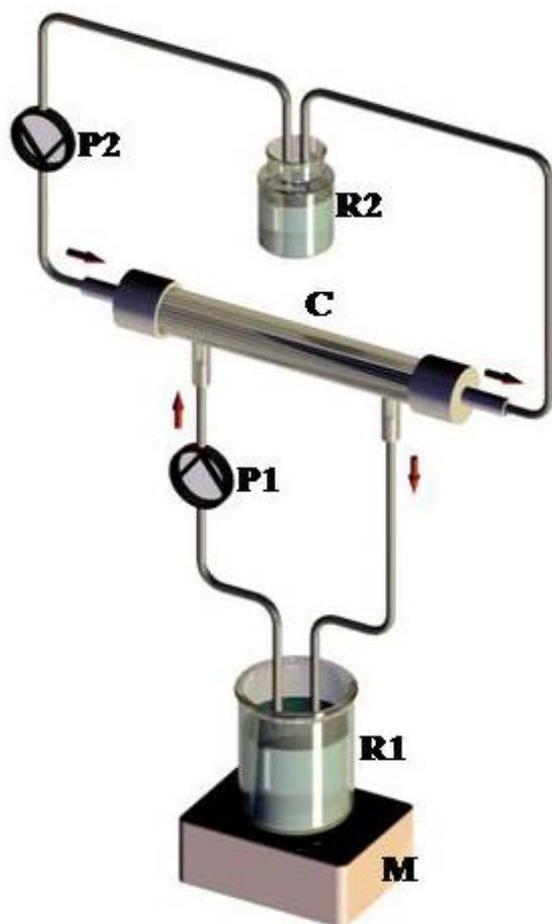


Fig. 1. Schematic of the experimental setup used for the SLM extraction of Sr(II) and Y(III): C – contactor, R1 – feed reservoir, R2 – stripping reservoir, P1, P2 – peristaltic pumps for the donor and acceptor phase, respectively, M – magnetic stirrer.

SLM extraction of Sr(II) and Y(III) was performed in a HF membrane contactor designed and constructed in our laboratory, which consisted of seven hydrophobic microporous polypropylene HF membranes enclosed in a glass shell with an inner diameter of 0.7 cm. Polypropylene HFs have been shown a good radiation stability and can be safely used for the separation of radionuclides [2,26]. The fibers were potted on both ends of the shell with epoxy resin. Membrane contactor was equipped with separate inlet and outlet tube connections for both aqueous phases. The membrane had a wall thickness of 50 μm , an inner diameter (d_i) of 280 μm , a mean pore size of 0.1 μm , and a porosity (ε) of 60% [27]. The effective length (L_{ef}) of each fiber in the contactor was 17 cm, and the (total) effective outer ($A_o =$

$\pi d_o N L_{ef} \varepsilon$; d_o is the outer diameter of the fiber, N is the total number of fibers in the contactor) and inner ($A_i = \pi d_i N L_{ef} \varepsilon$) surface area of the membranes was 8.5 and 6.3 cm², respectively. The organic phase immobilized in the pores of the membrane was 0.48 mol dm⁻³ (15%) DEHPA in dodecane. The volume of the organic phase was ~37 μ l, calculated from the equation:

$$V_o = \frac{\pi(d_o^2 - d_i^2)NL_{ef}\varepsilon}{4} \quad (3)$$

A schematic of the experimental setup is shown in Fig. 1. SLM extraction system consisted of a HF module (C), two reservoirs for the aqueous donor and acceptor solutions (R1 and R2, respectively), two peristaltic pumps (Perkin-Elmer, Waltham, Mass., USA), P1 and P2, tubes (PharMed[®], Cole-Parmer Instrument Company, Vernon Hills, Ill., USA) and magnetic stirrer (M). SLM was prepared by pumping the organic phase through the lumen of the HF at a low flow rate. After the pores were filled with the organic phase, both sides of the membrane were rinsed with sufficient amount of milli-Q water, prior to the introduction of the donor and acceptor solutions. The donor solution (5.7 mmol dm⁻³ of Sr(II) and 0.23 mmol dm⁻³ of Y(III) in 0.1 mol dm⁻³ HCl) with a total volume of 25 cm³ was fed at the shell side of the fibers and recirculated in a closed loop between the module and reservoir R1 using peristaltic pump P1. The flow rate of the donor phase was 0.8-4.7 cm³ min⁻¹ and the total holdup volume of the tubing used for the recirculation of the donor phase was 0.8 cm³. The donor phase was vigorously mixed in reservoir R1 by a magnetic stirring bar to obtain nearly ideal mixing conditions. The acceptor solution (3 mol dm⁻³ HCl) with a total volume of 4 cm³ was pumped through the lumen of the fibers using peristaltic pump P2 and recirculated between the module and reservoir R2. The flow rate of the acceptor phase was 0.8 or 1.9 cm³ min⁻¹ and the total holdup volume of the tubing used to circulate the acceptor phase was 0.5 cm³. The donor and acceptor phase flowed co-currently through the module.

All experiments were carried out at room temperature. Samples were periodically collected from the donor and acceptor reservoir to determine strontium and yttrium concentrations by ICP-OES. The withdrawn volume of each phase was sufficiently small to keep the total volume constant.

2.4. Theory

Y(III) ions preferentially reacted with DEHPA and the complex was transferred through the membrane against the concentration gradient of Y(III), due to a coupled transfer of H^+ ions in the opposite direction. The efficiency of Sr(II) and Y(III) mass transfer through the liquid membrane was evaluated using several parameters such as the extraction efficiency (E), the removal efficiency (E_R), the memory effect (M), the mean flux across the membrane (J_m), and the overall mass transfer coefficient (K_D). The extraction efficiency or yield was calculated as the amount of the metal ion (Sr(II) or Y(III)) found in the acceptor phase divided by the initial amount of metal ion in the donor phase:

$$E = \frac{n_A}{n_D^{in}} = \frac{C_A V_A}{C_D^{in} V_D} \quad (4)$$

where n_D^{in} is the initial number of moles of the respective metal ion in the donor phase, n_A is the number of moles of the respective metal ion collected in the acceptor phase at time t , C_D^{in} is the initial molar concentration of the respective metal ion in the donor phase, C_A is the molar concentration of the respective metal ion in the acceptor phase at time t , and V_D and V_A are the donor and acceptor volumes, respectively. E depends on the partition coefficient of the respective metal ion between the aqueous donor and organic phase, the flow rate of both aqueous phases, the rate of diffusion in the feed solution and through the membrane, and the efficiency of the stripping into the acceptor phase [17]. The removal efficiency represents the amount of the respective metal ion removed from the donor phase with respect to its initial amount in the donor phase:

$$E_R = \frac{n_D^{in} - n_D}{n_D^{in}} = \frac{C_D^{in} - C_D}{C_D^{in}} \quad (5)$$

where n_D and C_D are the number of moles and the molar concentration of the respective metal ion in the donor phase at time t , respectively. The memory effect is a fraction of the metal ion captured in the organic phase with respect to its amount initially present in the donor phase, and can be calculated as a difference between the removal and extraction efficiency ($M = E_R - E$).

The mean flux (J_m) of the respective ion across the membrane in a SLM system operated under closed-loop recirculation of aqueous phases is given by:

$$J_m = -\frac{Q_D E_R'}{A_o} C_D^{in} \exp\left(-\frac{Q_D E_R'}{V_D} t\right) \quad (6)$$

$$E_R' = 1 - \exp\left(-\frac{K_D A_o}{Q_D}\right) \quad (7)$$

where Q_D is the donor flow rate, E_R' is the removal efficiency per single pass of the feed stream, and K_D is the overall mass transfer coefficient based on the donor phase [21,28].

According to the resistance-in-series approach, the mass transfer of an ion through SLM proceeds via three steps: diffusion of the ion from the feed stream to the membrane interface, diffusion of the ion through the organic phase entrapped within the membrane pores, and diffusion of the ion from the stripping membrane interface to the bulk of the stripping (acceptor) phase. If the extraction is accompanied by chemical reactions, e.g. formation and decomposition of an ion-carrier complex at feed and stripping phase, respectively, the reaction kinetics parameters have to be included in the transport equation [29]. If the chemical reaction is fast, the overall mass transfer resistance (R), expressed in terms of the driving force in the donor phase, can be described as a sum of the three resistances (the resistance of the donor phase, the organic phase, and the acceptor phase):

$$R = \frac{1}{K_D} = \frac{1}{k_D} + \frac{d_o}{k_M d_{LM} m_D} + \frac{d_o m_A}{k_A d_i m_D} \quad (8)$$

where k_D , k_M , and k_A are the individual mass transfer coefficients of the donor phase, the organic phase and the acceptor phase, respectively, d_{LM} is the log mean diameter of the fiber, m_D is the partition coefficient between the organic phase and the aqueous donor phase, and m_A is the partition coefficient between the organic phase and the acceptor phase. Eq. (8) is valid for the donor phase flowing through the shell side and the acceptor phase flowing through the lumen of the fibers [30]. This configuration offers a larger surface area for the extraction step than the lumen-feed configuration.

The individual mass transfer coefficients of the donor and acceptor phase can be estimated using mass transfer correlations involving Sherwood, Schmidt and Reynolds numbers [31-33]. The membrane mass transfer coefficient can be predicted from the membrane morphology:

$$k_M = \frac{D\varepsilon}{\delta\tau} \quad (9)$$

where δ and τ are the membrane thickness and tortuosity of the pores, respectively, and D is the diffusivity of ion-carrier complex in the organic phase entrapped within the pores. D can be estimated from the Wilke-Chang correlation or the Scheibel equation [34].

The overall mass transfer coefficient in a SLM extraction system with closed-loop recirculation of both aqueous phases was determined experimentally using the equation [28]:

$$K_D = -\frac{Q_D}{A_o} \ln \left[1 - \frac{V_D}{Q_D} \frac{d \ln(C_D^{in} / C_D)}{dt} \right] \quad (10)$$

The individual mass transfer coefficients can be estimated using the aforementioned equations or graphically using the Wilson-plot method [35,36].

3. Results and discussion

3.1. Two-phase batch LLE

A two-phase batch LLE was performed to find the optimum conditions for the extraction of Sr(II) and Y(III) so that they can be applied for a SLM system. The initial concentration of both metals in the aqueous phase was kept constant, whilst the concentration of HCl in the aqueous phase and the concentration of DEHPA in the organic phase were varied over a wide range. DEHPA is a well-known extractant and frequently used for the LLE of metal ions due to its chemical stability, good kinetics of extraction, good loading and stripping characteristics, low solubility in aqueous phase, and availability in commercial quantities. The extraction of metal ions with DEHPA proceeds via a cation exchange

mechanism [37]. The obtained m_M values for the extraction of Sr(II) and Y(III) and the Y(III)-Sr(II) separation factors are listed in Table 1.

Table 1

The partition coefficients of Sr(II) and Y(III), m_Y and m_{Sr} , and separation factors, α , at different concentrations of HCl in the donor phase and different concentrations of DEHPA in the organic phase (Donor phase: 5.7 mmol dm⁻³ of Sr(II) and 0.23 mmol dm⁻³ of Y(III) in HCl; Organic phase: DEHPA in hexane, except in the case * in which case dodecane was used as the organic solvent; Phase volume ratio: 1:1; Contact time: 60 min).

$C_{HCl}, \text{mol dm}^{-3}$	$C_{DEHPA, org}, \%$	m_Y	m_{Sr}	α
0.1	5	283	0.03	9.4×10^3
0.1	15	420	0.02	2.1×10^4
0.1	40	480	0.02	2.4×10^4
0.1	15*	829	< 0.01	8.3×10^4
1.0	5	2	0.02	1.0×10^2
1.0	15	21	0.02	1.1×10^3
1.0	40	255	0.02	1.3×10^4
2.0	5	0.1	0.02	5
2.0	15	1.8	0.02	90
2.0	40	12	0.01	1.2×10^3

As can be seen from Table 1, the extraction of Sr(II) was negligible in the entire range of acidity investigated, as well as in the entire range of DEHPA concentration. The extraction of Y(III) was significantly affected by the HCl concentration in the aqueous phase and the DEHPA content in the organic phase. For a fixed DEHPA concentration in hexane, the partition coefficient of Y(III) decreased as the concentration of HCl increased. This can be explained by the fact that an increase in the donor acidity reduces the dissociation of DEHPA and Y(III) ions react with a deprotonated DEHPA. The similar results were obtained for the extraction of Sr(II) and Y(III) from nitric acid solutions using either DEHPA or bis(2-ethylhexyl) phosphonic acid (PC88A) as a carrier in the organic phase [2,38]. The highest Y/Sr separation factors for the system DEHPA/hexane of $(0.94-2.4) \times 10^4$ were achieved at 0.1 mol dm⁻³ HCl.

If the concentration of HCl in the donor phase remained constant, the partition coefficient of Y(III) increased with increasing concentration of the carrier in the organic phase and would reach a constant

limiting value at very high DEHPA concentration. As shown in Table 1, for each HCl concentration in the donor, the highest separation factors α were obtained using 40% DEHPA in hexane. Since the values of m_Y and α for the extraction from 0.1 mol dm^{-3} HCl were fairly similar using either 15 or 40% DEHPA in hexane, the lower DEHPA concentration will be used in further work to reduce the operating costs and environmental impact.

In order to investigate the effect of solvent type, the extraction of Sr(II) and Y(III) was performed with two different solvents, under the optimal conditions in terms of acidity of the donor solution and DEHPA concentration in the organic phase (0.1 mol dm^{-3} HCl and 15% DEHPA). The use of dodecane, instead of hexane, as a solvent for DEHPA, led to an increase in m_Y and α by a factor of ~ 2 and ~ 4 , respectively. Thus, 15% DEHPA in dodecane was used as the organic phase in all subsequent SLM extraction experiments.

3.2. Variations of process performances with time in a recirculating SLM extraction system

After optimization of the donor and organic phase conditions, the feasibility of separation Y(III) from Sr(II) was investigated using the membrane-assisted LLE in continuous HF membrane contactor shown in Fig. 1. Since DEHPA is well suited to extract selectively Y(III) from aqueous solutions, separation of Sr(II) from Y(III) in the applied SLM extraction system involves two separation stages: the extraction of Y(III) from the aqueous donor phase into the organic phase containing carrier molecules (by complexation of Y(III) with DEHPA molecules at the (donor solution)-membrane interface) and the re-extraction of Y(III) from the organic phase into the aqueous acceptor phase involving the release of Y(III) at the membrane-acceptor solution interface. At low concentrations of yttrium ($0.15 - 0.80 \text{ mmol dm}^{-3}$), binding of Y(III) to DEHPA may be explained by the formation of two organic metal species, $YA_3 \cdot 2HA$ and $YA_3 \cdot HA$ [37], where HA and A stand for DEHPA in the molecular and deprotonated form, respectively. The donor phase was chosen to flow on the shell side because this configuration offered a larger mass transfer area for the removal of Y(III) from the donor phase than the lumen-

stripping configuration. The donor and the acceptor phase were recirculated in a closed loop between the respective reservoirs and the module in order to improve the rate of mass transfer in both aqueous phases. The variations of the concentration of Y(III) ions in the donor and acceptor phase with time at five different donor flow rates are presented in Fig. 2. The acceptor flow rate was kept constant at $0.8 \text{ cm}^3 \text{ min}^{-1}$.

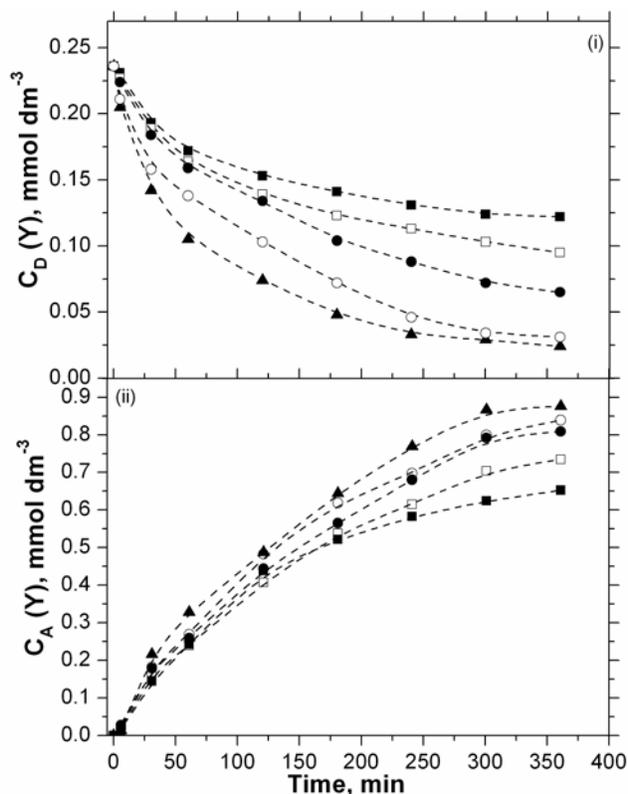


Fig. 2. Time dependence of Y(III) concentration in the donor and acceptor phase reservoir at different donor flow rates. Donor phase: 25 cm^3 , 5.7 mmol dm^{-3} Sr(II) and $0.23 \text{ mmol dm}^{-3}$ Y(III)/ 0.1 mol dm^{-3} HCl, pH 1; Acceptor phase: 4 cm^3 , 3 mol dm^{-3} HCl; Organic phase: 15% DEHPA in dodecane; Donor flow rates: (■) $0.8 \text{ cm}^3 \text{ min}^{-1}$; (□) $1.6 \text{ cm}^3 \text{ min}^{-1}$; (●) $2.4 \text{ cm}^3 \text{ min}^{-1}$; (○) $3.2 \text{ cm}^3 \text{ min}^{-1}$; (▲) $4.7 \text{ cm}^3 \text{ min}^{-1}$; The acceptor flow rate: $0.8 \text{ cm}^3 \text{ min}^{-1}$.

As shown in Fig. 2, the concentration of Y(III) in the donor phase reservoir decreased significantly during the first 4 h of operation and gradually reached a plateau afterwards. The concentration of Y(III) in the acceptor phase reservoir increased exponentially until a steady state was established after ~5 h of operation, indicating that after that time the mass fluxes of Y(III) from the donor to acceptor phase and

vice versa were equilibrated. The concentration of Y(III) in the donor and acceptor phase was depended on the flow rate of the donor phase. The minimum concentration of Y(III) in the donor phase and the maximum concentration of Y(III) in the acceptor phase were achieved at the highest donor flow rate of $4.7 \text{ cm}^3 \text{ min}^{-1}$. At the same time, as the donor flow rate increased from 0.8 to $4.7 \text{ cm}^3 \text{ min}^{-1}$, the concentration of Sr(II) in the donor phase was reduced by 4 to 8% compared to the initial Sr(II) concentration. The re-extraction of Sr(II) on the acceptor side of the membrane was virtually negligible after 360 min ($< 0.03\%$ of its initial concentration) and independent of the donor flow rate. The obtained results suggest that HF membrane contactor in recirculation mode of operation can be applied as a generator of radionuclide ^{90}Y in the form suitable for direct complexation and use in nuclear medicine. It should be noted that the process takes a relatively long time because of the limited surface (contacting) area of the laboratory-scale HF membrane contactor, which is more than 3 orders of magnitude smaller than the contacting area of a commercial LiquiCel[®] X50 membrane contactor [2], used for the ^{90}Sr - ^{90}Y separation. The improvement in the rate of Y(III) transport through SLM containing 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester as a result of increased membrane area is well documented [39].

3.3. *Effect of the phase flow rates*

The mass transfer in membrane contactors with recirculating loops is strongly influenced by the flow rate of the phases involved in the process. The effect of the extraction time on the process efficiency at the lowest and highest donor flow rate (0.8 and $4.7 \text{ cm}^3 \text{ min}^{-1}$) used in this work and the constant acceptor flow rate of $0.8 \text{ cm}^3 \text{ min}^{-1}$ is shown in Figs. 3 (i) and (ii). Both the removal and extraction efficiency of Y(III) increased with time before reaching a constant value after about 5 h. The terminal values of the removal and extraction efficiency were 48 and 44% at $Q_D = 0.8 \text{ cm}^3 \text{ min}^{-1}$, respectively. Thus, at $Q_D = 0.8 \text{ cm}^3 \text{ min}^{-1}$ almost all Y(III) extracted from the donor solution was re-extracted into the acceptor phase and the memory effect was very low. As Q_D increased to $4.7 \text{ cm}^3 \text{ min}^{-1}$, the removal efficiency of Y(III) increased markedly from 48 to 90%, but the extraction efficiency only moderately

increased from 44 to 59% indicating that a substantial fraction of Y(III) removed from the donor solution remained in the organic phase, which led to a memory effect of $\sim 30\%$. Since the decomplexation reaction at the membrane/acceptor interface was fast, it can be assumed that at $Q_D = 4.7 \text{ cm}^3 \text{ min}^{-1}$, there was a significant mass transfer resistance either in the organic phase (due to the high concentration of the complexes formed between DEHPA and metal ions that hindered the diffusion of Y(III)-DEHPA complex through the membrane) or in the acceptor phase (due to the insufficient contact area for the re-extraction of Y(III) from the organic to the acceptor phase). Similar results pointing out to the accumulation of metal ions such as Y, Zn, Cd, Cu, and Ni in SLM containing different acidic organophosphorus carriers (2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester or di-(2-ethylhexyl) dithiophosphoric acid) were reported elsewhere [39,40].

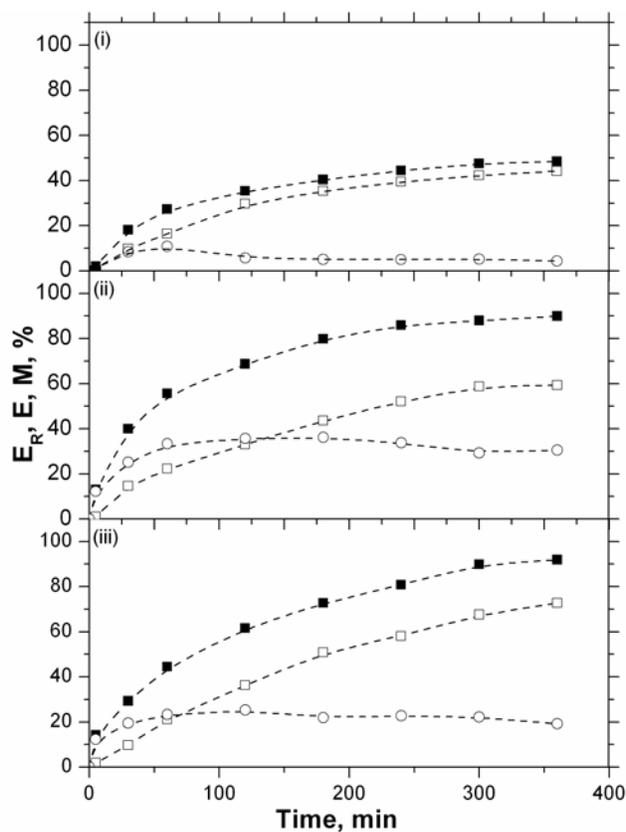


Fig. 3. Effect of the phase flow rates on the efficiency parameters E (\square), E_R (\blacksquare) and M (\circ). The phase flow rates: (i) donor $0.8 \text{ cm}^3 \text{ min}^{-1}$, acceptor $0.8 \text{ cm}^3 \text{ min}^{-1}$; (ii) donor $4.7 \text{ cm}^3 \text{ min}^{-1}$, acceptor $0.8 \text{ cm}^3 \text{ min}^{-1}$; and (iii) donor $4.7 \text{ cm}^3 \text{ min}^{-1}$, acceptor $1.9 \text{ cm}^3 \text{ min}^{-1}$. Donor phase: 25 cm^3 , 5.7 mmol dm^{-3} Sr(II)

and $0.23 \text{ mmol dm}^{-3}$ Y(III)/ 0.1 mol dm^{-3} HCl, pH 1; Acceptor phase: 4 cm^3 , 3 mol dm^{-3} HCl; Organic phase: 15% DEHPA in dodecane.

In order to improve the extraction efficiency of Y(III) from the donor to acceptor phase while keeping high removal efficiency, the flow rate of the donor phase was kept constant at the maximum value of $4.7 \text{ cm}^3 \text{ min}^{-1}$ and the flow rate of the acceptor phase was increased to $1.9 \text{ cm}^3 \text{ min}^{-1}$ (Fig. 3 (iii)). As can be seen from Figs. 3 (ii) and (iii), as the acceptor flow rate increased from 0.8 to $1.9 \text{ cm}^3 \text{ min}^{-1}$, the removal efficiency of Y(III) increased only marginally by $\sim 2\%$, but a considerable improvement in extraction efficiency was observed, with E increasing from 60 to 72%. Therefore, accumulation of Y(III) in the organic phase was lowered at higher acceptor flow rate and hence, the memory effect was reduced from 30 to 20%.

Table 2

The terminal concentrations of Y(III) in the donor (C_D^*) and acceptor phase (C_A^*) reservoirs after 360 min and the terminal efficiency parameters as a function of the donor flow rate. $Q_A = 0.8 \text{ cm}^3 \text{ min}^{-1}$, $V_D/V_A = 6.2$, $C_D^{in} = 0.23 \text{ mmol dm}^{-3}$, $C_A^{in} = 0$.

Q_D $\text{cm}^3 \text{ min}^{-1}$	C_D^* mmol dm^{-3}	C_A^* mmol dm^{-3}	E_R %	E %	M %
0.8	0.122	0.65	48.6	44.2	4.4
1.6	0.095	0.74	59.6	49.8	9.8
2.4	0.065	0.81	72.3	54.8	17.5
3.2	0.031	0.84	87.0	56.8	30.1
4.7	0.024	0.88	89.9	59.3	30.6

As shown in Figs. 2 and 3, the Y(III) concentration in the donor and acceptor phase reservoir and extraction efficiency parameters (E , E_R and M) are time dependent for any given flow rates of the phases until a quasi-steady state is reached. Under the experimental conditions of this work, a steady state was not fully established after 6 h of operation, so that the terminal concentrations of Y(III) in the donor and acceptor phase will be used instead of their true equilibrium values. In Table 2, the terminal values of C_D , C_A , E_R , E , and M are listed as a function of the donor flow rate at the constant acceptor phase flow rate of $0.8 \text{ cm}^3 \text{ min}^{-1}$. The obtained results indicate that the terminal (minimum) concentration of Y(III)

that can be reached in the donor phase decreased with increasing the donor phase flow rate, which is a typical behaviour for the donor-controlled membrane-based extraction [28,41]. As expected, the terminal Y(III) concentration in the acceptor phase increased with increasing the donor flow rate, but an increase of Y(III) concentration in the acceptor phase was lower than the corresponding decrease of Y(III) concentration in the donor phase, due to the accumulation of Y(III) in the organic phase. The terminal memory effect, which is a relative measure of the amount of Y(III) accumulated within the organic phase over 6 h, increased from 4 to 31 % as Q_D increased from 0.8 to 4.7 cm³ min⁻¹.

It can also be seen from the results in Table 2 that the removal efficiency of Y(III) increased significantly (from 49 to 87%) with increasing the donor flow rate from 0.8 to 3.2 cm³ min⁻¹, but the effect was less pronounced with further increase in the donor flow rate, probably due to saturation of the organic phase inside the pores of the membrane by the complexes formed between DEHPA and either Y(III) or Sr(II) inducing a slowdown in the rate of renewal of the interfacial contact area by a fresh organic phase. The extraction efficiency of Y(III) was less affected by the donor flow rate than the removal efficiency, indicating that a portion of Y(III) extracted from the donor phase remained in the organic phase due to a high extraction capacity of the extractant. It means that re-extraction of Y(III) from the organic to the acceptor phase is suppressed, and the degree of Y(III) re-extraction decreased with increasing the donor flow rate. The reason for the suppressed re-extraction of Y(III) at higher donor flow rates could be the fact that accumulated metal-DEHPA complexes increased the viscosity of the membrane phase, and thus the diffusion of the Y(III)-DEHPA complex toward the membrane-acceptor interfacial contact area was hindered. Another reason for the suppressed re-extraction of Y(III) could be insufficient surface contact area provided for the re-extraction in the lumen of the HFs compared to that on the shell side. Similar behavior was reported earlier for the extraction of aroma compounds in hollow fiber membrane contactors [30,42].

Fig. 4 shows the molar percent of Y(III) and Sr(II) in the donor phase before SLM extraction, as well as in the raffinate and acceptor phase after 360 min of SLM extraction. It is clear that the investigated SLM process is highly selective for Y(III). The concentration of Y(III) in the donor phase at the start of

the process was only 3.9 mol% (the molar ratio of Y(III) to Sr(II) was 1:25) and the final concentration of Y(III) in the acceptor phase was 99.6 mol% (the molar ratio of Y(III) to Sr(II) was 250:1). On the other hand, due to impermeability of the liquid membrane to Sr(II), the concentration of Sr(II) in the donor phase went up during the process from 96.1 to 99.6 mol%. The yield of Y(III) in the acceptor phase reached 60% after running the process for 360 min with only 0.4% of the initial amount of Y(III) remaining in the raffinate and 39.6% being trapped in the organic phase.

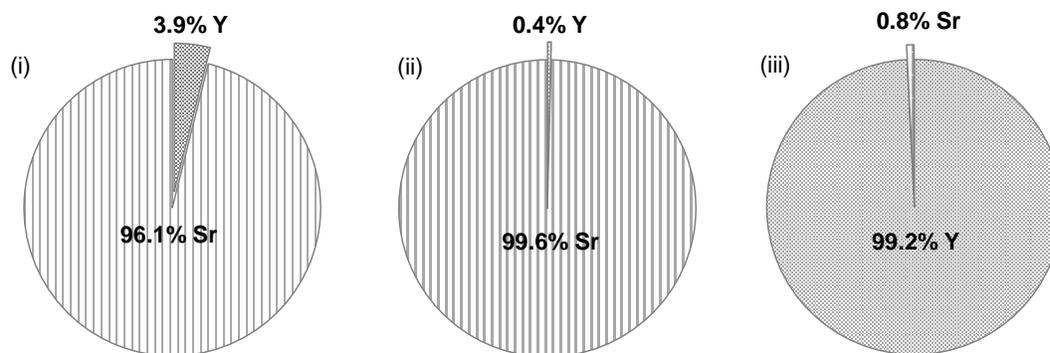


Fig. 4. The molar percent of Y(III) and Sr(II) in (i) donor phase before SLM extraction, (ii) raffinate phase after 360 min of SLM extraction, and (iii) acceptor after 360 min of SLM extraction. $Q_D = 4.7 \text{ cm}^3 \text{ min}^{-1}$, $Q_A = 0.8 \text{ cm}^3 \text{ min}^{-1}$, $C_D^{in} = 5.7 \text{ mmol dm}^{-3}$ Sr(II) and $0.23 \text{ mmol dm}^{-3}$ Y(III).

Table 3

The extraction efficiency parameters of Sr(II) after 360 min of operation as a function of the acceptor flow rate. $Q_D = 4.7 \text{ cm}^3 \text{ min}^{-1}$, $V_D/V_A = 6.2$, $C_D^{in} = 5.7 \text{ mmol dm}^{-3}$ Sr(II), $C_A^{in} = 0$.

Q_A $\text{cm}^3 \text{ min}^{-1}$	E_R %	E %	M %
0.8	8.1	0.02	8.08
1.9	12.8	0.20	12.6

It was shown in Fig. 3 (iii) that the yield of Y(III) can be improved by increasing the acceptor flow rate. However, the acceptor flow rate affects not only the extraction of Y(III), but also the extraction of Sr(II). As shown in Table 3, the amount of Sr(II) transferred into the acceptor phase at the acceptor flow rate of $1.9 \text{ cm}^3 \text{ min}^{-1}$ was ten times higher than that at $0.8 \text{ cm}^3 \text{ min}^{-1}$. Although the re-extraction of Sr(II) was still at low level with a yield of Sr(II) of only 0.2 %, the increased breakthrough of Sr(II) into the

acceptor solution is undesirable, because radioactive ^{90}Sr could be deposited in bones during a therapy with ^{90}Y radiopharmaceuticals, which might possibly cause bone cancer. As a result, the acceptor flow rate of $1.9\text{ cm}^3\text{ min}^{-1}$ will be regarded as excessive in the present ^{90}Sr - ^{90}Y generator system and will not be considered in further work.

3.4. Rate of Y(III) mass transfer

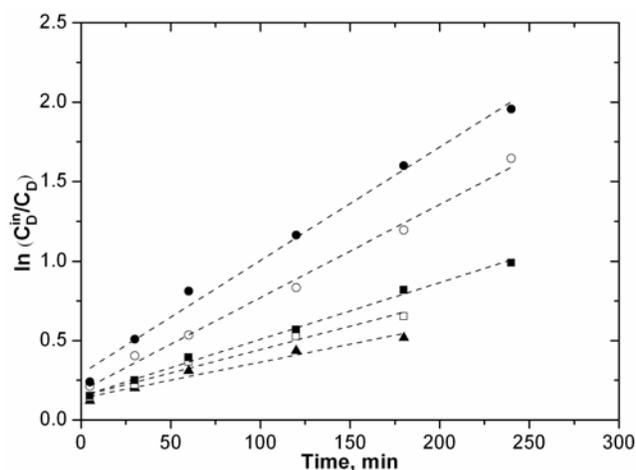


Fig. 5. The plot for the determination of the overall mass transfer coefficient. Donor phase: 25 cm^3 , 5.7 mmol dm^{-3} Sr(II) and 0.23 mmol dm^{-3} Y(III)/ 0.1 mol dm^{-3} HCl, pH 1; Acceptor phase: 4 cm^3 , 3 mol dm^{-3} HCl; Organic phase: 15% DEHPA in dodecane; Acceptor flow rate: $0.8\text{ cm}^3\text{ min}^{-1}$; Donor flow rates: (\blacktriangle) $0.8\text{ cm}^3\text{ min}^{-1}$; (\square) $1.6\text{ cm}^3\text{ min}^{-1}$; (\blacksquare) $2.4\text{ cm}^3\text{ min}^{-1}$; (\circ) $3.2\text{ cm}^3\text{ min}^{-1}$; (\bullet) $4.7\text{ cm}^3\text{ min}^{-1}$.

Table 4

The slope of the line in Fig. 5, the overall mass transfer coefficient, K_D , the coefficient of determination, R^2 , and the removal efficiency per single donor pass, E_R' , as a function of the donor flow rate, Q_D , for the extraction of Y(III) in recirculating SLM extraction system. $V_D/V_A = 6.2$.

Q_D $\text{cm}^3\text{ min}^{-1}$	$d\ln(C_D^{\text{in}}/C_D)/dt$ min^{-1}	$K_D \times 10^6$ m s^{-1}	R^2	E_R' %
0.8	0.0023	1.2	0.956	7.4
1.6	0.0031	1.6	0.972	5.0
2.4	0.0037	1.9	0.994	3.9
3.2	0.0058	2.8	0.991	4.4
4.7	0.0071	3.5	0.989	3.7

The overall mass transfer coefficient based on the donor phase concentration, K_D , for the investigated recirculating SLM extraction system was calculated from the experimental data using Eq. (10). Plotting $\ln(C_D^{\text{in}} / C_D)$ against time should give a straight line and the overall mass transfer coefficient can be calculated from the slope of that line. A graph of $\ln(C_D^{\text{in}} / C_D)$ against time at five different flow rates of the donor phase is shown in Fig. 5. As predicted by Eq. (10), good linear relationships between $\ln(C_D^{\text{in}} / C_D)$ and t were obtained, with correlation coefficients exceeding 0.95. The slopes of these lines and the overall mass transfer coefficients determined from the slopes are listed in Table 4. As can be seen from Table 4, K_D increased from 1.2 to $3.5 \times 10^{-6} \text{ m s}^{-1}$ with increasing the donor phase flow rate from 0.8 to $4.7 \text{ cm}^3 \text{ min}^{-1}$, which is generally observed trend for extraction systems with $m_D \gg 1$ [28].

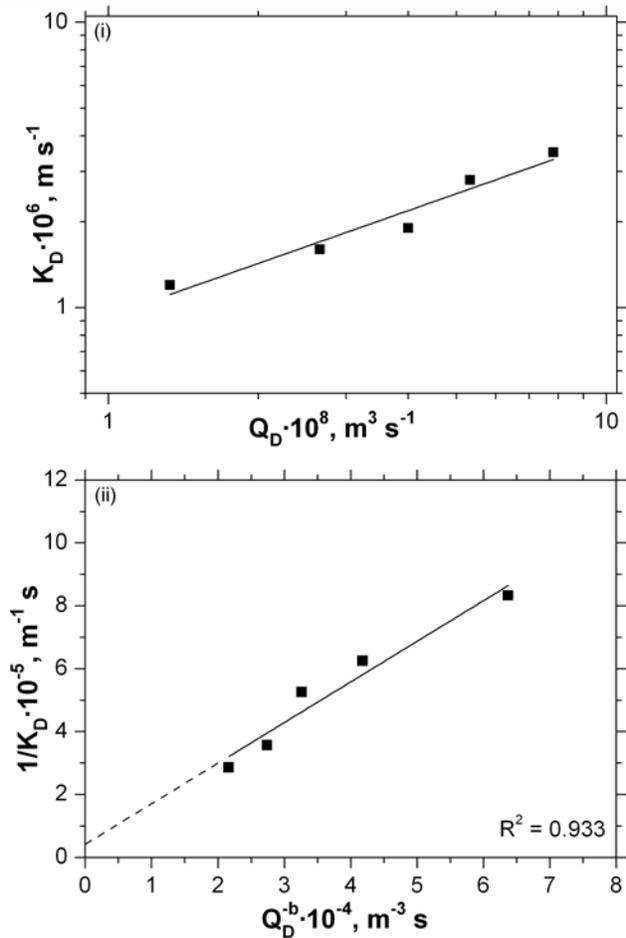


Fig. 6. (i) The effect of the donor flow rate on the overall mass transfer coefficient of Y(III) based on the donor phase. The acceptor phase flow rate was kept constant at $0.8 \text{ cm}^3 \text{ min}^{-1}$. (ii) The Wilson plot of $1/K_D$ vs. $1/Q_D^b$, where b is a slope of the best fit line in Fig. 6 (i).

Fig. 6 (i) is a plot of K_D versus donor phase flow rate, Q_D , on a log-log scale. A linear dependence was obtained, indicating that the overall mass transfer resistance ($1/K_D$) was controlled by the donor phase resistance, so that the overall mass transfer coefficient was approximately equal to the mass transfer coefficient in the donor phase, $K_D \approx k_D$. The overall mass transfer resistance ($1/K_D$) in the applied SLM extraction system is given by Eq. (8), which is valid if the reaction kinetics at both interfaces (donor-membrane and membrane-acceptor) can be neglected, i.e. if the overall kinetics is limited by the rate of mass transfer. In that case, mass transfer of Y(III) through supported liquid membrane takes place in three successive diffusion steps: diffusion of Y(III) through the boundary layer of the aqueous donor phase to the membrane interface, diffusion of Y(III)-DEHPA complex through the organic phase entrapped within the membrane pores, and diffusion of Y(III) through the boundary layer of the stripping phase.

The sum of the membrane and the acceptor mass transfer resistances can be determined graphically from the Wilson plot. This method assumes that the overall mass transfer resistance is controlled by the flow rate of the mass transfer-limiting phase which is the donor phase in this case. The Wilson plot of $1/K_D$ as a function of $1/Q_D^b$ is shown in Fig. 6 (ii). The value of the exponent, $b = 0.61$, was determined by a least-square fit of K_D versus Q_D (Fig. 6 (i) and Table 4). The correlation $Sh \propto Re^{0.61}$ for the calculation of the shell side mass transfer coefficient is very similar to $Sh \propto Re^{0.60}$, found by Prasad and Sirkar for shell-side flow through hollow fiber module with loosely packed fibers at $0 < Re < 500$ [43].

The intercept on the $1/K_D$ axis is equal to $0.42 \times 10^5 \text{ m}^{-1} \text{ s}$ and represents a sum of the membrane resistance and the resistance of the acceptor phase (the second and third term in Eq. (8)). The donor phase resistance is the major mass transfer resistance in the system and its contribution to the overall mass transfer resistance varies from 86% at the highest donor phase flow rate to 95% at the lowest Q_D value. The membrane mass transfer coefficient, k_M , predicted from Eq. (9) is $1.4 \times 10^{-6} \text{ m s}^{-1}$, which is based on $\varepsilon = 0.6$, $\delta = 50 \text{ }\mu\text{m}$, $\tau = 1.7$ (estimated from the Wakao-Smith relation [44]), and $D = 1.9 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ (estimated from the Scheibel equation [34]). Putting $k_M = 1.4 \times 10^{-6} \text{ m s}^{-1}$ into the

second right-hand term of Eq. (8) gives the organic phase resistance of $\sim 1 \times 10^3 \text{ m}^{-1} \text{ s}$, which is two orders of magnitude less than the intercept on the Wilson graph, suggesting that the mass transfer resistance of the acceptor phase (due to either small interfacial area between the organic and acceptor phase or small volume of the acceptor) could be the main reason for suppressed re-extraction of Y(III) into the acceptor phase. It may be concluded that the overall rate of the process in the recirculating SLM extraction system is controlled by the donor phase boundary diffusion. The mass transfer of Y(III) across the boundary layer of the donor phase strongly depends on the donor phase flow rate and consequently, when the donor flow rate is higher the applied system has better performances.

3.5. The influence of the donor flow rate on the molar flux of Y(III)

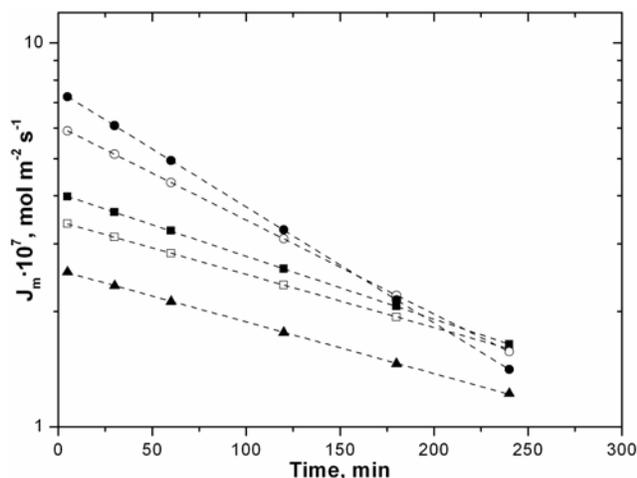


Fig. 7. The variation of the mean molar flux of Y(III) through the donor/organic phase interface with the time of extraction at different donor flow rates: (▲) $0.8 \text{ cm}^3 \text{ min}^{-1}$; (◻) $1.6 \text{ cm}^3 \text{ min}^{-1}$; (■) $2.4 \text{ cm}^3 \text{ min}^{-1}$; (○) $3.2 \text{ cm}^3 \text{ min}^{-1}$; (●) $4.7 \text{ cm}^3 \text{ min}^{-1}$. Acceptor flow rate: $0.8 \text{ cm}^3 \text{ min}^{-1}$.

The mean flux of Y(III) through the interface between the donor and organic phase in a SLM extraction system with closed loop recirculation of the aqueous phases depends on the donor phase flow rate, the volume of the donor phase reservoir, the removal efficiency per single pass of the donor phase through the module, the time elapsed since the process was started, and the donor/organic phase interface, as predicted by Eq. (6). The removal efficiencies per single pass of the donor phase, E'_R , at

different donor flow rates, calculated from Eq. (7), are listed in Table 4. The changes of the mean flux of Y(III) over time at different donor phase flow rates are shown in Fig. 7. Obviously, there is a negative linear relationship between J_m and t on a semi-log scale, as predicted by Eq. (6). Eq. (6) is valid when the change of concentrations in the respective aqueous phase reservoirs is negligible compared to the change in the aqueous phase concentrations along the module, which is satisfied if the system is sufficiently away from equilibrium (in this work, it is valid in the first 4 h of operation). The flux showed a descending trend with time, because the concentration gradient of Y(III) across the liquid membrane was gradually reduced and so did the driving force for the mass transfer. The flux of Y(III) decreased until a steady state was achieved, when the net flux became zero. The rate of flux decline was higher at the higher donor phase flow rates, which was according to Eq. (6).

4. Conclusions

A novel ^{90}Sr - ^{90}Y generator system was developed for separation of ^{90}Y from its long-lived parent, radionuclide ^{90}Sr based on a hollow fiber supported liquid membrane (SLM) system operated under closed-loop recirculation of both aqueous phases. In a simple two-phase extraction system, the partition coefficient of Y(III) increased with decreasing the concentration of HCl in the aqueous phase from 2 to 0.1 mol dm^{-3} HCl and increasing the concentration of DEHPA in the organic phase from 5 to 40%. The use of dodecane, instead of hexane, as a solvent for DEHPA, led to an increase in the Y/Sr separation factor by a factor of 4.

When the three-phase system was used for Y/Sr separation, the flux of Y(III) through SLM decreased with time until a steady state was established after about 5-6 h of operation. The donor phase resistance was the major mass transfer resistance in the three-phase system and its contribution to the overall mass transfer resistance varied from 86 to 95%, depending on the donor phase flow rate. The overall mass transfer coefficient of Y(III) through SLM was directly proportional to the donor flow rate raised to the power of 0.61. A yield of Y(III) in the acceptor phase increased as the flow rate of both aqueous phases increased and reached 72% at the acceptor flow rate of $1.9 \text{ cm}^3 \text{ min}^{-1}$ and the donor flow

rate of $4.7 \text{ cm}^3 \text{ min}^{-1}$. However, a breakthrough of Sr(II) through the liquid membrane also increased with increasing the flow rates in the systems, so that the flow conditions must be optimized to find a balance between the requirement for a high yield of Y(III) in the acceptor phase and a low breakthrough of Sr(II) through SLM.

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Abbreviations

DEHPA	di(2-ethylhexyl)phosphoric acid
SLM	supported liquid membrane
LLE	liquid-liquid extraction
FS	flat sheet
HF	hollow fiber
PP	polypropylene
PE	polyethylene
PTFE	polytetrafluoroethylene
PFA	poly(tetrafluoroethylene- <i>co</i> -perfluorovinylether)
PVDF	polyvinylidene fluoride

Symbols

A_o effective outer surface area of membrane, m^2

A_i	effective inner surface area of membrane, m^2
b	gradient of the line in Fig. 6 (i)
C_A	molar concentration of a metal ion in the acceptor phase at any time t , mol m^{-3}
C_A^*	terminal concentration of a metal ion in the acceptor phase, mol m^{-3}
C_D	concentration of a metal ion in the donor phase reservoir at any time t , mol m^{-3}
C_D^*	terminal concentration of a metal ion in the donor phase, mol m^{-3}
C_D^{in}	initial concentration of a metal ion in the donor phase reservoir, mol m^{-3}
d_i	inner diameter of a hollow fiber, m
d_o	outer diameter of a hollow fiber, m
d_{LM}	log mean diameter of a hollow fiber, m
E	extraction efficiency, -
E_R	removal efficiency, -
E'_R	removal efficiency per single pass of donor phase through module, -
J_m	mean molar flux of Y(III), $\text{mol m}^{-2} \text{s}^{-1}$
K_D	overall mass transfer coefficient based on the donor phase, m s^{-1}
k_D	mass transfer coefficient for the donor phase, m s^{-1}
k_M	mass transfer coefficient for the organic phase in the membrane pores, m s^{-1}

k_A	mass transfer coefficient for the acceptor phase, m s^{-1}
L_{ef}	effective length of hollow fibers, m
M	fraction of a metal ion captured in the organic phase divided by its initial amount in the donor phase (memory effect), -
m_A	partition coefficient between the organic phase and the acceptor phase, -
m_D	partition coefficient between the organic phase and the donor phase, -
n_A	number of moles of a metal ion present in the acceptor phase at any time t , mol
n_D	number of moles of a metal ion present in the donor phase at any time t , mol
n_D^{in}	initial number of moles of a metal ion in the donor phase, mol
Q_D	flow rate of the donor phase, $\text{m}^3 \text{s}^{-1}$
Q_A	flow rate of the acceptor phase, $\text{m}^3 \text{s}^{-1}$
t	time, s
V_A	volume of the acceptor phase, m^3
V_D	volume of the donor phase, m^3
V_o	volume of the organic phase, m^3

Greek letters

α	separation factor, -
δ	membrane thickness, m

ε membrane porosity, -

τ tortuosity of membrane pores, -

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Graphical abstract

