Mathematical modeling on non-dispersive extraction of germanium from aqueous solutions using Aliquat 336
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ABSTRACT
In this work, the mathematical modeling of the facilitated transport of germanium (non-dispersive extraction) through a flat sheet membrane with an Aliquat 336 carrier was described. The flat sheet supported liquid membrane (FSSLM) experiments were performed under conditions germanium ≈ 100 mg/L, tartaric acid concentration of 2.76 mmol/L, and carrier concentrations of 2.5–10%v/v. The extraction equilibrium, mass transfer, and diffusion equations based on Fick’s law were the principles of modeling. Modeling was carried out by programming in Matlab mathematical software to obtain the extraction ($K_{ex}$) and mass transfer constants ($K_m$) as the objective parameters. According to the model resolution, $K_{ex}$ and $K_m$ were found to be 0.178 and 9.25 × 10$^{-6}$/C$_0$2 cm/s, respectively. The correlation coefficients between model and experimental data relating to the Aliquat 336 concentrations of 2.5, 5, 7.5, and 10%v/v were found as 0.96, 0.98, 0.99, and 0.92. The parameters of root mean square error, bias, and scatter index showed the model accuracy. In addition, diffusion coefficients relating to Aliquat 336 concentrations of 2.5, 5, 7.5, and 10%v/v were calculated using mass transfer coefficients to be 2.4 × 10$^{-4}$, 2.23 × 10$^{-4}$, 1.91 × 10$^{-4}$, and 1.79 × 10$^{-4}$ cm$^2$/s, respectively.

Key words | Aliquat 336, germanium, mass transfer, modeling, supported liquid membrane

INTRODUCTION
Germanium is recognized as an important metalloid used in high-technology applications. One of the recent usages is as arrays in X-ray fluorescence microscopy (Agyeman-Budu et al. 2016). Lead–zinc–silver and copper ores, as well as coal fly ashes, are the main resources of germanium (Yellishetty et al. 2017). Due to the rare mined resources of germanium, the efficient recovery of germanium in metallurgical processes is currently important (Kamran Haghighi et al. 2018b, 2019). Several systems such as flotation (Matis et al. 1988; Hernández-Expósito et al. 2006), solvent extraction and ion exchange membrane (Kuroiwa et al. 2014; Nusen et al. 2015), adsorption (Marco-Lozar et al. 2007), membrane process (Takemura et al. 2013), ion exchange (Arroyo & Fernández-Pereira 2009), and precipitation (Liang et al. 2008) have been used to separate germanium from various media. Liquid membrane techniques have been introduced as attractive alternatives for the separation/removal of various species with low concentrations from aqueous solutions (Aguilar & Cortina 2008; Kılıç 2009; Koter et al. 2013). Emulation and hollow fiber supported liquid membranes (HFSLM) have been studied for the separation of germanium from various solutions (Taihong et al. 1999; Tutkun et al. 1999; Ozawa et al. 2000). Mathematical modeling is one of the tools that can be used to control the processes. These techniques with a combination of mass transfer phenomena create a valuable tool for developing facilitated transport models that can be used in practical applications such as the design and the development of further processes.

In order to develop a model for a facilitated transport of species via supported liquid membranes (SLM), some suppositions should be considered. Two common suppositions have been mentioned in the literature. The main difference of these suppositions whether or not to consider the
interfacial layer placed between the bulk solution and SLM (Ramkumar & Chandramouleeswaran 2015). In the latter supposition, the diffusion through the liquid membrane is the base of the model. This yields the desired results when the thickness of the mentioned interfacial layers tends to be zero by an efficient stirring around both sides of SLM (Koter et al. 2013; Ramkumar & Chandramouleeswaran 2015). Several studies used this supposition to study the facilitated transport of species (Mogutov & Kocheriginsky 1995; Mohapatra et al. 2012; ur Rehman et al. 2012). Due to the developed configuration of the SLM system of this study and agile impellers, which were placed as close as possible to the membrane surfaces, the interfacial layers were not considered for the model development.

A number of studies have investigated modeling the transport of various metals through SLM systems using Aliquat 336 as a carrier. A summary of a literature survey on species transport modeling using Aliquat 336 has been illustrated in Table 1. In an HFSLM, the system with the carrier of Aliquat 336, of mercury(II) was separated from petroleum-produced water (Chaturabul et al. 2015). This system was modeled on the convection–diffusion–kinetic principle. In another HFSLM system, tantalum(III) and niobium(III) were separated in a diluted hydrofluoric solution (Buachuang et al. 2011). In the mentioned study, a mass transfer modeling was presented with a good fitting between experimental and modeled data. Monitoring chromium(VI) was carried out using flat sheet supported liquid membranes (FSSLM) impregnated with Aliquat 336 (Castillo et al. 2002). The mathematical equations for modeling the system were achieved from diffusion processes and chemical reactions occurring within the FSSLM system. Mass transfer coefficient parameters were obtained in the mentioned system. Polyvinyl chloride-supported membranes with Aliquat 336 as the carrier have been used to transport cadmium(II) and copper(II) from HCl medium (Wang et al. 2000). The principles of mathematical modeling of this system were the chemical reaction kinetics, and the diffusion processes resulted in finding the diffusion parameters and the kinetic rates (Wang et al. 2000). In 1996, Alonso & Pantelides (1996) studied the modeling of the removal of chromium(VI) via HFSLM. The developed models were based on the convective and diffusive mass transport. As seen in the literature survey, most of the publications have modeled the species transport using Aliquat 336 through HFSLM but only one study has described a model for an FSSLM system. Furthermore, no methodical investigation has been carried out to study the influence of Aliquat 336 on the transport of germanium across an FSSLM. In addition, for the first time a new mathematical model, linked the liquid–liquid extraction and FSSLM parameters, was developed to calculate the mass transfer and equilibrium extraction constants in the present study.

This research presents the development of a mathematical model for the facilitated transport of germanium through FSSLM impregnated with Aliquat 336 with respect to the equilibrium equations, extraction reaction, Fick’s law, and diffusional principles. The validity of the obtained model is investigated using transport percentage curves and correlation coefficients. Finally, the objective parameters such as the mass transfer coefficients and the extraction constant were calculated.

Table 1 | A summary of a literature survey on species transport modeling using Aliquat 336

| Authors         | Methods       | Species         | Diluents         | Strip medium            | Method   | Reference                   |
|-----------------|---------------|-----------------|------------------|-------------------------|----------|-----------------------------|
| Chaturabul et al. | Numerical     | Mercury(II)     | Dichloromethane  | Thiourea water          | HFSLM    | Chaturabul et al. (2015)    |
| Buachuang et al. | Empirical equations | Tantalum(III)–niobium(III) | Kerosene | NaClO₄, thiourea, and HCl | HFSLM    | Buachuang et al. (2011)    |
| Castillo et al. | Empirical equations | Chromium(VI) | Kerosene & decanol | 1,5-Diphenylcarbazide (DPC) in H₂SO₄ | FSLSM | Castillo et al. (2002)    |
| Suren et al.    | Generating    | Mercury(II)     | Tetrahydrofuran  | Thiourea                | (PVC)-based membranes | Suren et al. (2013)     |
| Wang et al.     | Numerical     | Cadmium(II)–copper(II) | Toluene          | Chloride solution       | HFSLM    | Wang et al. (2000)        |
| Alonso et al.   | Numerical     | Chromium(VI)    | Kerosene & decanol | HCl                     | FSSLM    | Alonso & Pantelides (1996) |
| This study      | Numerical     | Germanium(IV)   | Kerosene & decanol | HCl                     | FSSLM    | –                           |
MATERIALS AND METHODS

Reagents

Tricaprylyl methyl ammonium chloride ([\(\text{CH}_3(\text{CH}_2)_7\text{NCH}_3\text{Cl}\)], namely Aliquat 336, was purchased from Alfa Aesar, Germany, with the formula weight of 404.17, density of 0.880, viscosity of 1,500 mPa at 30 °C, and purity of 88.2–93.0. The diluents for Aliquat 336 were kerosene and 1-decanol, which were supplied by Sigma-Aldrich and Merck, Germany, respectively. Desired volumes of germanium(IV) oxide (GeO\(_2\)), Sigma-Aldrich, Germany, were dissolved in pure distilled water to prepare the feed solution with a purity of 99.998% (Sigma-Aldrich A.C.S. Reagent). The other materials used in this study were analytical grade from Merck, Germany.

FSSLM experiments

All the transport experiments were run in the FSSLM system as shown in Figure 1 at room temperature (25 °C). The volume of the feed and strip phases was 220 mL. The flat sheet membranes used in this research were purchased from Millipore Durapore, Germany, with the material of polytetrafluoroethylene (PTFE) with the following characteristics: a diameter of 47 mm and the pore size of 0.45 μm. This membrane was impregnated with different concentrations of Aliquat 336 (2.5, 5, 7.5, and 10%v/v) followed by rinsing with water to eliminate the excess extractant remaining on the membrane surface. The effective area of the flat sheet membrane placed in a holder between two cells was measured at 11 cm\(^2\). Both phases were efficiently agitated with mechanical impellers to remove the effect of interfacial layers around the flat sheet membrane. Several samples of 0.5 mL volume were taken from the feed and strip phases at desired times and their content was analyzed for germanium using inductively coupled plasma (Agilent 700 Series).

A capillary u-tube viscometer was used to estimate the kinematic viscosity of Aliquat 336 with different concentrations. The ASTM D445 protocol was used in this estimation. To calculate the dynamic viscosity, the kinematic value was multiplied by density.

MATHEMATICAL MODELING

The principles used in this study were considered as the following statements.

(a) The extraction of germanium was based on the formation of germanium(IV)-tartrate (Ge(OH)\(_2\)T\(^2\)) anionic complexes, which could be extracted by the Aliquat 336 anionic exchanger (Equation (1)). The source of tartrate anions is from tartaric acid added to the solution (2.276 mmol/L equal to two times the germanium molar concentration in the feed phase). Equation (1) shows a
reaction described in the literature for the extraction of germanium by Alamine 356 (Kamran Haghighi et al. 2018a).

\[2(R_4NCI)_{(org)} + Ge(OH)_2T^2\rightarrow \text{aq}^{-} \]
\[\Rightarrow (R_4N)_2Ge(OH)_2T_{(org)} + 2Cl_{(aq)}^{-} \quad (1)\]

Subscripts \(org\) and \(aq\) indicate the organic and aqueous solutions, respectively. The extraction constant of this reaction can be written as Equation (2):

\[K_{ex} = \frac{[[(R_4N)_2Ge(OH)_2]_{(org)}][Cl_{(aq)}^{-}]}{[R_4NCI]_{(org)}[Ge(OH)_2T^2]_{(aq)}} \quad (2)\]

where the brackets refer to the molar concentrations of species. According to previous studies, mass transport is usually the rate-control step in the SLM transports; thus, it is supposed that the equilibrium reaction between the carrier and germanium anionic species happens instantly (Kolev et al. 2013). Furthermore, it was supposed that the overall concentration of the carrier \([L]_0\) was persistent in the membrane phase. Thus, Equation (3) was written as follows:

\[[L]_0 = 2 \times [(R_4N)_2Ge(OH)_2T^2]_{(org)} + [R_4NCI]_{(org)} \quad (3)\]

In order to simplify the mathematical formulas, \([L]_0\), \([(R_4N)_2Ge(OH)_2T^2]_{(org)}\), and \([R_4NCI]_{(org)}\) are replaced with \(L_0\), \(C_{Ge,org,i}\), and \(L_{free,i}\), respectively. Hence, Equation (3) was written as Equation (4):

\[L_{0,i} = 2C_{Ge,org,i} + L_{free,i} \quad (4)\]

The subscript \(i\) refers to different conditions (various concentrations of the carrier). Furthermore, \(L_{free,i}\) depicts the equilibrium concentration of Alquat 356. The germanium amount extracted by the carrier is ready to diffuse through the flat sheet membrane. With respect to Equation (3), Equation (2) was rewritten as Equation (4) and rearranged as Equation (5):

\[K_{ex} = \frac{C_{Ge,org,i}C^2_{Cl,aq,i}}{(L_{0,i} - 2C_{Ge,org,i})^2C_{Cl,aq,i}} \Rightarrow 
4K_{ex}C_{Cl,aq,i}(C_{Ge,org,i}^2 - 4L_{0,i}C_{ex}C_{Cl,org,i} + C^2_{Cl,org,i})(C_{Ge,org,i} - K_{ex}C_{Cl,org,i}L^2_{0,i}) = 0 \quad (5)\]

Equation (5) is in the form of a quadratic equation \((Ax^2 + Bx + C = 0)\) and can be dissolved to find a logic formula for \(C_{Ge,org,i}\) as Equation (6):

\[C_{Ge,org,i} = \frac{[C^2_{Cl,org,i} + 4K_{ex}L_{0,i}C_{Cl,org,i}]}{[4L_{0,i}K_{ex}C_{Cl,org,i} + C^2_{Cl,org,i}]^2 - (16K^2_{ex}C^2_{Cl,org,i}L^2_{0,i})^{0.5}}{8K_{ex}C_{Cl,org,i}} \quad (6)\]

It is noteworthy that the subscript \(aq\) refers to the feed phase.

(b) In order to find the value of mass transfer coefficient, the diffusion equation was written as Equation (7) (Danesi et al. 1981; Huang & Juang 1988):

\[J_{Ge,m,i} = K_m \times C_{Ge,org,i} \times \mu^{-\alpha} \quad (7)\]

where \(J_{Ge,m}, K_m, \mu, \) and \(\alpha\) refer to the flux of the germanium–carrier complex through the membrane, mass transfer constant, viscosity, and the power of the carrier’s viscosity (equal to 2/3), respectively. Afterward, the concentration of germanium in the feed phase can be calculated using Fick’s equation as in Equation (8).

\[J_{Ge,m,i} = -\frac{V}{A} \frac{\Delta C_{Cl,org,i}}{\Delta t} \Rightarrow 
C_{Cl,org,i}(t + \Delta t) = C_{Cl,org,i}(t) - \frac{A}{V} \Delta t \times J_{Ge,m,i} \quad (8)\]

where \(C_{Cl,org,i}(t)\) denotes the germanium concentration corresponding to an Alquat 356 concentration at a desired time. In addition, with respect to the simultaneous transport of germanium and chloride species (the first from the feed to the strip and the second vice versa) and the extraction equation (Equation (1)), the flux and the concentrations of chloride ions are achieved as Equations (9) and (10):

\[J_{Cl,i} = 2J_{Ge,m,i} \quad (9)\]

\[C_{Cl,org,i}(t + \Delta t) = C_{Cl,org,i}(t) - \frac{A}{V} \Delta t \times 2J_{Ge,m,i} \quad (10)\]

In this study, the values of \(K_m\) and \(K_{ex}\) are the objectives of the modeling, which will be used to describe the transport process of germanium in the presented FSSLM system.

(c) In the current modeling, a function was used to monitor gaps between the calculated germanium \((C_{Ge,org,cal}(t)) = (C_{Ge,org,i}(t))\) in the feed phase and similar experimental concentrations \((C_{Ge,org,exp}(t))\) at experimental times. This mathematical function is the Error function,
which was written as Equation (11):

$$\text{Error}(x) = \sum_{i=1}^{N} (C_{\text{Ge,aq,cal},i}(t) - C_{\text{Ge,aq,exp},i}(t))^2$$  \hspace{1cm} (11)

In order to show the accuracy of the model, root mean square error (RMSE), bias, and scatter index (SI) were calculated for the model. RMSE is calculated according to Equation (12) (Mentaschi et al. 2013; Najafzadeh & Zeinola-bedini 2018):

$$\text{RMSE} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (C_{\text{Ge,aq,cal},i} - C_{\text{Ge,aq,exp},i})^2}$$  \hspace{1cm} (12)

where $N$ is the number of data. Furthermore, $C_{\text{Ge,aq,cal},i}$ and $C_{\text{Ge,aq,exp},i}$ represent the values obtained from the model and experimental values, respectively. By considering the average of the values, another index for evaluating the model can be defined as the SI according to Equation (13) (Mentaschi et al. 2013):

$$\text{SI} = \sqrt{\frac{\sum_{i=1}^{N} ((C_{\text{Ge,aq,cal},i} - \bar{C}_{\text{Ge,aq,cal}}) - (C_{\text{Ge,aq,exp},i} - \bar{C}_{\text{Ge,aq,exp}}))^2}{\sum_{i=1}^{N} (C_{\text{Ge,aq,cal},i})^2}}$$  \hspace{1cm} (13)

where $\bar{C}_{\text{Ge,aq,cal},i}$ and $\bar{C}_{\text{Ge,aq,exp},i}$ are the average calculated and experimental values, respectively.

Another parameter to measure the accuracy of the model is the bias indicator defined in Equation (14) (Mentaschi et al. 2013):

$$\text{bias} = \bar{C}_{\text{Ge,aq,cal},i} - \bar{C}_{\text{Ge,aq,exp},i}$$  \hspace{1cm} (14)

RESULTS

Modeling configuration

In this research, Matlab mathematical software (R2014b) was used as a tool for programming and creating the FSSLM mass transfer model. The principles used in this model were introduced in the theoretical section. The overall configuration of the modeling is shown in Figure 2. It is noteworthy that experiments were carried out at four concentrations of Aliquat 336 (2.5, 5, 7.5, and 10%) as seen in Figure 2, in the first stage, a preliminary matrix with columns containing the number of conditions, the initial germanium concentration in the feed phase, the Aliquat 336 concentration in each condition, the number of times for each condition in which samples were taken, and the viscosity of various Aliquat 336 concentrations was formed. Afterward, the matrix of time was formed, which incorporated the experimental times. In the third step, another matrix including the experimental germanium concentrations in the feed phase corresponding to the times in the time matrix was created in Matlab.

In order to find the values of the objective parameters ($K_m$ and $K_{ex}$), three loops were considered as shown in
6. As seen in Figure 2, the final objective parameters are obtained when the minimum errors between calculated and experimental values are found.

The other notes about this configuration are listed below:

1. At the first step, the matrixes of \(N_{0,\text{condition}}\) (the number of experimental conditions), \([\text{Ge}]_0\) (initial germanium concentrations), \([L]_0\) (initial concentrations of Aliquat 336), \(N_{0,\text{times}}\) (the number of experimental times), and \([\text{Viscosity}]\) were formed. The time matrix \([T]\) and the feed experimental concentration matrix \([C(t)]_{\text{eq}}, i\) were also created at this step.

2. In each condition, the initial concentration of chloride ions in the feed phase is considered to be 0. In order to prevent the division by zero error, this value is equal to 0.000000001 mg/L.

3. In each condition, the initial germanium concentration (time = 0) in the organic phase is calculated using Equation (6). In this equation, the initial chloride concentration is close to 0, and the germanium concentration is equal to its initial concentration in the feed phase. Also, since the values of \(K_m\) and \(K_{ex}\) are necessary for the calculation of Equation (6), an initial guess is obtained from the fmincon function.

4. In the second loop, after calculating the concentration of germanium in the feed phase, to calculate the concentration of germanium in the organic phase, Equation (6) is again used to produce a new value called \(C_{\text{Ge,org}}(t + \Delta t)\).

5. Since the time is changing in the set of positive integer numbers, the calculations are carried out each minute. With respect to the restricted experimental points (times), the calculated values (from Equation (8)) corresponding to the experimental times are inserted into another defined matrix called the calculated matrix. The calculation continued until a final time of \(t_f\) (according to the final time of experiments). A concentration for a certain time and condition is compared to the corresponding value in the experimental concentration matrix.

6. As seen in Figure 2, the final objective parameters are obtained when the minimum errors between calculated and experimental values are found.

Table 2 | The initial conditions used for developing a model for the FSSLM of this study

| No. of the exp. | Initial Ge (mg/L) | Aliquat (v/v%) | Aliquat (mol) | Kinematic vis. (cSt) | Dynamic vis. (cP) |
|----------------|------------------|----------------|---------------|---------------------|------------------|
| 1              | 96.66            | 2.5            | 0.050         | 2.26                | 1.78             |
| 2              | 94.43            | 5              | 0.100         | 2.50                | 1.99             |
| 3              | 94.43            | 7.5            | 0.149         | 3.11                | 2.50             |
| 4              | 96.66            | 10             | 0.199         | 3.39                | 2.77             |

Model resolution

In order to model the facilitated transport of germanium through a flat sheet membrane impregnated with Aliquat 336, a series of experiments were conducted in four conditions as listed in Table 2.

The concentration of Aliquat 336 was selected in the range of 2.5–10%v/v because the transport of germanium was negligible in lower concentrations than 2.5%. On the other hand, since the Aliquat 336 is a viscous ionic liquid, the concentrations of more than 10%v/v were not efficient for the transport of germanium. According to the literature, in an SLM system in which Aliquat 336 was used as the carrier for the transport of tantalum and niobium, an increase in the carrier concentration enhanced the viscosity of the membrane phase, which resulted in hindering diffusion (Buachuang et al. 2011). Buachuang et al. (2011) showed that the transport efficiency of Ta(III) increased up to Aliquat 336 of 3%v/v; however, the transport decreased by increasing the carrier up to 4%v/v. This behavior can be justified according to the Stokes–Einstein equation in which diffusion has an inverse relation with viscosity (Miller 1924).

With respect to the configuration shown in Figure 2, a program code was written in Matlab software and the optimum objective parameters were finally found after several iterations using the minimization function called fmincon. Hence, the extraction constant \((K_{eq})\) and the mass transfer constant \((K_m)\) were found to be 0.178 and 9.25 \(\times 10^{-2}\) cm/s, respectively. The extraction equilibrium constant was found according to Equation (5) from the results of the model by the sum of errors, which tended to be minimum. This value was compared with the extraction constant obtained in various studies in the literature (Table 3). However, depending on the number of equilibria, the charge of the ions etc., it is difficult to compare the extraction constants and these types of constants. For instance, if the charge of species is different, the constant dimensions will not be the same (Ohmiya & Sekine 1996). As seen in
Table 3, the scale of the presented $K_{ex}$ values varies in the extensive range. Among these studies, the species having similarity to that in this study was chromium(VI). The $K_{ex}$ values were calculated in both liquid–liquid extraction (LLX) and SLM systems. In both systems, the extracted species was chromate ($CrO_4^{2-}$). The mathematical models were developed based on the transport principles and extraction mechanisms. As seen in Table 3, the dimension and the scale of the obtained values are in the range of this study’s value.

The other value obtained in the model of this study was $K_m$. Based on Equation (7), a value was found for the overall mass transfer constant. In order to understand the mass transfer in each concentration of the carrier, the values of mass transfer $K'_{m}$ were achieved by considering the viscosity values of the carrier. In this regard, the overall mass transfer constant was multiplied by $\mu^{-\alpha}$ for each concentration of Aliquat 336. Afterward, the diffusion coefficient ($D_m$) can be calculated based on Equation (15) developed by Prasad & Sirkar (1988):

$$K'_{m} = \frac{D_m \cdot \varepsilon}{\delta \cdot \tau} \quad (15)$$

In this equation, $\varepsilon$, $\delta$, and $\tau$ refer to porosity, membrane thickness, and tortuosity, respectively. The calculated values are illustrated in Table 4. The comparison of the mass transfer coefficient obtained in the current study and the corresponding values achieved in other SLM systems in which Aliquat 336 was applied as a carrier are illustrated in Table 5. As seen in this summary, most of the coefficients were obtained in HFSLM systems using Aliquat 336 with concentrations in the range of 2.5–10%v/v. In all these systems, the diffusions of species such as tantalum and chromium are much lower than that of germanium in this study.

Furthermore, in a polyvinyl chloride-based membrane system, the cadmium diffusion coefficient is 10^6 times less than the coefficient found in the current study. However, Chaturabul et al. (2015) developed an HFSLM system to transport mercury(II) using the carrier of Aliquat 336 (4%v/v). Since the mass transfer constant ($K'_{m}$) was calculated in the aforementioned system, only this value is presented in Table 5. The obtained $K'_{m}$ of 17.1 × 10^{-2} was about three times the value found in the current study. Consequently, it can be concluded that the system developed in the current research is an efficient procedure to transport germanium through the PTFE flat sheet membrane impregnated with Aliquat 336.

The validity of the model

The validity of the developed model was investigated by comparing the modeled and experimental curves. These curves were plotted for the four conditions (various Aliquat 336 concentrations) and the initial germanium concentration of the feed phase is shown in Table 1, with the temperature of 25°C and an HCl concentration of 1 M as the strip solution. The results are illustrated in Figure 3. This figure shows the plots of germanium concentration in the feed phase as a function of time in four Aliquat 336 concentrations. The modeled and
experimental curves are shown by continuous lines and the separate points, respectively. According to these plots, the germanium species concentration reduced in the feed phase by prolonging the time showing the transport of these species through the FSSLM. The overall tendency of the experimental and modeled data shows a good agreement between the data. As seen in Figure 3, the proportion of the transport rate in the Aliquat 336 concentration of 2.5%v/v is the slowest among the concentrations. In the other carrier concentrations, the transport of germanium was almost completed before 600 min. In order to evaluate the precision of the model for each concentration of Aliquat 336, related correlation coefficients were calculated. For this purpose, experimental and calculated values were plotted as scatter plots in Figure 4. As seen in this figure, the correlation coefficients are increased by enhancing the Aliquat 336 concentration, whereas the coefficient decreases to 0.92 at the carrier concentration of 10%v/v. This discordance can be seen in Figure 3(d). A similar result has been reported by Buachuang et al. (2011). With an enhancement of the Aliquat 336 concentration and after a specific concentration, the viscosity within the membrane increases. Therefore, this factor may hinder the mass transfer process followed by accumulating the species complexes in the liquid membrane. In addition, with an increase of the free carrier molecules, they cannot participate in the transport process and react with germanium species (Buachuang et al. 2011). This results in inaccurate transport curves such as the curve shown in Figure 3(d). In addition to the correlation coefficient, statistical parameters, namely RMSE, bias, and SI, have been used to evaluate the accuracy of the model. As seen in Figure 4, with respect to the data range (germanium concentration of 0–100 mg/L), values of RMSE, bias, and SI of the model corresponding to each Aliquat 336 concentration are low, showing the accuracy of the model. However, similar values for the model corresponding to the Aliquat 336 concentration of 10%v/v (RSME = 3.422, bias = −3.776, and SI = 0.189) are the highest among the concentrations. The reason for this increase has been discussed above.

**CONCLUSIONS**

In this work, the facilitated transport of germanium species from the neutral medium containing tartaric acid as the complexant across an FSSLM was modeled. The FSSLM experiments were performed under the following conditions: germanium ≈ 100 mg/L, tartaric acid concentration 2.76 mmol/L, and carrier concentrations of 2.5–10%v/v. Aliquat 336 was used as a carrier in this system. In order to develop a model, equations related to the extraction mechanism, the mass transfer, and the

### Table 4 | The obtained viscosity, mass transfer constant and diffusion coefficients

| Aliquat (%v/v) | \( \mu^v \) | \( K'_m \text{(cm/s)} \) | \( D_m \text{(cm}^2/\text{s)} \) |
|----------------|----------------|--------------------------|--------------------------|
| 2.5            | 1.47           | 6.30 \times 10^{-2}      | 2.4 \times 10^{-4}       |
| 5              | 1.58           | 5.85 \times 10^{-2}      | 2.23 \times 10^{-4}      |
| 7.5            | 1.84           | 5.02 \times 10^{-2}      | 1.91 \times 10^{-4}      |
| 10             | 1.97           | 4.69 \times 10^{-2}      | 1.79 \times 10^{-4}      |

### Table 5 | A summary of diffusion coefficients for various species extracted using Aliquat 336

| Authors         | Extracted species       | Aliquat (%v/v) | System | \( D_m \) (cm²/s) | Membrane          | Reference          |
|-----------------|-------------------------|----------------|--------|------------------|-------------------|--------------------|
| Buachuang et al. | Tantalum(III)           | 3              | HFSLM  | 3.74 \times 10^{-9} | Polypropylene     | Buachuang et al. (2011) |
| Alonso et al.   | Chromium(VI) (from HCl) | 10%            | HFSLM  | 2.5 \times 10^{-7} | Polypropylene     | Alonso & Pantelides (1996) |
| Alonso et al.   | Chromium(VI) (from wastewater) | –              | HFSLM  | 4.75 \times 10^{-5} | Polypropylene     | Alonso et al. (1994) |
| Castillo et al. | Chromium(VI)           | 0.2 (mol/L)    | FSSLM  | 1.64–2.44 \times 10^{-7} | PVDF             | Castillo et al. (2002) |
| Chaturabul et al. | Mercury(II)           | 4              | HFSLM  | \( K'_m = 17.1 \times 10^{-2} \) (cm/s) | Polypropylene methane | Chaturabul et al. (2015) |
| Wang et al.     | Cadmium(II)            | 30             | PVC-based | 3.85 \times 10^{-10} | Polyvinyl chloride | Wang et al. (2000) |
| This study      | Germanium(IV) (100 mg/L) | 5%            | FSSLM  | 2.23 \times 10^{-4} | PTFE              | –                  |
Figure 3 | The concentration of germanium in the feed phase plotted versus time at various concentrations of Aliquat 336 as the carrier: (a) 2.5%v/v; (b) 5%v/v; (c) 7.5%v/v; (d) 10%v/v (feed solution: 2.76 mmol/L tartaric acid; about 100 mg/L Ge(IV); stripping solution: 1 M HCl).

Figure 4 | Modeled concentration of germanium versus the experimental data for various concentrations of Aliquat 336 as the carrier: (a) 2.5%v/v; (b) 5%v/v; (c) 7.5%v/v; (d) 10%v/v (feed solution: 2.76 mmol/L of tartaric acid, Ge(IV) about 100 mg/L; stripping solution: 1 M HCl).
diffusion were derived. These equations were numerically solved using programming in a mathematical tool (i.e., Matlab software) to obtain objective parameters. The objective parameters of the equilibrium extraction constant ($K_{ex}$) and the overall mass transfer constant ($K_m$) were found to be $0.178$ and $9.25 \times 10^{-2}$ cm/s, respectively. The value of $K_{ex}$ was compared with similar values in the literature. With respect to viscosities, the values of mass transfer coefficients corresponding to Aliquat 336 concentrations of 2.5, 5, 7.5, and $10\%$v/v were found to be $6.30 \times 10^{-2}$, $5.85 \times 10^{-2}$, $5.02 \times 10^{-2}$, and $4.69 \times 10^{-2}$ cm/s, respectively. In addition, diffusion coefficients ($D_m$) relating to the Aliquat 336 concentrations of 2.5, 5, 7.5, and $10\%$v/v were calculated using mass transfer coefficients to be $2.4 \times 10^{-4}$, $2.25 \times 10^{-4}$, $1.91 \times 10^{-4}$, and $1.79 \times 10^{-4}$ cm$^2$/s, respectively. Finally, the model curves fit well with the experimental points, showing the validation of the model. The correlation coefficients between model and experimental data corresponding to Aliquat 336 concentrations of 2.5, 5, 7.5, and $10\%$v/v were calculated to be 0.96, 0.98, 0.99, and 0.92, respectively. With respect to the data range (germanium concentration 0–100 mg/L), values of RMSE, bias, and SI of the model corresponding to each Aliquat 336 concentration were low, showing the accuracy of the model. However, similar values for the model corresponding to the Aliquat 336 concentration of $10\%$v/v (RSME = 5.422, bias = $-5.776$, and SI = 0.189) are the highest among the concentrations. This model can be used as a useful tool in further SLM processes such as HFS-SLM with minor changes.

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**AUTHOR CONTRIBUTIONS**

H.K.H. made a significant contribution to every stage of this paper, such as the investigation (with the essential assistance of A.F. and A.M.S.) and analysis and preparing the paper. M.I. contributed to the conception of the paper. H.K.H. and A.F. designed the tests and presented a model for this paper. M.I. and H.K.H. finalized the paper by a critical revision of the paper.

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