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Transport of Thiourea through an Aliquat 336/Polyvinyl Chloride Membrane

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ABSTRACT

The transport of thiourea in acidic or neutral chloride solutions through a polyvinyl chloride (PVC) membrane containing immobilized Aliquat 336 was studied experimentally. No chemical interaction between thiourea and Aliquat 336 was observed. The acidity constant of thiourea at 1.0 ionic strength was 13.7 and its distribution constant for acidic solutions and neat Aliquat 336 was 4.20. A mathematical model assuming ideal mixing in the solutions on both sides of the membrane and Fickian diffusion in the membrane was developed and used for the determination of the diffusion coefficient of thiourea in membranes with 30, 40, and 50 wt% Aliquat 336 content. The corresponding values are estimated to be $5.5 \times 10^{-13} \text{ m}^2\text{s}^{-1}$, $1.2 \times 10^{-12} \text{ m}^2\text{s}^{-1}$ and $3.5 \times 10^{-12} \text{ m}^2\text{s}^{-1}$, respectively. The transport properties of PVC membranes with other plasticizers [*bis*(1-butylpentyl) adipate, dioctylphenyl phosphonate, and *n*-decanol] were compared to the Aliquat 336/PVC membrane.

Key Words. Aliquat 336; Thiourea; Diffusion coefficient; Membrane transport; PVC membrane

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INTRODUCTION

Recent papers (1, 2), describe a novel polymer liquid membrane for extracting gold(III) from hydrochloric-acid solutions. This membrane, which consisted of the quaternary ammonium chloride extractant, Aliquat 336, immobilized in a polyvinyl chloride (PVC) matrix, was cast from a tetrahydrofuran solution as a thin, homogeneous, and mechanically stable film. Membranes contained from 30 to 50 wt% Aliquat 336. Aliquat 336 acts as a plasticizer for PVC, thus membranes are rubbery and flexible. Transport studies were carried out with this membrane using a conventional two-compartment glass transport cell (Fig. 1) (1). The feed phase contained gold(III) chloride in 2.5 M hydrochloric acid, and the strip phase was 0.25 M thiourea in a mixture of hydrochloric and sulfuric acids (2.5 M).

The transport of gold(III), which proceeded well initially, ceased after about half the gold had been transported, and it was found that thiourea had transported from the strip phase to the feed phase. It was assumed that thiourea in the feed phase then complexed with gold(III) and prevented further transport. A similar phenomenon involving transport of thiourea from the strip phase to the feed phase was also observed by Kokoi et al. for supported liquid membranes (3).

In this paper the transport of thiourea through Aliquat 336/PVC membranes was studied experimentally. A mathematical model describing this process was developed and utilized to determine the diffusion coefficient of thiourea in Aliquat 336/PVC membranes with varying Aliquat 336 content. The transport properties of PVC membranes with other plasticizers (*bis*[1-butylpentyl]

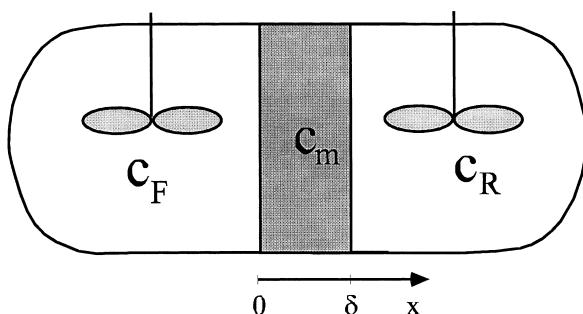


FIG. 1 Scheme of the two-compartment transport cell (F , R , and m refer to feed solution, receiver solution, and the membrane).

adipate, dioctylphenyl phosphonate, and *n*-decanol) were compared to the Aliquat 336/PVC membrane.

EXPERIMENTAL

Reagents and Apparatus

Aliquat 336 (Aldrich), a mixture of quaternary ammonium chlorides and a small amount of octanol and decanol, was used as received. High-molecular-weight powdered PVC (Fluka) was used for the preparation of the membranes. *Bis*(1-butylpentyl) adipate, dioctylphenyl phosphonate, and decanol (all Fluka) were used without further purification. Tetrahydrofuran (Mallinkrodt) was passed through an activated alumina column to remove the stabilizer and peroxides. Thiourea (Sigma) was used as received. All other chemicals were of analytical reagent grade.

The spectrophotometric measurements were performed using a Shimadzu UV-Visible Model 240 spectrophotometer (Japan) with 10-mm quartz cuvettes.

A thermostat bath and digital thermoregulator (Ratek Instruments, Victoria, Australia) were used to circulate the water through jacketed compartments of the diffusion cell to maintain the temperature of the thiourea solutions at $25 \pm 0.1^\circ\text{C}$ during the mass transport experiments.

Electrospray mass spectrometry (ES-MS) measurements were carried out in the positive-ion mode by a VG BIO-Q ES MS (Micromass, UK) using 40-V cone voltage and 3.79-kV capillary voltage. The carrier was a 1 : 1 methanol–water solution at a flow rate of $5.0 \mu\text{L min}^{-1}$.

The thicknesses of the membranes were measured using a microscope with a calibrated lens (Nikon Labophot-2, Japan).

Determination of the Acidity Constant of Thiourea (K_a)

Two mL of a 5.03×10^{-4} M thiourea solution was added to each of five 25 mL volumetric flasks, and a series of solutions was prepared by adding volumes of 1.76 M HCl (0.0, 3.0, 6.0, 9.0, and 13.2 mL) and 2.00 M KCl (12.5, 9.7, 6.8, 4.0, and 0.0 mL) and filling the remaining volume with distilled water. The purpose of the KCl was to adjust the ionic strength in each solution to 1.0. The absorbance of all solutions was measured at 236 nm. This enabled the concentration of the neutral form of thiourea to be obtained using the molar absorptivity of thiourea ($12,300 \text{ cm}^2 \text{ mol}^{-1}$). The absorbance of the protonated form of thiourea was ascertained to be negligible at this wavelength. The concentration of the protonated form of thiourea was obtained by difference.

Determination of the Distribution Constant of Thiourea (K)

Neat Aliquat 336

An aqueous solution (50 mL) containing 5.7×10^{-3} M thiourea and 1.0 M HCl was stirred with 5.0 g (5.6 mL) of neat Aliquat 336 at 30°C for 48 h. After allowing the mixed phases to separate overnight, 1.5 mL was centrifuged for 10 min to ensure complete separation of the Aliquat 336. Then, 1.0 mL of the aqueous phase was diluted to 50.0 mL with distilled water, the absorbance measured at 236 nm, and the concentration of thiourea was calculated. The concentration of thiourea in the Aliquat 336 phase was obtained by difference.

Aliquat 336/PVC Membrane

Three aqueous solutions (25 mL each) containing 3.54×10^{-5} M thiourea and 1.0 M NaCl; 4.42×10^{-5} M thiourea, 0.02 M HCl, and 1.0 M NaCl; and 4.54×10^{-5} M thiourea, and 1.00 M HCl, respectively, were stirred with pieces of 50 wt% Aliquat 336/PVC membranes (total mass of 0.78 g in each solution). The concentration of thiourea in the solutions was monitored spectrophotometrically daily for 40 d.

Interaction between Aliquat 336 and Thiourea

The UV-visible and ES-MS spectra of solutions of thiourea in neat Aliquat 336 obtained in the distribution studies were recorded.

Membrane Preparation

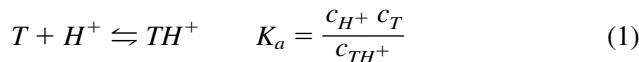
PVC membranes with a total mass of 800 mg and containing 30, 40, and 50 wt% of the plasticizer (Aliquat 336, *bis*[1-butylpentyl] adipate, dioctylphenyl phosphonate, and *n*-decanol) were prepared as described previously (1).

Transport Experiments

Transport experiments were carried out in a two-compartment glass cell with the membrane sandwiched between the compartments (Fig. 1). The area of the membrane exposed to the feed and receiver solutions was 962 mm², and the volumes of the compartments were either both 100 mL or both 210 mL. The feed solution was 0.25 M thiourea prepared by dissolving the solid in a premixed solution containing HCl and KCl and adjusted to an ionic strength of 1.0 (except for the high-acidity solution). Samples (0.2 mL) from the receiver solution were withdrawn (an equivalent volume of blank solution was added to the feed solution to maintain constant volume) at various time intervals and their absorbances measured at 236 nm. The concentration of thiourea was calculated using molar absorptivity.

MATHEMATICAL MODEL

The protolytic equilibria (Eq. 1) in both the feed and the receiver solutions (Fig. 1) are characterized by the acidity constant of protonated thiourea (K_a , Eq. 1).



where H^+ , T , and TH^+ refer to the protons, and the neutral and the protonated thiourea in the solutions, respectively.

The model does not include a chemical reaction between the membrane and thiourea. Because it can be expected that the Aliquat cation is very hydrophobic, it was assumed that ion exchange between this cation and protonated thiourea would be unlikely. Thus only neutral thiourea would be able to diffuse through the membrane. The concentration of neutral thiourea (c_T) in the feed and the receiver solutions can be defined by

$$c_{T,F} = \frac{1}{1 + c_{H^+,F}/K_a} \bar{c}_F \quad (2)$$

$$c_{T,R} = \frac{1}{1 + c_{H^+,R}/K_a} \bar{c}_R \quad (3)$$

where $\bar{c} = c_T + c_{TH^+}$ is the total concentration of thiourea.

The distribution of neutral thiourea between the solutions and the membrane (at $x = 0$ and $x = \delta$, Fig. 1) is characterized by the distribution constant (K , Eq. 4).

$$(c_m)_{x=0,\delta} = K c_T \quad (4)$$

Assuming that both solutions are ideally mixed and the mass transport through the membrane is the result of Fickian diffusion only, the mass transfer of thiourea from the feed to the receiver solution (Fig. 1) can be described by Eq. (5) with initial and boundary conditions (6)–(8)

$$\frac{\partial c_m}{\partial t} = D_m \frac{\partial^2 c_m}{\partial x^2} \quad (5)$$

where t is the time, and D_m is the diffusion coefficient of thiourea in the membrane.

$$c_m(0,x) = 0 \quad (6)$$

$$\left(\frac{\partial c_m}{\partial x} \right)_{x=0} = \frac{V}{S} \frac{1}{D_m} \frac{d \bar{c}_F}{dt} \quad (7)$$

$$\left(\frac{\partial c_m}{\partial x} \right)_{x=\delta} = -\frac{V}{S} \frac{1}{D_m} \frac{d \bar{c}_R}{dt} \quad (8)$$

where S is the exposed area of the membrane, and V is the solution volume in each compartment of the diffusion cell (Fig. 1).

Taking into account Eq. (4) and the protolytic equilibria in the feed and receiver solutions (Eqs. 2 and 3), boundary conditions (7) and (8) will be transformed into

$$\left(\frac{\partial c_m}{\partial x} \right)_{x=0} = \frac{V}{S} \frac{1}{D_m} \frac{1 + c_{H^+,F}/K_a}{K} \left(\frac{\partial c_m}{\partial t} \right)_{x=0} \quad (7)$$

$$\left(\frac{\partial c_m}{\partial x} \right)_{x=\delta} = -\frac{V}{S} \frac{1}{D_m} \frac{1 + c_{H^+,R}/K_a}{K} \left(\frac{\partial c_m}{\partial t} \right)_{x=\delta} \quad (8)$$

If the acidity constant is very high the thiourea is predominantly neutral and inequality (9) will hold. As a result, the boundary conditions (7) and (8) can be simplified accordingly.

$$c_{H^+}/K_a \ll 1 \quad (9)$$

The mathematical model consisting of Eq. (5) with initial condition (6) and boundary conditions (7) and (8) was numerically solved by the alternating-direction finite difference method (4). A computer program for the numerical solution of the model mentioned above was written in MS Quick C® and run on a PC.

The experimental extraction data can be fitted by the model outlined above to determine D_m provided the acidity constant (K_a) and the distribution constant (K) of thiourea at the ionic strength used are known. An initial estimate of D_m can be calculated by Eq. (10) valid for the initial stages of the mass-transfer process, when it can be assumed that the concentration of the feed solution (\bar{c}_F) is constant and that a linear concentration gradient within the membrane, $\partial c_m / \partial x = [c_m(t,0) - c_m(t,\delta)]/\delta$, is established very rapidly.

$$D_m = \frac{V}{S} \frac{\delta}{c_F} \frac{c_R}{t} \frac{1 + c_{H^+,F}/K_a}{K} \quad (10)$$

RESULTS AND DISCUSSION

The membrane transport of thiourea depends on the protolytic properties of thiourea, its interaction with Aliquat 336, and its diffusion coefficient in the membrane, which will be affected by the Aliquat 336 content.

Acidity Constant of Thiourea (K_a)

The acidity constant of protonated thiourea was reported by Janssen to be 15.5 (5); however, this value was obtained for solutions containing high concentrations of sulfuric acid. Thus, the acidity value was determined in this work under conditions that matched the transport studies. The acidity cons-

tant in chloride solutions was calculated to be 13.7 ± 0.4 at an ionic strength of 1.0.

Distribution Constant of Thiourea between the Solution and the Aliquat 336/PVC Membrane (K)

It was not possible to determine K by simply equilibrating the membrane with a thiourea solution because, even after 40 d, equilibrium had not been reached. Thus, the distribution constant (K) was determined for acidic solutions of thiourea and neat Aliquat 336 and found to be 4.20. This value was assumed to be valid for the membrane-solution system.

Interaction between Aliquat 336 and Thiourea

The examination of solutions of thiourea in Aliquat 336 using ES-MS and UV-Visible spectrometry failed to show any chemical interaction between the two compounds. However, the work reported in this paper demonstrates that thiourea is soluble in Aliquat 336 and this solubility plays an important role in the transport of thiourea through the PVC-based membranes. The driving force for transport is assumed to be the concentration difference of thiourea between the two compartments, and the mass transfer through the membrane the result of Fickian diffusion only.

Effect of the Solution and Membrane Composition

The transport of thiourea was studied using identical feed and receiver solutions consisting of 1.0 M NaCl, or 0.29, 1.16, or 2.55 M HCl and following the transport of thiourea from the feed to the receiver side (Fig. 2). The initial concentration of thiourea in the feed solution was 0.25 M, and a 140 μm thick membrane containing 50 wt% Aliquat 336 was used. For 1.0 M NaCl and 0.29 M HCl, thiourea is equally distributed between the feed and receiver solutions at equilibrium. For higher acid concentrations (1.16 and 2.55 M), there is a deviation from this behavior, particularly at longer times. This cannot be explained by the protonation of thiourea since K_a levels are very high, and only 8% and 16% of the total concentration of thiourea is protonated in 1.16 M and 2.55 M HCl, respectively. This deviation is most likely the result of partial oxidation of the thiourea by dissolved oxygen. This process is accelerated by the presence of acid (6). The first oxidation product is thought to be thioperoxydicarbonimidic diamide (TDD) (7), which decomposes further only very slowly. TDD is a base that can easily attract two protons because the acidity constants of the corresponding conjugated acids are very low, i.e., 3.2×10^{-6} and 2.2×10^{-8} , respectively (7). Similarly to protonated thiourea, TDD cannot penetrate the membrane. Note that TDD has similar spectrophotometric properties to thiourea, with an absorption maximum at 241 nm and a molar

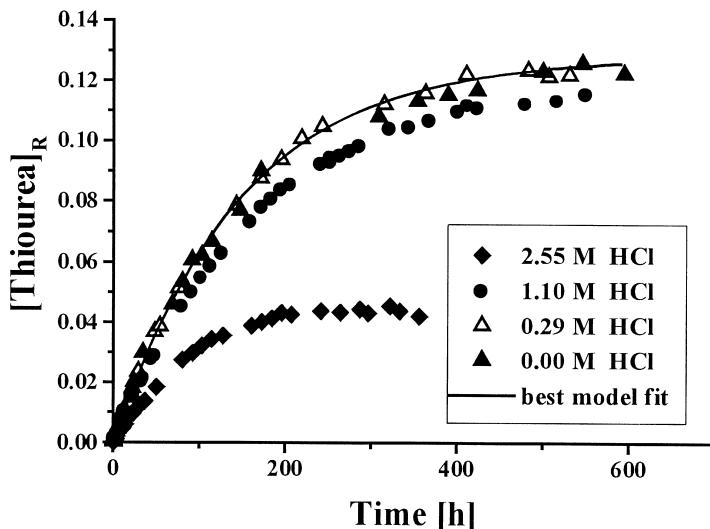


FIG. 2 Effect of acid concentration on the transport of thiourea through a 50 wt% Aliquat 336/PVC membrane.

absorptivity of $16,600 \text{ cm}^2 \cdot \text{mol}^{-1}$, and thus is difficult to differentiate from thiourea.

Because the mathematical model does not take into account the oxidation of thiourea in strongly acid solutions, the diffusion coefficient (D_m) of thiourea in the membrane was determined only for transport experiments between neutral or slightly acidic solutions. Thus, D_m corresponding to the best fit of the mathematical model to the experimental data for 1.0 M NaCl and 0.29 M HCl was found to be $3.5 \times 10^{-12} \text{ m}^2 \cdot \text{s}^{-1}$.

The transport of thiourea through membranes containing 30 and 40 wt% Aliquat 336 was studied using 0.25 M thiourea in 0.29 M HCl in the feed compartment of the transport cell, with 0.29 M HCl in the receiver compartment. By fitting the model to these data the value of D_m for the 30 and 40 wt% membranes was found to be $5.5 \times 10^{-13} \text{ m}^2 \cdot \text{s}^{-1}$ and $1.2 \times 10^{-12} \text{ m}^2 \cdot \text{s}^{-1}$, respectively. These results, including those for the 50 wt% membrane mentioned above, are shown in Fig. 3, where the solid lines represent the best model fit to the experimental data. The rate of transport of thiourea increases almost exponentially with increasing Aliquat 336 concentration (Fig. 4). This dependence can be described successfully by the following empirical equation

$$D_m = 2.43 \times 10^{-18} C^{3.627} \quad (11)$$

where C is the concentration of Aliquat 336 in wt%.

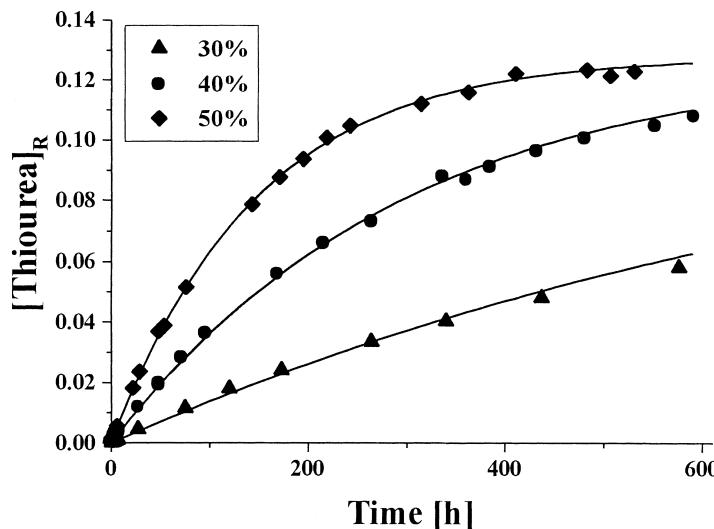


FIG. 3 Effect of Aliquat 336 content in the membrane on the transport of thiourea (feed solution: 0.25 M thiourea in 0.3 M HCl and 0.70 NaCl; receiver solution: 0.30 M HCl and 0.70 NaCl; — best model fit).

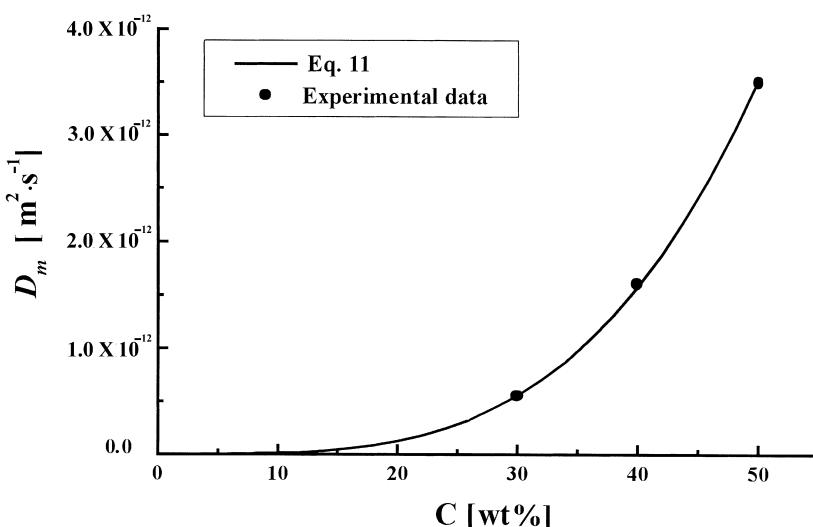


FIG. 4 D_m obtained by fitting the model to the experimental data (Fig. 3) and calculated by Eq. (11).

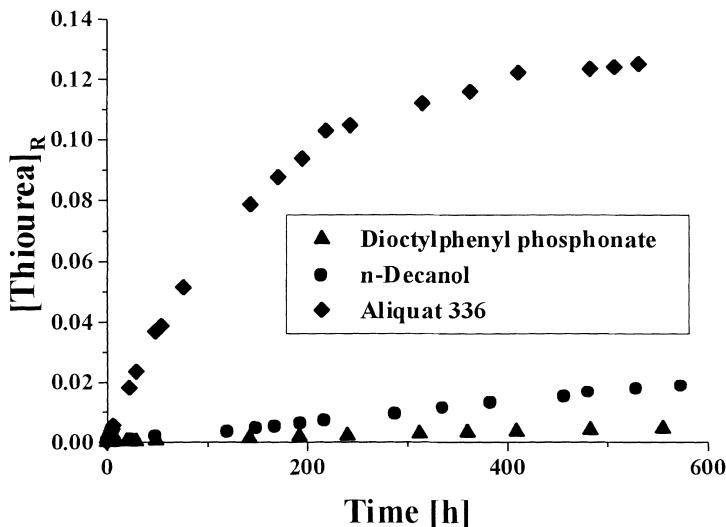


FIG. 5 Effect of the plasticizer (50 wt%) on the transport of thiourea (solutions composition as in Fig. 3).

Effect of the Plasticizer

A number of other organic compounds act as plasticizers for PVC, and some were examined in PVC membranes for their ability to transport thiourea. Thus, membranes were prepared containing 50 wt% *bis*(1-butylpentyl) adipate, diethylphenyl phosphonate, and *n*-decanol. These membranes were placed in the transport cell with 0.25 M thiourea in 1.0 M HCl in the feed compartment, and 1.0 M HCl in the receiver compartment. The results (Fig. 5) show that the rate of transport of thiourea is extremely slow compared to Aliquat 336. In fact, the rate for *bis*(1-butylpentyl) adipate is so slow that it is not included in the figure. The reason for this behavior is the very low solubility of thiourea in these other plasticizers compared to Aliquat 336.

CONCLUSIONS

This paper describes the transport of thiourea through a membrane consisting of Aliquat 336 immobilized in PVC. The diffusion of thiourea is facilitated by its solubility in Aliquat 336 and confirms the explanation provided previously (1) for the failure of an Aliquat 336/PVC membrane to transport gold(III) quantitatively from an HCl feed solution to a receiver solution con-

taining thiourea. In this system, thiourea diffuses through the membrane and complexes the remaining gold(III) in the feed solution, hence preventing its transport. Another reason for the failure to use thiourea as a stripping reagent in strong acidic solutions is its partial oxidation resulting in the formation of a cationic product that can neither penetrate the membrane nor complex with gold(III).

A mathematical model for the transport of thiourea through the Aliquat 336/PVC membrane was developed. It assumes Fickian diffusion in the membrane and takes into account the protolytic equilibria in both the feed and the receiver solutions. The model was successfully used for the determination of the diffusion coefficient of thiourea in membranes with varying Aliquat 336 content.

NOMENCLATURE

c	concentration (mol L^{-1})
\bar{c}	total concentration of thiourea (mol L^{-1})*
C	Aliquat 336 concentration in the membrane (wt%)
D_m	diffusion coefficient ($\text{m}^2 \cdot \text{s}^{-1}$)
F	refers to feed solution
H^+	refers to protons
K	distribution constant
K_a	acidity constant (mol L^{-1})
R	refers to receiver solution
S	exposed area of the membrane
t	time (s)
T	refers to thiourea
TH^+	refers to protonated thiourea
V	solution volume in each compartment of the diffusion cell (m^3)
x	axial distance (m)

Greek Symbols

δ	thickness of the membrane (m)
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*Subscripts F , R , and m refer to the feed solution, the receiver solution, and the membrane, respectively, while H^+ , T , and TH^+ refer to the protons, and the neutral and the protonated thiourea, respectively.

REFERENCES

1. G. Argiopoulos, R. W. Cattrall, I. C. Hamilton, S. D. Kolev, and R. Paimin, "The Study of a Membrane for Extracting Gold(III) from Hydrochloric Acid Solutions," *J. Membr. Sci.*, **138**, 279 (1998).
2. S. D. Kolev, G. Argiopoulos, R. W. Cattrall, I. C. Hamilton, and R. Paimin, "Mathematical Modelling of Membrane Extraction of Gold(III) from Hydrochloric Acid Solutions," *Ibid.*, **137**, 261 (1998).
3. T. Kakoi, M. Goto, K. Kondo, and F. Nakashio, "Extraction of Palladium by Liquid Surfactant Membranes Using New Surfactants," *Ibid.*, **84**, 249 (1993).
4. B. Carnahan, H. A. Luther, and J. O. Wilkes, *Applied Numerical Methods*, Wiley, New York, 1969.
5. M. J. Janssen, "Physical Properties of Organic Thiones, IV: The Basicity of the Thiocarbonyl Group in Various Thiones," *Recl. Trav. Chim. Pay-Bas*, **81**, 650 (1962).
6. M. Hoffmann, and J. O. Edwards, "Kinetics and Mechanism of the Oxidation of Thiourea and N',N'-dialkylthioureas by Hydrogen Peroxide," *Inorg. Chem.*, **16**, 3333 (1977).
7. L. G. Rio, C. G. Munkley, and G. Stedman, "Kinetic Study of the Stability of $(\text{NH}_2)_2\text{CSSC}(\text{NH}_2)_2^{2+}$," *J. Chem. Soc., Perkin Trans.*, **2**, 159 (1996).

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