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Selective separation of yttrium(III) through a liquid membrane system using 2-thenoyltrifluoroacetone as an extractant carrier

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Abstract

2-Thenoyltrifluoroacetone has been offered as a mobile carrier in organic phase for the transport and selective separation of yttrium from aqueous media using a liquid membrane system. Perceivably, the use of n-propylamine (PA) in the source phase enhances the transport of yttrium ions. The extraction and stripping conditions have entirely been evaluated and explained. The suggested method has been utilized for the separation of yttrium(III) from its binary mixtures with strontium(II) and some other cations such as Ni^{2+}, Co^{2+}, Ag^+, Fe^{2+}, Al^{3+}, Cu^{2+}, Hg^{2+} and Cs^+ in aqueous solutions of pH 5.4 in the presence of PA, while 1 M nitric acid was acting as a stripping agent in the receiving division. Cyanide ion and 5-sulfosalicylic acid have been used as masking agents to minimize the interferences from different transition metal ions and Al^{3+} in the source phase, respectively. ^{90}Y in secular equilibrium with ^{90}Sr in the source phase, was transferred to receiving phase and separated completely from its long-lived parent isotope. The activity of the transported ^{90}Y was found to decay with a half-life 64.17 ± 0.05 h. The purity of yttrium-90 was comparable or better than the other applied liquid membrane systems for purification of yttrium-90.

Keywords Liquid membrane · Yttrium(III) · Strontium(II) · 2-Thenoyltrifluoroacetone · n-Propylamine · Lewis cell

Abbreviations

HTTA	2-Thenoyltrifluoroacetone
PA	n-Propylamine
PC-88A	2-Ethylhexyl phosphonic acid mono 2-ethylhexyl ester
KSM-17	2-Ethylhexyl-2-ethylhexyl phosphonic acid
CMPO	Octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide
Cyanex 272	Bis (2,4,4-trimethylphenyl)phosphinic acid
TOPO	Tri-n-octylphosphine oxide
EDTA	Ethylene diamine tetraacetic acid
TBP	Tributyl phosphate
BLM	Bulk liquid membrane
SP	Source phase
RP	Receiving phase
MP	Membrane phase
k_e	Apparent rate constant of extraction step
k_s	Apparent rate constant of stripping step
J_{max}	Maximal flux
Gy (unit)	Gray
Bq (unit)	Becquerel
η	Viscosity
cP (unit)	Centipoise
i.d.	Internal diameter

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Introduction

Yttrium is a valuable element from the industrial viewpoint. This element is utilized for nuclear programs including the construction of control rods for nuclear reactors, as well as the production of glass, ceramics and microwave equipment. In the tumor therapy investigations, ^{90}Y is used for generating the labeled monoclonal antibodies, albeit devoid of ^{90}Sr isotope (Pedersen 1967). ^{90}Y is generated from ^{90}Sr but to analyze of the both isotopes in the environmental samples and radioactive wastes are particularly difficult and

complicated, because both of the isotopes are β emitters. One of the indirect methods for measuring ^{90}Sr in the reactor waste, as a complex medium, is separation and measurement of ^{90}Y produced from ^{90}Sr via conducting repeated extractions with tributyl phosphate and detecting its Cherenkov radiation (Martin [1987]). Therefore, the development of the novel techniques to separate yttrium(III) ions from the complex media is a major challenge.

In recent years, the various types of liquid membrane techniques as a valuable tool for separation of metal ions, particularly with very low concentrations are fast emerging (Li [1968], [1971]). These techniques possess the obvious advantages in comparison with traditional methods such as solvent extraction, e.g., the simultaneous extraction and stripping operations, raising the restrictions of organic phase loading, the cost-effective use of expensive complexing agents.

Extensive investigations on liquid membrane techniques for the separation of yttrium have been reported. Mohapatra et al. ([2016]) have evaluated multiple diglycoamide-functionalized calix[4]arenes for separation of carrier-free ^{90}Y from ^{90}Sr via flat-sheet-supported liquid membrane. PC-88A was used as a carrier for separation of ^{90}Y by hollow fiber-supported liquid membrane (Kandwal et al. [2011]). The radiation stability of extractant was observed up to 1000 kGy. Ramanujam et al. ([2001]) developed a generator system for preparation of ^{90}Y from ^{90}Sr present in the high level waste of the Purex process utilizing a supported liquid membrane and KSM-17 as a carrier. In the other investigation, a two-stage-supported liquid membrane system was developed for the separation of carrier-free ^{90}Y using KSM-17 and CMPO as extractants (Dhami et al. [2007]). Kopunec and Manh ([1991]) demonstrated transport of yttrium(III) from nitrate medium through liquid membrane containing TOPO in n-dodecane, supported on a nucleoporous filter, into a receiving solution with EDTA. Kunthakudee et al. ([2016]) reported the selective separation of yttrium ions from other rare earth elements utilizing a hollow fiber-supported liquid membrane and Cyanex272 as an extractant. In the other study, synergistic effect between Cyanex272 and TBP was observed by Ramakul et al. ([2009]) for separation of yttrium by means of microporous hydrophobic hollow fiber-supported liquid membrane. A novel idea of transport of yttrium (III) metal ions through fiber-supported liquid membrane in two-stage processes, i.e., source to membrane and membrane to stripping phase has been investigated by Gaikwad and Rajput ([2010]). The fiber-supported liquid membrane was impregnated with PC-88A. Goto et al. ([1992]) used 2-ethyl-hexylphosphonic acid mono-2-ethyhexyl ester as carrier in a hollow fiber membrane extractor for separation of yttrium from the heavy rare earth metals holmium and erbium.

The most compounds employed as a carrier in the above liquid membrane systems are amongst the acidic ligands.

The most important advantage of such ligands is the possibility to modulate the selectivity and efficiency of the transport by controlling the pH of the aqueous source and/or stripping phases (Ramakul et al. [2009]). Another category of acidic ligands, ß-diketones, are well known as beneficial chelating agents in analytical chemistry and radiochemistry, and as a result of their acidic characters, they have been employed for transport of lanthanides from liquid membrane (Sugiura et al. [1989]). Hence in the present work, we were interested in studying one of β-diketones, i.e., HTTA as a mobile carrier in bulk liquid membrane system for the selective separation of yttrium in the presence of ^{90}Sr and several other interfering ions.

Experimental

Materials and reagents

HTTA, n-propylamine, carbon tetrachloride, dichloromethane, chloroform, arsenazo III, the acids and salts used were purchased from Merck chemical company. A stock solution of 0.01 M yttrium (III) was prepared from YCl$_3$·6H$_2$O (Merck). Ni^{2+}, Cu^{2+}, Co^{2+}, Cs$^+$, Sr^{2+}, Hg^{2+}, Al^{3+} and Ag$^+$ solutions were prepared from the corresponding reagent grade nitrate salts (Merck). Doubly distilled water was used throughout.

Apparatus

GBC Cintra 6 spectrophotometer was used for the measurement of yttrium ion concentration in the aqueous phases in the absence of interfering ions, using arsenazo III as an indicator at 650 nm (Savvin [1961]).

The samples of both aqueous phases containing Ni^{2+}, Co^{2+}, Cu^{2+}, Ag$^+$, Al^{3+}, Sr^{2+}, Fe^{2+} and Hg^{2+} ions were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP/AES, Varian Liberty 150 AX Turbo). Also atomic absorption spectrometer (AAS, Varian Spectra 200) was used for the measurement of cesium ion concentration in the aqueous phases.

The activities of β-emitters ^{90}Sr and ^{90}Y were measured by a liquid scintillation counter (Wallac Quantulus^{TM} 1220).

The pH of solutions was adjusted using a Metrohm 620 pH meter equipped with a combined glass-saturated calomel electrode.

Transport tests were performed utilizing the bulk liquid membrane (BLM) apparatus, in which a cylindrical glass cell (4.0 cm, i.d.) keeping a glass tube (2.0 cm, i.d.), separated the two aqueous phases (Fig. 1). The distance of the lower rim of the interior glass tube and bottom of the reservoir was 1.0 cm. The tests were accomplished by using a thermostated
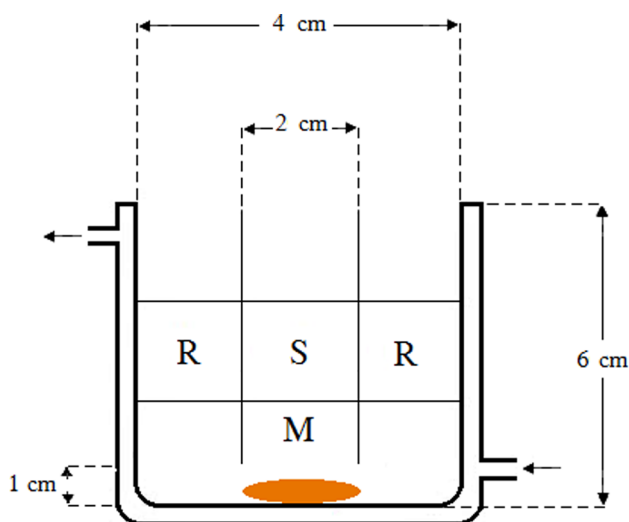
Fig. 1 Schematic diagram of liquid membrane apparatus for transport of Y(III) ions. *S* source phase, *R* receiving phase, *M* membrane phase

Fig. 2 Diagram for extraction of Y(III) and Sr(II) at pH 2.3-7. Conditions: Aqueous phase (A.P.), 5 ml of 1.0×10^{-3} M Y(III) or Sr(II) and 1% PA buffered at pH 2.3-7; Organic phase (O.P), 5 ml of 0.02 M HTTA in CHCl$_3$; time of extraction, 24 h

apparatus (Wise Circu, Korea) to maintain the controlled temperature.

Procedure

All transport tests were accomplished at the ambient temperature of 25 ± 1 °C. To perform the facilitated transport, the dichloromethane membrane phase (20 mL) containing 0.02 M HTTA was poured the bottom of the cell. Then 10 ml of 1 M nitric acid as receiving phase and 5 ml aqueous phase as feed phase containing Y(III) or a binary mixture of metal ions along with 1%(v/v) PA at a fixed pH of 5.4 were poured into the outer and interior cylinders, respectively (The mentioned aqueous phases were saturated initially with pure dichloromethane by pre-contacting these phases with dichloromethane to avoid the huge loss of the membrane phase with a significant effect on the mass transfer). The organic membrane was magnetically stirred with a magnetic stirrer using a 2.0 cm Teflon-coated stirrer bar. The concentration of yttrium ion in the absence of the interfering ions in the two feed and receiving phases was measured by spectrophotometry after 8.5 h using arsenazo (III) as an indicator.

An analogous transport experiment was performed in lack of the carrier for reference. Detailed circumstances of the tests performed in order to attain optimal conditions are illustrated in the tables and figures. The reproducibility of the above system was studied by performing three replicate transport experiments. The percentage of Y(III) ion transport (%T) across the membrane was calculated as the percentage of Y(III) transported from the feed to the receiving phase, measured at 8.5 h, according to the following equation:

$$\%T = 100 \frac{C_{rt} \times V_r}{C_0 \times V_f},$$ (1)

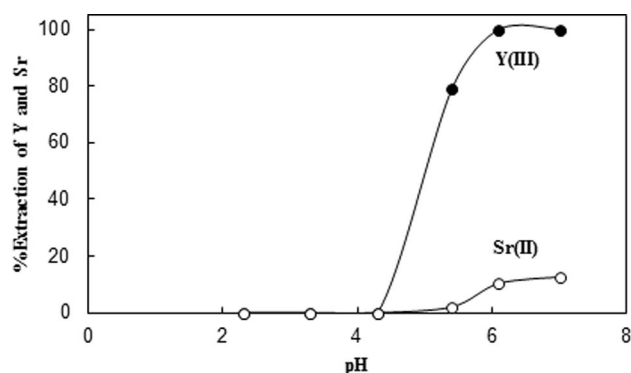where C_0 and C_{rt} are the concentrations of yttrium(III) in feed and receiver compartments at time 0 and t, respectively. Also, V_f and V_r indicate the volumes of feed and receiving phases, respectively. The percentage of Y(III) ion transport after 8.5 h was 89.71 ± 1.6%.

Preliminary experiments on the solvent extraction of Y (III) and Sr (II) ions with HTTA extractant

A knowledge of extractive behavior of the extractant applied as a carrier is necessary for complete separation of the metal ions by means of the facilitated transport. So, we decided to scrutinize the extractive behavior of yttrium and strontium in chloroform by HTTA extractant. Obviously, this test could specify our strategy to accurately design the experiments of the selective transport of yttrium (III) by the liquid membrane systems. Solutions containing 1×10^{-3} M Sr (II) or 1×10^{-3} M Y(III) with 1% (v/v) PA and adjusted at pH 2.3–7 were extracted by the same volume of chloroform solution (0.02 M HTTA). Determination of yttrium (III) and strontium (II) ion concentrations in aqueous phases was made by spectrophotometry and ICP-AES, respectively. As seen in Fig. 2, there was no extraction at pH of 2.3–3.4 for Y (III) and Sr (II) ions. At pH range 5.4–7, yttrium (III) ions were extracted between 78.8 and 100%, while in the same pH range the extraction of strontium (II) ions would not exceed 12.57%. At around pH 5.4, the extraction percentage of strontium was quite small, but almost 78.8% of the yttrium was extracted. Therefore, it appears that only the pH adjustment is sufficient to achieve in the selective separation of yttrium (III) from strontium (II) by extraction with HTTA in chloroform.

Results and discussion

Transport mechanism

HTTA is listed among β-diketones and its enolic form has a substitutable hydrogen atom and therefore can be considered as a mono-acidic ligand (HR). At the feed phase/membrane interface, the Y(III) ions, possibly as $Y(PA)^{3+}$ complex, are absorbed into the membrane as the result of strong complex formation with HTTA. At this step, the carrier and $Y(PA)^{3+}$ complex impart protons and PA to the source phase as HPA^+ due to complex formation with yttrium ion. The neutral yttrium-carrier complex (YR_3) thus produced diffuses down its concentration gradient. On the other direction of the membrane, the Y(III) ion is liberated into the aqueous receiving phase as a result of the stripping action of the H^+ ion. The liberated protonated carrier (HR) then diffuses back across the membrane to the feed phase/membrane interface and the cycle will be recurred. The concentration polarization of various species was reduced to the smallest possible amount by continuing and alike stirring throughout the experiment. The main outcome is the transport of yttrium(III) from the aqueous feed phase to the aqueous stripping phase across the bulk of the organic membrane phase, at the cost of the counter-transport of the equivalent quantities of the protons.

Effect of pH in source phase on the transport process

The pH of the source phase is expected to affect the extractive characters of the mobile carrier HTTA as an acidic ligand. To illustrate the influence of hydrogen-ion concentration, the transport tests of yttrium (III) ions (primary concentration of 1.0×10^{-3} M) with 1% (v/v) PA from the source aqueous phase, via a chloroform membrane phase consisting 0.02 M HTTA, to 1 M nitric acid solution versus pH of the source phase in the range of 2.3–7.0 were performed (Fig. 3). The pH values higher than 7 were not investigated due to hydrolysis and precipitation of yttrium (III) ions (Gaikwad and Rajput 2010).

The experimental results indicate that with increasing the pH of the source phase up to 5.4, the transport of yttrium ions from the source phase to the membrane phase and its liberation to the receiving phase is augmented. At higher pH values, the yttrium transport will remain practically constant. By increasing pH, the proton concentration gradient between the source and receiving phases increases, therefore, the driving force for the transport of yttrium is augmented and a larger amount of yttrium (III) ions is transferred. At lower pH values, the yttrium (III)
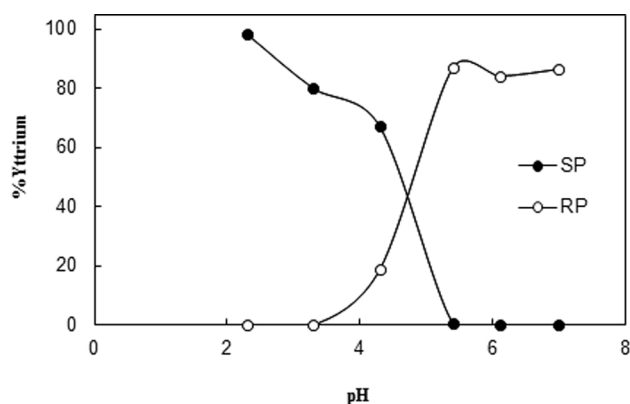

Fig. 3 Effect of pH in source phase on transport process. Conditions: Source phase (SP), 5 ml of 1.0×10^{-3} M Y(III) and 1% PA; Liquid membrane phase (MP), 20 ml of 0.02 M HTTA in $CHCl_3$; Receiving phase (RP), 10 ml of 1 M HNO_3; time of transport, 8.5 h

ion transport slackens. The slackened transport of yttrium (III) ions to the receiving phase at lower pH values can be chiefly pertaining to the augmented rivalry of proton with yttrium ion for the mobile carrier HTTA in the membrane phase (Shamsipur et al. 2009). The optimal pH of 5.4 was chosen, because at this pH, there is a maximal transfer of yttrium(III) ions to the receiving phase and also, according to the extraction diagram of Y (III) and Sr (II) (Fig. 2), the less interference effect of strontium ions in all likelihood, is underway.

Effect of PA in source phase on the transport process

In order to investigate the effect of PA, the experiments related to yttrium ion transport (primary concentration of 1.0×10^{-3} M) were carried out under the following conditions:

I.   In the presence of 1% (v/v) PA in the source phase, by chloroform liquid membrane phase containing 0.02 M HTTA and 1 M nitric acid as a receiving phase.
II. In the absence of PA in the source phase, by chloroform liquid membrane phase containing 0.02 M HTTA and 1 M nitric acid as a receiving phase.
III. In the presence of 1% (v/v) PA in the source phase, by chloroform liquid membrane phase without HTTA carrier and with 1 M nitric acid as a receiving phase.

All conditions (I) to (III) were set out in the range of pH 2.3–7.0. The experimental results are shown in Fig. 4. As is evident, in the case of binary system, the percentage of transport of yttrium ions increased over the pH range of 3.3–5.4 and achieved a plateau in the pH range 5.4–7 with 86.25–86.95% transport level; while, in the absence of PA
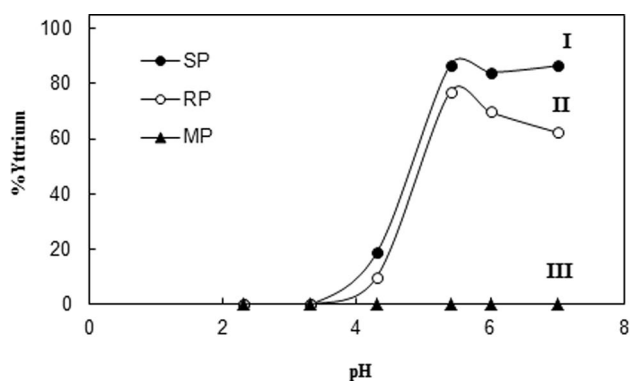
Fig. 4 Effect of PA in source phase on transport process. I: HTTA + PA; II: HTTA; III: PA. Conditions: Source phase (SP), 5 ml of 1.0×10^{-3} M Y(III); Liquid membrane phase (MP), 20 ml of CHCl$_3$; Receiving phase (RP), 10 ml of 1 M HNO$_3$; time of transport, 8.5 h

Fig. 5 Effect of the carrier concentration in organic phase on transport process. Conditions: Source phase (SP), 5 ml of 1.0×10^{-3} M Y(III) and 1% PA in pH = 5.4; Liquid membrane phase (MP), 20 ml of different concentrations of HTTA in CHCl$_3$; Receiving phase (RP), 10 ml 1 M HNO$_3$; time of transport, 8.5 h

in the source phase, the amount of transported yttrium ions reduced over the pH range 3.3–7. Also, it is worth mentioning that PA alone was unable to transport the yttrium ions.

Schweitzer and Mccarty (1963) have observed a similar behavior with regard to the solvent extraction of yttrium with β-diketones. According to these authors, the addition of an amine to the system in the pH range, where hydrolysis of yttrium(III) is important, causes that amine to compete successfully with the hydroxide ion to form an aqueous complex of the type Y(amine)$^{3+}$ which is broken in the extraction step with β-diketones. This phenomenon leads to an increase in the extraction efficiency of yttrium (III) in the solvent extraction, and similarly in our study to an enhancement in the transport percentage, possibly due to the presence of a complex of the type Y(PA)$^{3+}$ in the source phase which prevents the hydrolysis of yttrium(III) in solution.

Effect of HTTA concentration in the membrane phase on the transport process

The effect of the mobile carrier concentration on the transport of yttrium ion through the organic liquid membrane was investigated and the experimental results are represented in Fig. 5. As is seen, the percentage transport of yttrium ion is augmented with increasing concentration of HTTA from 0 to 0.02 M, while there is no appreciable transport in lack of the carrier. However, a diminutive decrease in yttrium transport will happen with growing the HTTA concentration in the liquid membrane from 0.02 to 0.1 M (Nowier et al. 2000; Altin et al. 2011). It should be noted that despite the initial augmentation of extraction of yttrium(III) ions to the membrane with increasing HTTA concentration, but further increase in the latter beyond 0.02 M may cause an increase in the membrane viscosity which in turn results in a reduction in the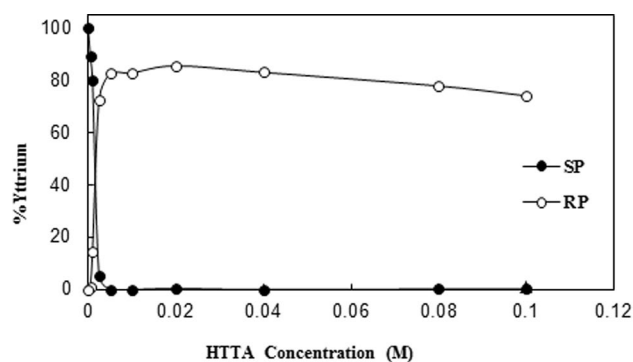 diffusion coefficient of the created complex between the carrier and yttrium ions in the liquid membrane according to Wilke–Chang equation (Hines and Maddox 1985).

Effect of the diluent type in the membrane phase on the transport process

The nature of diluent such as polarity, viscosity and other physical properties affects the transport efficiency (Musikas et al. 1992). The selected diluent must be immiscible with the water, less viscous, less volatile and at the same time it must possess an appropriate polarity (Noble and Way 1987; Mulder 1996). In order to assess effect of the diluent type, the transport experiments were carried out using chloroform, dichloromethane and carbon tetrachloride in the membrane phase. Under the identical experimental conditions, the experimental results indicated that the transport efficiency of yttrium ions to the receiving phase diminishes in the order CH$_2$Cl$_2$ (89.71%) > CHCl$_3$ (88.59%) > CCl$_4$ (77.69%). A blend of a variety of physical characters which simultaneously affect the transport phenomenon can intervene in the behavior perceived herein. For example, CH$_2$Cl$_2$ possesses the lowest viscosity ($\eta = 0.44$ cP) compared with CHCl$_3$ ($\eta = 0.58$ cP), CCl$_4$ ($\eta = 0.97$ cP) (Memon et al. 2014) which results in an increase in the rate of the Y(III)-HTTA complex transport in the organic membrane phase (Nezhadali et al. 2016). Also, the acid constant of HTTA carrier is a parameter strongly dependent on the organic liquid membrane properties such as polarity and/or polarizability. Compared with CCl$_4$ and CHCl$_3$ with the dielectric constants of 2.24 and 4.81, respectively, CH$_2$Cl$_2$ with a dielectric constant of 9.08 (Memon et al. 2014) can lead to a larger acid constant of the carrier and hence increase the extraction rate of yttrium from the source phase to the membrane (Rezaei and Nedjate 2003; Han et al. 2017). Thus, the success of utilizing dichloromethane as an organic membrane lies in the fact

that it is less viscous and more polar in comparison to both chloroform and carbon tetrachloride.

Effect of the acid concentration in the receiving phase on the transport process

The influence of the alteration in nitric acid concentration in the receiving phase, on the yttrium transport efficiency was also studied and the results are represented in Fig. 6. As seen, the percentage of yttrium ion transport increases with augmenting concentration of nitric acid up to 1 M. By further addition of acid concentration the yttrium transport efficiency decreases.

The low transport at low acidities may be ascribed to the insufficient proton concentration to break the Y(III)-HTTA complex at receiving phase/membrane interface (Shamsipur et al. 2010). At very high acidity, the transport was again low presumably because of the hydrolysis and degradation of the carrier itself (Nanda et al. 2004). Thus, a solution of nitric acid 1 M was used as a receiving phase in the following experiments.

Effect of the transport time

The effect of time on yttrium ion transport through the liquid membrane was investigated under the optimal experimental conditions. The alteration of yttrium concentration in the liquid membrane, the source and the receiving solutions versus time is illustrated in Fig. 7. It is clear that the extraction of yttrium ion from the source phase to the organic membrane takes place almost completely after 2 h. Nevertheless, the liberation of yttrium ion from the membrane phase into the receiving phase accomplishes at a lower rate. Thus, we simply presume that the release of yttrium ion from its complex with HTTA is the rate-determining step of the membrane
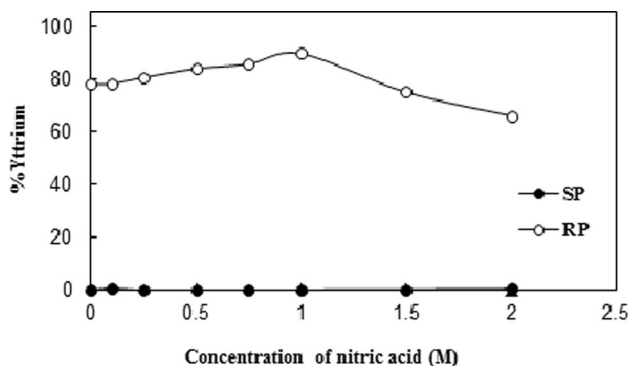

Fig. 7 Effect of transport time. Conditions: Source phase (SP), 5 ml of 1.0×10^{-3} M Y(III) with 1% PA and pH = 5.4; Liquid membrane phase(MP), 20 ml of 0.02 M HTTA in CH_2Cl_2; Receiving phase (RP), 10 ml of 1 M HNO_3

transport (Dadfarnia and Shamsipur 1992). Under the optimum conditions, the transport of yttrium ion from the source aqueous phase into the receiving aqueous phase attains a maximum value in the transport time of 8.5 h. After 8.5 h, the yttrium ions transport remains practically constant.

The temperature effect

The influence of the temperature on the yttrium transport efficiency was studied under the optimal experimental conditions. Figure 8 indicates the alteration of the yttrium ion concentration in the source, membrane and receiving phases versus the temperature. It is evident that the percentage of yttrium transport to receiving phase is augmented with temperature in the range of 6–25 °C. At the higher temperature, the process efficiency remains almost constant.

Various effects must be envisaged to explicate the results. The effect of the temperature on the complexation and decomplexation reactions of yttrium ion at each of the

Fig. 6 Effect of the concentration of the acid used in the receiving phase. Conditions: Source phase (SP), 5 ml of 1.0×10^{-3} M Y(III) with 1% PA and pH = 5.4; Liquid membrane phase (MP), 20 ml of 0.02 M HTTA in CH_2Cl_2; Receiving phase (RP), 10 ml of different concentrations of nitric acid; time of transport, 8.5 h
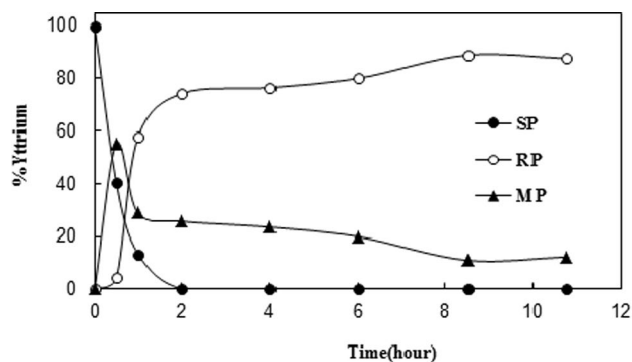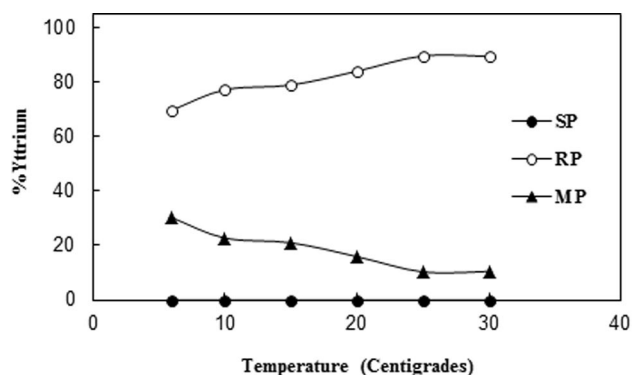

Fig. 8 Temperature effect. Conditions: source phase (SP), 5 ml of 1.0×10^{-3} M Y(III) with 1% PA and pH = 5.4; Liquid membrane phase, 20 ml of 0.02 M HTTA in CH_2Cl_2; Receiving phase (RP), 10 ml 1 M nitric acid; time of transport, 8.5 h

membrane interfaces is one of them (Muthuraman et al. 2009). As the membrane viscosity depends on the temperature, the influence of the temperature on the diffusion of the transferred species through the membrane should not be disregarded in the transport process. When the operating temperature rises, the cohesive force between the organic membrane molecules diminishes but the kinetic energy of the membrane molecules increases. This process reduces the fluid shear stress paving the way for the organic membrane molecules to become more mobile, thus reducing the viscous resistance of the membrane phase (Chang 2016). Subsequently, Y(III)-HTTA complex can diffuse at a much more rapid rate across the membrane phase with the rising temperature, and this is consistent with both the Wilke–Chang correlation and Stokes–Einstein equation (Cussler 2009). Nevertheless, the distribution of the mobile carrier HTTA also hinges on the temperature and must be considered for interpreting the experimental results (Yaftian et al. 2006).

Effect of stirring rate

In the present study, under the previous optimum conditions, stirring speed of the membrane phase was increased in the range of 100–200 rpm in order to optimize uniform mixing of the solution and to minimize thickness of aqueous boundary layers. The variation of yttrium (III) concentration in both source and receiving phases with the different rotating speeds of stirrer was measured by spectrophotometry. The change of Y (III) concentration in the membrane phase was determined by the mass balance between the phases.

By means of a kinetic model that is commonly used to describe the transport behavior of the metal ions through the liquid membranes on the basis of the kinetic laws related to the two consecutive irreversible first-order reactions (He and Ma 2000), "first-order apparent rate constants" of the extraction (k_e) and the stripping (k_s) stages were obtained and are presented in Table 1. Indeed, both of the values of k_e and k_s are functions of the extraction reaction, stripping reaction and the solute diffusion rate. Also, the values of k_e and k_s are interrelated with each other (Zhang et al. 2009).

Table 1 Effect of stirring rate on kinetic parameters

Stirring rates (rpm)	K_e (h^{-1})	K_s (h^{-1})	J_{max} (h^{-1})	% Transport
100	1.03	0.41	0.22	66.32
150	1.71	0.71	0.38	78.11
200	1.81	1.17	0.53	89.71

Conditions: source phase (SP), 5 ml of 10^{-3} M Y^{3+} with 1% PA and pH = 5.4; liquid membrane phase (MP), 20 ml of 0.02 M HTTA in CH$_2$Cl$_2$; receiving phase (RP), 10 ml 1 M nitric acid; time of transport, 8.5 h

As this table shows, the transport rate of yttrium ions through the liquid membrane is affected by the stirring speed, because the apparent rate constants of extraction and stripping steps and maximal flux (J_{max}) increase with the augmentation of the rotating speed of the stirrer in the range of 100–200 rpm. This indicates that within the stirring velocity range examined, diffusion is the rate determining step in the transport processes from the source phase to the membrane phase and the membrane phase to the receiving phase, respectively (Ma et al. 2001; Davarkhah et al. 2013). It should be taken into account the fact that kinetic experiments should not be carried out at the speeds greater than 250 rpm because of the turbulence and hydrodynamic instability at the two interfaces; in particular, the deformation of the interface of the source/membrane phases became more pronounced, in the sense that the interface area was increased by the bulge creation. Therefore, the kinetic tests in this study were accomplished at 200 rpm in order to retain the same hydrodynamic conditions.

Selectivity of bulk liquid membrane system for transport of Y(III)

In order to appraise the selectivity of the liquid membrane system suggested, yttrium ion transport in the presence of strontium and other various metal ions in the source phase was investigated. Table 2 comprises the list of the percentage transport of Y(III) and M^{n+} cations (i.e., Sr^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+}, Ag$^+$, Al^{3+}, Cs$^+$ and Hg^{2+}) which were available with yttrium ion in equimolar concentrations of 1.0×10^{-4} M, to the receiving phase. As it is apparent from Table 2, in the lack of a masking agent in the source phase, while the interfering effects of some metal ions including Sr^{2+}, Cs$^+$ and Ag$^+$ is insignificant (0.0–7.5%), other cations tested illustrate intermediate (i.e., Hg^{2+} 54.22%, Ni^{2+} 51.63%, Co^{2+} 58.05%, Fe^{2+} 58.09%, Cu^{2+} 64.94%) and high (i.e., Al^{3+} 100%) interfering effects.

This is because HTTA is a well-known multipurpose chelating agent for a variety of metal ions. Therefore, it was mandatory to add an appropriate masking agent to remove the interference effects of these ions during selective transport of yttrium(III) from the aqueous media. Hence, in the subsequent step, the selectivity of yttrium transport in the presence of Co^{2+}, Cu^{2+}, Ni^{2+}, Fe^{2+}, Ag$^+$ and Hg^{2+} ions was investigated at the pH 5.4 and in the presence of 1.0×10^{-2} M CN$^-$ as a masking agent, in the source solution. The experimental results of this sequence of transport experiments are also presented in Table 2. As it is perceived from Table 2, in the presence of 1.0×10^{-2} M CN$^-$, the transport of the interfering metal ions was slightly diminished. The selectivity of yttrium transport in the next step was studied in the presence of 1.0×10^{-1} M CN$^-$ as a masking agent in the source solution. The results of these series

Table 2 Amount of yttrium ions transported from various cation mixtures through the membrane[a]

No.	Mixture	% Transported into receiving phase	% Remaining in membrane phase	% Remaining in source phase
I	Y^{3+} [a]	78.70	20.27	0.03
	Cu^{2+}	64.94	34.49	0.57
II	Y^{3+} [b]	79.23	20.73	0.04
	Cu^{2+}	64.22	35.37	0.41
III	Y^{3+} [c]	86.03	10.04	3.93
	Cu^{2+}	0.00	0.00	100
IV	Y^{3+} [a]	79.18	31.41	0.29
	Co^{2+}	58.05	41.32	0.63
V	Y^{3+} [b]	78.09	21.69	0.22
	Co^{2+}	53.93	41.01	5.06
VI	Y^{3+} [c]	83.48	15.89	0.63
	Co^{2+}	0.00	15.78	84.22
VII	Y^{3+} [a]	79.71	20.00	0.29
	Ni^{2+}	51.63	45.41	2.96
VIII	Y^{3+} [b]	77.66	21.99	0.35
	Ni^{2+}	46.41	51.32	2.27
IX	Y^{3+} [c]	81.56	17.48	0.96
	Ni^{2+}	1.09	12.64	86.27
X	Y^{3+} [a]	79.13	20.54	0.33
	Fe^{2+}	58.09	39.58	2.33
XI	Y^{3+} [b]	77.78	21.99	0.23
	Fe^{2+}	52.70	37.22	10.08
XII	Y^{3+} [c]	83.05	15.98	0.97
	Fe^{2+}	2.57	15.34	82.09
XIII	Y^{3+} [a]	70.08	29.88	0.04
	Ag^+	0.70	99.17	0.13
XIV	Y^{3+} [a]	75.26	20.71	4.03
	Al^{3+}	100	0.00	0.00
XV	Y^{3+} [d]	82.58	17.25	0.17
	Al^{3+}	15.49	45.23	39.28
XVI	Y^{3+} [e]	84.67	14.70	0.63
	Al^{3+}	0.00	0.00	100
XVII	Y^{3+} [a]	87.07	12.13	0.80
	Sr^{2+}	0.00	0.00	100
XVIII	Y^{3+} [a]	78.99	11.93	0.08
	Cs^+	7.52	12.88	79.60
XIX	Y^{3+} [a]	78.07	21.22	0.71
	Hg^{2+}	54.22	29.67	16.11
XX	Y^{3+} [b]	79.79	19.45	0.76
	Hg^{2+}	50.56	30.78	18.66
XXI	Y^{3+} [c]	83.09	16.48	0.43
	Hg^{2+}	0.00	0.00	100

[a]Conditions: source phase (SP), 5 mL of 1.0×10^{-4} M of each cation in the binary mixture with pH = 5.4 and 1% nPA; Liquid membrane phase (MP), 20 ml of 0.02 M HTTA in CH_2Cl_2; Receiving phase (RP), 10 ml 1 M nitric acid; time of transport, 8.5 h

[b]In the presence of 0.01 M CN^-

[c]In the presence of 0.1 M CN^-

[d]In the presence of 0.01 M 5-sulfosalicylic acid

[e]In the presence of 0.1 M 5-sulfosalicylic acid

of transport tests are also illustrated in Table 2. As it is seen from Table 2, in the presence of 1.0×10^{-1} M CN^-, the transport of these interfering ions was significantly diminished (0.00–2.57%).

The cyanide ions function as masking agent can be justified on the basis of the theory of hard and soft acids and bases. The cyanide ion is among the "soft" ligands which have very little affinity to bond with rare earth elements. The most stable complexes of cyanide ion form with lower valances of the soft cations of groups IB, IIB and VIIIB depicted in the periodic table. Thus, yttrium with the behavior quite similar to the rare earth elements, is considered as a hard acid and has no tendency to form a complex with cyanide ion, while the elements such as Cu^{2+}, Co^{2+}, etc. are considered as soft or medium acids with high affinity to form a complex with the cyanide ions.

Other masking agent, i.e., sulfosalicylic acid in the source phase was used for the selective transport of yttrium in the presence of Al^{3+}. Applying this masking agent in the concentrations of 0.01 and 0.1 M led to a decrease in the transport of Al^{3+} from the 100 to 15.49 and to 0.00%, respectively.

Separation of yttrium-90 from strontium-90

In the previous section, in the light of the transport behavior of inactive yttrium(III), especially in a relatively high concentration (1×10^{-4} M) in the presence of strontium(II) with the same concentration, we observed that yttrium(III) could be extracted almost quantitatively into the receiving phase. To evaluate the method effectiveness for separation of the trace amounts of yttrium-90 from strontium-90 (in secular equilibrium with yttrium-90), two modes of execution for the transport tests were prescribed. Thus, the previous optimized transport parameters with the higher amounts of yttrium were utilized in two separate tests for extraction of yttrium-90 from the source phase containing an equilibrium mixture of yttrium-90 and strontium-90, either the inactive yttrium carrier (1×10^{-4} M) was used or not. After the transport time of 8.5 h (prior optimized time), the donor and receiving phases were sampled and measured by a liquid scintillation counter at different times. The results indicated the transport efficiency of 91.41% in both cases for yttrium-90 after 8.5 h.

Theoretically, and thanks to the previous optimized results for inactive yttrium with a relatively high concentration (1×10^{-4} M), at the beginning of the separation of the phases after 8.5 h, the source phase was expected to contain merely strontium-90 and the receiving phase was anticipated to include yttrium-90 only. Our assumption was affirmed by the liquid scintillation spectrum from strontium-90 counting in the source phase at the initial moments after separating of the phases. This spectrum showed only one peak

arising from strontium-90. As the time passed, yttrium-90 was expected to grow gradually in the source phase. A peak merely from yttrium-90 was observed in the receiving phase at the beginning of the phase separation whose height reduced gradually with time due to the decay of yttrium-90 to zirconium-90.

To evaluate the purity of the yttrium-90 product that entered into the receiving phase under the optimal transport conditions, its process of decay was aligned with the function of time. Logarithm of yttrium-90 activity versus time is shown in Fig. 9. The half-life or $t_{1/2}$ of 64.17 ± 0.05 for yttrium-90 was calculated by the slope of the straight line. Thus, the purity of isolated yttrium-90 was estimated to be 99.99%.

The performance of the developed BLM system dealt with this research work, was compared in terms of the half-life for isolated yttrium-90 in the receiving phase as a criterion for its purity and the acidity in the liquid phases with
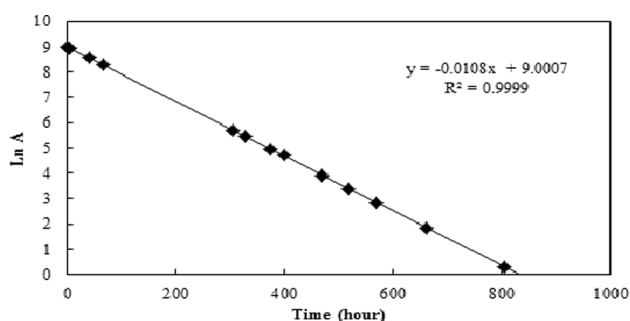

Fig. 9 Logarithm of ^{90}Y activity in the receiving phase as a function of time

the other liquid membrane systems cited in the literature for separating and purifying yttrium-90, the results of which are given in Table 3. As is seen, the purity of yttrium-90 in most cases is comparable or better than the other applied liquid membrane systems for purification of yttrium-90. Also, the acidity of feed and receiving phases in the current study is lower than other systems in many instances.

The use of HTTA as an extractant-carrier to separate yttrium-90 from strontium-90 in the other formats of membranes such as the supported liquid membrane and polymer inclusion membrane, is the subject of another research project to work on in our laboratory.

Conclusion

Yttrium(III) ions are liable to be separated effectively from strontium ions in aqueous solutions by the chloroform liquid membrane containing HTTA as a carrier. The optimum conditions for the transport of yttrium include: the donor phase of pH 5.4 with 1% (v/v) PA, the liquid membrane containing 0.02 M HTTA in dichloromethane, and 1 M nitric acid solution as a receiving phase. Under the achieved optimum conditions, the trace Y-90, in the equilibrium with Sr-90, is quantitatively transportable to the receiving phase and prone to be separated from its long-lived parent isotope. The transported Y-90 decays with a half-life of 64.17 ± 0.05 h which indicates the purity of 99.99% for isolated yttrium-90. Also, under the same optimal conditions and in the presence of appropriate masking agents in the donor phase, it is possible to separate yttrium (III) from the dual mixtures with other cations such as Cu^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+}, Ag^+, Al^{3+}, Cs^+

Table 3 Comparison of liquid membrane systems for ^{90}Y separation and purification

Extractant	Technique	Feed phase	Receiver	Half-life obtained	Remark	References
N,N,N′,N′-tetraoctyl diglycoamide (TODGA)	SLM	HCl 6 M	HCl 0.01 M	69.72 h	Contaminated with ^{90}Sr	Dutta and Mohapatra (2013)
Di-(2-thylhexyl)phosphoric acid (D2EHPA)	SLM	HNO$_3$ 1 M	HNO$_3$ 4 M	64.17 h	Reasonably pure	Naik et al. (2010)
Bis(2-ethylhexyl) phosphonic acid (PC88A)	HFSLM	HNO$_3$ 0.1 M	HNO$_3$ 3 M	64.70 h	Reasonably pure	Kandwal et al. (2011)
2-ethylhexyl 2-ethylhexyl phosphonic acid (KSM-17) Octyl(phenyl)-N,N-diisobutylcarbamoyl-methylphosphine oxide (CMPO)	Two-stage SLM	HNO$_3$ 0.01 M HNO$_3$ 3 M	CH3COOH 1 M	~ 64 h	Reasonably pure	Dhami et al. (2007)
Diglycolamide-functionalized Calix[4]arenes	SLM	HNO$_3$ 3 M	DOTA 0.01 M EDTA 0.01 M	64.29 h 64.05 h	Reasonably pure	Mohapatra et al. (2016)
2-Thenoyltrifluoroacetone (HTTA)	BLM	pH = 5.4	HNO$_3$ 1 M	64.17 h	Reasonably pure	Present work

and Hg^{2+}. Cyanide ions and 5-sulfosalicylic acid as masking agents are utilized to mask various transition metal and Al^{3+} ions in the donor phase, respectively. The current study may be particularly beneficial to the separation of yttrium from the complex media, presenting an indirect method for measuring ^{90}Sr in radwastes. Also, this novel technique can be considered as a candidate to prepare yttrium-90 for generating the labeled monoclonal antibodies and peptides.

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