Separation of As(III) and As(V) by hollow fiber supported liquid membrane based on the mass transfer theory

Tatchanok Prapasawat, Prakorn Ramakul, Chairit Satayaprasert, Ura Pancharoen[†]
and Anchaleeporn W. Lothongkum*

Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University,
Patumwun, Bangkok, Thailand 10330
*Department of Chemical Engineering, Faculty of Engineering,
King Mongkut's Institute of Technology Ladkrabang, Ladkrabang, Bangkok, Thailand 10520

Abstract−Separation of As(III) and As(V) ions from sulphate media by hollow fiber supported liquid membrane has been examined. Cyanex 923 was diluted in toluene and used as an extractant. Water was used as a stripping solution. The extractability of As(V) was higher than As(III). When the concentration of sulphuric acid in feed solution and Cyanex 923 in liquid membrane increased, more arsenic ions were extracted into liquid membrane and recovered into the stripping solution. The mathematical model was focused on the extraction side of the liquid membrane system. The mass transfer coefficients of the aqueous phase (k_i) and organic phase (k_m) are 7.15×10^{-3} and 3.45×10^{-2} cm/s for As(III), and 1.07×10^{-2} and 1.79×10^{-2} cm/s for As(V). Therefore, the rate-controlling step for As(III) and As(V) in liquid membrane process is the mass transfer in the aqueous film between the feed solution and liquid membrane. The calculated mass transfer coefficients agree with the experimental results.

Key words: Arsenic, Separation, Liquid Membrane, Hollow Fiber, Mass Transfer

INTRODUCTION

The widespread occurrence of arsenic is hazardous due to its carcinogenic and mutagenic properties; furthermore, the toxicity is dependent on its oxidation states [1]. It is an unwanted waste generated from the processing of a variety of ores including those of copper, gold, nickel, lead and zinc [2]. In the electrorefining of copper to produce cathodes of high purity from impure anode copper, certain impurity elements such as nickel, arsenic, antimony and bismuth dissolve in the copper-bearing acidic electrolyte solution. Among these impurities, arsenic is the most commonly found because of its occurrence in the corresponding raw material. The typical electrolyte contains (g/L): Cu 30-60, As 1-7, Ni 1-20, Sb 0.1-0.7 and H_2SO_4 150-250 [3]. The predominant arsenic species are arsenite (As(III)) and arsenate (As(V)). In strongly acidic solutions, As^{3+} exists in the form of AsO^+. The undissociated form is present in the pH range from -2 to 11. pK_1 of about 10 is reported for H_3AsO_3. The acid H_3AsO_4, in which arsenic has +5 valency, is a much stronger acid with pK_a values similar to H_3PO_4 and equal to pK_1 2.2, pK_2 6.9 and pK_3 11.5 at 25 °C. In refining solutions, arsenic exists in the form of undissociated arsenic acid H_3AsO_4.

The extraction of As(III) and As(V) is of practical importance. From previous literature, it is noted that inorganic arsenicals are generally more toxic than organic arsenicals, and trivalent forms are more toxic than pentavalent forms [4]. Bogacki [5] recovered As(V) from sulphuric acid solution by solvent extraction but it highly consumed solvent and had no stripping phase.

Liquid membrane is a hydrometallurgical process for metal recovery from aqueous solutions and seems to be a promising approach due to the selectivity and the facilitated transportation of the desired metal ions [6]. The simultaneous extraction and stripping operation of the liquid membrane system is very unique. Metal ions can move from low to high concentration solutions. Many works have applied liquid membrane supported by the hollow fiber known as supported liquid membrane to recover valuable metals as well as fermentation products [7,8] pollutants [9] pharmaceutical products [10,11] rare earth metals [12-16], heavy metals [17,18] and radioactive metals [19] due to their advantage of accomplishing the extraction and stripping operation with very high enrichment factors in a single stage.

In this study, we focused on the separation of arsenite (As(III)) and arsenate (As(V)) from aqueous solution by the hollow fiber supported liquid membrane and on the modeling of this process. The extractability of As(III) and As(V) ions at various conditions was considered. A model which described the transport mechanism was presented. The effect of H_2SO_4 concentration on the permeability coefficient was studied and the values of the aqueous phase mass transfer coefficient (k_i) and the organic phase mass transfer coefficient (k_m) were calculated and the rate-controlling step was found.

THEORY

1. Liquid Membrane Mechanism for Separation of Arsenic

The liquid membrane consists of an organic extractant solution. The transport mechanism of the arsenic ions through the liquid membrane is schematically illustrated in Fig. 1 The liquid membrane is between the aqueous solution initially containing arsenic ions (feed solution) and the aqueous solution initially containing no arsenic ions (stripping solution). Transportation of ions results from the con-

[†]To whom correspondence should be addressed.
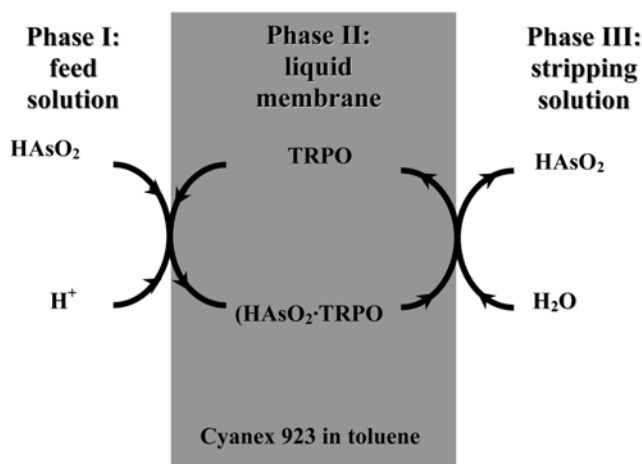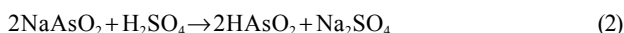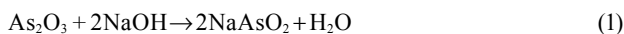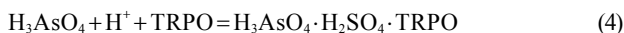E-mail: ura.p@chula.ac.th

$$HAsO_2 \cdot H \cdot TRPO + H_2O \rightarrow HAsO_2 + H^+ + TRPO \quad k_a = 5.8 \times 10^{-3} \quad (5)$$

$$H_3AsO_4 \cdot H \cdot TRPO + H_2O \rightarrow H_3AsO_4 + H^+ + TRPO \quad k_a = 5.8 \times 10^{-10} (6)$$

The transport mechanism of arsenic ions is shown in Fig. 1. The transport occurs in the hollow fiber module as shown in Fig. 2. Inside of the hollow fiber module, it consists of a liquid membrane and two sides for aqueous solutions. The liquid membrane is trapped in hydrophobic micropore and this liquid membrane separates the feed and stripping solutions. The feed solution and the stripping solution flow countercurrently.

2. The Extraction Equilibruim

At the concentration of TRPO 30% (v/v), most of the arsenic ions are extracted. The extraction equilibrium (K_{ex}) of As(III) can be expressed by Eq. (7).

$$K_{ex} = \frac{[HAsO_2 \cdot H^+ \cdot TRPO]}{[HAsO_2][H^+][TRPO]} \tag{7}$$

The distribution ratio for arsenic, D is given by

$$D = \frac{[HAsO_2 \cdot H^+ \cdot TRPO]}{[HAsO_2]} = K_{ex}[H^+][TRPO] \tag{8}$$

In the same way, the extraction equilibrium of As(V) can be written same as that of As(III). The values of K_{ex} for As(III) and As(V) extracted by TRPO were 0.2811 and 0.451 (L/mol)^2, respectively.

3. Estimation of Permeability Coefficients

Considering linear concentration gradients, fast interfacial reactions and the distribution ratio of metal ions between the feed phase and the membrane phase are much higher than that between the membrane phase and the stripping phase; the final equation for permeability coefficient could be expressed as suggested by Danesi [21].

$$V_f \ln\left(\frac{C_f}{C_{f,0}}\right) = -AP\frac{\phi}{\phi+1}t \tag{9}$$

where

$$\phi = \frac{Q_f}{PL\varepsilon\pi Nr_i} \tag{10}$$

P is the permeability coefficient. C_f and $C_{f,0}$ are arsenic ions concentration at time t and 0, respectively, A and V_f are effective area of the membrane and volume of the feed, respectively. Q_f is the volumetric flow rate of the feed solution that flows through the tube side. From the plot of $V_f \ln(C_f/C_{f,0})$ and t in Eq. (9), the permeability coefficient can be obtained from the slope ($-AP(\phi/\phi+1)$) by analytical calculation. L, N, r_i, and ε are the length of the hollow fiber, number of hollow fibers in the module, internal radius of the hollow fiber and porosity of the hollow fiber, respectively.

4. Mass Transfer Modeling

The mathematical model of the hollow fiber supported liquid membrane for the separation of arsenic by using the permeability coefficient depends on three of mass transfer resistances because the number of steps of the transport mechanism is three. The first is the resistance when the liquid flows through the hollow fiber lumen. The second resistance is the diffusion of the complex arsenic ion through the liquid membrane that is immobilized in the porous wall of the fiber. The third resistance is due to the stripping solution and organic interface outside of the fiber. The mass transfer resistance
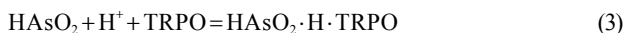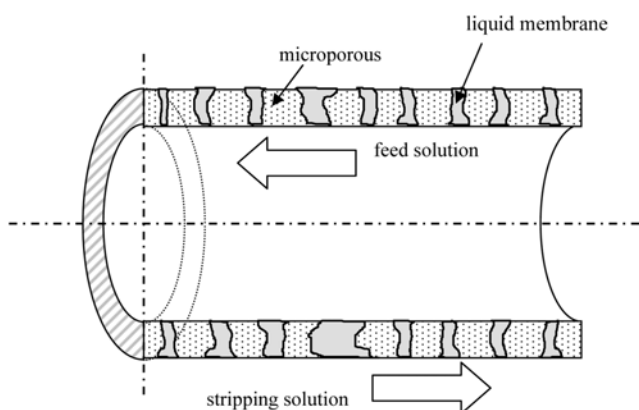

Fig. 1. Schematic representation of arsenic coupled transport with TRPO (Cyanex 923) for As(III) ions.

centration gradient between feed and stripping solutions [17,20].

The As_2O_3 in presence of high sulphuric concentration results in anion complex form as shown in Eqs. (1)-(2)

$$As_2O_3 + 2NaOH \rightarrow 2NaAsO_2 + H_2O \tag{1}$$

$$2NaAsO_2 + H_2SO_4 \rightarrow 2HAsO_2 + Na_2SO_4 \tag{2}$$

Trialky phosphine oxide (TRPO) molecules in the liquid membrane phase will form a neutral species, which are extractable into the organic phase. As(III) and As(V) ions in sulphuric acid can be extracted as Eqs. (3)-(4)

$$HAsO_2 + H^+ + TRPO = HAsO_2 \cdot H \cdot TRPO \tag{3}$$

$$H_3AsO_4 + H^+ + TRPO = H_3AsO_4 \cdot H_2SO_4 \cdot TRPO \tag{4}$$

From Eq. (3) and Eq. (4) we found that the As(III) and As(V) in sulphate solution are anion complex form as $HAsO_2$ and H_3AsO_4, respectively. From this result, As(III) and As(V) can be extracted by Cyanex 923 (TRPO) as it reacts with anions only.

In the presence of water in the stripping phase, As(III) and As(V) dissolved from the complex ions by Eq. (5) and (6), respectively.

Fig. 2. Flow pattern in hollow fiber supported liquid membrane [17].

is the reciprocal of the mass transfer coefficient as follows [22].

$$\frac{1}{P} = \frac{1}{k_i} + \frac{r_i}{r_{lm}}\frac{1}{P_m} + \frac{r_i}{r_o}\frac{1}{k_s} \quad (11)$$

Where; r_{lm} is the log-mean radius of the hollow fiber, k_i and k_s are the aqueous phase and the stripping phase mass transfer coefficients in the tube and shell sides. P_m is the membrane permeability, which is related to the distribution ratio (D) in Eq. (8) and the relation of D and P_m is in Eq. (12) [22].

$$P_m = Dk_m \quad (12)$$

By combining Eqs. (7) and (12), the following equation is obtained

$$P_m = K_{ex}k_m[H_2SO_4][TRPO] \quad (13)$$

where k_m is the membrane mass transfer coefficient.

By substituting P_m in Eq. (13) into Eq. (11) and assuming that the stripping reaction is instantaneous, the contribution of the stripping phase is neglected. Therefore, Eq. (11) is expressed as

$$\frac{1}{P} = \frac{1}{k_i} + \frac{r_i}{r_{lm}}\frac{1}{K_{ex}k_m[H_2SO_4][TRPO]} \quad (14)$$

EXPERIMENTAL

1. Chemicals

For feed solution, As_2O_3, NaOH, H_2O_2 and H_2SO_4 were used. They were A.R grade and supplied by Merck Ltd. Toluene was supplied by Fisher Scientific UK Ltd. Cyanex 923 was supplied by Cytec Canada Inc. without purification. It contains about 93% trialkyl phosphine oxide [23].

2. Apparatus

• The Liqui-Cel® Laboratory Liquid/Liquid Extraction System which is composed of two gear pumps, two variable speed controllers, two rotameters and four pressure gauges, was used.

• The Liqui-Cel® Extra-Flow module offered by CELGARD LLC (Charlotte, NC; formerly Hoechst Celanese), shown in Fig. 3, was used as a support material. This module uses Celgard® microporous polyethylene fibers that are woven into fabric and wrapped around a central tube feeder that supplies the shellside fluid. Woven fabric allows more uniform fiber spacing, which in turn leads to higher mass transfer coefficients than those obtained with individual fibers. The property of hollow fiber module is shown in Table 1. The fiber is potted into a solvent-resistant polyethylene tubesheet and shell casing in polypropylene.

• Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) was used to measure the concentrations of arsenic.
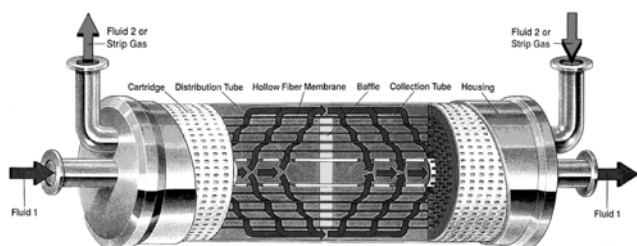

Fig. 3. The Liqui-Cel® Extra-Flow module.

Table 1. Properties of the hollow fiber module [24]

Properties	Descriptions
Materials	Polypropylene
Fiber ID	240 mm
Fiber OD	300 mm
Pore size	0.05 mm
Number of fiber	240 mm
Porosity	30%
Contact area	1.4 m²
Area per unit volume	29.3 cm²/cm³
Module diameters	6.3 cm
Module length	20.3 cm

3. Procedures

Cyanex 923 contains about 93% of the active substance and 7% water. The reagent was diluted with toluene, and its 2-40% v/v solution was used.

Synthetic As(III) solutions in sulphuric acid were used. A sample of 0.132 g As_2O_3 was mixed with about 0.4 M NaOH and 10 ml of water stirred and heated to dissolve solids. Then water and sulphuric acid were added to obtain the solutions with the required concentration of H_2SO_4 (0.2-1 M) in 5 L of the solution. The stock solutions were further diluted with sulphuric acid of high concentration to obtain less concentrated As(III) solutions.

The solutions of As(V) were obtained according to the method given by Suzuki [23].

A sample of As_2O_3 (0.132 g) was mixed with 5 ml 0.4 M NaOH and 5 ml H_2O_2. The mixture was heated for 3 h to dryness. Then the solid was dissolved in 20 ml of water and diluted with H_2SO_4 (0.2-1 M) to obtain the required As(V) concentration and rinsed with water until 5 L solution was obtained.
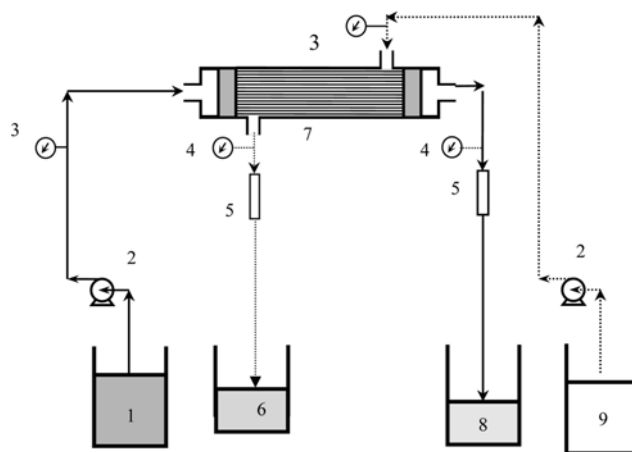

Fig. 4. Schematic countercurrent flow diagram for one-through-mode operation in hollow fiber supported liquid membrane.
1. Feed reservoir
2. Gear pump
3. Inlet pressure gauges
4. Outlet pressure gauges
5. Flow meters
6. Outlet stripping solution reservoir
7. Hollow fiber module
8. Raffinate reservoir
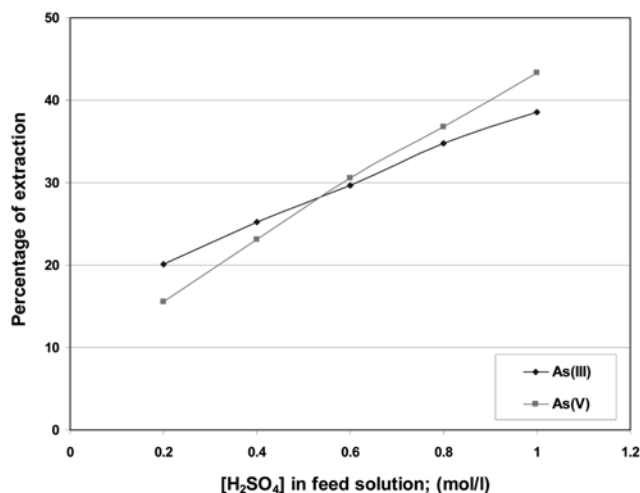9. Inlet stripping solution reservoir

Fig. 5. Effect of H_2SO_4 concentration on the extraction of arsenic.

Fig. 6. Effect of extractant concentration (Cyanex 923) on the extraction of arsenic.

Fig. 7. Plot of [$HAsO_2 \cdot H_2SO_4 \cdot TRPO$] and [$HAsO_2$][$H^+$][$HSO_4^-$][TRPO] at equilibrium for As(III).

Fig. 8. Plot of [$H_3AsO_4 \cdot H_2SO_4 \cdot TRPO$] and [$H_3AsO_4$][$H^+$][$HSO_4^-$][TRPO] at equilibrium for As(V).

The organic phase was introduced by capillary action by filling the hollow fiber lumen with organic solution and maintained for 1 h; then the organic phase was removed from the module by gravity. The excess feed and stripping solutions were fed counter- currently upward by two gear pumps (Masterflex) at the flow rates of 100 cm³/min. The feed solution was circulated through the inner side of the hollow fiber and the stripping on the outer side. The flow diagram is shown in Fig. 4.

RESULTS AND DISCUSSION

1. The Effect of H_2SO_4 Concentration on the Extraction of Arsenic

The percentage of extraction of As(III) and As(V) from 0.2-1.0 mol/L of sulphuric acid is shown in Fig. 5. The extraction of both As(III) and As(V) increases when the concentration of sulphuric acid increases. From Eqs. (3)-(4), the principle of Henryi Louis Le Chatelier, when hydronium ions concentration was increased, As(III) and As(V) ions were extracted more and convert to the product.

The extraction of As(V) is higher than As(III). This process shows that the extractability is poor when sulphuric concentration is lower than 0.4 M but abruptly increases when the H_2SO_4 concentration is higher than 0.4 M.

2. The Effect of Extractant Concentration on the Extraction of Arsenic

From Fig. 6, when the concentration of the extractant (Cyanex 923) increases, the percentage of the extraction of arsenic increases up to 30% (v/v) of Cyanex 923. The extraction of arsenic decreases from the extraction equation, Eqs. (3)-(4). When the Cyanex 923 concentration is over 30% (v/v), the percentage of extraction decreases due to an excessive increase in extractant concentration that produces the higher viscosity of the liquid membrane, which therefore generates a lower diffusion speed of the species that affects the mass transfer process [13].

3. Calculation of Equilibrium Constant and Distribution Ratio

The equilibrium constant (K_{ex}) and distribution ratio (D) of arsenic can be calculated from Eqs. (7)-(8) by using the solvent extraction process. The equilibrium constants of As(III) and As(V) are shown
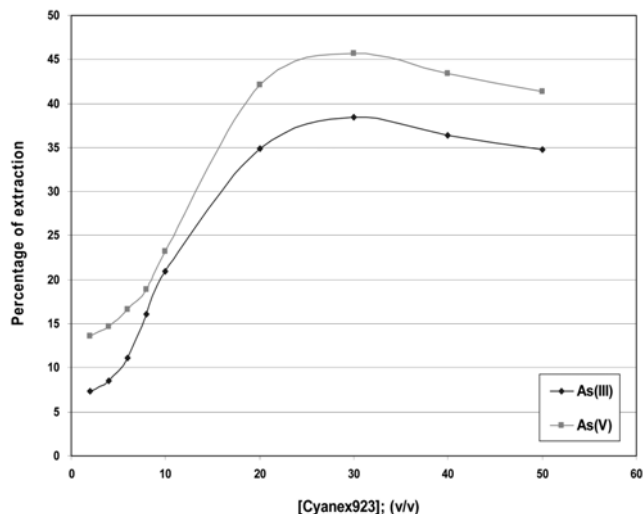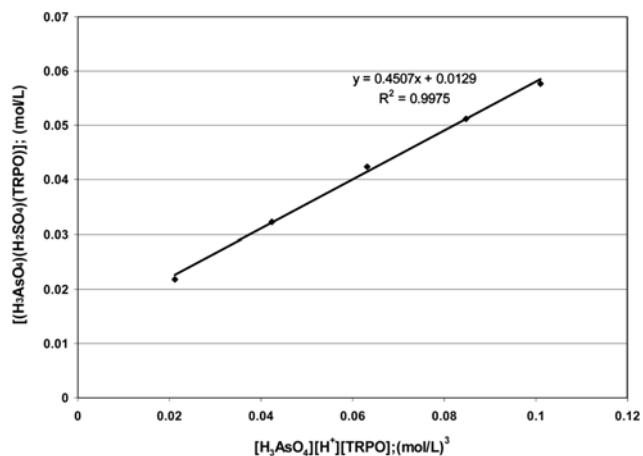
Table 2. The distribution ratios (D) and permeabilities (P) at different concentrations of sulphuric acid

| [H₂SO₄] (M)	As(III)		As(V)	
	D (-)	P×10⁵ (cm/s)	D (-)	P×10⁵ (cm/s)
0.2	0.201	2.26	0.156	2.04
0.4	0.252	3.62	0.232	3.47
0.6	0.297	4.42	0.306	4.76
0.8	0.348	5.66	0.367	6.11
1.0	0.385	7.54	0.434	7.58
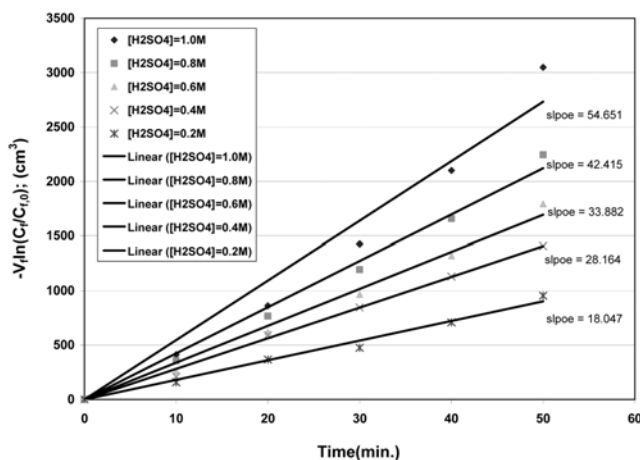
Fig. 9. Plot of $-V_f \ln(C_f/C_{f,0})$ of As(III) of the feed against time at different H₂SO₄ acid concentrations.
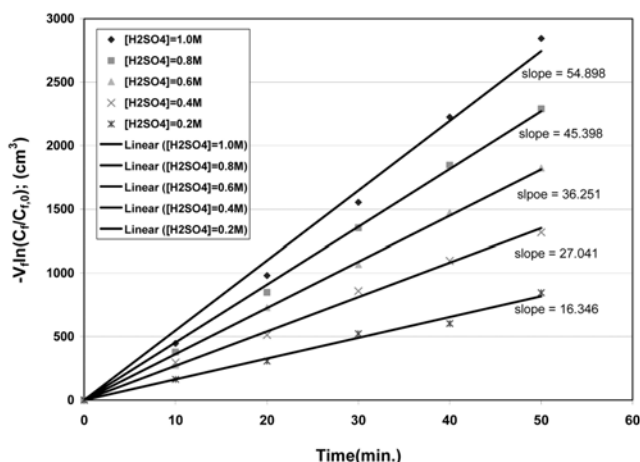
Fig. 10. Plot of $-V_f \ln(C_f/C_{f,0})$ of As(V) of the feed against time at different H₂SO₄ acid concentrations.

in Figs. 7-8, respectively. The slopes of these graphs are the equilibrium constant values which are 0.2811 (L/mol)² and 0.4507 (L/mol)² for As(III) and As(V), respectively. The distribution ratios and permeabilities are shown in Table 2.

3. Calculation of Permeability

The permeabilities can be calculated from Eqs. (9)-(10) for arsenic ions at the H₂SO₄ concentration 0.2-1.0 M, shown in Figs. 9-10 and Table 2 for As(III) and As(V), respectively.

4. Calculation of the Mass Transfer Coefficient and the Dif-
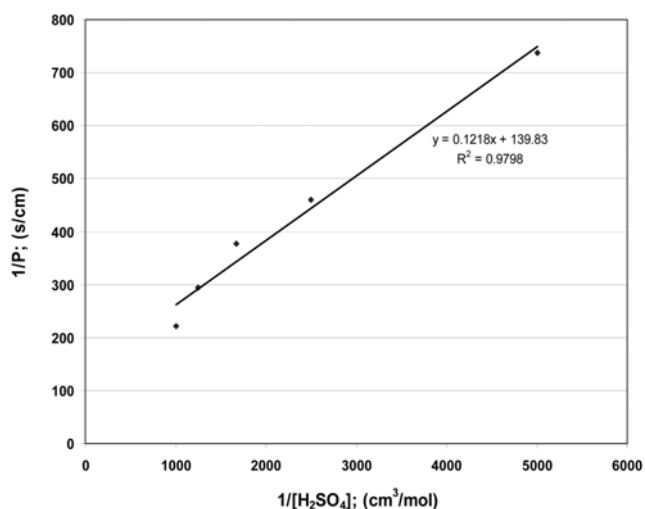
Fig. 11. Plot of 1/P as a function of 1/[H₂SO₄] for As(III).
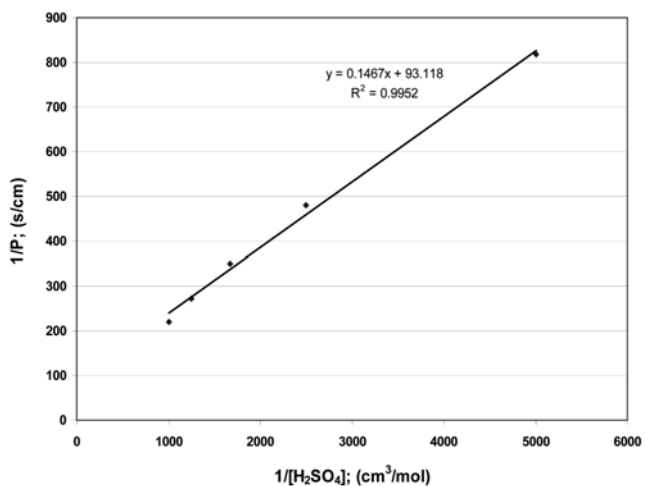
Fig. 12. Plot of 1/P as a function of 1/[H₂SO₄] for As(V).

fusion Coefficient

The aqueous phase and membrane mass transfer coefficients, k_i and k_m can be evaluated by using Eq. (14) and the plot of 1/P as a function of 1/[H₂SO₄] at different H₂SO₄ concentrations as shown in Figs. 11-12 for As(III) and As(V). A straight line with the slope of $r_i/(r_{lm}K_{ex}k_m[TRPO])$ and the ordinate of $1/k_i$ is obtained. Thus, from Figs. 11-12, the values of k_i and k_m are calculated from the slopes and ordinate, which are $7.15×10^{-3}$ and $3.45×10^{-2}$ cm/s for As(III) and $1.07×10^{-2}$ and $1.79×10^{-2}$ cm/s for As(V). The membrane mass transfer coefficients (k_m) are higher than the aqueous feed mass transfer coefficient (k_i). The aqueous feed mass transfer coefficient (k_i) of As(V) is higher than that of As(III). According to these results, the rate-controlling step is the mass transfer in the aqueous film between the feed solution and liquid membrane. Thus, the extraction of As(V) is higher than As(III).

CONCLUSIONS

The efficiency of extraction depends on the concentration of sulphuric acid in the feed solution and Cyanex 923 concentrations in

the liquid membrane, and valency of the arsenic. The extraction of arsenite and arsenate increases when the concentrations of sulphuric in feed solution and Cyanex 923 increase. The extraction efficiency of As(III) is more than that of As(V). The maximum extraction of arsenic is at 30% (v/v) of Cyanex 923 in liquid membrane. The mass transfer coefficients of the aqueous phase (k_i) and organic phase (k_m) are 7.15×10^{-3} and 3.45×10^{-2} cm/s for As(III), and 1.07×10^{-2} and 1.79×10^{-2} cm/s for As(V). Therefore, the rate-controlling step is the mass transfer in the aqueous film between the feed solution and liquid membrane.

ACKNOWLEDGMENT

NOMENCLATURE

A　　: effective area of the membrane [cm²/s]
C_f　　: concentration of feed solution at t time [M]
$C_{f,0}$　: concentration of feed solution at t= 0 [M]
k_i　　: aqueous phase mass transfer coefficient [cm/s]
k_m　　: organic phase mass transfer coefficient [cm/s]
k_s　　: stripping mass transfer coefficient [cm/s]
K_{ex}　: extraction equilibrium [-]
D　　: distribution ratio [-]
L　　: length of the fiber [cm]
N　　: number of hollow fibers in the module [-]
P_m　　: membrane permeability [cm/s]
P　　: permeability
r_{lm}　: the log-mean radius of the hollow fiber [cm]
r_i　　: internal radius of the hollow fiber [cm]
r_o　　: external radius of the hollow fiber [cm]
V_f　　: volume of the feed reservoir [cm³]
Q_f　　: volumetric flow rate of feed solution that flows through the tube side [cm³/s]
t　　: time [min]

Greek Letters
ε　　: porosity, of the hollow fiber module [-]

REFERENCES

1. W. R. Cullen and K. J. Reimer, *Chem. Rev.*, **89**, 713 (1989).
2. J. Szymanowski, *Hydroxyoximes and copper hydrometallurgy*, CRC Press, Boca Raton, 1 (1993).
3. J. Szymanowski and M. Wiœniewski, *Polish J. Appl. Chem.*, **40**, 3 (1996).
4. R. Eisler, *A review of arsenic hazards to plants and animals with emphasis on fishery and wildlife resources*, In J. O. Nriagu, Ed. Arsenic in the environment, Part II: Human health and ecosystem effects, John Wiley & Sons, Inc., New York, 185-259 (1994).
5. M. B. Bogacki, M. Wisniewski and J. Szymanowski, *Journal of Radioanalytical and Nuclear Chemistry*, **228**(1-2), 57 (1997).
6. G. Schultz, *Desalination*, **68**, 191 (1988).
7. T. Hano, M. Matsumoto, S. Venoyama, T. Ohtake, Y. Kawano and S. Miura, *Bio. Separation*, **3**, 321 (1993).
8. R. Basu and K. K. Sirkar, *AIChE J.*, **37** (1991).
9. C. M. Yun, R. Prasad and K. K. Sirkar, *In. Eng. Chem. Res.*, **31**, 1709 (1992).
10. R. Prasad and K. K. Sirkar, *J. Membr. Sci.*, **47**, 235 (1989).
11. R. Basu and K. K. Sirkar, *J. Membr. Sci.*, **75**, 131 (1992).
12. W. Patthaveekongka, N. Vijitchalermpong and U. Pancharoen, *Korean J. Chem. Eng.*, **20**, 1092 (2003).
13. U. Pancharoen, P. Ramakul and W. Patthaveekongka, *J. Ind. Eng. Chem.*, **11**(6), 926 (2005).
14. P. Ramakul, W. Pattaweekongka and U. Pancharoen, *J. Chin. Inst. Chem. Engrs.*, **36**(5), 1 (2005).
15. P. Ramakul, W. Pattaweekongka and U. Pancharoen, *Korean J. Chem. Eng.*, **23**, 85 (2006).
16. P. Ramakul, E. Songkun, W. Pattaweekongka, M. Hronec and U. Pancharoen, *Korean J. Chem. Eng.*, **23**, 117 (2006).
17. P. Ramakul and U. Pancharoen, *Korean J. Chem. Eng.*, **20**, 724 (2003).
18. P. Ramakul, K. Nakararueng and U. Pancharoen, *Korean J. Chem. Eng.*, **21**, 1212 (2004).
19. U. Pancharoen, P. Ramakul, W. Patthaveekongka and M. Hronec, *J. Ind. Eng. Chem.*, **12**(5), (2006).
20. C. Porter Mark, *Handbook of industrial technology membrane*, New Jersey, Noyes publications (1990).
21. P. R. Danesi, *J. Membr. Sci.*, **20**, 231 (1984).
22. N. S. Rathore, J. V. Sonawane, Anil Kumar, A. K. Venugopalan, R. K. Singh, D. D. Bajpai and J. P. Shukla, *J. Memb. Sci.*, **189**, 119 (2001).
23. M. Wisniewski, *Hydrometallurgy*, **46**, 235 (1997).
24. Hoechst Celanese Corporation, Operating Manual Laboratory Liquid/Liquid Extraction System (1995).
25. A. Kumar, R. Haddad, G. Benzal, R. Ninou and A. M. Sastre, *J. Membr. Sci.*, **174**(17), (2000).