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Permeation and modeling studies on Ge(IV) facilitated transport using trioctylamine through supported liquid membrane

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Abstract−Germanium transport from a solution containing tartaric acid by a flat sheet supported liquid membrane (FSSLM) using trioctylamine (TOA) as a carrier and polytetrafluoroethylene (PTFE) as a membrane was investigated. A mass transfer model was developed to monitor the transport process based on experimental results. The effect of parameters such as feed solution pH, TOA concentration, initial germanium concentration, and strip hydrochloric acid concentration on the germanium flux and the transport percentage were studied. A high permeation was observed at a feed solution pH of 3.00, 40%v/v TOA and 5 mg/dm^3 Ge^{4+}. At HCl concentrations of 1-3 mol/dm^3, the germanium transport was complete. Finally, based on the mass transfer model, the aqueous and organic resistance values were 11,802 and 860.85 h/cm, respectively. The validity of the model was investigated by fitting the model and experimental data. The correlation coefficient of 0.99 showed the validity of the model.

Keywords: Transport, Permeation, Supported Liquid Membrane, Mass Transfer Modeling, Germanium

INTRODUCTION

Germanium has been known as a strategic metalloid used in various industries such as semiconductors, etc. [1]. According to the literature and industrial works, zinc and coal ores are the primary resources of germanium [2,3]. Therefore, investigations on the separation of germanium from various effluents can be vital in the view of environmental engineering and industrial chemistry. Solvent extraction is a typical hydrometallurgical process used to purify germanium solutions [3-6]. The supported liquid membrane (SLM) is a method used for the recovery and the separation of species from aqueous solutions. Some researchers have declared that this technology can challenge the solvent extraction process. Lower consumptions of solvents and energy, as well as phase separation issues, are the advantages of SLM systems. Since organic extractants are used as carriers in liquid membranes, their behavior for the transport of species across membranes should be investigated. Several extractants such as KELEX 100 [7,8], LIX 63 [6,9], TOA [4], Ionquest 801 [5,6] and Cyanex 301 [5] have been used for the liquid-liquid extraction (LLX) of germanium from aqueous solutions. Separation of germanium using flat sheet supported liquid membranes has rarely been investigated in the literature. Nevertheless, other membrane processes such as nano-filtrations [10], anion exchange membranes of RX-1 [11,12], porous hollow-fibers [13-18], polysulfone membranes [19], and liquid suspension membranes [20] have been used to recover germanium from aqueous solutions.

Trioctylamine (TOA) diluted in kerosene has been applied to extract germanium-catechol complexes [4,21] from coal fly ash effluents. Furthermore, trioctylamine was used to remove germanium-catechol/sodium oxalate from sulfuric acid medium [22]. Germanium-tartaric acid is another anionic compound that can be extracted using TOA [23]. Catechol, tartaric acid, and similar reagents can convert germanium to an anionic complex, which can be extracted by extractants with the anion exchange behavior.

In this study, an FSSLM system containing a polytetrafluoroethylene (PTFE) membrane filter impregnated with the carrier of trioctylamine (TOA) was used to transport germanium anionic compounds formed by using tartaric acid from a synthetic solution. Also, the effect of the pH, the concentrations of germanium, TOA and HCl in the strip/receiving solution on the germanium transport was investigated. Finally, the mass transfer kinetic model was developed to find germanium transport parameters through the FSSLM system.

THEORY

Tri octyl amine (TOA) is an amine extractant having anion exchange behavior. Therefore, to extract germanium, it must be in the form of anionic species. According to the literature [23,24], germanium neutral species can be converted to anionic complexes by tartaric acid. The reaction between germanium neutral species and tartaric acid results in producing $Ge(C_4H_4O_6)_3^{2-}$. This species can be extracted by an amine extractant such as TOA. Xiong, Liang, Fan, Xu and Huang [23] proposed an overall reaction for the anionic complexation as Eq. (1):

$$3C_4H_6O_6+H_2GeO_3 \text{ (in a neutral solution)} \\ =H_2Ge(C_4H_4O_6)_3+3H_2O=Ge(C_4H_4O_6)_3^{2-}+2H^++3H_2O \tag{1}$$

Note that the protonated molecules of TOA (its cationic form) can extract anionic species. Acidic solutions such as diluted sulfuric

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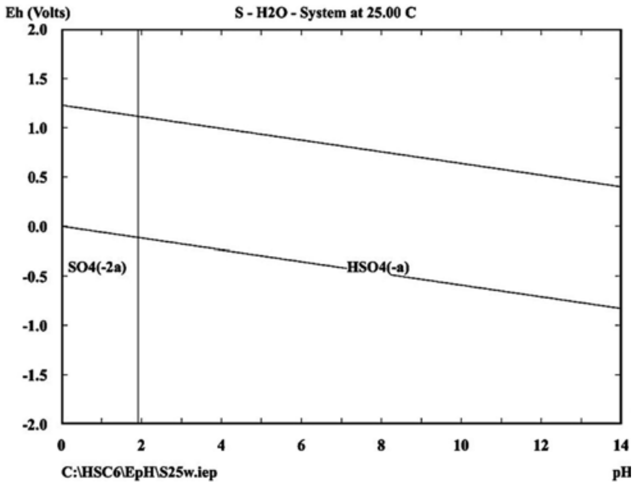

Fig. 1. Eh-pH diagram of the sulfuric acid system (HSC 6.0 software).

acids can convert TOA molecules to their protonated form. The reaction by which an amine extractant is converted to a protonated amine extractant was proposed by Liu, Yang, Lu, Shang, Lu and Zhao [24] as Eq. (2):

$$R_3N_{(org)}+H_2SO_{4\,(aq)}=[R_3NH]^+\,[HSO_4]^-_{(org)} \tag{2}$$

The extraction mechanism by which a tartaric-germanium complex is extracted from an aqueous solution using protonated TOA is as Eq. (3):

$$\begin{aligned}&2\,[R_3NH]^+\,[HSO_4]^-_{(org)}+H_2Ge(C_4H_4O_6)_{3\,(aq)}\\&\quad=[R_3NH]^+_2\cdot[Ge(C_4H_4O_6)_3]^{2-}_{(org)}+2H_2SO_{4\,(aq)}\end{aligned} \tag{3}$$

To show why HSO_4^- participated in the extractant protonation, instead of SO_4^{2-}, an Eh-pH diagram was constructed by the HSC 6.0 software as shown in Fig. 1. In this figure, the type of sulfuric acid species at various pHs can be seen. At pHs higher than 2, the first ionization of sulfuric acid occurs. Since the pH of the feed solution in all experiments and conditions in this study is higher than 2, it can be concluded that only one mole of H^+ dissociates from one mole of sulfuric acid. Therefore, in Eq. (3), the concentration of H_2SO_4 is equal to one mole of H^+. In equations presented in the following, the concentration of sulfuric acid has been replaced by the concentration of a proton. Moreover, as seen in Eq. (3), the pH variance between the feed and receiving solutions can be considered as a driving force for transferring germanium species. The equilibrium constant (K) of Eq. (3) is written as Eq. (4):

$$\begin{aligned}K&=\frac{\{[R_3NH]^+_2[Ge(C_4H_4O_6)_3]^{2-}\}_{(org)}\cdot[H_2SO_4]^2_{(aq)}}{\{[R_3NH]^+[HSO_4]^-\}^2_{(org)}\cdot[H_2Ge(C_4H_4O_6)_3]_{(aq)}}\\&=\frac{[Ge^{4+}]_{org}\cdot[H^+]^2_{aq}}{[TOA]^2_{org,\,eq}\cdot[Ge^{4+}]_{aq}}\end{aligned} \tag{4}$$

By supposing that the ion dissolution in the extractant phase is negligible, the concentration of a germanium-TOA complex is approximately equal to the germanium concentration in the organic phase. The concentrations of $\{[R_3NH]^{2+}[Ge(C_4H_4O_6)_3]^{2-}\}_{(org)}$, $[H_2SO_4]^2_{(aq)}$, $\{[R_3NH]^+[HSO_4]^-\}_{(org)}$, and $[H_2Ge(C_4H_4O_6)_3]_{(aq)}$ are equal to $[Ge^{4+}]_{org}$, $[H^+]^2_{aq}$, $[TOA]^2_{org,eq}$, and $[Ge^{4+}]_{aq}$. The equilibrium at this condition can be demonstrated using the germanium distribution coefficient as Eq. (5):

$$D_{Ge}=\frac{[Ge^{4+}]_{org}}{[Ge^{4+}]_{aq}}=\frac{[GeTOA_2]_{org}}{[Ge^{4+}]_{aq}}=K\frac{[TOA]^2_{org}}{[H^+]^2_{aq}} \tag{5}$$

In addition, the overall transport can be described in supported liquid membrane processes. The germanium flow in the interfacial layer of SLM is indicated by J and can be evaluated by Eq. (6):

$$J_{aq}=-D_{aq}\frac{d[Ge^{4+}]_{aq}}{dx} \tag{6}$$

where D_{aq} is the diffusion coefficient and dx indicates a differential form of the boundary layer. By integrating Eq. (6) at the steady condition, Eq. (7) was obtained:

$$J_{interfacial\ layer}=\frac{D_{aq}}{l}([Ge^{4+}]_{aq}-[Ge^{4+}]_{aq,\,i}) \tag{7}$$

As seen in Eq. (6), after the integration, dx is converted to a thickness of the layer (l), and i indicates the interfacial condition. $[Ge^{4+}]_{aq}$ shows the concentration of germanium in the bulk of the solution. The interfacial concentration is an equality such as the equilibrium concentration because the mentioned reaction is supposed to be very fast. This reaction is supposed to be very fast. Eq. (8) shows this equality:

$$D_{Ge}\approx\frac{[Ge^{4+}]_{org,\,i}}{[Ge^{4+}]_{aq,\,i}} \tag{8}$$

The flux by which germanium species are transported through the membrane (J_m) can be written as Eq. (9):

$$J_m=-D_m\frac{d[Ge^{4+}]_{org}}{dx} \tag{9}$$

Due to the strong acidic condition of the receiving solution, it can be supposed that the concentration of $[GeTOA_2]_{org}$ in the interface layer of the membrane of the receiving solution is negligible. Thus, by integrating and considering this supposition, Eq. (10) can be written as follows:

$$J_m=\frac{D_m}{\delta}[Ge^{4+}]_{org,\,i} \tag{10}$$

In this equation, δ indicates the membrane thickness. Since the two aforementioned fluxes (J_m and J_i) are equal at a steady state condition, the overall flux of J can be written using Eqs. (6), (7) and (9) as Eq. (11):

$$J=\frac{D_{Ge^{4+}}[Ge^{4+}]_a}{D_{Ge^{4+}}l/D_{interfecial}+\delta/D_m}=P[Ge^{4+}]_{aq} \tag{11}$$

In this equation, P is the permeability coefficient. Since the concentration of germanium varies by prolonging time, the overall flux of germanium can be represented by Eq. (12):

$$J=-\left(\frac{V}{A}\right)\left(\frac{d[Ge^{4+}]}{dt}\right) \tag{12}$$

where V indicates the volume of the feed solution and A depicts the effective area of the membrane.

By combining Eqs. (11) and (12) followed by their integration, Eq. (12) is written as Eq. (13):

$$\ln\left(\frac{[\mathrm{Ge}^{4+}]_{feed}}{[\mathrm{Ge}^{4+}]_{feed,\,t}}\right) = -\frac{\mathrm{APt}}{\mathrm{V}} \tag{13}$$

Consequently, P can be evaluated using Eq. (13). Finally, the germanium transport percentage (%) at any time can be calculated as Eq. (14):

$$\%\mathrm{E} = 100 \times \frac{([\mathrm{Ge}^{4+}]_{feed,\,0} - [\mathrm{Ge}^{4+}]_{feed,\,t})}{[\mathrm{Ge}^{4+}]_{f,\,0}} \tag{14}$$

EXPERIMENTAL PROCEDURE

1. Reagents

To synthesize a particular concentration of the germanium solution, the desired amount of GeO_2 purchased from Merck, Germany was dissolved in deionized water. Tartaric acid used to form the anionic complexation was purchased from Merck, Germany. To form germanium anionic complexes in the aqueous phase, an amount of tartaric acid equal to ten-times the germanium molar mass in the solution was added to the feed phase. According to the literature, the neutral form of germanium (H_2GeO_3) was converted to produce $Ge(C_4H_4O_6)_3^{2-}$ after adding tartaric acid [23]. H_2SO_4 and NaOH from Merck were used to adjust the pH. HCl from Merck was also used as the strip/receiving solution. The commercial extractant namely trioctylamine (TOA) was supplied by Merck, Germany. To convert TOA into its ammonium salt, the extractant was acidified with 0.5 mol/dm^3 H_2SO_4 before use in the experiments.

2. Experimental System

Flat sheet supported liquid membrane experiments were carried out in a system with two cells, one for the feed phase with a volume of 250 mL and another for the strip phase with the same volume. Fig. 2 shows a schematic of the FSSLM system used in the present study along with schematized interfacial reactions (introduced in section 2) for the germanium transport through the membrane with TOA as a carrier. The cells shown in this figure were connected together with a flange part, as a flat sheet membrane that could be placed between them. After placing a membrane, its effective area was found to be 9.62 cm^2. To prepare a liquid membrane, the membrane was impregnated with the desired composition of TOA diluted in kerosene for a few hours. The impregnated membrane was washed with distilled water to eliminate extra carriers. After this step, the membrane was ready to be placed between the cells in a flange part. The polymeric membrane was a polytetra fluoroethylene (PTFE) Millipore membrane having a porosity of 75%, pore size of 0.45 μm, diameter of 47 mm and thickness of 50 μm. Fig. 3 illustrates the SEM micrographs of this membrane provided by the supplier. The solutions in the feed and strip phases were agitated with impellers at room temperature (25±1 °C). The permeation coefficient P (cm/h) is an important parameter for controlling the system, obtained from the slopes of the plots in which $-\frac{\mathrm{V}}{\mathrm{A}}\ln\left(\frac{[\mathrm{Ge}^{4+}]_{feed}}{[\mathrm{Ge}^{4+}]_{feed,\,t}}\right)$ was plotted vs. time, based on Eq. (13).

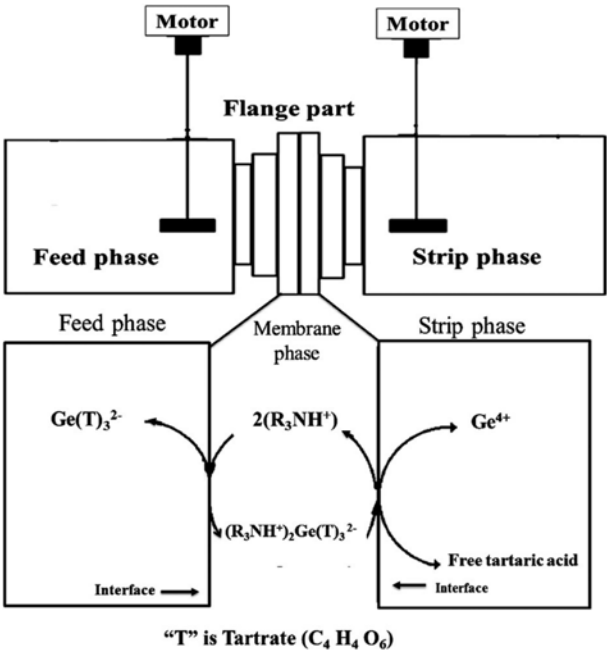

Fig. 2. Schematic of the FSSLM system and interfacial reactions used in the present study.

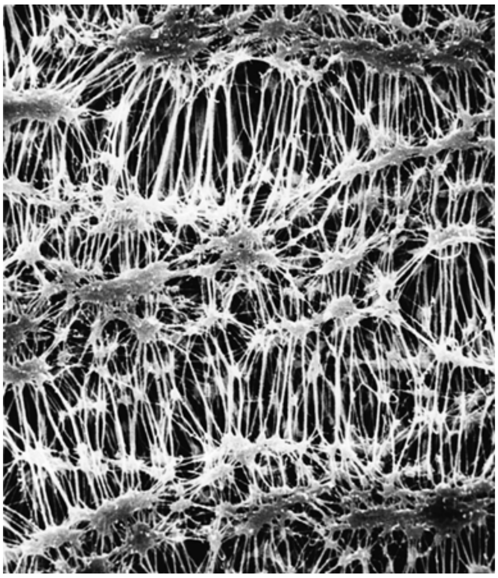

Fig. 3. SEM micrographs of the PTFE membrane used in the current study presented by Merck Millipore [25].

Appropriate volumes of samples from the feed and strip phases were taken at desired times followed by analyzing the germanium concentration using an inductively coupled plasma mass spectrometry (ICP-MS) Varian.

RESULTS AND DISCUSSION

1. Evaluation on Influence of Tartaric Acid and Protonated TOA on the Liquid-liquid Extraction of Germanium

To understand the influence of tartaric acid on the extraction of germanium, a series of liquid-liquid extraction experiments were

Table 1. The influence of tartaric acid and protonated TOA on the liquid-liquid extraction of germanium

The condition of experiment	DGe	%EGe
TOA-without tartaric	0	0
Protonated TOA-without tartaric	0.020	1.990
TOA-with tartaric	20.140	95.270
Protonated TOA-with tartaric	121.554	99.184
Strip (TOA with tartaric)	16.541	94.299

conducted in the presence and the absence of tartaric acid by non-protonated and protonated TOA with sulfuric acid. The extraction experiments were performed by solutions containing 100 mg/dm^3 of germanium. The amount of tartaric acid used was ten-times the mole mass of the germanium content in the solution. The results are illustrated in Table 1. High extraction efficiencies were obtained in the presence of tartaric acid. The extraction efficiency of protonated TOA is greater than that of the non-protonated one. The addition of tartaric acid decreased the pH to a value of 3. In this case, partial protonation of TOA was achieved. For this reason, untreated TOA can extract a part of germanium in the presence of tartaric acid (see Table 1). Therefore, the addition of tartaric acid was necessary for the extraction of germanium by TOA in the SLM process. The corresponding reactions are shown in Eqs. (1) to (3).

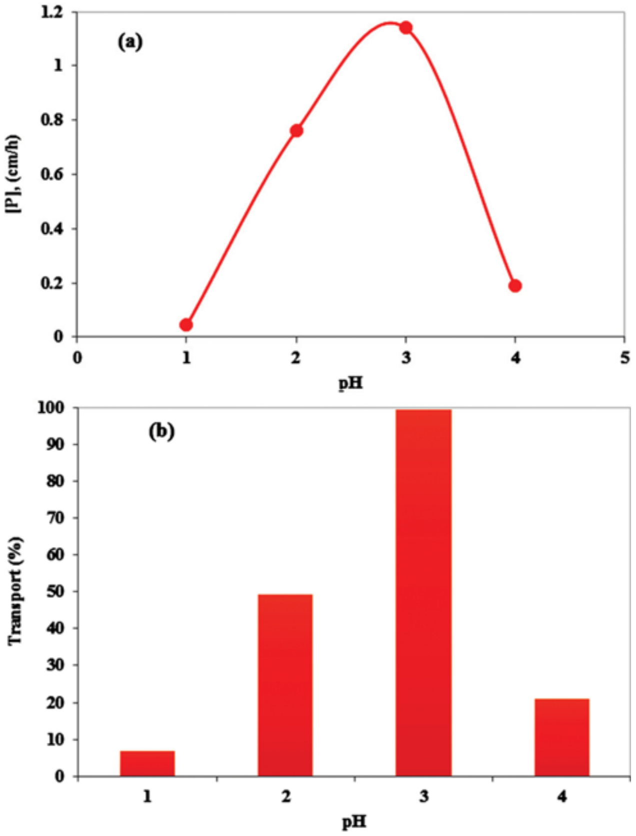

Fig. 4. (a) Effect of pH on germanium permeability and (b) on transport percentage in an FSSLM system using TOA as a carrier (feed pH: 3±0.1, germanium concentration: 60 mg/dm^3, TOA concentration: 40%v/v, time: 22 h, HCl concentration: 3 mol/dm^3).

2. Effect of pH

The transport of germanium species from solutions with a tartaric acid amount equal to ten-times the Ge molar mass in the feed (as a complexant of Ge^{+4}) was studied using 40%v/v of TOA in the pH range of 1-4, and the germanium concentration of 60 mg/dm^3. The pH of the feed solution was obtained as 3±0.1 after adding tartaric acid. It means that a pH of 3 was obtained without adding any adjutant reagents. Fig. 4(a) and (b) show the effect of the pH on the permeability coefficient and the transport percentage of germanium, respectively. As seen in Fig. 4(a), by increasing the pH from 1 to 3, the permeability coefficient for germanium increases from 0.045 to 1.14 cm/h and then it decreases to 0.19 cm/h as the pH increases from 3 to 4. No fluxes were observed at pHs less than 1 and more than 4. In pHs more than 4.00, permeation rates of germanium were reduced since the concentration of the $\{[R_3NH]_2^+[Ge(C_4H_4O_6)_3]^{2-}\}_{(org)}$ complex decreased at the interfacial levels of feed and membrane phases. Fig. 4(b) illustrates the effect of the pH on the transport percentage. As seen, the transport percentage of germanium decreased at high acidities. This reduction occurred due to the weak acid dissociation constant (K_a) of tartaric acid ($C_4H_6O_6$). With decreasing the pH of the feed solution (i.e., equal to an increase in the solution acidity), the dissociation of tartaric acid was stopped. According to Eq. (1) and Le Chatelier's principle, with an enhancement of hydronium cations, the reaction of Eq. (1) went forward to the left. Under an equilibrium condition, anionic species of $Ge(C_4H_6O_6)_3^{-2}$ decreased and permeation rates of germanium were reduced because the concentration of the $\{[R_3NH]_2^+[Ge(C_4H_4O_6)_3]^{2-}\}_{(org)}$ complex decreased at the interfacial levels of feed and membrane phases. On the other hand, since H_2GeO_3 is an acid with a low K_a, it is dissociated to $HGeO_3^-$ and GeO_3^{2-} species followed by decreasing the amounts of $Ge(C_4H_6O_6)_3^{2-}$. Thus, the transport percentage of germanium decreases in the low acidity. Consequently, with a decrease in the number of active germanium anions involved in the transport reaction, the germanium transport rate decreased.

3. Effect of Extractant Concentration

To evaluate the effect of the TOA concentration on the transport and the flux of germanium species through the FSSLM system with TOA, various volume percentages of TOA in the range of 10-50%v/v were studied. This range was selected according to the liquid-liquid extraction experiments. The initial pH of feed solutions was kept at 3±0.1. All experiments were conducted under the condition of germanium concentration of 60 mg/dm^3 in the feed solution, TOA of 40%v/v, time of 22 h, and 3 mol/dm^3 HCl in the receiving solution. Fig. 5(a) and (b) illustrates the effect of the TOA concentration on the transport percentage and the flux (J) of germanium, respectively. According to Fig. 5(a), with an increase of the TOA concentration from 10 to 50%v/v, the transport percentage increases to 100%. In addition, with an enhancement of the TOA concentration from 10 to 40%v/v, the flux increase from 4.23 to 9.63×10^{-4} mol/cm^2·h (Fig. 5(b)). In the mentioned figure, the flux and the permeability were inclined as the TOA concentration increased up to 50%. According to Eq. (3), with an enhancement of TOA up to 50%v/v, the complex of germanium-tartrate-TOA was formed, resulting in an increase of the germa-

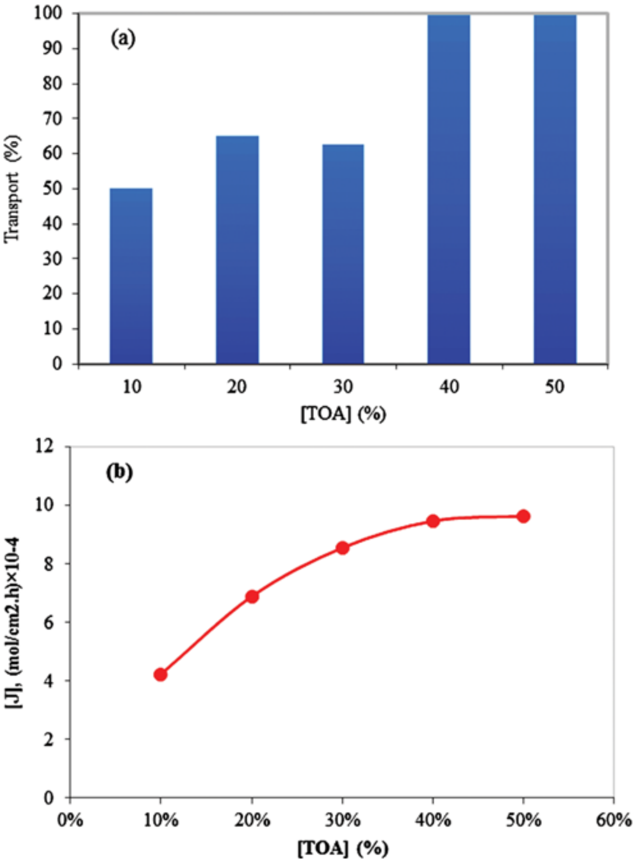

Fig. 5. Effect of carrier concentration on (a) transport percentage and (b) flux (J) of germanium in an FSSLM system using TOA as a carrier (feed pH: 3, germanium concentration: 60 mg/dm^3, time: 22 h and HCl concentration: 3 mol/dm^3).

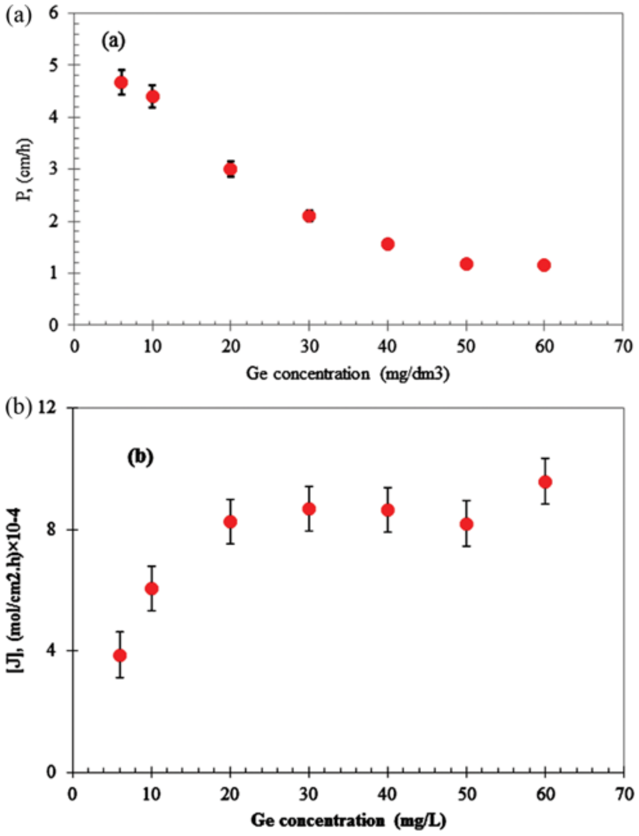

Fig. 6. Effect of germanium concentration on (a) permeability and (b) flux of germanium in an FSSLM system using TOA as a carrier (feed pH: 3, TOA concentration: 40 v/v%, and HCl concentration: 3 mol/dm^3).

nium transport at the interface of the feed solution-membrane. According to a few studies [23], a modifier can be used to modify the extractant. In this regard, tributyl phosphate (TBP) was added to TOA. The liquid-liquid extraction experiments showed that this addition improves the extraction efficiency and the separation process. Therefore, to improve the SLM efficiency, an amount equal to 5%v/v was added to the TOA extractant (40%v/v) diluted by kerosene. However, as soon as the PTFE membrane was placed in the mentioned organic solution, PTFE was dissolved and disrupted. Thus, TBP as a modifier was not used in the SLM studies.

The unit of J in this study is mol/cm^2·h. It can be easily converted to various units such as mol/m^2·s, mol/cm^2·h etc. The values of J obtained in this study are comparable to the other studies. For example, the facilitated transport study of vanadium species through FSSLM using TOA as the carrier showed a maximum flux of about 50×10^{-6} mol/m^2·s equal to 5×10^{-9} mol/cm^2·s [26]. The investigation on the transport of Co(II) and Li(I) using FSSLM containing Cyanex 272 showed fluxes of 82.20×10^{-6} mol/m^2 s (equal to 8.22×10^{-9} mol/cm^2 s) and 0.918×10^{-6} mol/m^2 s (equal to 0.918×10^{-10} mol/cm^2 s), respectively [27]. The Mo(VI) transport through an FSSLM impregnated in Alamine 336 as the mobile carrier was carried out and the results showed that the maximum flux for Mo(VI) reached about 1.6×10^{-9} mol/cm^2 s [28]. There are many works with similar values, which can be found in the literature. In the case of this study, the highest value of the germanium flux reached an approximate value of 9.5×10^{-4} mol/cm^2·h, which is equal to 2.67×10^{-7} mol/cm^2 s. Therefore, with a glance at the mentioned values, it can be seen that the flux of this study is greater than that reported in the literature.

4. Effect of Initial Metal Concentrations

To find the effect of the initial germanium concentration on the flux and the transport of the germanium species through the FSSLM system with TOA, various concentrations of germanium in the range of 5-60 mg/dm^3 were used. The TOA concentration in the membrane phase and the pH of the initial feed solution were kept at 40%v/v and 3, respectively. The HCl concentration of the receiving solution was set to 3 mol/dm^3. Fig. 6(a) and (b) shows the results. As shown in Fig. 6(a), the germanium permeability coefficient decreased from 4.68 to 1.15 cm/h by increasing the germanium concentration. Evidently, this occurred due to an increase in the active area of the transport when pores were occupied by species complexes. Furthermore, according to Fig. 6(b), with an increase in the initial concentration of germanium in the feed solution from 5 to 60 mg/dm^3, the germanium flux value (J_{Ge}) gradually increased from 3.87×10^{-4} to 9.58×10^{-4} mol/m^2 h. This enhancement possibly occurred because with an increase of the germanium concentration in the feed solution, the accessibility of germanium anion species to the feed-membrane boundary was enhanced. Therefore, the interfacial chemical reaction shown in Eq. (3) went forward to the right, leading to an increased flux as shown in Fig. 6(b). As seen in this figure, after the germanium concentration of 20 mg/dm^3, slight variations were observed. With respect to the literature, this behavior took place owing to the saturation of membrane pores with germanium species-carrier complexes. In addition, the formation of a layer of the carrier at the membrane boundary layer is possibly another reason for this behavior [29].

5. Effect of HCl Concentration in the Receiving Solutions

The strip reagent in the receiving solution has an essential role in species transportation through the SLM. Since the supported membrane phase is saturated with the species-carrier, the removal of the metal complex by a reagent is vital; without this step, the permeation rate is impacted. In this regard, in the present study, HCl solutions with various concentrations were used as the receiving solution. To investigate the effect of HCl on the stripping of germanium in the receiving phase, the concentration range of HCl was varied from 1 to 4 mol/dm^3 and the parameters such as the feed solution pH and the TOA concentration were kept constant at 3.00 and 40%v/v, respectively. Fig. 7(a) and (b) illustrates the effect of the HCl concentration on the transport percentage and the flux (J) of germanium, respectively. As shown in Fig. 7(a), with an enhancement in the concentration of HCl, the transport percentage of germanium from the feed phase to the receiving phase decreased. And, according to Fig. 7(b), there was no significant difference between germanium fluxes belonging to various concentrations of HCl in receiving solutions. The transport of germanium in the HCl concentration range of 1-3 mol/dm^3 was completed after 10 h; however, the flux of germanium at the HCl concentration of 4 mol/dm^3 in the strip phase was not decreased to zero due to the incomplete transport at the time of 10 h. This incomplete transport occurred due to the high acidity that took place while the pH of the feed solution decreased in the contact of feed-membrane-HCl, followed by protonating tartaric acid and the loss of germanium-tartrate anionic species in the interfacial face. As illustrated in Fig. (2), stripped germanium species can be in the form of Ge^{4+}, because at low pH values corresponding to HCl solutions with concentrations more than 1 mol/dm^3, germanium-tartrate is not a stable complex, resulting in decomposing and converting to germanium cation and tartaric acid. Everest and Harrison [30] investigated the complexes formed between tartaric acid and germanium using ion-exchange techniques. They declared that at pHs<1.24 (in the presence of hydrochloric acid), the sorption of free tartrate on the resin was seen, meaning the decomposition of Ge-tartrate. According to the tartaric acid speciation diagram, free tartaric acid molecules are dominant species at pH values less than 1 [31]. Furthermore, the presence of Ge^{4+} in the acidic solutions with pHs lower than 1 was reported in the literature [5,9]. Germanium in the form of Ge^{4+} can be recovered by various techniques such as the precipitation using tannin [32,33]. The remaining solution after filtering germanium precipitates contained free tartaric acid, which can be reused.

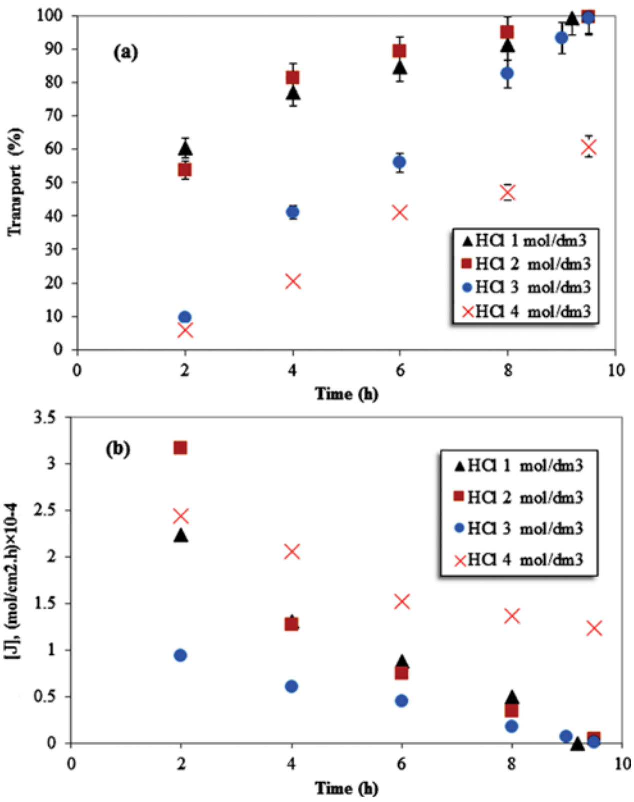

Fig. 7. Effect of HCl concentration on (a) transport percentage and (b) flux (J) of germanium in an FSSLM system using TOA as a carrier (feed pH: 3, germanium concentration: 5 mg/dm^3, and TOA concentration: 40%v/v).

6. Membrane Stability

The stability of an SLM system is a significant issue in membrane processes. The extractant defeat from the membrane pores occurs in unstable SLM systems. The pressure gradient, the mobile carrier solubility, the pore blockage due to the precipitation, and the gel creation caused the instability. A full discussion of the instability mechanisms has been reported in a review paper [34]. To enhance the membrane stability, several methods were suggested. The re-impregnation of membranes was reported in the literature [35]. At the optimum TOA concentration of 40%v/v, the pH of 3, and the germanium concentration of 5 mg/dm^3, the stability experiments were conducted. The capability of the impregnated membrane was investigated after six cycles. According to the results, the TOA-membrane used could transport about 98% of germanium during 10 hours and only less than 2% of the transport percentage had decreased. Subsequently, the reusability/recyclability of the FSSLM system used in this study for the germanium transport was possible.

7. Transfer Model

To evaluate the transfer of germanium species through the membrane, a mass transfer kinetic model was developed. At the first step, some assumptions were considered to develop a model. It is supposed that the transport of germanium is in the form of germanium-tartrate in both interfacial phases and only resistances of the membrane and aqueous diffusions exist. Furthermore, reactions at interfacial layers are fast, and the carrier concentration in the membrane and the interfacial layer of the feed side is considered the same because the germanium concentration in the interface of the feed side is much smaller than the carrier concentration of the membrane body. After the diffusion of germanium species through the membrane and reaching the strip side, the migration of ions from the interfacial layer to the strip bulk is fast.

In this study, we assumed that 2 moles of the extractant participated in the reaction as mentioned in Eq. (3). Considering Eqs. (3) to (5), the value of K was 0.04. According to Fick's law, Eq. (15) was obtained for the germanium flux through the interfacial layer in the feed phase:

$$J_{aq} = -D_{aq}\left(\frac{\partial[\mathrm{Ge}^{4+}]}{\partial x}\right) = \frac{1}{\Delta_{aq}}([\mathrm{Ge}^{4+}]_{0,f} - [\mathrm{Ge}^{4+}]_{i,f}) \tag{15}$$

Similar to Eq. (15), the germanium flux through the interfacial layer in the membrane can be written as Eq. (16):

$$J_m = \frac{1}{\Delta_{org}}([(\mathrm{R_2GeT_3})_{(org)}]_{i,f} - [(\mathrm{R_2GeT_3})_{(org)}]_{i,s}) \tag{16}$$

To simplify the equations, T was replaced with ($C_4H_4O_6$). According to the assumptions, Eq. (16) was rewritten as Eq. (17):

$$J_m = \frac{1}{\Delta_{org}}([\mathrm{Ge}^{4+}]_{(org),\,i,f}) \tag{17}$$

Δ_{aq} and Δ_{org} are called the mass transfer coefficient (or the diffusional resistance) for the aqueous boundary layer and the membrane phase, respectively. Using Eq. (4), the transported germanium can be obtained from Eq. (18):

$$[\mathrm{Ge(IV)}]_{(org)} = \frac{\mathrm{K}\cdot[\mathrm{TOA}]^2_{(org)}\cdot[\mathrm{Ge}^{4+}]_{(aq)}}{[\mathrm{H}^+]^2_{(aq)}} \tag{18}$$

Hence, using the last equation, the germanium flux in the membrane phase can be obtained as Eq. (19):

$$J_m = \frac{1}{\Delta_{org}}\left(\frac{\mathrm{K}\cdot[\mathrm{TOA}]^2_{(org)}\cdot[\mathrm{Ge}^{4+}]_{(aq)}}{[\mathrm{H}^+]^2_{(aq)}}\right) \tag{19}$$

With respect to this equation, the equilibrium concentration of germanium in the aqueous phase can be found as Eq. (20):

$$[\mathrm{Ge}^{4+}]_{(aq)} = [\mathrm{Ge}^{4+}]_{i,f} = \left(\frac{\Delta_{org}\cdot J_m\cdot[\mathrm{H}^+]^2_{(aq)}}{\mathrm{K}\cdot[\mathrm{TOA}]^2_{(org)}}\right) \tag{20}$$

Therefore, by replacing $[\mathrm{Ge(IV)}]_{i,f}$ in Eq. (15) and with regard to the steady state condition ($J_{aq}=J_m=J$), J and P are obtained as Eqs. (21) and (22), respectively. These equations have combined the equilibrium and diffusivity conditions.

$$J = \frac{\mathrm{K}[\mathrm{TOA}]^2_{org}\cdot[\mathrm{Ge}^{4+}]_{0,f}}{\Delta_{org}[\mathrm{H}^+]^2 + \Delta_{aq}(\mathrm{K}[\mathrm{TOA}]^2)} \tag{21}$$

$$P = \frac{\mathrm{K}[\mathrm{TOA}]^2}{\Delta_{org}[\mathrm{H}^+]^2 + \Delta_{aq}(\mathrm{K}[\mathrm{TOA}]^2)} \tag{22}$$

Using Eq. (22), the values of Δ_{aq} and Δ_{org} can be obtained from the intercept and the slope of Eq. (23) as follows:

$$\frac{1}{P} = \Delta_{aq} + \Delta_{org}\cdot\frac{[\mathrm{H}^+]^2}{(\mathrm{K}[\mathrm{TOA}]^2_{org})} \Rightarrow y = \Delta_{aq} + \Delta_{org}\cdot(x) \tag{23}$$

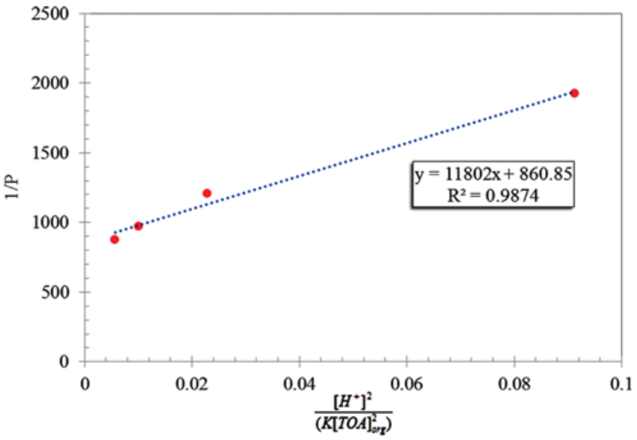

Fig. 8. The plot of 1/P vs. $\frac{[\mathrm{H}^+]^2}{(\mathrm{K}[\mathrm{TOA}]^2_{org})}$ of Eq. (23) for experimental data.

Fig. 8 illustrates the plot of y vs. x mentioned in Eq. (23). As seen, the trend line equation was found with a high correlation coefficient showing the proper fitting of the plotted line. Hence, the values of 11,802 and 860.85 h/cm (3.27 and 0.27 s/cm) were obtained for Δ_{org} and Δ_{aq}, respectively. Using these values, the values of P can be recalculated by Eq. (22). The calculated values were termed

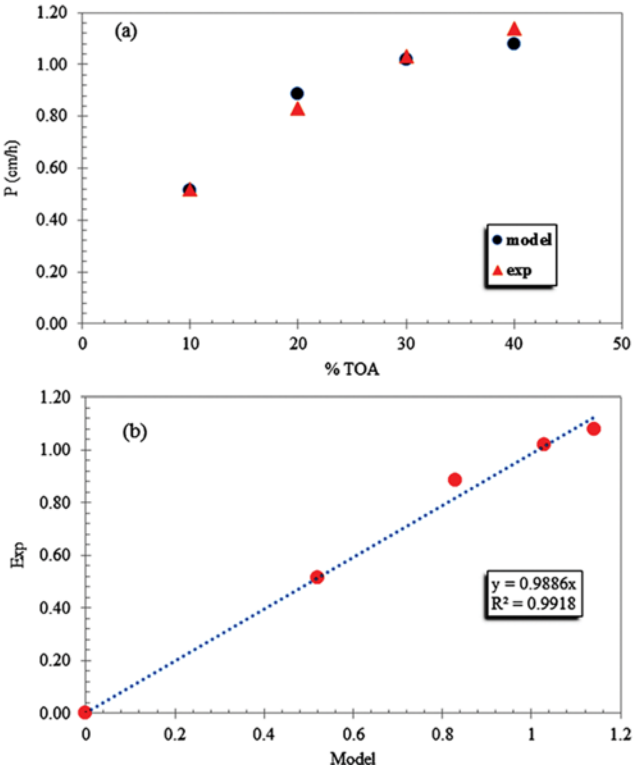

Fig. 9. (a) Germanium permeability coefficient vs. TOA concentration corresponding to model (▲) and experiment (●) results and (b) experimental permeability coefficient vs. predicted permeability coefficient (feed pH: 3, germanium concentration: 60 mg/dm^3, and HCl concentration: 3 mol/dm^3).

the model data.

Fig. 9(a) and (b) was constructed to compare the experimental and model data in various TOA concentrations and to obtain the correlation of the experimental and model data, respectively. In Fig. 9(a), the validity of the mass transfer model is reasonable. The high correlation coefficient of (R^2=0.99) obtained in Fig. 9(b) shows that the model could be adequately used to introduce the data.

CONCLUSION

For the first time, the transport of germanium was conducted by the FSSLM process using TOA as a mobile carrier. From the view of the equilibrium study, the transport percentage of germanium was enhanced with an enhancement of the TOA concentration. Furthermore, the best germanium permeability was at a pH of 3 due to the formation of germanium tartrate anionic species at this pH. There was an insignificant transport of germanium achieved below or above the feed pH of 3.00. The HCl concentration of 1-3 mol/dm^3 formed sufficient protons to break down the germanium tartrate-TOA complex and transform germanium through the membrane containing TOA. Therefore, a complete transport of germanium from a solution at a pH of 3.00, using 40%v/v TOA and the hydrochloric acid concentration range of 1-3 mol/dm^3 was obtained in this process. With regard to the mass transfer model, the values of 11,802 and 860.85 h/cm were obtained for Δ_{org} and Δ_{aq}, respectively. The validity of the mass transfer model carried out using the comparison of the model and experimental data showed that the model could be validated to introduce the SLM system.

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