Permeation of europium through immobilised supported liquid membrane†

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The transport of europium through a porous supported liquid membrane (SLM) containing PC-88A (EHPNA) and Versatic 10 (VA 10) as immobilised carriers has been carried out. The results demonstrated that transport increases with increasing stirring speed, and reaches a constant value beyond a certain rotation speed. The permeability coefficient increases with the increase in carrier concentration in a certain range. The dependence of permeabilities on the pH of both the source and receiving solutions have been explored. The permeability coefficient has been calculated by taking into account the mass balance. The effects of complexing agents such as succinic, malonic and citric acid on permeability coefficient of europium has been investigated. Under similar experimental conditions the effect of complexing agents on permeation of europium has been found as: citric acid > succinic acid > malonic acid. Permeation coefficient of europium has been found greater with PC-88A in comparison with that of Versatic 10. The effect of complexing agents using in receiving phase has been explored. The mechanism of transport of europium in supported liquid membrane has been suggested. The developed methods have been used for the exploration of its utility for synthetic samples.

Liquid membranes containing acidic extractants have been studied as a new separation and pre-concentration technique. However, the continuous and simultaneous extraction and stripping operations are very interesting, attractive and effective because it can remove metal ions from a low concentration with uphill transport to high concentration. Mainly, two types of liquid membranes, viz., emulsion liquid membrane and supported liquid membrane, have been explored by utilising several extractants as mobile carriers for recovery and separation of several metal ions.

In order to consider its practical applications, supported liquid membrane (SLM) consisting of two aqueous phases separated by a solid support could be very useful for the separation and pre-concentration of metal ions from low concentration aqueous solutions, because it reduces the extractant cost and the recovery of metal ion can be achieved in single stage continuous operation. However, it is necessary to have a suitable choice of carriers and hydrophobic porous supports with high stability. Basically support material should not be affected by the acids, alkali or organic solvents.

The present paper deals with parameters affecting the permeability and effect of complexing agent on transport of europium in the acidic extractant supported liquid membrane system.

Experimental Procedure

Reagents—The commercial acidic extractants, 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHPNA or PC-88A) (Daihachi Chemical Industry Co. Ltd, Japan), and Versatic 10 acids (VA 10) (Shell Chemicals), were used. The appropriate concentrations of acidic extractants were utilised for the immobilisation on cellulose triacetate membrane. The concentration of acidic extractant in the prepared organic solution was estimated volumetrically with potassium hydroxide in ethyl alcohol by using the indicator phenolphthalein. The organic solutions were prepared by diluting a desired amount of extractant with hexane. Europium(III) solution was prepared by dissolving an appropriate quantity of europium trioxide in hydrochloric acid. After evaporating any excess acid, the solution was diluted to 250 mL with distilled water. The solution was standardized complexometrically at pH 5 with xylene orange as the indicator. All other chemicals used were of analytical grade.

Apparatus—A digital pH meter, type 120 (EICO, India) with glass and calomel electrodes was used. The experimental apparatus used to measure the permeability is schematically shown in Fig. 1. Two 35 and 20 mL round flasks are joined with a joint. A membrane (SLM) with an interface...
cial area of 11.94 cm² is placed in the joint to separate the two compartments. Solutions were poured into the flasks through the sampling ports. The solutions are independently stirred with paddle stirring system in all experiments. The experiments have been performed at 25 ± 0.6°C. Flasks with different joint diameters have been used to evaluate the dependence of the permeability on the membrane area, A, and the volume of the aqueous solutions, V. A Hitachi-220 double beam microprocessor controlled spectrophotometer was used for the estimation of metal ion concentration from the samples.

Preparation of SLM—The microporous cellulose triacetate membrane with thickness 30 μm, pore size 0.02-0.05 μm and porosity 45% was clamped in between two round bottom flasks. The microporous thin sheet membrane was impregnated with PC-88A (EHPNA) or Versatic 10 acids dissolved in hexane, and excess extractant was removed with the help of filter paper. The acidic extractant incorporated in the microporous support was estimated to be about 0.1 mL by weighing the membrane before and after immobilisation.

Procedure—Source solution containing europium ion with a suitable concentration and 0.01 M sodium acetate was taken in a bigger cell. The pH of solution was adjusted to desired value by using dilute solutions by hydrochloric acid or sodium hydroxide. The receiving phase was 0.01 M sodium acetate with the appropriate concentration of hydrogen ion. The source and receiving solutions were separated by SLM without leakage. The support was quite stable during the experiment. The samples of the source and receiving solutions were pipetted at time intervals. Europium concentrations in two aqueous solutions were estimated by measuring the absorbance at 575 nm after colour development with Arsenazo I indicator at pH 7.50.

Results and Discussion

Europium extraction equilibrium—The extraction equilibrium of europium(III) from aqueous 0.01 M sodium acetate solution with acidic extractant in the simplest form is expressed as follows.

\[ M^{3+}_{\text{aq}} + 3HL_{\text{org}} \rightleftharpoons ML_3(\text{org}) + 3H^+_{\text{aq}} \]  \( \ldots (1) \)

where \( M^{3+} \) stands for metal ion, HL for acidic extractant, org for organic phase and aq for aqueous phase. However, the complexation mechanism of lanthanide ion with acidic extractants basically depends on the ratio of acidic extractant to metal ion concentration and pH of aqueous solution.

\[ M^{3+}_{\text{aq}} + n(\text{HL})_2_{\text{org}} \rightleftharpoons ML_3 \cdot (2n-3)\text{HL}_{\text{org}} + 3H^+_{\text{aq}} \]  \( \ldots (2) \)

\( n \) represents the number of dimeric acidic extractant taking part in complexation. The complexation and cleavage of complex are the important steps in the membrane system for the effective transport of metal ion. This is illustrated in Fig. 2 in order to compare the bulk and supported liquid membranes.

Ion transport—In order to investigate the permeation behaviour of metal ion in SLM, the following mechanisms are proposed. The transport flux \( J \) of metal ions \( (M^{3+}) \) can be expressed as follows.

\[ J = \pm \frac{V}{A} \cdot \frac{dC^{M^{3+}}}{dt} \]  \( \ldots (3) \)

\( V \) is volume, \( A \) stands for contact surface area and, \( t \) for time. Where minus sign indicates the decrease in concentration of metal ion in source phase. Transport flux \( J \) of metal ions in the kinetic process can be calculated by plotting the values of concentration of metal ion versus time,
and using values of $V$ and $A$. Under the optimized conditions of experimental studies, the diffusion and chemical reaction fluxes of ion transport are assumed to be equalled to each other. The rates for the forward and backward extraction processes of metal ion in a supported liquid membrane at interface I (Fig. 2) can be expressed by Eq. (3). The net forward ion transport flux ($J_f$) of extraction process at interface I (Fig. 2) is given by Eq. (4).

\[
J_f = J_{f,s} - J_{b,s} = k_{f,s}[M^{3+}]_s[(HL)]_{2,m}^3 - k_{b,s}[ML_3 \cdot 3 HL]_m[H^+]_s^3 \quad \ldots (4)
\]

where $f$ stands for forward, $b$ for backward, $s$ for source phase and $m$ for membrane. However, the net backward ion transport flux ($J_b$) of stripping process at interface II (Fig. 2) is expressed by Eq. (5).

\[
J_b = J_{b,s} - J_{f,s} = k_{b,s}[ML_3 \cdot 3 HL]_m[H^+]_r^3 - k_{f,s}[M^{3+}]_r[(HL)]_{2,m}^3 \quad \ldots (5)
\]

$r$ represents the receiving phase. Thus kinetic process of ion transport of metal ion can be occurring continuously in two steps as forward and backward extraction processes. However, during these two step kinetic process, the ion transport flux for forward and backward extraction processes $J_f$ and $J_b$, fluxes are higher than those of reverse fluxes. Under these conditions, the fluxes observed are $J_{f,s} > J_{b,s}$ and $J_{b,s} > J_{f,s}$.

In SLM system, forward and backward extraction processes were carried out in a single system. At the interface I (Fig. 2) the extraction process is taking place, and its reaction equation and equilibrium constant expressions are given as follows.

\[
M^{3+} + 3(HL)_{2,m} \rightleftharpoons ML_3 \cdot 3 HL_m + 3H^+ \quad \ldots (6)
\]

\[
K_F = \frac{[ML_3 \cdot 3 HL]_m[H^+]_r^3}{[M^{3+}]_r[(HL)]_{2,m}^3} \quad \ldots (7)
\]

At the interface II (Fig. 2) there exists stripping process (backward extraction), and its reaction equation and equilibrium constant expressions are given as

\[
ML_3 \cdot 3 HL_m + 3H^+_r \rightleftharpoons M^{3+} + 3(HL)_{2,m} \quad \ldots (8)
\]

\[
K_B = \frac{[M^{3+}]_r[(HL)]_{2,m}^3}{[ML_3 \cdot 3 HL]_m[H^+]_r^3} \quad \ldots (9)
\]

where $K_F$ and $K_B$ refer to extraction and stripping equilibrium constants at the interfaces I and II, respectively. From Eqs (7) and (9), one can write the following Eq. (10).

\[
K_F \cdot K_B = \frac{[M^{3+}]_r[H^+]_r^3}{[M^{3+}]_r[H^+]_r^3} \quad \ldots (10)
\]

Eq. (10) predicts the steady state dynamics of SLM system. It has strong capability of preconcentration of metal ion depending on the metal ion concentration and $pH$ of source and receiving phases.

Distribution ratio ($D_F$) at interface I (Fig. 2) for the forward extraction process can be expressed as follows.

\[
D_F = \frac{[ML_3 \cdot 3 HL]_m}{[M^{3+}]_r} = K_F \frac{[(HL)]_{2,m}^3}{[H^+]_r^3} \quad \ldots (11)
\]

Distribution ratio ($D_B$) at interface II (Fig. 2) for the stripping process is given by Eq. (12).

\[
D_B = \frac{[ML_3 \cdot 3 HL]_m}{[M^{3+}]_r} = \frac{1}{K_B} \frac{[(HL)]_{2,m}^3}{[H^+]_r^3} \quad \ldots (12)
\]

From Eqs (11) and (12), the expression for ratio of distribution ratio of metal ion extraction and stripping processes can be written as follows.

\[
\frac{D_F}{D_B} = \frac{K_F}{K_B} \quad \ldots (13)
\]

From Eq. (13), it is clear that $D_F$ and $D_B$ values are inversely proportional to their respective $pH$ of source and receiving solution, respectively.

The forward and backward extraction fluxes for SLM systems are defined as shown in Fig. 2, and Eqs (4) and (5). The net ion transport flux of metal can be given for the continuous transport of ions from source to receiving phase through membrane phase.

\[
J = [(HL)]_{2,m}(k_{f,s}[M^{3+}]_r - k_{b,s}[M^{3+}]_r) + (ML_3 \cdot 3 HL]_m \\
\times (k_{b,s}[H^+]_r^3 - k_{f,s}[H^+]_r^3) \quad \ldots (14)
\]

However, kinetic process can be expressed as follows.

\[
J_{b,s} = k_{b,s}[ML_3 \cdot 3 HL]_m[H^+]_r^3 \quad \ldots (15)
\]

\[
J_{f,s} = k_{f,s}[M^{3+}]_r[(HL)]_{2,m}^3 \quad \ldots (16)
\]

However, from the Eqs (15) and (16), it is clear that the forward extraction flux ($J_{f,s}$) at interface I,
and backward extraction flux ($J_{b,x}$) must be higher than those of their respective reverse extraction fluxes in order to enable us to keep the continuous ion transport of metal from source to receiving phase through membrane phase.

\[
J_{b,x} = \frac{k_{b,x}}{k_{e,x}} \cdot D_e \frac{[M^{3+}]_{aq}}{[[HL]_2]_{m}} \quad \ldots (17)
\]

\[
J_{e,x} = \frac{k_{e,x}}{k_{b,x}} \cdot \frac{1}{D_B} \frac{[H^+]_{m}}{[[HL]_2]_{aq}} \quad \ldots (18)
\]

**Extraction mechanism**—Some chemical reactions involved in liquid membrane for the monomeric and dimeric forms of EHPNA are given as follows. The dimerisation constant $k_{d,1}$ of ligand in membrane phase is expressed by Eq. (19).

\[
k_{d,1} = \frac{[[HL]_2]_m}{[HL]_m^2} \quad \ldots (19)
\]

The distribution constant of ligand between membrane and aqueous phase is given by Eq. (20).

\[
k_{d} = \frac{[HL]_m}{[HL]_{aq}} \quad \ldots (20)
\]

The dissociation constant of ligand in aqueous phase is expressed by Eq. (21).

\[
k_a = \frac{[H^+]_{aq} [L^-]_{aq}}{[HL]_{aq}} \quad \ldots (21)
\]

However, the distribution ratio of ligand, $D_I$, is given by Eq. (22).

\[
D_I = \frac{[[HL]_2]_m + [HL]_m}{[HL]_{aq} + [L^-]_{aq}} \quad \ldots (22)
\]

The distribution ratio of ligand in terms of other equilibrium constants of ligand can be expressed as follows.

\[
D_I = k_d [k_{d,1} [k_d]_{aq} + 1] \quad \ldots (23)
\]

\[
1 + k_a [H^+]_{aq}
\]

The extraction equilibrium of lanthanide-EHPNA complexes extracted into organic phase is given in general by Eq. (2). However, value of $2n-3$ is being found 3. The extraction equilibrium constant of the complexes is expressed by following Eq. (24).

\[
K_{ex} = \frac{[ML_3 \cdot 3HL]_{org} \cdot [H^+]_{aq}^3}{[M^{3+}]_{aq}[[HL]_2]_{org}^3} \quad \ldots (24)
\]

However, overall stability constant ($\beta$) of complex formation between lanthanide ion and chelating reagent EHPNA is expressed by Eq. (25).

\[
\beta = \frac{[ML_3 \cdot 3HL]_{aq}}{[M^{3+}]_{aq} [L^-]_{aq} [HL]^3_{aq}} \quad \ldots (25)
\]

Distribution of M-EHPNA complex between membrane and aqueous phases can be given by the following Eq. (26).

\[
k_{d,m} = \frac{[ML_3 \cdot 3HL]_m}{[ML_3 \cdot 3HL]_{aq}} \quad \ldots (26)
\]

The extraction equilibrium constant $K_{ex}$ can be expressed in terms of stability constant $\beta$ of $ML_3 \cdot 3HL$ complex in the aqueous phase, its distribution constant, $k_{d,m}$, the distribution constant of the extractant EHPNA, $k_d$, the dimerization constant of the extractant EHPNA, $k_{d,1}$, and dissociation constant $k_a$.

\[
K_{ex} = \frac{\beta \cdot k_{d,m} \cdot k_3}{k_d^6 \cdot k_{d,1}} \quad \ldots (27)
\]

In supported liquid membrane, the concentration of metal ion in source solution at time $t$ is given by the Eq. (28).

\[
[M^{3+}]_s = [M^{3+}]_0 \times e^{-\frac{[A]_s}{P_e} t} \quad \ldots (28)
\]

However, permeability coefficient, $P$, is related to ion transport flux as follows.

\[
P = \frac{J}{C_i} \quad \ldots (29)
\]

where $C$ stands for the concentration of metal ion in source solution at time $t$. Under the unequal volume conditions of source, membrane and receiving phases, the distribution ratios of metal ion in supported liquid membrane at interfaces I and II are expressed by following Eq. (30).

\[
\frac{D_E}{D_B} = \frac{V_i}{V_s} \times \frac{[M^{3+}]_s}{[M^{3+}]_0} \quad \ldots (30)
\]

However, distribution ratios $D_E$ and $D_B$ are related to permeability coefficient as follows.

\[
\frac{D_E}{D_B} = \frac{V_i}{V_s} \times \frac{[M^{3+}]_s}{[M^{3+}]_0} \times e^{[A]_s/P_t} \quad \ldots (31)
\]
From the Eqs (11) and (27), one gets following expression at the interface I (Fig. 2).

\[ D_f = \frac{\beta \cdot k_{dm} \cdot k_a^3}{k_{d1}^6 \cdot k_{d1}^3} \left( \frac{[HL]_{2,ln}^{3}}{[H^+]_a^3} \right) \ldots (32) \]

However, stripping equilibrium constant at interface II (Fig. 2) can be expressed in terms of other ligand and complex constant involved in the process as follows.

\[ K_B = \frac{\beta' \cdot k_{dm} \cdot k_a^3}{k_{d1}^6 \cdot k_{d1}^3} \ldots (33) \]

where \( \beta', k_{dm}, k_a', k_d, k_d' \) express the reverse constants of the processes at the interface I actually which are taken place at interface II. Hence, Eq. (12) can be written as follows.

\[ D_B = \frac{k_{d1}^6 \cdot k_{d1}^3}{\beta' \cdot k_{dm} \cdot k_a^3} \left( \frac{[HL]_{2,ln}^{3}}{[H^+]_a^3} \right) \ldots (34) \]

However, one can write the following equation from Eqs (17) and (32)

\[ J_{bs} = \frac{k_{bs}}{k_{bs}} \cdot \frac{\beta \cdot k_{dm} \cdot k_a^3}{k_{d1}^6 \cdot k_{d1}^3} \ldots (35) \]

Eq. (36) is obtained from Eqs (18) and (34)

\[ J_{bs} = \frac{k_{bs}}{k_{bs}} \cdot \frac{\beta \cdot k_{dm} \cdot k_a^3}{k_{d1}^6 \cdot k_{d1}^3} \ldots (36) \]

The metal ion concentration in receiving phase at time \( t \) from the Eqs (31), (32) and (34) can be given as follows.

\[ [M^{3+}]_r = \frac{\beta \cdot k_{dm} \cdot k_a^3}{k_{d1}^6 \cdot k_{d1}^3} \times \left( \frac{[HL]_{2,ln}^{3}}{[H^+]_a^3} \right) \times e^{-[A/V]_b \cdot Pt} \ldots (37) \]

Above Eq. (37) can be written as follows.

\[ [M^{3+}]_r = K_f \cdot K_B \times \frac{V}{V_r} \times [M^{3+}]_b^3 \times [H^+]_a^3 \times e^{-[A/V]_b \cdot Pt} \ldots (38) \]

In order to assess the distribution of metal ion at interfaces I and II in supported liquid membrane system, it is essential to signify the role of ligand and metal ion-ligand complex constants involved in the processes. It is well illustrated by the Eqs (32) and (34). However, the dependence of forward and backward extraction fluxes in SLM system on these constants is explained by Eqs (35) and (36). The variation of metal ion concentration in receiving phase by taking into account the ligand and metal ion-ligand complex constants including hydrogen ion concentration in source and receiving phases, volume of source and receiving phases and area of contact is significantly given by the Eq. (37). Moreover, Eq. (38) takes into account the extraction and stripping equilibrium constant during the transport of metal ion from source to receiving phase through membrane phase. This valuable data helps us in selecting a suitable carrier for the membrane system.

**Mass balances**—The free concentration of metal ion and EHPNA can be calculated as follows.

\[ [M^{3+}]_{aq} = C_m^{ini} - \left( \frac{V}{V_{org}} \right) [ML_3 \cdot 3HL]_{org} \]

\[ -[ML_3 \cdot 3HL]_{aq} \ldots (39) \]

\[ ([HL]_{2,org}) = C_m^{ini} - 6 \left( \frac{V}{V_{org}} \right) [ML_3 \cdot 3HL]_{aq} - [HL]_{org} \]

\[ -[HL]_{aq} - [L^-]_{aq} \ldots (40) \]

The counter transport of hydrogen ions in source from membrane and receiving phases can be evaluated as follows.

\[ [H^+]_{sc} = 3[M^{3+}]_r + 3[ML_3 \cdot 3HL]_{org} \ldots (41) \]

where \( sc \) represents the coupled transport of hydrogen ions in source from membrane and receiving phases. \( [M^{3+}]_{aq} \) stands for the free metal ion in aqueous phase. Where \( ini \) represents the initial concentration.

In order to present the data and assess the experimental variables, the permeability coefficient values were evaluated and presented. The plots of the logarithm of the concentration ratio at time \( t \) to the initial concentration in the source solution, \([Eu^{3+}]_{b0}/[Eu^{3+}]_{b0} \) vs \( t \) give a series of straight lines. Such plots are illustrated for EHPNA system in Fig. 3. From the slopes of the plots \( \log [Eu^{3+}]_{b0}/[Eu^{3+}]_{b0} \) vs \( t \), the value of permeability coefficient, \( P \) was calculated.

**Effect of stirring speed**—In order to achieve effective transport of europium in an SLM system, it is essential to explore the diffusion process and chemical reaction, and their fluxes. The chemical reaction between europium (III) and EHPNA or
Versatic 10 is to be considered fast. The effect of stirring speed on diffusion of europium through aqueous bulk solution including membrane diffusion has been explored. The stirring of both phases source and receiving were carried out from 50 to 130 rpm (Fig. 4). It was observed that the permeability coefficient increases in both the systems of EHPNA and Versatic 10 in the range from 50 to 75 rpm. It indicates that diffusion of europium in bulk solutions increases with increase in stirring speed. However, permeability coefficient remains constant in the range from 75 to 130 rpm for both systems. It can be inferred that the diffusion processes were equalled to chemical reactions. Further studies were carried out under these conditions at 90 rpm.

Effect of pH of the source solution—In a liquid membrane system, pH is being one of the significant driving forces for the transport of metal ion. In order to assess the significant role of pH of source solution in transport of europium, pH variation studies of source solution has been carried out. The $P$ values are plotted against $pH$ values of the source solution. $P$ values increased with the increase in $pH$ for EHPNA in the range 1.5-5.0, however, after it remains unaffected. It shows that the complexation and extraction at the interface of source and membrane solutions favours with the increase in $pH$ of source phase (Fig. 5a). The change in permeability coefficient for Versatic 10 was observed in the range 3-5.75. Moreover, above this $pH$ range it remains unchanged. Since the concentration of acetate ion maintained equal in source and receiving phases, the change in acetate ion had a minor effect on $P$ values. However, quantitative and effective permeation of europium for EHPNA can be carried out in efficient fashion at lower $pH$ in comparison to that of Versatic 10.

Effect of acid concentration in receiving phase—Since the extraction and stripping processes in SLM system are carried out simultaneously for continuous transport of metal ion, it is significant to explore the effect of acid concentration in receiving phase in order to enhance effective ion transport by making efficient stripping process at the interface of membrane and receiving solutions. The effect of acid concentration in receiving solution in both the systems EHPNA and Versatic 10 on the permeability coefficient has been studied in the range 0.05-1 $M$ (Fig. 5b). It was observed that the permeability coefficient decreases with the decrease in acid concentration in the receiving solution. However, the stripping process of europium from membrane phase is easier under the same conditions for Versatic 10 in comparison to that of EHPNA (Fig. 5b).

Effect of europium ion concentration—The SIM system is being recognised as economically viable, efficient and effective for the separation and preconcentration of metal ion. It is necessary for the extraction and stripping process to be carried out in efficient fashion at lower $pH$ in comparison to that of Versatic 10.
to explore the effect of metal ion concentration on permeability coefficient. The effect of europium ion concentration on the permeability has been studied in the range from $10^{-6}$ to $10^{-2}$ M. Since at lower concentration of europium, $P$ values observed are similar (Fig. 6). In the range $10^{-4}$-5$\times10^{-3}$ M, $P$ value decreases with the increase in metal ion concentration for EHPNA and Versatic 10 (Fig. 6) systems. It significantly shows that the preconcentration of europium ion can be carried out in efficient manner from dilute solutions.

**Effect of carrier concentration**—The metal ion carrier plays a significant role in the SLM system in order to make it effective transport and economically viable. Therefore, it is essential to investigate the effect of carrier concentration on the permeability of metal ion. The effect of EHPNA and Versatic 10 concentrations on the permeability coefficient of europium was studied in the range from $10^{-5}$ to 2 M. It was observed that the permeability coefficient of europium increases with the increase in EHPNA and Versatic 10 concentrations in the range $10^{-5}$ to 0.02 M, and $10^{-5}$ to 0.075 M, for EHPNA and Versatic 10, respectively. However, above these concentration ranges, it remains the same in the case of both the systems (Fig. 7). Thus, it is possible to carry out effective separation and preconcentration of europium at minimum concentration of acidic extractants which makes the SLM system economically viable in comparison with that of liquid-liquid extraction.

**Effect of complexing agents**—By use of complexing agents in source solution in order to investigate its effect on extraction of metal ion at interface of source and membrane solutions, and consequently its effect on the permeability. For such studies, citric, succinic and malonic acids were selected for EHPNA and Versatic 10 systems. In first instant studies, the concentrations of citric, succinic and malonic acids in source solutions were varied in the range $10^{-6}$ to $10^{-3}$ M. It was significantly observed that with the increase in concentration of these complexing agents, the competition towards complexation with europium increases, and in effect permeability coefficient decreases for EHPNA (Fig. 8a) systems. However, the sequence of effect of complexing agents on permeability coefficient of europium observed in the decrease in order was citric $>$ succinic $>$ malonic. It indicates that citric acid is more competitive towards complex formation with europium in comparison with that of succinic and malonic acids by using EHPNA and Versatic 10 as carriers. Moreover, the effect of complexing agents significantly effective for Versatic 10 in comparison to that of EHPNA (Fig. 8). It can be seen that the concentration of complexing agents above $10^{-5}$ M is effective to make use of it for improving selectivity for the separation and preconcentration methods for europium.

In an SLM system $pH$ of source phase is an important factor for the complexation of europium. Since dissociation of EHPNA, Versatic 10, citric, succinic and malonic acids does depend on the $pH$ of aqueous solution, and in addition to this, the complexation of europium with these acids also depends on its $pH$. Thus, $pH$ is an important parameter to assess the permeability of europium in an SLM system. Effect of $pH$ of source solution in presence of citric, succinic and malonic acids has been studied in the range 1-6.5 for the EHPNA and Versatic 10 systems. However, during the $pH$ dependency it was observed that in case of EHPNA system, the decrease in the permeability coefficient with the variation in $pH$ of source solution from $pH$ 1.5 to 5.5 (Fig. 9a). It indicates that the competition of complexation of europium with citric, succinic and malonic acids become competitive to EHPNA in the extraction
process. The results observed in the case of Versatic 10 are described in Fig. 9b. Decrease in permeability of europium with respect to pH from 3 to 6.5 has been observed. However, these results show that the complexation of europium with EHPNA and Versatic 10 in presence of complexing agent in the competitive order can be given as follows EHPNA > Versatic 10.

The effect of complexing agent in receiving phase—The effect of hydrochloric acid concentration on permeability of europium (III) has been given in Table 1. It indicates that the effective transport of europium ion can be carried out with the increase in acid concentration in receiving phase. Different nitric acid concentrations in receiving phase have been used in order to check the permeability of europium. However, results observed were similar to those of hydrochloric acid. Other complexing agents tested in receiving phase at pH 4.5 were ammonium thiocyanate (1-3 M), sodium nitrate (1-4 M), citric acid (10^-2, 10^-2 M) and EDTA (10^-2-10^-3 M). However, none of them was found to be effective for ion transport of europium. However, permeation of metal ion at interface I (Fig. 2) favours with the increase in DF values, rotation speed, mineral acid concentration, carrier concentration and complexing agent concentration. For example, when SlM containing acidic extractant, it is possible to transport europium efficiently above pH 4 for EHPNA and pH 5 for Versatic 10 from the source solution affecting the permeability coefficient of metal ion.

Thus, use of complexing reagent in receiving phase at higher pH has no effect on ion transport at interface I. Therefore, effective complexing reagent towards metal ion in receiving phase at low pH < 1 should be efficient for ion transport. However, permeation of metal ion at interface I (Fig. 2) favours with the increase in $D_F$ values in which $k_{d1}$, $k_{d2}$, $k_a$, $\beta$ and $k_{dm}$ values are essentially required high. $D_F$ value is inversely proportional to hydrogen ion concentration in source solution. $D_F$ increases with the decrease in hydrogen ion concentration in source solution. However, ligand and metal ion-acidic extractant complex constants are controlling $D_F$ with respect to hydrogen ion concentration in source solution. Thus, the presence of complexing reagent in source solution affects the permeability coefficient of metal ion.

The obtained data can be effectively used for selecting the optimum experimental conditions such as pH values, rotation speed, mineral acid concentration, carrier concentration and complexing agent concentration. For example, when SLM containing acidic extractant, it is possible to transport europium efficiently above pH 4 for EHPNA and pH 5 for Versatic 10 from the source solution.

Table 1—Effect of hydrochloric acid concentration on enrichment of europium(III), source phase 35 mL, receiving phase 20 mL, carrier 0.1 M EHPNA

<table>
<thead>
<tr>
<th>Source phase pH</th>
<th>Receiving phase HCl, M</th>
<th>$P$ cm/min</th>
<th>$[Eu^{3+}]$, 6 h</th>
<th>Recovery %</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5</td>
<td>0.5</td>
<td>5 x 10^-3</td>
<td>105</td>
<td>75</td>
</tr>
<tr>
<td>3.5</td>
<td>1.5</td>
<td>5.6 x 10^-3</td>
<td>135</td>
<td>80</td>
</tr>
<tr>
<td>3.5</td>
<td>2.0</td>
<td>6 x 10^-3</td>
<td>140</td>
<td>85</td>
</tr>
<tr>
<td>3.5</td>
<td>3.0</td>
<td>7 x 10^-3</td>
<td>170</td>
<td>88</td>
</tr>
<tr>
<td>3.5</td>
<td>4.0</td>
<td>8.2 x 10^-3</td>
<td>180</td>
<td>89</td>
</tr>
</tbody>
</table>

Fig. 8—Plots of log $P$ vs log [complexing agent] for EHPNA and Versatic 10 systems, Eu(III) = 1.65 x 10^-3 M, EHPNA = 0.05 M, Versatic 10 = 0.1 M, hydrochloric acid concentration in receiving solution = 0.3 M, and rpm = 90

Fig. 9—Plots of log $P$ vs pH of source solution in presence of complexing agents, Eu(III) = 1.65 x 10^-3 M, EHPNA = 0.05 M, Versatic 10 = 0.1 M, hydrochloric acid concentration in receiving solution = 0.3 M, and rpm = 90
Enrichment of europium(III) concentration—In order to achieve uphill and active transport of europium, the experiments with EHPNA and Versatic 10 as carriers were carried out by starting with equal concentrations of europium(III) in source and receiving solutions. Europium concentration in the source solution (pH 4.5) gradually decreased from its initial value of $10^{-4}$ M, whereas that in volume of the receiving solution 20 mL with 0.3 M hydrochloric acid increased with stirring time and eventually received double the initial concentration. After stirring for 200 min, more than 98% of the europium in source solution was transported through the liquid membrane against its concentration gradient, and the concentration in the receiving solution was about 100 times higher than that in the source solution.

The variation of europium enrichment factor is essentially controlled by the volume ratio of the source to receiving solutions, $\frac{V_s}{V_r}$. The concentration of europium through supported liquid membranes of EHPNA and Versatic 10 from 35 mL of the source solution initially containing $5 \times 10^{-6}$ M europium(III) to 20 mL of receiving solution with no initial europium(III), the europium was effectively concentrated into small volume of receiving solution by continuous transport. The results obtained show the enrichment factor for europium(III) to be 1.75.

Stability of SLM—The stability of cellulose triacetate support has been assessed under the feasible conditions for SLM system. The SLM has been continuously used for 50 days. During the 35 days of experiments, the $P$ values remain unaffected, however, there is decrease in $P$ values after this period (Fig. 10). The reasons could be the durability of membrane support, and effective transport of metal ion with carrier. The durability of membrane support has been found satisfactory. Moreover, the loss of acidic extractant in aqueous phase causes the decrease in permeability coefficient. The results show that frequently impregnation of membrane support is essential for the long time run.

Prediction of metal ion concentration in kinetic process—Fig. 11 illustrates the three different permeability coefficient cases of simulation curves for the prediction of metal ion concentration in source and receiving phases by using essential constants involved in the Eq. (38). From these data, it signifies the role of important constants of ligand and metal ion-ligand complexes are involved in the process of ion transport at the interfaces I and II (Fig. 2). However, for the stability two of the main factors responsible are durability of support material and continuous entrapment of carrier in pores of support material without loss in aqueous phase. The loss of carrier in aqueous phase can be minimized by selecting the favourable constants of ligand and metal ion-ligand complex from Eqs (23) and (27), respectively.

Conclusion

The permeation of europium in an SLM consisting of source, membrane phase immobilised on support, and receiving phases in which EHPNA and Versatic 10 in hexane as carriers have significantly been dependent on different parameters such as pH of aqueous solutions, carrier concentration and stirring speed. However, permeability an important characteristic for the efficient and effective operation of an SLM system has been explored. The extraction and ion transport mechanisms are proposed for the transport of metal ion in SLM system. The proposed method of enrichment of metal ion is useful for the pre-concentration. However, the simulation curves for
the continuous ion transport of metal ion give the status of kinetic process including metal ion concentration in source and receiving phases.

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References