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L. Boyadzhiev[a]; K. Dimitrov[a]
[a] INSTITUTE OF CHEMICAL ENGINEERING, BULGARIAN ACADEMY OF SCIENCES, SOFIA, BULGARIA

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# Kinetics of Silver Extraction with Triisobutylphosphine Sulfide

L. BOYADZHIEV and K. DIMITROV
INSTITUTE OF CHEMICAL ENGINEERING
BULGARIAN ACADEMY OF SCIENCES
1113 SOFIA, BULGARIA

## ABSTRACT

Kinetics of silver extraction from nitrate solutions with triisobutylphosphine sulfide dissolved in *n*-octane was studied. Experiments were carried out in a rotating diffusion cell. The rate constants of forward and reverse chemical reactions were evaluated: the former $k_f^* = 1.064 \times 10^{-3}$ m$^9$/(mol$^3$·s) and the latter $k_r^* = 2.085 \times 10^{-1}$ s$^{-1}$. The value obtained for the activation energy shows that the process of silver extraction with triisobutylphosphine sulfide is a predominantly diffusion-controlled process.

## INTRODUCTION

Silver can be recovered from silver-containing aqueous solutions or wastewaters by liquid–liquid extraction using various selective extractants, e.g., macrocyclic ethers [DB18C6 (1), DC18C6 (2, 3), DKP18C6 (2), Kryptofix 22 DD (4), etc.], trioctylphosphine oxide (TOPO) (1), 16,19-dioxa-13,22-dithiohexatriacontane (COST) (5), 2,2′,2″-tris(benzothiophenyl) triethylamine (6), triisobutylphosphine sulfide (TIBPS) (7–10), triisooctylthiophosphate (11), butylthiododecanoic acid (12), *o*,*o*-di-*n*-butyl α-phenylaminophenylmethanethiophosphate (13), etc.

Among these extractants, particular attention is paid to TIBPS, which is highly selective for silver (8, 14). In an acidic nitrate medium, TIBPS molecules react with the silver and nitrate ions according to

$$Ag^+ + 2TIBPS + NO_3^- \rightleftarrows Ag(TIBPS)_2NO_3 \tag{1}$$

where the silver ion is coordinately solvated by TIBPS through the sulfur-donating atom and is paired with a nitrate ion as in the cases of extraction with oxygen-containing neutral solvating extractants such as TOPO or TBP (9).

Equilibrium studies of the process and the selective extraction of silver by TIBPS from nitrate solutions containing several metal ions are described elsewhere (8–10).

The purpose of the present work was to elucidate the transfer kinetics of the process of silver extraction with TIBPS using a diffusional cell with a rotating membrane.

## MECHANISM OF MASS TRANSFER

The reaction described by Eq. (1), assumed to take place in the aqueous phase, is first order with respect to silver. It can be written

$$Ag^+ \underset{k_r}{\overset{k_f}{\rightleftharpoons}} Ag(TIBPS)_2NO_3 \qquad (2)$$

where

$$k_f = k_f^*[NO_3^-]_F[TIBPS]_F^2 \qquad (3)$$

$$k_r = k_r^* \qquad (4)$$

The scheme adopted for silver mass transfer in the diffusional cell is shown in Fig. 1. According to this scheme, the mass fluxes of silver are

$$J_1 = k_F \frac{S}{V_F}(X_F - X_{FM}) \qquad (5)$$

$$J_2 = k_f X_{FM} - k_r Y_{FM} \qquad (6)$$

$$J_3 = \frac{D_M}{\delta_M}\frac{S}{V_M}\epsilon(\overline{Y_{MF}} - \overline{Y_{MS}}) \qquad (7)$$

$$J_4 = k_S \frac{S}{V_S}(\overline{Y_{MS}} - \overline{Y_S}) \qquad (8)$$

where the overbar denotes the concentration in the organic solution.

The partition of the complex $Ag(TIBPS)_2NO_3$ between the aqueous phase $F$ and the organic phase $S$ is given by the distribution coefficient $m_C$:

$$m_C = \overline{Y_{MF}/Y_{FM}} \qquad (9)$$

Equation (5) describes the diffusion of silver ions from the bulk of the aqueous phase to the reaction zone—a thin aqueous layer adhering to

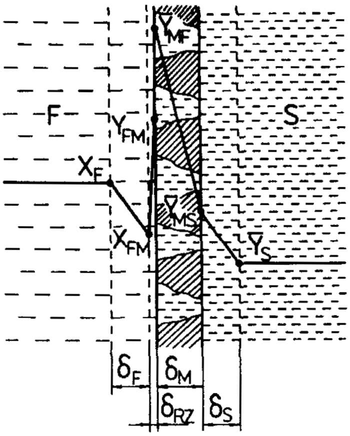

FIG. 1 Assumed silver concentration profiles across the boundary layers $\delta_F$ and $\delta_S$, reaction zone $\delta_{RZ}$, and the stagnant liquid in the membrane pores $\delta_M$.

the interface where Reaction (1) takes place. Equation (6) presents the conversion rate of the silver cation into a Ag complex according to Eq. (1). Equations (7) and (8) refer to the diffusional fluxes of the silver–organic complex in the stagnant organic liquid (filling the open membrane pores) and in the diffusional layer adjacent to the inner membrane wall, respectively. Since the volumes of both reaction zones and the volume of the organic liquid in the membrane pores can be neglected compared to the bulk of the two liquid phases *F* and *S*, the above-mentioned fluxes are practically equal:

$$J_1 = J_2 = J_3 = J_4 = J \tag{10}$$

Solving the set of Eqs. (5)–(10) yields

$$J = k_0\left(X_F - \frac{1}{m_C K}\overline{Y_S}\right) \tag{11}$$

where

$$K = \frac{k_f}{k_r} = \frac{k_f^*[NO_3^-]_F[TIBPS]_F^2}{k_r^*} = K^*[NO_3^-]_F[TIBPS]_F^2 \tag{12}$$

and

$$\frac{1}{k_0} = \frac{V_F}{S}\frac{1}{k_F} + \frac{1}{k_f} + \frac{V_M}{S}\frac{\delta_M}{m_C K D_M \epsilon} + \frac{V_S}{S}\frac{1}{m_C K k_S} \tag{13}$$

It was of interest to estimate the contribution of each term on the right-hand side of Eq. (13) to the overall process resistance, denoted on the left-hand side as $1/k_0$.

## EXPERIMENTAL

### Reagents and Methods of Analysis

Commercial triisobutylphosphine sulfide (>96%) under the trade name CYANEX 471 × (kindly supplied by Cyanamid Canada, Inc.) was used as supplied. *n*-Octane (Fluka), nitric acid (Riedel-de Haen), silver nitrate (Fluka), dimethyldichlorosilane (Fluka), and toluene (Merck) were also used.

The concentration of silver in the aqueous phase was measured by atomic absorption spectrometry using a Perkin-Elmer 3030 instrument and its concentration in the organic phase was found by solute mass balance. The concentration of hydrogen ions in the aqueous phase was measured by a pH meter OP-211/1 (Radelkis).

### Equipment

The kinetics of the extraction process was studied by means of the diffusional cell similar to the cell used by Tallarico et al. (15), shown in Fig. 2. It consists of two coaxial cylindrical vessels: the outer double-wall

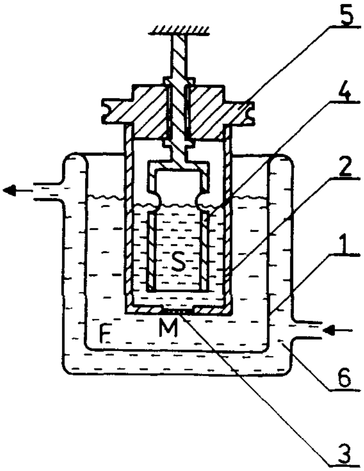

FIG. 2 Diagram of the rotating diffusional cell: (1) outer vessel, (2) rotating cylinder, (3) membrane, (4) baffle, (5) driven grooved pulley, (6) water jacket.

glass cylinder 1 contains the aqueous phase and the inner cylinder 2 of diameter 40 mm made of Plexiglas, contains the organic phase. The contact between the liquids takes place through the porous membrane 3, 10 mm in diameter, fixed in the center of the bottom of the inner vessel. A Teflon baffle 4, shaped as a hollow cylinder is placed in the inner compartment. The inner cylinder is rotated with a constant velocity by means of an electric motor 5. The outer cylinder 1 and the baffle 4 are immobile. In this way the solutions on both sides of the membrane are stirred without allowing stagnant zone formation in the vessels. Constant temperature of the solutions was maintained by means of a thermostat and a water jacket 6. Periodically small samples were taken from the aqueous phase for determining silver concentration. The concentration of silver in the organic phase was calculated from its mass balance.

The membrane used was of the type GS of Millipore of thickness $\delta_M = 0.22\ \mu m$ and porosity $\epsilon = 0.75$. In order to remove the impurities in its pores, the membrane was washed several times with distilled water. Subsequently the inner cylinder was kept in a desiccator for 12–16 h for membrane drying. Prior to use, the membrane was made hydrophobic by treating with 2–3 drops of a 2% solution of dimethyldichlorosilane in toluene. After drying the membrane was ready for use.

The following liquid phases were used in the study: 120 ml of a 0.2 mM aqueous solutions of silver nitrate acidified with nitric acid to pH = 1.2 (outer compartment) and 20 ml of a 0.06 M solution of TIBPS in *n*-octane (inner compartment).

Unless otherwise stated, the experiments were carried out at 293 K.

The equilibrium concentration of the extractant in the aqueous phase F was obtained as follows: equal volumes of distilled water and a 0.05 M solution of TIBPS in *n*-octane were set in contact by intense mixing. After reaching the equilibrium distribution and complete phase separation, the aqueous solution was mixed with an equal volume of pure *n*-octane whereby the extractant dissolved in water passed to the organic phase. After reaching the new equilibrium distribution and phase separation the organic phase was contacted with an equal volume of a $5 \times 10^{-4}$ M solution of silver nitrate. The excess of silver reacts quantitatively with the extractant present in the organic phase. The concentration of TIBPS in the organic phase (i.e., the equilibrium concentration of TIBPS in the aqueous phase) was determined by the difference in the initial concentration of silver in the aqueous solution and that after contacting with the organic phase. For the conditions of the experiment ($\overline{Y_S} = 60\ \text{mol/m}^3$) the equilibrium concentration of the extractant in the aqueous phase was $[\text{TIBPS}] = 1.48 \times 10^{-2}\ \text{mol/m}^3$, and therefore the partition coefficient is $m_E = 4.054 \times 10^3$.

Precise determination of the silver complex distribution coefficient $m_C$ was not possible due to the analysis limitation. It was only found that $m_C > 5 \times 10^5$.

## RESULTS AND DISCUSSION

The analysis of Eq. (11) revealed that for $K^* = 5.1 \times 10^{-3}$ m$^9$/mol$^3$ (10) and $[NO_3^-] = 63.3$ mol/m$^3$, the term $1/m_CK \ll 1$. Since $X_F \gg (1/m_CK)\overline{Y_S}$, for the conditions of the experiment, the expression for the flux $J$ (Eq. 11) can be simplified to

$$J = k_0X_F \tag{14}$$

The silver flux across the membrane, $J'$, is

$$J' = k_0'X_F \tag{15}$$

where

$$J' = \frac{V_F}{S}J \tag{16}$$

and

$$k_0' = \frac{V_F}{S}k_0 \tag{17}$$

where $k_0'$ (Eq. 17) is the overall mass transfer coefficient in m/s.

Taking into account that $1/m_CK \ll 1$, the last term in Eq. (13) is much less than the first one and therefore it could also be neglected. The diffusivity of the complex in the filled membrane pores, calculated by the method of Wilke (16), was $D_M = 6.32 \times 10^{-10}$ m$^2$/s. For the third right-hand term in Eq. (13), representing the mass transfer resistance in the membrane, a value of $7.365 \times 10^{-6}$ s$^{-1}$ was obtained. This value is much less than the experimental overall values obtained for $1/k_0$. It follows, then, that the third term in Eq. (13) can also be neglected.

According to Levich (17), the mass transfer resistance in the aqueous boundary layer, adjacent to the rotating membrane, can be expressed as

$$\frac{1}{k_F} = \frac{\delta_F}{D_F} = 1.61D_F^{-2/3}\nu^{1/6}\omega^{-1/2} \tag{18}$$

Therefore, taking into account Eq. (17), Eq. (13) becomes

$$\frac{1}{k_0'} = 1.61D_F^{-2/3}\nu^{1/6}\omega^{-1/2} + \frac{S}{V_F}\frac{1}{k_f} \tag{19}$$

Experiments were carried out with rotation velocities of 100, 150, 200, and 250 rpm. Figure 3 represents the amount of silver transported across the membrane versus time. The slopes of the lines are the silver fluxes $J'$ [mol/(m$^2$·s)]. A possible explanation of the line curvatures might be the unavoidable transformation of silver ion into elementary silver under the combined effect of the reductors present in the commercial extractant and the light.

Figure 4 demonstrates the dependence of $k_0'$ on the cell rotation velocity. On increasing the rotation velocity, $k_0'$ increases also, and asymptotically tends to a constant value ($k_{0,\max}'$). Rotation velocities over 250 rpm have no effect on the rate of silver transportation, which means that in these conditions both diffusional resistances of the boundary layers become negligible compared to the reduced overall transport resistance. Since the latter is much higher than the mass transfer resistance of the stagnant liquid in the membrane pores, as mentioned above, one may conclude that the transport process depends on the rate of the chemical Reaction (1) only.

$$\left[\frac{1}{k_0'}\right]_{\omega\to\infty} = \frac{S}{V_F}\frac{1}{k_f} \tag{20}$$

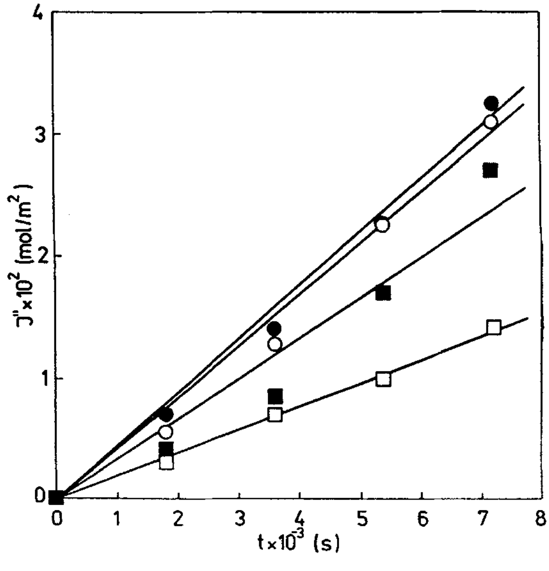

FIG. 3 Silver mass transferred across the membrane (mol/m$^2$) as a function of time: (□) ω = 100 rpm, (■) ω = 150 rpm, (○) ω = 200 rpm, (●) ω = 250 rpm

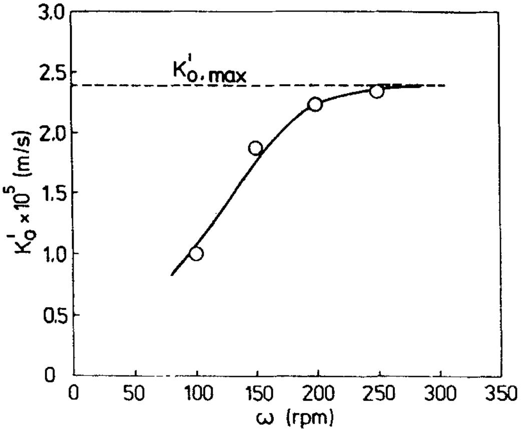

FIG. 4 Effect of rotation velocity ω on the overall mass transfer coefficient $k'_0$.

Relationship (20) permits calculation of the apparent rate constant of the forward chemical reaction $k_f$:

$$k_f = \frac{S}{V_F}\frac{J'}{X_F} \tag{21}$$

For the conditions of the experiments, its value was $k_f = 1.483 \times 10^{-5}$ $s^{-1}$. However, the real rate constant $k_f^*$, presented by Eq. (3), was $k_f^* = 1.064 \times 10^{-3}$ $m^9/(mol^3 \cdot s)$. By considering the value of the equilibrium constant $K^*$ the rate constant of the reverse reaction $k_r = k_r^* = 2.085 \times 10^{-1}$ $s^{-1}$ can be calculated.

Taking into account that the flux $J'$ is proportional to the rate constant $k_f$, the Arrhenius equation can be written as

$$J' = A \exp\left[-\frac{E}{RT}\right] \tag{22}$$

or

$$\ln J' = -\frac{E}{R}\frac{1}{T} + \ln A \tag{23}$$

where $E$ is the activation energy, $R$ is the universal gas constant, $T$ is the temperature, and $A$ is a frequency index.

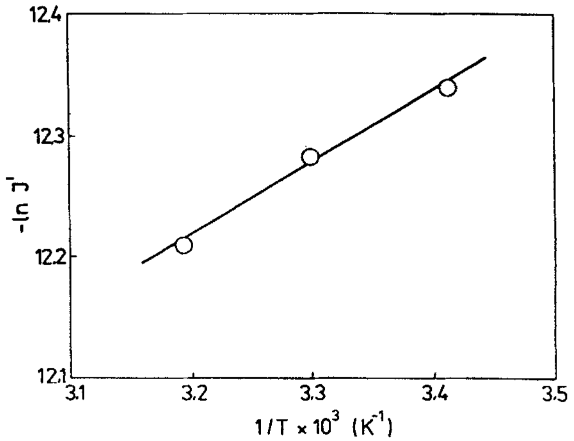

FIG. 5 Temperature effect on the mass flux $J'$.

Hence, the activation energy can be found from a plot of ln $J'$ versus $1/T$. This is illustrated in Fig. 5 for the temperatures of 293, 303, and 313 K. From the slope of the straight line, the value of the activation energy $E$ of the process was evaluated: $E = 4.948$ kJ/mol. This relatively low value for the activation energy ($E < 10$ kJ/mol) confirms the initial assumption that the process of silver extraction with triisobutylphosphine sulfide is diffusionally controlled. At very intensive stirring of both liquids only, not common in the usual liquid–liquid extraction processes, the mass transfer resistance can be eliminated (18).

## CONCLUSION

A relatively low value for the activation energy, found after the elimination of mass transfer resistances by intensive stirring of both liquid phases, shows that silver extraction with TIBPS is a predominantly diffusion-controlled process. However, the important temperature effect on the extraction rate also proves that resistance due to the reaction rate is not negligible but is larger than membrane resistance itself. By using the equilibrium and kinetic data obtained for a diffusional cell with rotating membrane, rate constants for the forward and reverse chemical reaction were evaluated. Their values are $k_f^* = 1.064 \times 10^{-3}$ m$^9$/(mol$^3$·s) and $k_r^* = 2.085 \times 10^{-1}$ s$^{-1}$, respectively.

## SYMBOLS

| | |
|---|---|
| $A$ | frequency factor [mol/(m$^2$·s)] |
| $D$ | diffusity (m$^2$/s) |
| $E$ | activation energy (kJ/mol) |
| $J$ | mass flux [mol/(m$^3$·s)] |
| $J'$ | mass flux [mol/(m$^2$·s)] |
| $J''$ | mass transferred (mol/m$^2$) |
| $K$ | pseudoequilibrium constant (—) |
| $K^*$ | equilibrium constant (m$^9$/mol$^3$) |
| $k_F$ | local mass transfer coefficient in the aqueous phase (m/s) |
| $k_M$ | local mass transfer coefficient in the membrane (m/s) |
| $k_S$ | local mass transfer coefficient in the organic phase (m/s) |
| $k_f$ | pseudoforward reaction rate constant (s$^{-1}$) |
| $k_f^*$ | forward reaction rate constant [m$^9$/(mol$^3$·s)] |
| $k_r$ | pseudoreverse reaction rate constant (s$^{-1}$) |
| $k_r^*$ | reverse reaction rate constant (s$^{-1}$) |
| $k_0$ | overall mass transfer coefficient (s$^{-1}$) |
| $k_0'$ | overall mass transfer coefficient (m/s) |
| $k'_{0,\max}$ | maximum overall mass transfer coefficient (m/s) |
| $m_E$ | distribution coefficient of extractant (—) |
| $m_C$ | distribution coefficient of silver complex (—) |
| $R$ | universal gas constant [kJ/(mol·K)] |
| $S$ | membrane area (m$^2$) |
| $T$ | temperature (K) |
| $V$ | volume (m$^3$) |
| $X$ | silver ion concentration (mol/m$^3$) |
| $Y$ | silver complex concentration (mol/m$^3$) |

### Greek

| | |
|---|---|
| $\delta$ | diffusional layer thickness (m) |
| $\epsilon$ | porosity (—) |
| $\nu$ | kinematic viscosity (m$^2$/s) |
| $\omega$ | angular velocity (s$^{-1}$) |

### Subscript

| | |
|---|---|
| F | in the bulk of the aqueous phase |
| FM | at the water/oil interface, water solution side |
| MF | at the water/oil interface, membrane solution side |
| M | in the bulk of the membrane phase |
| MS | at the internal membrane wall |

RZ in the reaction zone
S in the bulk of the organic phase

### Superscript

— in the organic phase

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