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# Non-dispersive extraction of Ge(IV) from aqueous solutions by Cyanex 923: Transport and modeling studies

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**Abstract:** A transport process was studied from an aqueous solution containing oxalic acid and 100 mg/L Ge using a flat sheet supported liquid membrane (FSSLM) system. Cyanex 923 immobilized in a polytetrafluoroethylene membrane was employed as a carrier. The solution chemistry and related diagrams were applied to study the transport of germanium. The effectual parameters such as oxalic acid, carrier concentration, and strip reagent composition were evaluated in this study. Based on the results, the oxalic acid concentration of 0.075 mol/L and the carrier concentration of 20 %v/v were the condition in which the efficient germanium transport occurred. Among strip reagents, NaOH (0.04-0.1 mol/L) had the best efficiency to transport germanium through the SLM system. Furthermore, the permeation model was obtained to calculate the mass transfer resistances of the membrane ($\Delta_m$) and feed ($\Delta_f$) phases. According to the results, the values of 1 and 1345 s/cm were evaluated for $\Delta_m$ and $\Delta_f$, respectively.

**Keywords:** Germanium; Supported liquid membrane; Transport; Cyanex 923; Modeling

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## 1. Introduction

Germanium is a strategic metalloid mainly used in a wide range of high-technology devices Liu, *et al.* [1]. Germanium is found in lead-zinc ores [1] and coal fly ashes [2]. In the view of hydrometallurgy, the leach solutions obtained from zinc plant residues and coal fly ashes contain germanium along with the other metals. The most important elements that can be found in these solutions are heavy metals such as zinc, nickel, cobalt, etc. [3,4]. The germanium separation from these solutions is a vital objective to obtain a purified germanium product.

Gasification coal fly ashes (GCFAs) containing germanium can be leached with water to dissolve germanium as water-soluble species [5]. Several processes have been developed to recover and separate germanium from impurities such as precipitation [6], flotation [7], ion-exchange [8], distillation [2], adsorption [9], liquid-liquid extraction (LLX) [10], and supported liquid membrane (SLM) [11-13]. Among these techniques, the LLX processes have been extensively applied to separate germanium from aqueous solutions [14,15]. However, some disadvantages such as high loss of extractant, high capital cost, difficult operation, etc. make this method inappropriate for treating low concentrations of ions. The supported liquid membrane techniques have been introduced as alternative methods to overcome these disadvantages [16]. High selectivity, easy operation, low consumption of carrier, and the one-step process are some advantages of SLMs [17-20].

Liu, et al. [1] reported oxalic acid as an efficient reagent to dissolve germanium from zinc residues. Therefore, one of the important leachates containing germanium is oxalate solution. In order to separate germanium from this type of solution, a few studies have been carried out. Liquid-liquid extraction of germanium from zinc leachates containing oxalic acid solutions has been carried out using tertiary amines in the literature [21,22]. Since the species of germanium oxalates are in the neutral form ($H_2Ge(C_2O_4)_3$) [15], it was anticipated that a neutral extractant could be used to extract germanium. In this regard, Cyanex 923 (four trialkyl phosphine oxides) with solvation extraction behavior was selected. Solvent extraction experiments using Cyanex 923 showed good efficiency for the extraction of germanium from oxalate solutions [15]. On the other hand, in order to overcome the challenges mentioned for an LLX system, an SLM system containing Cyanex 923 was firstly developed to transport germanium from an oxalate solution.

Cyanex 923 has been widely used in SLM systems. The permeation of cadmium ($H_{(n-2)}CdCl_n$ ) from wastewater containing chloride anions has been investigated through SLM processes using Cyanex 923 [23]. Chromium(VI) neutral species ($H_2CrO_4$) were transported across an FSSLM system using Cyanex 923 from chloride solutions [24]. Zinc(II) species in the form of $H_nZnCl_{(2+n)}$ were permeated by a solid-SLM from chloride medium using Cyanex 923 [25]. In addition, an FSSLM system has been used to transport $HFeCl_4$ species through a PVDF membrane with the carrier of Cyanex 923 from a solution containing chloride ions [26]. Alguacil, *et al.* [27] investigated the transport of Au(III) in the form $HAuCl_4$ through a PVDF membrane film impregnated in Cyanex 923 from an HCl solution. Results showed good transport efficiency for gold species. Neutral complexes of uranium(VI) ($UO_2(H_2PO_4)_2$) were separated through an SLM system from phosphoric acid solutions using the mobile carriers containing 2-ethyl hexyl phosphoric acid mono-2-ethyl hexyl ester (PC88A) and Cyanex 923 [28].

The presented research describes a flat-sheet supported liquid membrane (FSSLM) process with a Cyanex 923 carrier, in which the facilitated transport of germanium species is carried out from a solution containing oxalic acid. Significant parameters affecting the transport of germanium such as germanium concentration in the feed phase, carrier composition, oxalic acid concentration, membrane type, and NaOH concentration in the strip phase have been investigated in detail. Finally, a mass transfer model was developed to find $\Delta_{aq}$ and $\Delta_{org}$ values which are the resistances corresponding to the species diffusion through the feed-membrane interfacial layer and membrane phase, respectively.

## 2. Experimental

### *2.1. Materials*

Cyanex 923 consisting of four trialkyl phosphine oxides (93%) was supplied by CYTEC Inc., NJ, USA. Various concentrations of Cyanex 923 (5-30 %v/v) as a carrier were prepared by dissolving it in kerosene (Sigma-Aldrich, MO, USA). In all experiments, purified water used was supplied through a water purifier (Siemens, Germany). Solutions used in this study contained 100 mg/L of germanium which were prepared by dissolving $GeO_2$ (99.99%) from Sigma-Aldrich. Desired amounts of oxalic acid powder from Panreac, Barcelona, Spain were added to the aforementioned solutions to prepare various oxalate concentrations in the range of 0.05-0.2 mol/L. Sodium hydroxide (NaOH) was used to prepare stripping phases.

Poly tetra fluoro ethylene (PTFE) and polyvinylidene difluoride (PVDF) flat sheet hydrophobic membranes with the characteristics being porosity of about 85%, 47 mm diameter, pore size of 0.45 µm, and diameter of 47 mm from Millipore, KGaA, Darmstadt, Germany were used in the present study.

### *2.2. Membrane experiments*

FSSLM experiments were carried out in a system including two cells attached together with a flanged chamber between the cells in which a membrane filter could be placed. The effective membrane area was calculated to be 11 cm$^2$. The configuration of this system was introduced elsewhere [23]. In order to prepare membranes for experiments, PTFE membranes were put in Cyanex 923 solutions for 30 min. The carrier molecules fill membrane pores by capillarity in this time. Afterward, each membrane was taken out from a Cyanex 923 solution and washed with water to remove additional carriers. Finally, each membrane was placed between two cells. The samples with volumes of 0.5 mL from both phases were taken to evaluate the concentration of ions during the experiments. The composition of solutions was determined using an inductively coupled plasma atomic emission spectroscopy (ICP-AES Agilent, USA). The reproducibility of experimental values was calculated in the range of ± 5% and illustrated as error bars in figures.

### *2.3. Transport equations*

Transport phenomena in SLM processes principally occur in three steps including the reaction of species with the carrier at the feed-membrane interface, diffusion across the membrane and stripping at the membrane–strip interface. According to the literature, the flux of species (*J*) can be found by disregarding the concentration of germanium in the strip phase with respect to Eq. (1) [17]:

$$J = P_f C_f \tag{1}$$

In this equation, $P_f$ and $C_f$ represent the permeability coefficient at the feed–membrane interface and the ions concentration in the feed phase, respectively. Furthermore, the flux can be written according to Fick's first law in a differential form as Eq. (2):

$$J = -\frac{V}{A}\left(\frac{dC_f}{dt}\right) \tag{2}$$

Where *V* and *A* are the volume of the feed phase and the membrane efficient area, respectively. With respect to Eqs. (1), the integration form of Eq. (2) can be written as Eq. (3):

$$\ln(C_{f,0} / C_{f,t}) = -\frac{AP_f t}{V} \tag{3}$$

Where $C_{f,0}$ and $C_{f,t}$ depict the concentration of ions in the feed phase at the initial time and time of '*t*', respectively. Hence, the permeability coefficient can be evaluated from the slope corresponding to the plot of $\ln(C_{f,0} / C_{f,t})$ against $t$. Furthermore, the transport efficiency (%T) of germanium is calculated as Eq. (4):

$$\%T = \frac{C_{f,t}}{C_{f,0}} \times 100 \tag{4}$$

## 3. Solution chemistry

Germanium dioxide can be dissolved in water. However, this dissolution is slowly carried out as an intermediate tetra-hydroxide. These species can be converted to germanic acid with the solubility product ($K_{sp}$) of $2.39\times10^{-4.5}$ as Eq. (5) [29]:

$$2H_2O + GeO_2 \Leftrightarrow Ge(OH)_4 = H_2GeO_3 + H_2O \tag{5}$$

Germanium can form various complexes with organic acids such as tartaric acid, citric acid, oxalic acid, etc. Oxalic acid is a possible complexant which forms various complexes with germanium. According to the literature and observations, the solubility of germanium increases in the presence of oxalic acid in aqueous solutions (Liu et al., 2017b). The formation of germanium anionic and neutral species has been reported. For instance, Pokrovski et al. (2000) described that germanium (0.02 mol/L) and oxalic acid (0.1 mol/L) form anionic species of $Ge(OH)_2(ox)_2^{2-}$ ("ox" depicts oxalate) at pHs below 7. Furthermore, Liu et al. (2017a) introduced $Ge(ox)_3^{2-}$ as an anionic complex of germanium and oxalic acid. The concentrations of germanium and oxalic acid in the latter study were reported to be 0.013 and 0.67 mol/L, respectively. However, others [15,29] reported the formation of neutral species of trisoxalato germinates as Eq. (6):

$$3H_2C_2O_4 + GeO_2 \Leftrightarrow H_2Ge(C_2O_4)_3 + 2H_2O \tag{6}$$

In the current study, germanium neutral soluble species in the form of trisoxalatogermanate have been considered as predominant species participated in the reactions.

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## 4. Results and discussions

### *4.1. Determination of the extraction mechanism by slope analysis*

With respect to the "solution chemistry" section and the literature review [23,30,31], the probable extraction reaction of germanium using Cyanex 923 can be written as Eq. (7):

$$2H^{+}_{(aq)} + nL_{(org)} + Ge(C_2O_4)_3^{2-}{}_{(aq)} \xleftrightarrow{Kex} H_2Ge(C_2O_4)_3.nL_{(org)} \quad (7)$$

Where $L$ and $K_{ex}$ depict the organic extractant (Cyanex 923) and the equilibrium constant, respectively. In order to find the number of extractant molecules that participated in the reaction, a series of liquid-liquid extraction experiments were conducted and the results were reported elsewhere [15]. According to Eq. (7), $K_{ex}$ can be written as Eq. (8):

$$K_{ex} = \frac{[H_2Ge(C_2O_4)_3.nL]_{(org)}}{[H^+]^2_{(aq)}[L]^n_{(org)}[Ge(C_2O_4)_3^{2-}]_{(aq)}} \quad (8)$$

Since $\frac{[H_2Ge(C_2O_4)_3.nL]_{(org)}}{[Ge(C_2O_4)_3^{2-}]_{(aq)}}$ is equal to the distribution coefficient ($D$) at an equilibrium state, Eq. (8) can be written as Eq. (9):

$$K_{ex} = \frac{D}{[H^+]^2[L]^n} \quad (9)$$

By taking the logarithm of Eq. (9), Eq. (10) was rearranged:

$$\log(D) = \log K_{ex} + 2\log[H^+] + n\log[L] \quad (10)$$

According to solvent extraction experiments [15], $n$=4 was proposed for the number of Cyanex 923 molecules reacted with transported germanium species at the condition similar to the present study.

### *4.2. Determination of appropriate oxalic acid concentrations in the feed phase*

With respect to the "solution chemistry" section, germanium was transported across FSSLM as a neutral complex (trisoxalato germanate) using Cyanex 923. The transport efficiency depends on the complexation of germanium and oxalate. Therefore, the concentration of oxalic acid is a significant parameter for transport. In this regard, a series of experiments were conducted at the oxalic acid concentration in the range of 0.05-0.2 mol/L with the carrier concentration of 20 %v/v. Figures 1a and b illustrate the obtained results. As seen in these figures, the transport efficiency and permeation coefficients decrease at lower and higher values of this range. Moreover, at the oxalic concentration of 0.075 mol/L, the maximum permeation coefficient and transport efficiency were found to be $9.97 \times 10^{-4}$ cm/s and 88%, respectively. The species of germanium at various oxalic acid concentrations have been illustrated in Figure 2. As seen in this figure, at lower oxalic acid concentrations, the dissociation of oxalic acid ($H_2ox$) is not complete and the germanium is in the form of $Ge(OH)_4$. However, by increasing the oxalic acid concentration (up to 0.1 mol/L), the concentration of $ox^{2-}$ enhances results in increasing $H_2Ge(C_2O_4)_3$ and consequently the germanium transport. On the other hand, with more enhancement of oxalic acid concentration, the concentration of germanium oxalates decreases resulting in the decrease in the germanium transport at a higher oxalic acid concentration (>0.1 mol/L).

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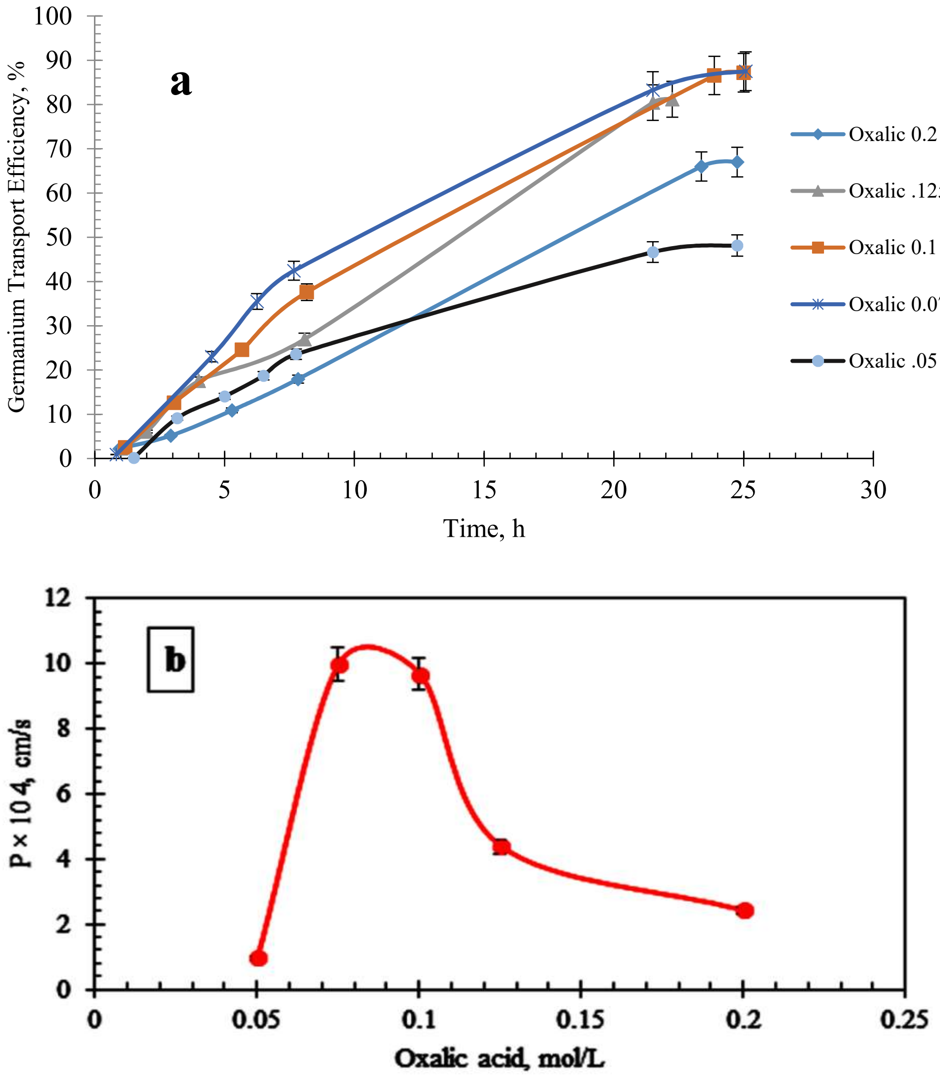


**Figure 1.** The effect of oxalic acid concentration on (a) transport and (b) permeability coefficient of germanium in the FSSLM system ([Cyanex 923] = 20 %v/v, temperature of 22°C, and [NaOH]= 0.1 mol/L).

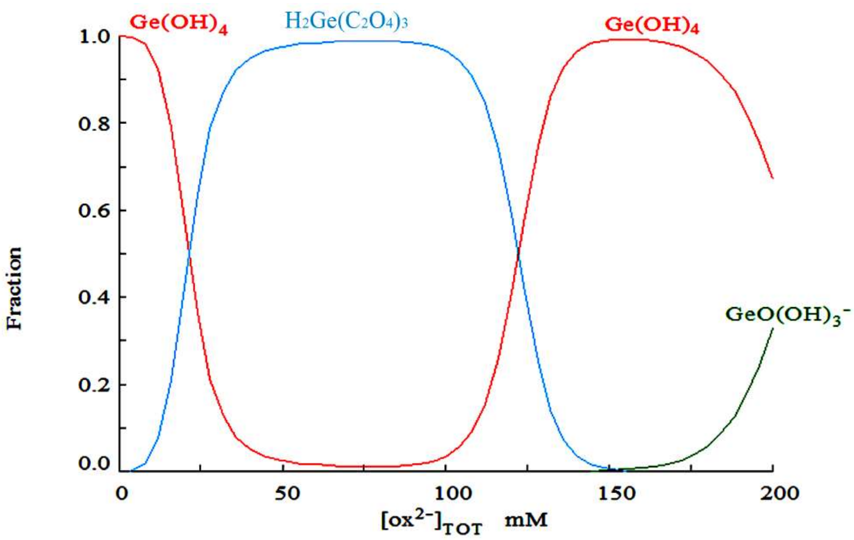


**Figure 2.** Species of germanium in various oxalic acid concentrations and 100 mg/L Ge (calculated by Medusa software).

### *4.3. Evaluation of appropriate carrier concentration*

The presence of mobile carriers in a membrane phase is necessary for the transport phenomena; however, an excess amount enhances the viscosity and decreases transport [32]. Therefore, in order to obtain efficient transport, determining an optimum concentration of the carrier is important. In the present study, the range of 0-30 %v/v for the Cyanex 923 concentration was selected with respect to the liquid-liquid extraction experiments. All FSSLM experiments were conducted at the oxalic acid concentration of 0.075 mol/L, the temperature of 22°C, and the NaOH concentration of 0.1 mol/L. The result has been plotted in Figures 3a and b. As seen in this figure, the complete reaction between species and the carrier does not occur at lower concentrations of the carrier. The germanium transport efficiency rises to about 88% when the carrier concentration increases from 10 %v/v to 20 %v/v. Moreover, with increasing the carrier concentration, the curves corresponding to Cyanex 923 of 30 and 25 %v/v are shifted down, showing the decrease in germanium transport. In Figure 3b, this behavior can be observed in the reduction of the permeability coefficient. The mentioned reduction may occur due to the enhancement of Cyanex 923 viscosity and its precipitation in pores of the membrane [33]. According to the aforementioned discussion, the concentration of 20 %v/v was selected as an optimum concentration.

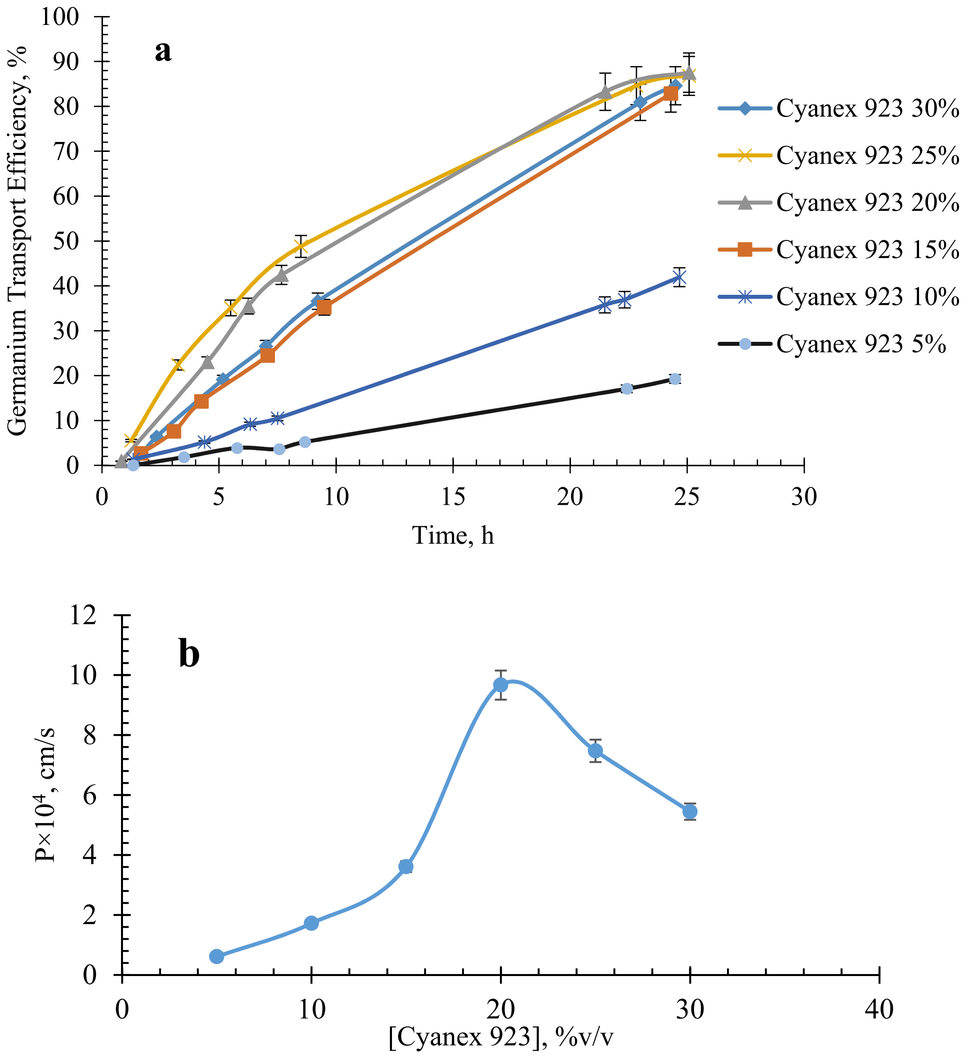


**Figure 3.** Effect of the carrier concentration on (a) transport and (b) permeability coefficient of germanium in the FSSLM system ([Oxalic acid] = 0.075 mol/L, temperature of 22°C, and [NaOH] = 0.1 mol/L).

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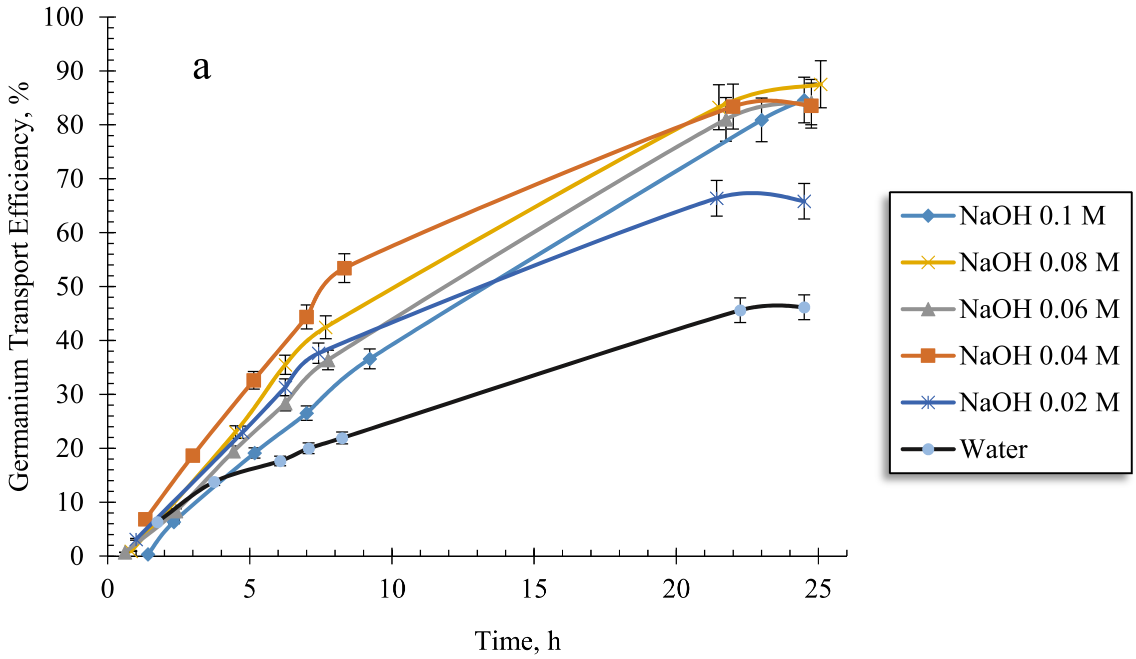
*4.4. Investigation on appropriate strip reagent*

In order to select efficient reagent/reagents for stripping germanium from the loaded organic carrier, a series of liquid-liquid extraction experiments were conducted and the results have been published elsewhere [15]. Among several reagents such as ammonium chloride ($NH_4Cl$), sodium hydroxide (NaOH), catechol ($C_6H_6O_2$), citric acid ($C_6H_8O_7$), ammonia ($NH_3$), sodium sulfate ($Na_2SO_4$), and sulfuric acid ($H_2SO_4$), NaOH was selected as an efficient reagent for stripping germanium from 20 %v/v Cyanex 923. Thus, FSSLM experiments were conducted to evaluate the effect of the NaOH concentration on the transport of germanium with the carrier concentration of 20 %v/v Cyanex 923 and an oxalic acid concentration of 0.075 mol/L in the feed phase. The results can be seen in Figures 4a and b.



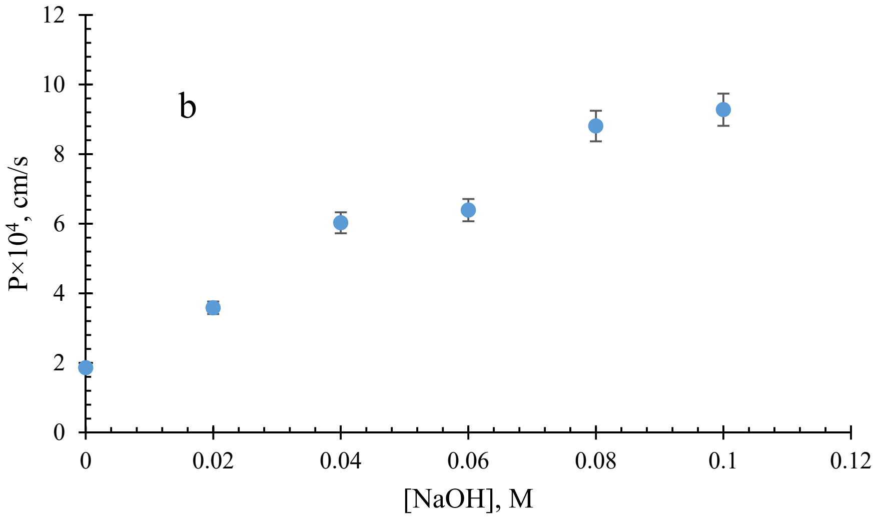




**Figure 4.** Effect of NaOH concentration on (a) transport and (b) permeability coefficient of germanium in the FSSLM system ([Oxalic acid] = 0.075 mol/L, the temperature of 22°C, and [Cyanex 923] = 20 %v/v).

As seen in these figures, the transport efficiency and the permeability coefficient increase with an enhancement of NaOH concentration. About 87% of germanium was transferred to the strip

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phase at concentrations in the range of 0.04-0.1 mol/L. The transport efficiency corresponding to the NaOH concentration of 0.02 mol/L is approximately 66%. Furthermore, according to Figure 4b, the permeability coefficient rises to 9.28 × $10^{-4}$ cm/s at the NaOH concentration of 0.1 mol/L. This is due to the increase in the amount of $OH^-$ anions which enhances the de-complexation rate at the interface of the strip side [30]. The probable reaction for stripping species from the loaded carrier can be written as Eq. (11) [15]:

$$H_2Ge(C_2O_4)_3 \cdot 4L_{(org)} + 2OH^- \Leftrightarrow 4L_{(org)} + Ge(C_2O_4)_3{}^{2-}{}_{(aq)} + 2H_2O_{(org)} \quad (11)$$

### *4.5. Effect of membrane type on transport*

In order to know the effect of membrane type on the transport of germanium, an experiment was conducted at the condition of 100 mg/L Ge and oxalic acid of 0.075 mol/L, and the NaOH concentration of 0.1 mol/L with a polyvinylidene difluoride (PVDF) membrane.

As seen in Figure 5, there is not a significant difference between the transport efficiencies corresponding to the PTFE and PVDF membranes obtained from the experiments conducted under a similar condition. However, the overall transport efficiency of the PTFE membrane is somewhat greater than that of PVDF. The germanium permeability coefficients of the PVDF and PTFE membranes were obtained to be 3.14 × $10^{-4}$ and 9.28 × $10^{-4}$ cm/s, respectively. Therefore, the germanium permeability through the PTFE membrane is approximately 3 times the PVDF permeability. Similar results have been reported by Adnan, *et al.* [34]. Various parameters such as higher tortuosity of PVDF membranes result in reducing their permeability [35].

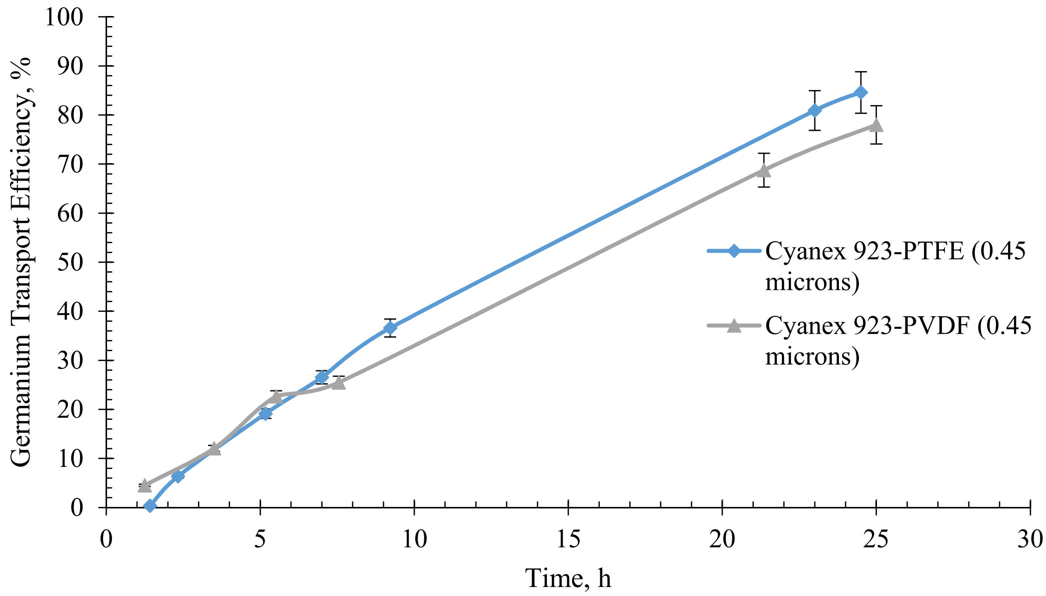


**Figure 5.** Transport efficiency of germanium versus time across PTFE and PVDF ([Oxalic acid] = 0.075 mol/L, the temperature of 22°C, [Cyanex 923] = 20 %v/v, and [NaOH] = 0.1 mol/L).

### *4.6. Permeability model*

The permeation of germanium through the FSSLM (with PTFE membrane) was modeled to find the mass transfer resistances. To model the mentioned system, it was assumed that species transported through SLM were performed by diffusing and the chemical reactions took place instantly [36]. Figure 6 illustrates how germanium oxalates permeate through a PTFE membrane containing Cyanex 923 based on the following steps:

(i) In the feed phase, germanium oxalates and protons diffuse to the interface layer.

(ii) Diffused species and Cyanex 923 molecules react together in the mentioned layer.

(iii) The produced complexes permeate across the membrane toward the membrane-strip interface layer.

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(iv) NaOH detaches germanium-Cyanex 923 complexes at the membrane-strip phase interface. Thus, germanium species are stripped from the organic carrier.

(v) The unloaded carrier molecules permeate inversely toward the feed phase.

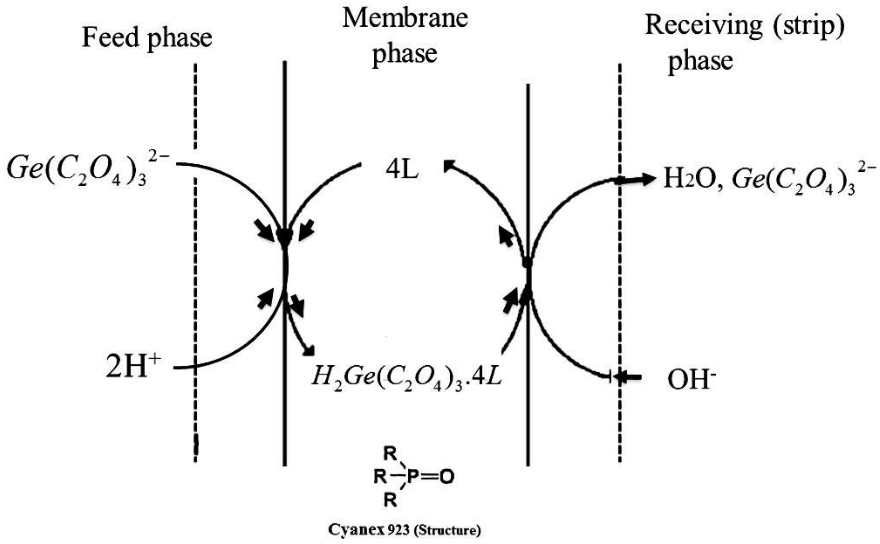


**Figure 6.** A schematic transport of germanium through FSSLM-Cyanex923.

The extraction reaction of germanium by Cyanex 923 has been described in Eq. (7) with *n*=4. According to an LLX model developed by Kamran Haghighi, *et al.* [37], the extraction equilibrium constant of the aforementioned reaction was calculated to be 2056. The germanium flux can be obtained using Fick's first diffusion law. Hence, the fluxes at the feed-membrane boundary layer and the membrane phase ($J_f$ and $J_m$, respectively) can be presented as Eqs. (12) and (13):

$$J_f = \frac{1}{\Delta_f}([Ge(IV)]_f - [Ge(IV)]_{bl,f}) \quad (12)$$

$$J_m = \frac{1}{\Delta_m}([H_2Ge(ox)_3.4R]_{bl,f} - [H_2Ge(ox)_3.4R]_{bl,s}) \quad (13)$$

Where $\Delta_m$ and $\Delta_f$ depict the resistances corresponding to the membrane phase and the feed phase boundary layer, respectively. Subscripts of *f*, *bl*, and *s* show feed, boundary layer, and strip, respectively. Moreover, $[Ge(IV)]_f$, $[H_2Ge(ox)_3.4R]_{bl,f}$, and $[H_2Ge(ox)_3.4R]_{bl,s}$ represent the germanium concentration in the feed phase, the feed-membrane, and the strip-membrane boundary layers, respectively. It is noted that since the germanium concentration in the strip-membrane boundary layer is lower than that in the feed-membrane boundary layer, $[H_2Ge(ox)_3.4R]_{bl,s}$ has been neglected. Hence, Eq. (13) can be rewritten as Eq. (14):

$$J_m = \frac{1}{\Delta_m}([H_2Ge(ox)_3.4R]_{bl,f}) \quad (14)$$

Since the chemical reactions instantly took place, the flux values in the feed-membrane layer and the membrane phase are equal ($J_f = J_m = J$). Therefore, overall $J$ can be found as Eq. (15):

$$J = \frac{K[H^+]^2[R]_{org}^{\ 4}[Ge(IV)]_f}{\Delta_m + \Delta_f(K[H^+]_{aq}^2[R]_{org}^4)} \quad (15)$$

Regarding Eq. (1), the permeability coefficient is also written as Eq. (16):

$$P = \frac{K[H^+]^2[R]_{org}^{\ 4}}{\Delta_m + \Delta_f(K[H^+]_{aq}^2[R]_{org}^4)} \quad (16)$$

By arranging Eq. (16), Eq. (17) was found to obtain the mass transfer resistances:

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$$\frac{1}{P} = \Delta_f + \frac{\Delta_m}{(K[H^+]_{aq}^2[R]_{org}^4)} \quad (17)$$

By plotting $\frac{1}{(K[H^+]_{aq}^2[R]_{org}^4)}$ versus $1/P$ and the corresponding trend line, the intercept and slope values ($\Delta_f$ and $\Delta_m$, respectively) can be found. The mentioned plot was shown in Figure 7. According to this plot, the values of 1 and 1345 s/cm were found for $\Delta_m$ and $\Delta_f$, respectively.

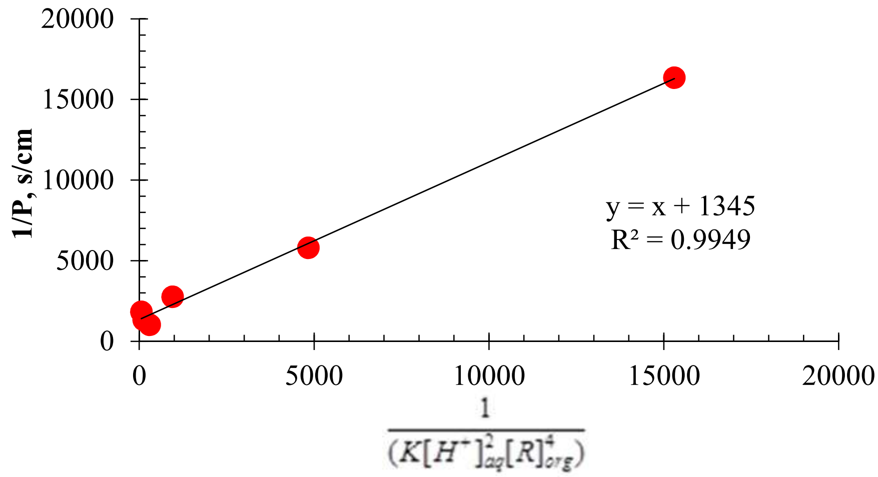


**Figure 7.** The plot of $1/P$ vs. $\frac{[H^+]^4}{(K[R]_{org}^4)}$ (100 mg/L of Ge, [Oxalic acid] = 0.075 mol/L, the temperature of 22°C, [Cyanex 923] = 20 %v/v, and [NaOH] = 0.1 mol/L).

## 5. Conclusion

This paper focused on studying the transport of germanium across an FSSLM system from aqueous solutions using Cyanex 923. The main achievement of this study was that germanium and oxalate can form neutral species which can be extracted and transported by Cyanex 923 through an FSSLM system. Results showed that the oxalic acid concentration is vital for the transport of germanium because extractable germanium oxalate species are not formed in out range of the optimum values. An optimum concentration of oxalic acid for the complete transport of germanium was found in a concentration range of 0.075-0.1 mol/L. The investigation on the effect of the Cyanex 923 concentration in the membrane phase showed that the concentration of 20 %v/v was appropriate for the complete germanium transport. Due to the inverse effect of viscosity in the higher concentrations of Cyanex 923 on germanium transport, Cyanex 923 concentrations more than 20 %v/v were not proposed as optimum conditions. Several stripping reagents were classified based on liquid-liquid extraction experiments to select appropriate reagents used in the FSSLM system. Accordingly, NaOH was chosen as an efficient stripping reagent for the FSSLM system. The NaOH concentrations of 0.04-0.1 mol/L were the range in which the maximum germanium transport achieved. Finally, a permeation model was developed to find the mass transfer resistances. As a result, the values of 1 and 1345 s/cm were found for $\Delta_m$ and $\Delta_f$, respectively.

**Author Contributions:** H.K.H made a significant contribution to every stage of this paper, such as the investigation, analysis, methodology and visualization. M.I. contributed to the conceptualization, project administration, validation and supervision of the paper. MTC contributed to the investigation for the paper. A.M.S contributed to the funding acquisition, investigation and resources provision for the paper. M.I. and H.K.H finalized the paper by a critical revision.

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