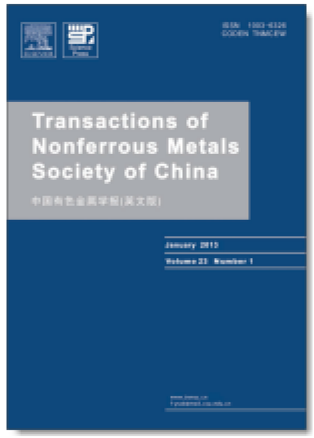

Germanium transport across supported liquid membrane with Cyanex 923: Mathematical modeling

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Keywords:	Supported liquid membrane, Cyanex 923, Germanium, Transport, Mathematical modeling
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Germanium transport across supported liquid membrane with Cyanex 923: Mathematical modeling

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Abstract

A mathematical model was developed to monitor the facilitated transport of germanium(IV) from oxalic acid solutions through a flat sheet supported liquid membrane (FSSLM) containing Cyanex 923. This model presented a reliable calculation of the extraction constant (K_{ex}= 2.057 × 10^3 1/mol^4). The FSSLM model was solved according to the extraction reaction, Fick's law, and diffusional transport. Consequently, the overall mass transfer coefficient (K_{org}) was found to be 3.84 cm/s. Using this value, diffusion coefficients for various Cyanex 923 concentrations in the range of 5 to 30 %v/v were calculated. Finally, the accuracy of the models was investigated.

Keywords: Supported liquid membrane; Cyanex 923; Germanium; Transport; Mathematical modeling

1. Introduction

The role of germanium in strategic uses such as semiconductors, catalysts, fiber optics, etc. has caused companies and countries to separate it from various resources [16]. Important primary resources of germanium are classified into zinc sulfide ores and fly ashes. Leachates or wastewaters released from plant processing of the mentioned materials may contain germanium. In order to separate germanium from these effluents, various techniques have been developed. Liquid-liquid extraction (LLX) [22], ion exchange [18], ion flotation [9], adsorption [28], precipitation [12], and emulsion liquid membrane (LM) [16], etc. are some of these techniques applied to separate germanium from aqueous solutions. Liquid membrane separation is a type of technique combining the extraction and stripping stages of liquid-liquid extraction processes in a single step. Some advantages such as energy saving, low investment and operational cost due to the lower consumption of extractants have made this technique effective in industrial usages [24]. Bulk LM (BLM), supported LM (SLM), and emulsion LM (ELM) are three types of developed membranes. In flat sheet SLM techniques, a membrane impregnated in a carrier, i.e. commonly a hydrophobic membrane, transports species from a feed phase to a receiving/strip phase based on the chemical potential gradient [24,26,27,29].

Mathematical modeling helps to better recognize the application and performance of SLM systems [21]. It can be useful for designing an effective operation and scaling up SLM systems [15]. The modeling of ion transport through a liquid membrane is carried out according to one of the following assumptions: (a) considering diffusion layers existing in the organic-aqueous interface [14], (b) considering that an organic molecule (carrier) leaves the membrane phase and reacts with aqueous species in the aqueous phase [6], (c) ignoring the presence of static layers formed between the liquid membrane and aqueous phase existing in the feed and strip sides [10]. The third assumption has been considered to develop a mathematical model in the present study. In this assumption, only the diffusion across SLM has taken place in the system. It is noted that an appropriate agitation of the feed/strip phases is necessary to eliminate the aforementioned interfacial layer. In the current study, a developed SLM system with well-designed impellers was used to eliminate the interfacial layers.

Several works studied the transport modeling of various species using Cyanex 923 as a carrier. Table 1 shows a summary of these studies. A kinetic model was obtained to describe parameters of the cadmium transport, including diffusions of ions, carrier, and carrier-ions across diffusion layers and interfacial chemical reactions [8]. Alguacil and Alonso (2003) [7] found the flux of chromium transported using Cyanex 923 in an FSSLM system with the basis of a model calculated using Fick's law. A permeation model illustrating the facilitated transport mechanism of iron(III) across a liquid membrane impregnated in Cyanex 923 was developed by Alguacil and Martínez (2000) [4]. Mass transfer resistances and diffusion coefficients were found using this model. The transport model of gold(III) across a SLM using Cyanex 923 diluted in n-decane was used to find resistances and diffusion coefficients [5]. Another model was developed to predict the membrane phase composition containing PC88A and Cyanex 923 in the physicochemical transport of uranium(VI) [17]. A mathematical model showing the transport rate is developed by Sastre et al. (1998) [3]. Based on this model, equations in which a relationship was found between the permeability coefficient and diffusion, equilibrium parameters as well as the concentrations of reagents were described. Furthermore, parameters such as diffusion resistances were calculated by means of the aforementioned model. Recently, Kamran Haghighi et al. (2018) [31] developed a mass transfer model to find transport resistances existing in the membrane phase and the boundary interface layer.

The aim of this paper is modeling the germanium(IV) facilitated transport from neutral media using an organophosphorus carrier called Cyanex 923. The development of a mathematical model for the germanium(II) liquid-liquid extraction resulted in determining the extraction equilibrium constant. This constant was the basis of FSSLM modeling. Using this constant, another mathematical model was developed according to the extraction equilibrium equation, Fick's law, and diffusional transport to image the behavior of germanium transport across the membrane. The diffusion and transport parameters were found using this model. The goodness of the obtained models was evaluated by comparing the correlations of experimental and model data.

Table 1. A Summary of a literature survey on species transport modeling using Cyanex 923.

Authors	Methods	Species	Diluents	Strip medium	Metho	Refs.
Alonso et al.	Kinetics	Cd(II)	Solvesso 100	HCl	FSSLM	[8]
Alguacil et al.	Fick's law	Cr(VI)	Cumene & Solvesso 100	Hydrazine Sulfate	FSSLM	[7]
Alguacil et al.	Empirical equations	Fe(III)	Xylene, toluene, n-decane and carbon	NaCl	FSLSM	[4]
Alguacil et al.	Empirical equations	Au(III)	n-decane	sodium thiocyanate &		[5]
Sastre et. al	Empirical equations	Au(III)	Cumene, kerosene and toluene	HCl	solid-SLM	[3]
Singh et al.	-	U(VI)	n-dodecane	$(NH_4)_2CO_3$	FSLSM	[17]

2. Experimental procedure

2.1. Reagents

An organophosphorus organic extractant called Cyanex 923 (four trialkylphosphine oxides) with the composition of 93% was provided by CYTEC Inc., USA. In all experiments, kerosene from Sigma-Aldrich was used to dilute Cyanex 923. A synthetic solution was prepared by dissolving germanium(IV) dioxide (GeO_2) with the purity of 99.998 % (Sigma-Aldrich A.C.S. Reagent) in distilled water. The other reagents used were analar grade from Merck, Germany.

2.2. Experiments

In order to find the extraction equilibrium constant of the LLX system, a series of experiments were conducted by shaking organic and aqueous phases with O:A ratio of 1 in separatory funnels by means of a mechanical shaker (SBS Instruments SA, Spain). The time of each experiment was 15 min followed by separating aqueous and organic phases. After the phase separation, a 0.5 mL sample from the aqueous phases was taken to be analyzed by means of an Inductively Coupled Plasma (ICP) (Agilent 700 Series, US). It is noted that the germanium concentration of organic phases was found by mass balancing. All aqueous phases used in the experiments contained 100 mg/L Ge and oxalic acid of 0.1 mol/L. Furthermore, the Cyanex 923 composition as the carrier was varied in the range of 5 to 30 %v/v.

FSSLM experiments were conducted in the cells introduced elsewhere [13]. The feed and receiving cells had volumes of 220 mL separated with a membrane module in which a flat sheet membrane impregnated with various concentrations of Cyanex 923 was used. The membrane used was a Millipore Durapore poly tetra fluoro ethylene (PTFE) membrane with a diameter of 47 mm and a pore size of 0.45 μm. The porosity, membrane thickness, and tortuosity of this membrane were 85%, 30 μm, and 1.18, respectively [19]. This membrane was impregnated with different concentrations of the organic phase followed by rinsing with water to eliminate the excess organic carrier remaining on the membrane surface. The effective area of the membrane was calculated to be 11 cm^2. As mentioned before, in order to eliminate the interfacial layers, solutions in the cells were efficiently agitated with well-organized mechanical impellers. In each experiment, samples with volumes of 0.5 mL were taken from the feed/receiving phases at desired durations followed by analyzing the germanium concentration of the solution by means of ICP (Agilent 700 Series).

Since the kinematic viscosity was used in FSSLM modeling, it was calculated for various concentrations of Cyanex 923 using a "Capillary U-Tube Viscometer" supplied from SCHOTT Instruments. The constant viscometer was determined to be 0.01 by the supplier. Calculations were carried out on the basis of the ASTM D445 standard. In order to find the kinematic viscosity, transit time for various concentrations of the carrier was multiplied by the mentioned constant. To evaluate the dynamic viscosity, kinematic values were multiplied by the corresponding density.

3. Modeling

3.1. Liquid-liquid extraction

In order to model the extraction of germanium from a solution containing oxalic acid, a series of mass balance and chemical equilibrium equations were considered. In the equilibrium condition, equations corresponding to species reacted in aqueous and organic phases were obtained. In order to obtain these equations, the germanium extraction mechanism of Cyanex 923 from a solution containing oxalic acid should be described. Since Cyanex 923 extracts species as the solvation mechanism, it is predicted that neutral species of germanium are extracted. With respect to the previous works, neutral species of trisoxalato germanates formed in aqueous solutions as in Eq. (1) [30]:

$$3H_2C_2O_4 + GeO_2.H_2O \Leftrightarrow H_2Ge(C_2O_4)_3 + 3H_2O \quad (1)$$

The aim of modeling for the LLX system was to find the extraction equilibrium constant used in FSSLM modeling. For this purpose, a series of experiments were conducted in the carrier concentrations of 1-30 %v/v. The overall reaction between trisoxalato germanates and Cyanex 923 can be written as Eq. (2) [30]:

$$H_2Ge(C_2O_4)_{3(aq)} + 4L_{(org)} \Leftrightarrow H_2Ge(C_2O_4)_3.4L_{(org)} \tag{2}$$

Subscripts *aq* and *org* represent aqueous and organic phases, respectively. The extraction equilibrium constant for this reaction is written as Eq. (3):

$$K_{ex} = \frac{[H_2Ge(C_2O_4)_3.4L]_{(org)}}{[H_2Ge(C_2O_4)_3]_{(aq)}[L]_{eq}{}^{4}{}_{(org)}} \tag{3}$$

Where brackets show the concentration and eq subscript depicts the equilibrium condition. In order to simplify the mathematical formulas, $[L]_{eq}$, $[H_2Ge(C_2O_4)_3.4L]_{(org)}$, and $[H_2Ge(C_2O_4)_3]_{(aq)}$ are replaced with L_{eq}, $C_{Ge,org,i}$, and $C_{Ge,aq.\exp,i}$, respectively. Obtaining K_{ex} was carried out based on minimizing the sum of squares (SS) attained between the experimental and modeling extraction efficiency. The corresponding calculations were conducted using the solver technique in Excel 2016 software. For this purpose, solver dedicated a value to K_{ex}. Using this value, the germanium concentration in the organic phase was again calculated using Eq. (3). Then, the model extraction efficiency can be found using Eq. (4).

$$\%E = \frac{C_{Ge,org}}{C_{Ge,0}} \tag{4}$$

Where E_{model} and E_{exp} are the extraction efficiencies obtained from the model and experiments. Finally, the sum of square values based on extraction efficiencies of experiments and model were obtained as Eq. (5):

$$SS = \sum_{i=1}^{N} (\%E_{\mathrm{model}} - \%E_{\mathrm{exp}})^2 \tag{5}$$

Where, i and N depict counter and the number of experiments, respectively. The mentioned dedication continued until the best K_{ex} was found in a condition in which SS between the model and experimental values were minimum.

3.2. Flat sheet supported liquid membrane

As mentioned before, the extraction equilibrium constant (K_{ex}) of the LLX system found using the corresponding model was used in the formulation of the FSSLM system. Matrixes were used in the mathematical programming in the Matlab software as follows:

(a) A matrix includes columns of the germanium initial concentration, Cyanex 923 concentration, the number of samples in each carrier concentration, and the corresponding viscosities.

(b) A time matrix includes times of the taken samples in each condition (i which shows the initial concentration of the carrier) imported in each row.

(c) A matrix called the concentration matrix containing the germanium concentrations of the feed solution at times mentioned in the time matrix.

Resistances in the interfacial layers have been ignored during the modeling due to the good agitation of solutions by impellers placed close to the membrane phase. According to the literature, the interfacial resistances are usually ignored in rough models [25]. In the present study, the model was created based on Fick's law as in Eqs. (6) and (7):

$$J_{Ge,i}(t) = K_{org} \times C_{Ge,org,i}(t) \times \mu^{-\alpha} \tag{6}$$

$$J_{Ge} = -\frac{V}{A}\frac{dC_{Ge,org}}{dt} \tag{7}$$

Where J_{Ge} is the germanium flux through the membrane, K_{org} represents an overall mass transfer coefficient; μ is the dynamic viscosity, α is a constant value representing the power of the carrier's viscosity, V is the volume equal to 220 mL and A is the membrane effective area equal to 11 cm^2.

For easiness, the germanium concentration transported by Cyanex 923 was represented with $C_{Ge, org.i.}$ In order to create a model, the Matlab 2012 software was used to write a program as shown in Fig. 1 and the following procedure:

(a) The concentration of germanium transported ($C_{Ge,org,i}(t)$)by Cyanex 923 with a specific concentration (*i*, e.g. *i*=1 represents the concentration of 5 %v/v) was calculated at the time of t with respect to the experimental germanium concentration of the feed phase ($C_{Ge,aq,\exp,i}$) as the extraction equilibrium reaction represented in Eq. (3). This calculation is as Eq. (8):

$$C_{Ge,org,i}(t) = C_{Ge,aq,\exp,i}(t) \times K_{ex} \times L_{eq}^{4} \tag{8}$$

(b) In each loop, *fmiccon* generated values for K_{org} and α. Using these values, $J_{Ge}(t)$ was calculated using Eq. (6). The calculated germanium concentration ($C_{Ge,aq,cal,i}(t)$) in the feed phase at the time of *t* in various experimental conditions (*i*) was obtained using Eq. (7) and rewritten as Eq. (9):

$$C_{Ge,aq,cal,i}(t) = C_{Ge,aq,\exp,i}(t-1) - \frac{A}{V} \times \Delta t \times J_{Ge,i}(t) \tag{9}$$

In this equation, $C_{Ge,aq,cal,i}(t-1)$ depicts the germanium concentration in the feed solution at the time of *t*-1. At the condition of *t*=1, this concentration shows the initial germanium concentration in the feed phase. Furthermore, Δt is the time interval of the calculations (here is 1 min).

(c) The objective values of this study are K_{org} and α. Their optimum values were found based on minimization of the sum of squares using the *fmincon* function (see Fig. 1). After obtaining values of calculated germanium concentrations for a loop ($C_{Ge,aq,cal,i}(t)$), the sum of square (SS) function was calculated from the squared differences between the calculated and experimental values as Eq. (10):

$$Error = \sum_{i=1}^{N} (C_{Ge,aq,cal,i}(t) - C_{Ge,aq,\exp,i}(t))^2 \tag{10}$$

(d) If the error function was minimized, the objective values of K_{org} and α produced using *fmincon* would be optimized, otherwise, new values were generated to continue calculations according to the aforementioned procedures.

4. Results and Discussion

4.1. Liquid-liquid extraction

The LLX system was modeled to find the extraction equilibrium constant based on minimizing the sum of squares (SS) for differences between experimental and calculated extraction efficiencies according to the procedure mentioned in the modeling section. To construct the model, experimental parameters such as the carrier concentration, the initial concentration of germanium, and the experimental results such as the extraction efficiency are required. Table 2 illustrates the initial conditions of experiments at room temperature used for modeling. The solver method tried to find a K_{ex} value by which the SS function was minimized. In each step, a proposed K_{ex} was used to calculate the concentration of germanium in the organic solution using Eq. (8) followed by evaluating a value for the extraction efficiency using Eq. (4) called the calculated extraction efficiency ($\%E_{cal}$). Finally, using the optimum value of K_{ex}, the *SS* value was found. According to the results, a value of 2056.83 $1/mol^4$ was obtained for the extraction equilibrium constant of the Cyanex 923 solvent extraction system. In addition, the value of 3.83×10^{-3} was found for the minimized SS function. In order to evaluate the accuracy of the LLX model, the plot of extraction efficiency vs. the extractant concentration was constructed as in Fig. 2. As seen in this figure, the model curve has a good fit to the experimental points. The plot of the model extraction efficiency versus experimental results and the regression line showed a correlation coefficient of 0.96, indicating that model values are close to the values obtained from the experiments. Since a specific membrane was used in all experiments with Cyanex 923, the value of K_{ex} obtained in the LLX system can be used in the SLM system. This supposition is usually considered in similar modeling [20].

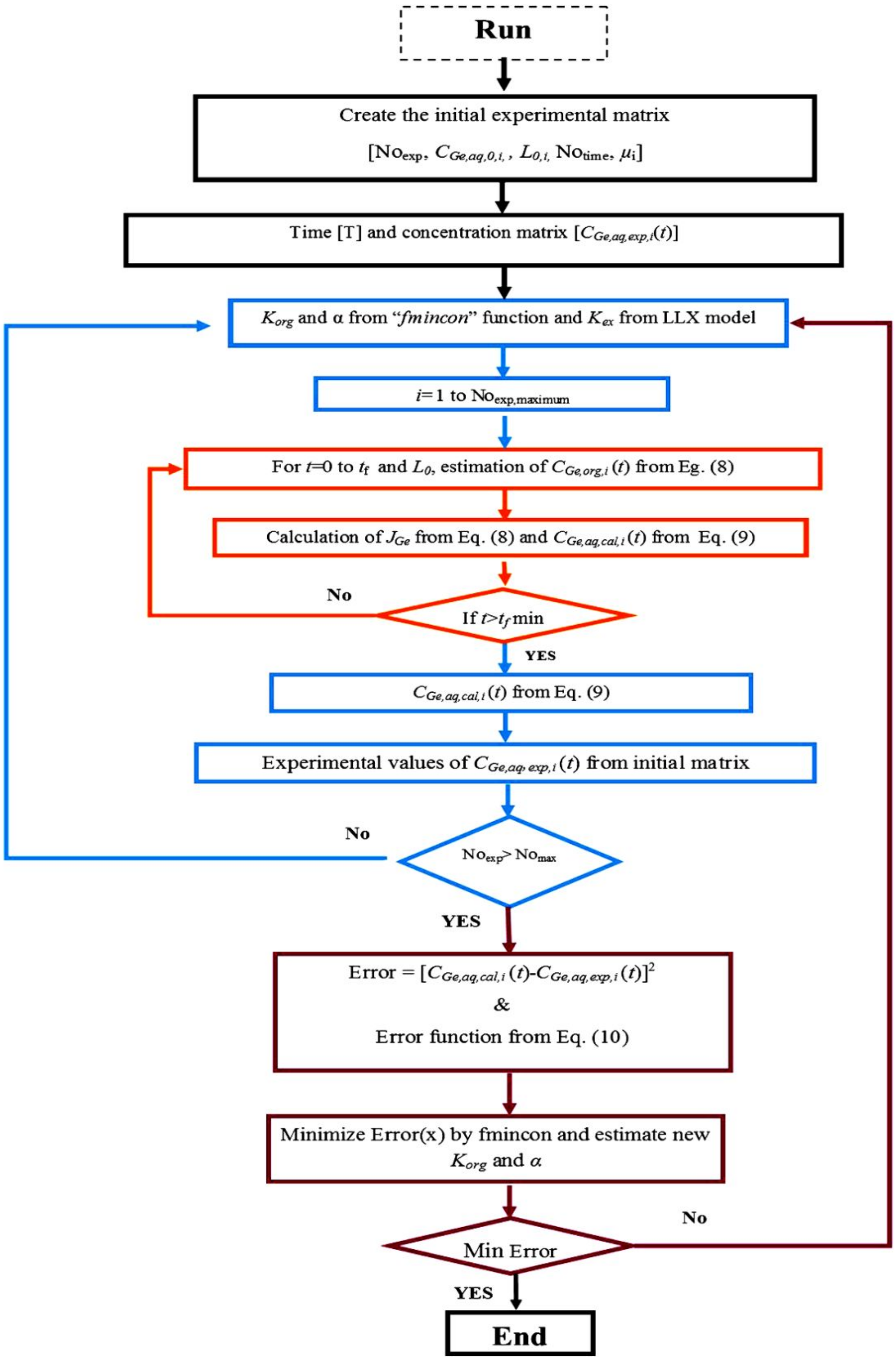

Fig. 1. Flowchart of the modeling procedure used to develop the model of this study.

Table 2. The initial conditions of the LLX system at room temperature used for modeling

Cyanex923, %v/v	$C_{Ge, 0,i}$ mol/L	Cyanex 923, mol/L	$C_{Ge, org}$, mol/L	$\%E_{exp}$
30	0.0011	0.7586207	0.00114469	99.89
25	0.0011	0.6321839	0.00114482	99.90
20	0.0011	0.5057471	0.00114056	99.53
15	0.0011	0.3793103	0.0011177	97.54
10	0.0011	0.2528736	0.00103318	90.16
7.5	0.0011	0.1896552	0.00083177	72.59
5	0.0011	0.1264368	0.000595127	51.93
2.5	0.0011	0.0632184	0.00015446	13.48
1	0.0011	0.0252874	4.9284E-05	4.30

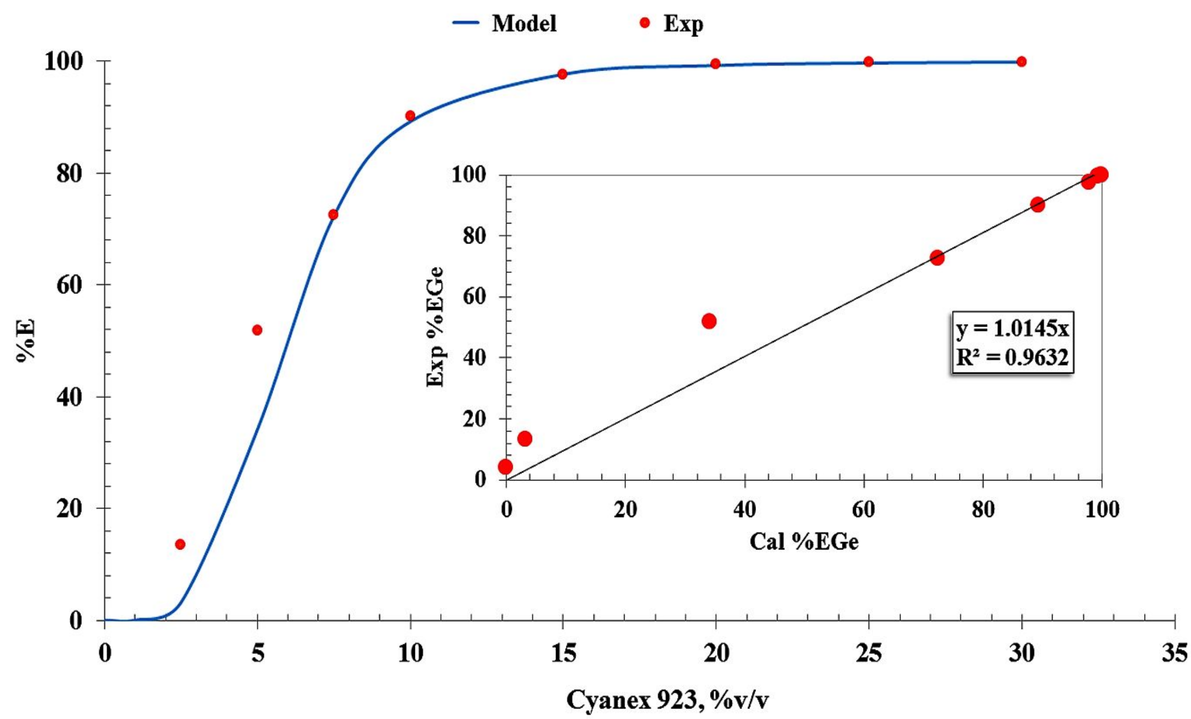

Fig. 2. Model and experimental extraction efficiencies obtained in the LLX system versus Cyanex 923 concentration (the main plot) and the regression line showing the correlation of experimental and model data (the smaller plot).

4.2. Flat sheet supported liquid membrane

In order to model the germanium transport across the PTFE membrane containing Cyanex 923, the extraction equilibrium constant, the equilibrium reaction, Fick's law, and diffusional transport, were used. In the equilibrium equation, the extraction equilibrium constant (K_{ex}) obtained from the LLX model was used. Fig. 1 showed the procedure used in modeling. Experimental data used for the construction of the FSSLM model are listed in Table 3.

Table 3. The initial conditions used for developing a model for the FSSLM of this study.

i	$C_{Ge,0,i}$ mg/L	Cyanex923, %v/v	Cyanex 923, mol/L	Kinematic Vis., mm^2/s	Dynamic Vis., mPa.s
1	94.31	5	0.126	2.10	1.85
2	94.55	10	0.252	2.35	2.07
3	94.23	15	0.378	2.70	2.38
4	109.21	20	0.505	3.27	2.88
5	86.30	25	0.631	3.76	3.31
6	95.04	30	0.757	3.89	3.42

The goal of FSSLM modeling was to find germanium diffusion parameters controlling the transport process. As seen in this table, various concentrations of Cyanex 923 in the range of 5-30% were used in the PTFE membrane. According to Fig. 1, the germanium concentration in the feed phase and the related times were used in the modeling process. In order to follow the instructions shown in Fig. 1 and introduced in the "Modeling" section, a series of program codes were written in Matlab R2014b software. As seen in this figure, modeling was carried out in two loops; first a loop corresponding to time placed within the main loop, in which the germanium concentration was calculated for each minute and a condition (i=Cyanex 923 concentration), and second the main loop for changing i. For comparing the calculated values with the experimental ones, model germanium concentrations corresponding to times of experimental points were kept. Finally, the optimum values were found when the error function was minimized.

With respect to Eq. (6), the overall mass transfer coefficient (K_{org}) found by the program is called the overall K_{org}. This value was found to be 3.84 cm/s. Furthermore, the power of the carrier's viscosity was obtained to be 0.60. Hiss and Cussler (1973) [1] reported that the power of the carrier's viscosity for a viscous solvent is about 2/3. This agreement between the values can confirm the accuracy of the model. Moreover, the values of the mass transfer coefficient (K_m) corresponding to different carrier concentrations can be obtained by multiplying the overall mass transfer coefficient by $\mu^{-\alpha}$. Using the mass transfer coefficient for each carrier concentration (K_m), the diffusion coefficient (D_m) can be calculated using the equation reported by Prasad and Sirkar (1988) [2] as Eq. (11):

$$K_m = \frac{D_m.\varepsilon}{\delta.\tau} \tag{11}$$

In this equation, porosity, membrane thickness, and tortuosity were shown by ε, δ, and τ, respectively. The values of D_m calculated using Eq. (11) were illustrated in Table 4. As seen in this table, the values of D_m decreased with increasing Cyanex 923 concentration. This decrease possibly occurs due to an enhancement of the carrier viscosity. Diffusion coefficients (D_m) obtained were compared with D_m achieved in the literature that worked on the facilitated transport of various metals and species through a membrane containing Cyanex 923. Table 5 illustrates this comparison.

Table 4. The values of mass transfer and diffusion coefficients for various concentrations of Cyanex 923 in the FSSLM system.

Cyanex 923, %v/v	K_m, cm/s	D_m, cm^2/s
5	4.50×10^{-2}	8.50×10^{-4}
10	2.28×10^{-2}	4.30×10^{-4}
15	9.91×10^{-2}	1.87×10^{-4}
20	3.11×10^{-2}	5.87×10^{-5}
25	1.36×10^{-2}	2.57×10^{-5}
30	1.11×10^{-2}	2.09×10^{-5}

Table 5. The evaluation of the diffusion coefficients in the literature.

System	Diluent	Support	D_m, cm^2/s	Ref.
Fe-Cyanex 923 (10 %v/v)	Xylene	PVDF	3.3×10^{-6}	[4]
Au-Cyanex 923 (5 %v/v)	n-decane	PVDF	9.91×10^{-8}	[5]
Cr-Cyanex 923 (20 %v/v)	Cumene	PVDF	7.78×10^{-4}	[7]
Cd-Cyanex 923 (10 %v/v)	Kerosene	PVDF	6.4×10^{-8}	[8]
U- PC88A (0.15 M) and Cyanex 923 (0.15 M)	n-dodecane	PTFE	3.90×10^{-6}	[17]
Ge-Cyanex 923 (10 %v/v)	Kerosene	PTFE	4.30×10^{-4}	This study

As seen in this table, in the Fe-Cyanex 923 (10 %v/v) system, first K_{ex} was calculated and then diffusion rates of iron species across the feed diffusion layer-membrane were used to calculate the rate of the Fe(III) transport. Using these rates, Fick's first law was applied to find the iron flux through the membrane. The model parameters being the aqueous and organic resistances were found followed by calculating the diffusion coefficient using the obtained organic resistance [4]. Moreover, Alguacil et al. (2001) [5] developed a similar model for the facilitated transport of gold(III) using Cyanex 923 across a PVDF membrane with 125 μm thickness, porosity of 75% and pore size of 22 μm. In the above mentioned studies, iron(III) and gold(III) were transported as $HFeCl_4$ and $HAuCl_4$ from chloride media using Cyanex 923. In a model developed by Alguacil and Alonso (2003) [7], diffusional fluxes of chromium(IV) at interfacial layers and the membrane phase were determined by two equations. These fluxes had a relationship with corresponding diffusion coefficients. The carrier and the membrane were Cyanex 923 and PVDF with characteristics similar to those explained above. Alonso et al. (2006) [8] used diffusion rates of cadmium species through the feed diffusion layer and the membrane to evaluate the rate of the cadmium transport and to model the facilitated transport of cadmium species through a PVDF membrane using Cyanex 923. The procedures used in the mentioned study were similar to that reported by Alguacil and Martínez (2000) [4]. Since three types of cadmium species namely $CdCl_2$, $HCdCl_3$, and H_2CdCl_4 existed in the aqueous solutions, three K_{ex} were calculated and used to determine diffusional flux equations. The values obtained in the aforementioned studies have been listed in Table 5. As seen in this table, most D_m values are lower than the diffusion coefficient obtained in the current study. However, the D_m value of the Cr-Cyanex 923 (20 %v/v) system is slightly higher than that of this study. The validity of the model was determined by comparing the experimental and calculated data. In this regard, a series of plots corresponding to calculated and experimental results were plotted. Plots were constructed for six Cyanex 932 concentrations mentioned in Table 3. Fig. 3 illustrates plots of germanium concentration in the feed phase obtained from experimental and model results as a function of time. The continuous lines and the circular points depict the calculated and experimental data, respectively. With respect to these plots, the germanium concentration decreased in the feed phase over time, meaning that the transport of these species occurred through the FSSLM. The inclination of the experimental points to the model curves shows the accuracy of model points to experimental ones. As seen in Fig. 3(a), the transport rate corresponding to the Cyanex 932 concentration of 5 %v/v is very low, as less than 10% of germanium is transported after 1468 min. However, in the mentioned plot, the model curves have a good tendency to the experimental points. In the other carrier concentrations, the transport rates were gradually increased. Another way to investigate the model accuracy is to show the correlations between experimental and calculated data. This purpose was carried out by plotting the calculated concentrations as a function of experimental results (Fig. 4). According to this figure, correlation coefficients are higher than 92%, showing good agreement between experimental and model data. With respect to the literature, values for correlation coefficients above 0.9 show a good fit with high correlation in a regression plot [11,23]. However, since the transport of germanium corresponding to the Cyanex 923 concentration of 5%v/v is very low, the correlation line could not intercept the origin. Thus, the corresponding correlation coefficient could not be obtainable.

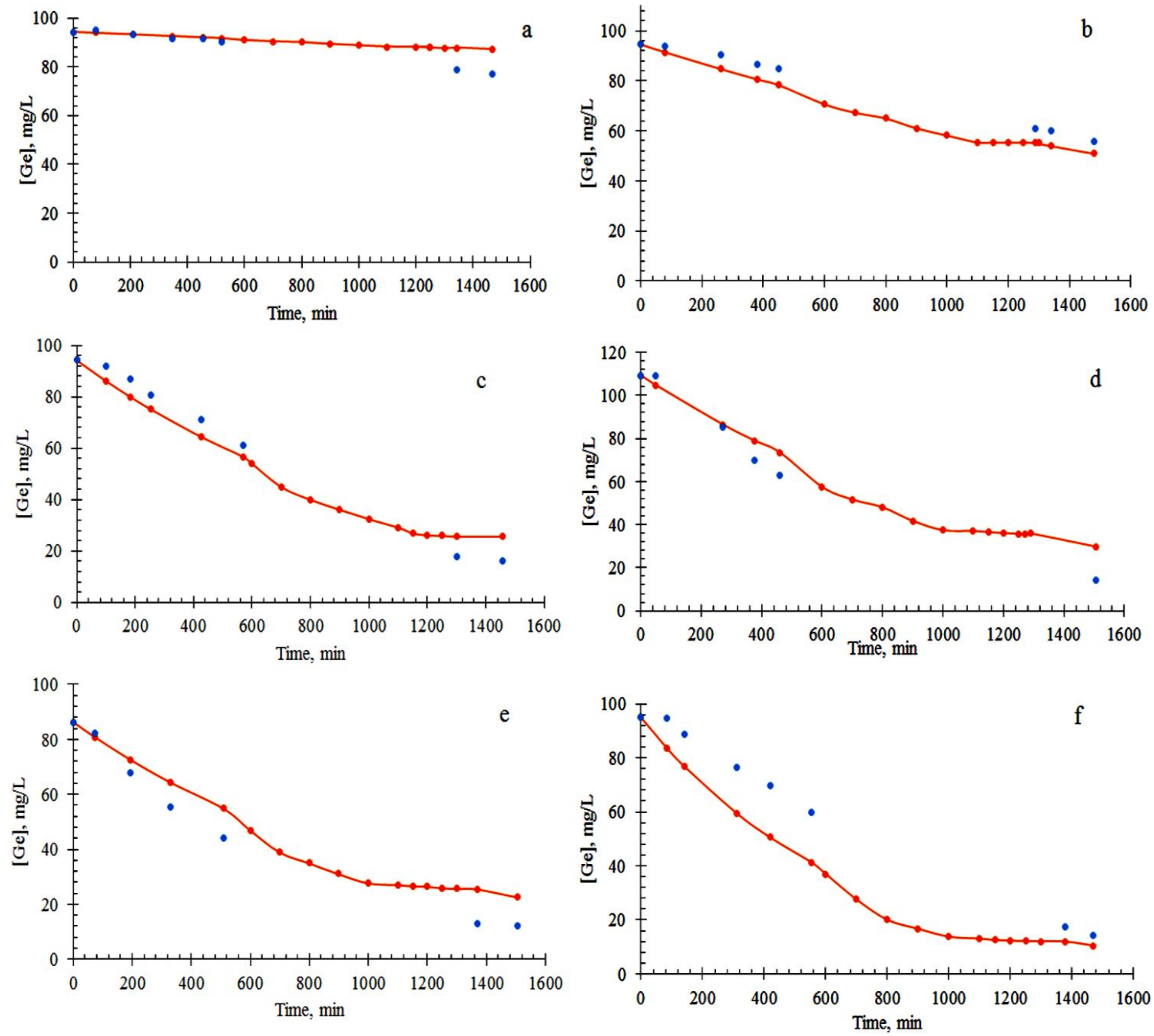

Fig. 3. Model and experimental concentrations of germanium in the feed phase versus time for Cyanex 923 concentrations of (a) 5 %v/v, (b) 10 %v/v, (c) 15 %v/v, (d) 20 %v/v, (e) 25 %v/v, and (f) 30 %v/v.

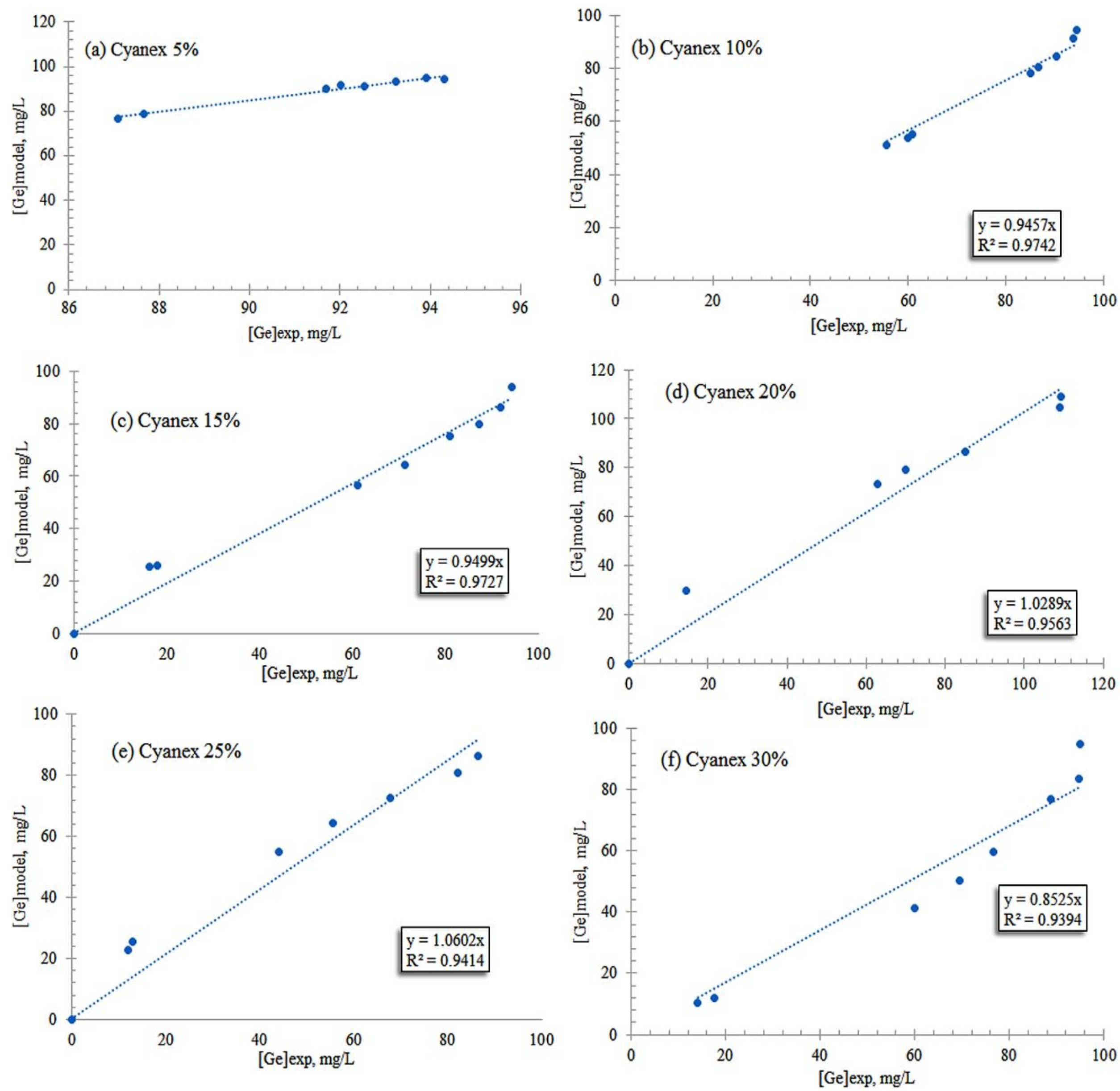

Fig. 4. Regression lines showing the correlation of experimental and model data for Cyanex 923 concentrations of (a) 5 %v/v, (b) 10 %v/v, (c) 15 %v/v, (d) 20 %v/v, (e) 25 %v/v, and (f) 30 %v/v.

5. Conclusion

A mathematical model was developed to facilitate the transport of Ge(IV) from oxalic acid solutions across FSSLM composed of the Cyanex 923 and a PTFE disc membrane. This model was based on an LLX model, by which the extraction equilibrium constant was found (K_{ex}= 2057 1/mol^4). The FSSLM model curves fitted to the results obtained from FSSLM experiments for various carrier concentrations. This model resulted in determining the overall mass transfer and diffusion coefficients for the PTFE membranes containing 5%, 10%, 15%, 20%, 25% and 30% (v/v) Cyanex 923. With respect to results, it was possible to fit the model curves to experimental extraction data for all carrier concentrations. As a result, a good agreement between the model and experimental data showed the accuracy of the model. The model can be applied for depth understanding the processes occurring during the facilitated transport of germanium. Moreover, the mentioned models can be valuable for further investigation and designation of hollow-fibre SLM and LLX processes.

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Symbols

A= membrane effective area [cm^2]

$C_{Ge,\mathrm{aq},0}$ = initial concentration of germanium in the feed phase [mol/L]

$C_{Ge, \mathrm{cal, aq, i}}(t)$= calculated (model) concentration of germanium in the feed phase at the time of t [mol/L]

$C_{Ge, \mathrm{exp,aq,,i}}(t)$= experimental concentration of germanium in the feed phase at the time of t [mol/L]

$C_{Ge,org,i}$= concentration of germanium in organic phase in LLX system [mol/L]

J_{Ge} = flux of germanium [mol/s.cm^2]

i= the condition number [-]

K_{org}= overall mass transfer coefficient [cm/s]

K_{ex} = extraction equilibrium constant [1/mol^4]

Leq= equilibrium concentration of Cyanex 923 [mol/L]

$\mathrm{No_{exp}}$ = the number of experiments [-]

$\mathrm{No_{exp,\ maximum}}$ = the final number of experiments [-]

$\mathrm{No_{time}}$= the number of samples taken at individual times [-]

$L_{0,\mathrm{i}}$= initial concentration of Cyanex 923 at the condition of i [mol/L]

[T] = matrix containing times in which samples were taken [-]

t_f = final time in which a sample was taken [min]

V=volume of phase [mL]

μ_i= Dynamic viscosity of carrier with various concentration [mm^2/s]

α= power of the carrier's viscosity [-]

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