**Separation Science and Technology**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

# A Kinetic Model for Pb$^{2}$ Flotation with Sodium Dodecylsulfate in a Batch Column

A. Uribe-Salas[a]; R. Pérez-Garibay[a]; F. Nava-Alonso[a]; M. Castro-Román[a]
[a] CINVESTAV-IPN Unidad Saltillo, Ramos Arizpe, Coah, México

**To cite this Article** Uribe-Salas, A. , Pérez-Garibay, R. , Nava-Alonso, F. and Castro-Román, M.(2005) 'A Kinetic Model for Pb$^{2}$ Flotation with Sodium Dodecylsulfate in a Batch Column', Separation Science and Technology, 40: 15, 3225 — 3237
**To link to this Article: DOI:** 10.1080/01496390500385426
**URL:** http://dx.doi.org/10.1080/01496390500385426

*Separation Science and Technology*, 40: 3225–3237, 2005
Copyright © Taylor & Francis LLC
ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390500385426

# A Kinetic Model for $Pb^{2+}$ Flotation with Sodium Dodecylsulfate in a Batch Column

**A. Uribe-Salas, R. Pérez-Garibay, F. Nava-Alonso, and M. Castro-Román**
CINVESTAV-IPN Unidad Saltillo, Ramos Arizpe, Coah, México

**Abstract:** The flotation kinetics of $Pb^{2+}$ ion with sodium dodecylsulfate (SDS) was studied with the aim of validating a model developed based on the considerations presented by Nicol et al. (1). The study was conducted under experimental conditions similar to those used by Liu and Doyle (2), namely, 1 L of solution at pH = 4 containing $1 \times 10^{-4}\,M\,Pb^{2+}$ and 0.4% v/v ethanol as frother; the metal:collector molar ratio was varied from 1:1 to 1:4. The experiments were performed in a 0.057 m diameter column using an air flow rate in the range of $6.1 \times 10^{-5}$ to $12.2 \times 10^{-5}\,m^3/min$. Results show the kinetics of the flotation is first order with respect to collector concentration (SDS), with a rate constant directly depending on the bubble surface area rate ($A_b$, $m^2/min$), the slope of the adsorption isotherm of the surfactant onto the bubble-liquid interface (*a*), and cross-sectional area of the flotation cell (A), and inversely depending on the volume of the (well-mixed) lead-bearing solution.

**Keywords:** Flotation, sodium dodecylsulfate, kinetic model, batch column

## INTRODUCTION

Flotation is a physicochemical method of separation with a broad spectrum of applications in the fields of mineral processing and effluent treatment. There exist several methods to treat aqueous effluents which are characterized in

Received 16 March 2005, Accepted 2 September 2005

Address correspondence to A. Uribe-Salas, CINVESTAV-IPN Unidad Saltillo, Carr. Saltillo-Monterrey km 13, 25900, Ramos Arizpe, Coah, México. E-mail: alejandro.uribe@cinvestav.edu.mx

terms of the material to be floated: ion flotation and precipitate flotation, among others. The flotation of soluble-ionic species has received several names with the aim of distinguishing it from the process that floats the precipitate formed as a consequence of the chemical reaction that takes place between the ionic species and a chemical reagent added to the solution for that purpose. The flotation of ionic species has been called ion flotation by Sebba (3), to convey the fact that the species that adhere to the gas bubble are the ions; foam fractionation by Grieves and Keyle (4), to remark the fact that ions in the solution are divided into two fractions: the aqueous solution and the froth phase, and foam extraction by Nicol et al. (1), to describe the process where the colligend is transported to the froth as a counterion of an ionic species of opposite charge, that has surfactant properties and is therefore adsorbed onto the gas-water interface; this last process is illustrated in Fig. 1.

It is worth remarking that in all the cases, the precipitation of a compound formed by the colligend $M^{n+}$ and the collector anion $S^-$ may take place in the froth (or in the aqueous stream that overflows the cell), where a sufficiently high concentration for the precipitation to occur is reached.

In the present work, the kinetics of $Pb^{2+}$ removal by flotation using sodium dodecylsulfate as collector is experimentally studied. The results are interpreted in terms of a kinetic model developed based on considerations put forward by Nicol et al. (1). The experiments were performed in slightly acid solutions (pH 4) containing 0.04% (v/v) ethanol as frother and varying the gas flow rate in the range of $6.1 \times 10^{-5}$ to $12.2 \times 10^{-5}\ m^3/min$.

## The Kinetic Model

It is accepted that the adsorption of the collector onto the gas-liquid interface is a relatively fast process. Some researchers report that once the gas bubble is

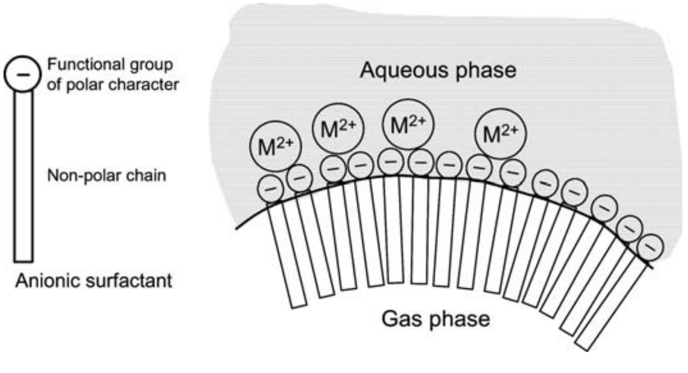

*Figure 1.* Adsorption of the anionic surfactant $SDS^-$ (e.g., dodecylsulfate) onto the gas-water interface and transport of the colligend cation $M^{2+}$ (e.g., $Pb^{2+}$), as a counterion [adapted from Liu and Doyle (2001b)].

formed and initiates its ascension through the liquid column, the equilibrium is reached within a distance of ca. 0.01 m, or in a period of time of 0.1 second. According to Nicol et al. (1), it is reasonable to assume that for the moment when the bubble has started to rise, its surface must be in equilibrium with the concentration of the collector in the bulk of the solution. This means mass transfer phenomena do not play a significant role in the flotation kinetics, and that the differences observed in the flotation kinetics of the different metal ions are due to selectivity only (i.e., chemical affinity between the collector and metal ion).

According to the above, the adsorption isotherm of a particular collector may provide a direct way of predicting the flotation kinetics. In this regard, it is known that at relatively low collector concentrations (e.g., those used in ion flotation), the adsorption isotherm may be described by the equation:

$$\Gamma = a \times [C] \tag{1}$$

where $\Gamma$ is the adsorption density of the collector on the bubble surface ($mol/m^2$); $a$ is the slope of the adsorption isotherm (m) and [C] is the collector concentration ($mol/m^3$).

Hence, the rate at which the collector adsorbed on the bubble surface reaches the overflow of the cell in a continuous flotation reactor (e.g., the concentrate stream), per unit area of cross-sectional area of the cell is given by Nicol et al. (1):

$$\frac{Q_{overflow}}{A} \times [C]_{overflow} = \frac{A_b}{A} \times \Gamma, \ \text{mol/min/m}^2 \tag{2}$$

where $Q_{overflow}$ is the volumetric overflow rate ($m^3/min$); $[C]_{overflow}$ is the concentration of the collector ($mol/m^3$) in the overflow; $A_b$ is bubble surface area rate ($m^2/min$); $A$ is the cross-sectional area of the cell ($m^2$); $\Gamma$ ($=a$ [C]) is the adsorption density of the collector on the bubble surface; $a$ is the slope of the adsorption isotherm (m) and [C] is the collector concentration in the bulk solution.

The bubble surface area rate ($A_b$) is related to the bubble surface area flux, $S_b$ (5, 6), through the following expression:

$$S_b = \frac{6J_g}{d_b} = \frac{A_b}{A} = \frac{A_v \times Q_g}{A} \tag{3}$$

where $J_g$ is the superficial gas rate (m/min) and $d_b$ is average bubble diameter (m); $A_v$ is the specific bubble surface area (bubble surface per unit volume of gas, $m^2/m^3$), and $Q_g$ is the volumetric air flow rate ($m^3/min$).

Assuming that the surfactant adsorption onto bubble surface is instantaneous as noted by Nicol et al. (1), and that once the surfactant reaches the froth zone it disappears (e.g., forms a precipitate with the metal, which in fact happens (e.g., Scorzelli et al. (7)), the batch flotation of the surfactant in a well-mixed cell is given by the following expression:

$$-\frac{dM}{dt} = A_b \times \Gamma, \ \text{mol/min} \tag{4}$$

where $-dM/dt$ is the rate of disappearance of the surfactant from the aqueous solution (mol/min).

Since the volume of the aqueous solution (V) remains practically constant, and the adsorption density equation ($\Gamma = a[C]$) holds for relatively small concentrations:

$$-\frac{1}{V}\frac{dM}{dt} = -\frac{d[C]}{dt} = \frac{A_b}{V} \times a[C], \ \text{mol/min/m}^3 \tag{5}$$

Integrating:

$$-\frac{[C]}{[C]_o} = \exp(-k \times t) \tag{6}$$

with

$$k = \frac{aA_b}{V} \tag{7}$$

In order to solve Eq. (6), it is necessary to know the volume of solution (V), the bubble surface rate ($A_b$) and the slope of the collector adsorption-isotherm ($a$). In this work a value of $a = 2.86 \times 10^{-5}$ m was obtained from the surface tension data reported by Liu and Doyle (2) for SDS-$Pb^{2+}$ aqueous solutions, following the analysis described in the literature [see Kelly and Spottiswood (8), and summarized in Appendix 1.

The strategy used to evaluate the validity of the model was to fit experimental results to Eq. (6) in order to obtain the rate constant (termed $k_{experimental}$), and to compare the values with those obtained with Eq. (7) and knowledge of $a$, $A_b$, and V (termed $k_{model}$).

## EXPERIMENTAL

### Apparatus

A 5.7 cm diameter and 1 m height transparent-flotation column was used (Fig. 2). Bubbles were generated by bubbling air through a 2 cm diameter and 2.5 cm height rigid sparger, which had a pore diameter of 3 μm.

The air velocity fed to the column was regulated by means of a calibrated flow meter equipped with a pressure manometer. In the experiments 1 liter (e.g., $V = 1 \times 10^{-3}$ m$^3$) of the aqueous solution containing the lead ion was used. The aqueous solution was conditioned in a conditioning tank and was fed to the column using a peristaltic pump [Masterflex Mod. 7518-10].

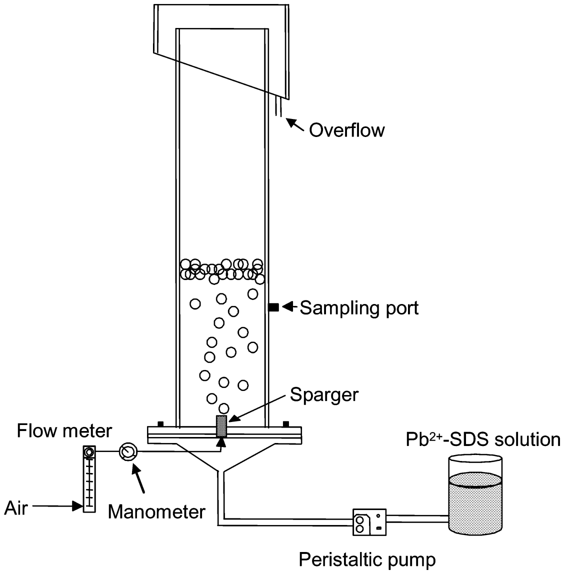

*Figure 2.* Schematic diagram of the experimental apparatus used in this work. In batch operation there is no overflow.

During the tests, samples of the aqueous solution in the column were taken from a sampling port located at ca. 0.3 m from the sparger.

In order to measure the surface area rate ($A_b$), photographs of the bubbling zone of the column were taken using a water box to avoid optical distortion due to light refraction (9), using a Nikon D100 digital camera equipped with a 105 mm macro lens. The bubble size distribution was obtained making use of an image analyzer; this was expressed both as bubble surface rate and bubble size-density function.

## Methodology

The experiments were performed at room temperature (around 25°C) using 1 liter of an aqueous solution containing $1 \times 10^{-4}$ M $Pb^{2+}$ and varying concentrations of sodium dodecylsulfate (SDS) in order to have metal:collector molar ratios from 1:1 to 1:4. The ionic strength of the solution was kept constant by adding $3 \times 10^{-4}$ M NaCl, while the pH of the solution was fixed at 4 by adding $HNO_3$ solution; at this pH the predominant species is the $Pb^{2+}$ ion, from the point of view of thermodynamics (Fig. 3). In all the experiments 0.4% v/v of ethanol was used as frother, with the objective of minimizing the effect on bubble size of the varying concentration of SDS as the flotation of the SDS-Pb couple proceeds. The kinetics of the ion flotation was varied by varying the air flow rate ($Q_g$) from $6.1 \times 10^{-5}$ to $12.2 \times 10^{-5}$ $m^3/min$.

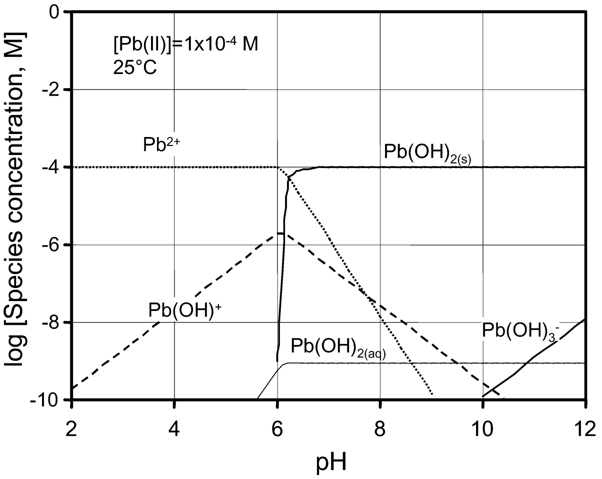

***Figure 3.*** Speciation diagram of the $Pb^{2+}$-$H_2O$ system at 25°C and $a$[Pb(II)] = $1 \times 10^{-4}$ M. Note $Pb^{2+}$ is the thermodynamically stable species at pH 4. Equilibrium data were taken from Sun and Skold [2001].

This flotation system has been very well documented by Doyle and coworkers [see Liu and Doyle, (2, 10)].

During the experiments, samples of about 3 mL of solution were carefully sucked from the interior of the column using a syringe, avoiding as much as possible the entrainment of air bubbles. The samples were prepared with 1 mL of solution and 99 mL of de-ionized water acidified to pH = 1 with $HNO_3$ in order to prevent precipitation of the hydroxides. Samples were analyzed by absorption spectrometry [Perkin Elmer Mod. 2380].

### Reagents

The analytical reagents used in this work were lead nitrate ($PbNO_3$), sodium dodecylsulfate (SDS: $CH_3(CH_2)_{11}SO_4Na$), ethanol acohol (99% v/v), sodium chloride (NaCl), nitric acid $HNO_3$, and sodium hydroxide NaOH. All reagents were supplied by Aldrich.

## RESULTS AND DISCUSSION

### Effect of Collector Concentration

Figure 4 presents the ratio $[Pb^{2+}]/[Pb^{2+}]_o$ as a function of flotation time for different initial collector (SDS) concentrations. These concentrations are reported in terms of Pb:SDS molar ratios; a molar ratio of 1:1 means equal

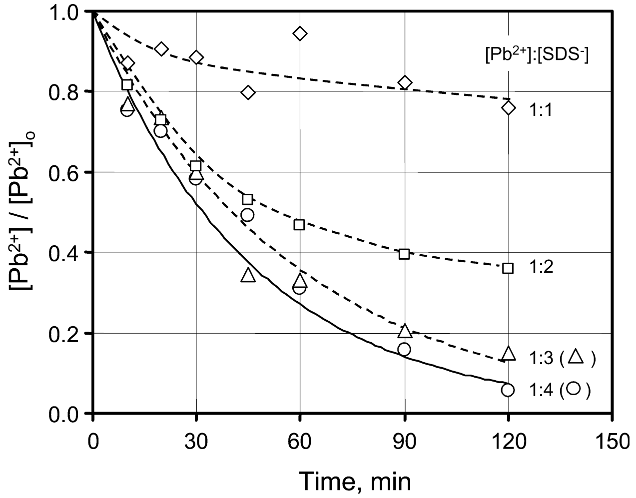

***Figure 4.*** Evolution of the $[Pb^{2+}]/[Pb^{2+}]_o$ ratio during $Pb^{2+}$ flotation ($[Pb^{2+}]_o = 1 \times 10^{-4}$ M) at different Pb:SDS molar ratios. pH = 4; $Q_g = 6.1 \times 10^{-5}\,m^3/min$ ($J_g = 0.024$ m/min); 0.4% v/v ethanol; $3 \times 10^{-3}$ M $NaNO_3$.

concentrations of lead ion and SDS were used ($1 \times 10^{-4}$ M), while a molar ratio of 1:4 means $[Pb^{2+}] = 1 \times 10^{-4}$ M and $[SDS] = 4 \times 10^{-4}$ M. The mechanism of lead flotation is linked to the natural adsorption of SDS anions onto the water-air interface, since the lead ions adsorb also as counter-ions in order to balance the electric charge of the adsorbed anions.

Figure 4 shows complete flotation is possible if the dodecylsulfate anion is present in excess of the stoichiometric molar ratio (i.e., one mole of $Pb^{2+}$ per two moles of $SDS^-$). When this is the case, flotation of lead ion may reflect with certain accuracy the flotation of the collector. It is worth remarking that lead and dodecylsulfate are floated as aqueous species and that eventually, they precipitate in the top of the froth bed in the form of $PbSDS_{2(s)}$, as a consequence of the increased concentration of both aqueous species due to the natural (e.g., gravity driven) drying of the froth. The figure shows that for molar ratio 1:4, the data may be adjusted to Eq. (6) written for $[Pb^{2+}]$, to give a rate constant of 0.019 $min^{-1}$.

## Effect of Air Flow Rate

Since the flotation rate constant depends directly on the volumetric air flow rate $Q_g$ [e.g., see Eq. (6)], experiments at different $Q_g$ were performed with the aim of corroborating such a linear dependency. Figure 5 presents the metal removal curves obtained at three different air flow rates: $6.1 \times 10^{-5}$, $9.1 \times 10^{-5}$, and $12.2 \times 10^{-5}\,m^3/min$. Relatively low air velocities are used

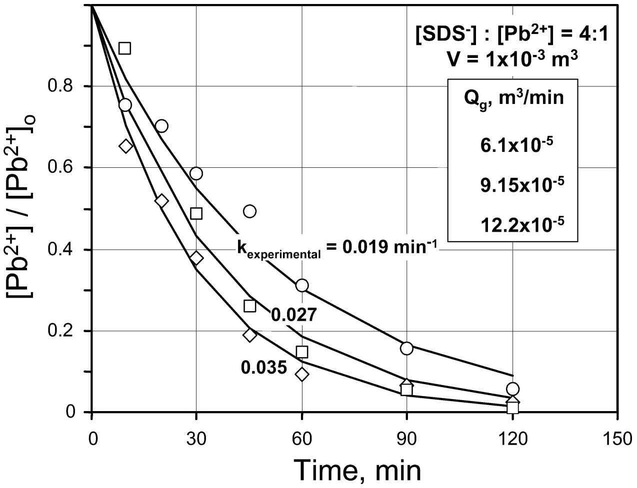

*Figure 5.* Effect of air velocity on the flotation kinetics of $Pb^{2+}$ ($[Pb^{2+}]_o = 1 \times 10^{-4}$ M) with SDS ($4 \times 10^{-4}$ M). pH 4; 0.4% v/v ethanol; $3 \times 10^{-3}$ M $NaNO_3$.

due to the fairly small bubbles encountered under the experimental conditions used. As shown in Fig. 6, about 80% of the air volume is in form of bubbles between 0.25 to 0.5 mm. This bubble diameter does not allow the use of air velocities typical of bubble columns and flotation columns, due to the risk of "frothing" the column.

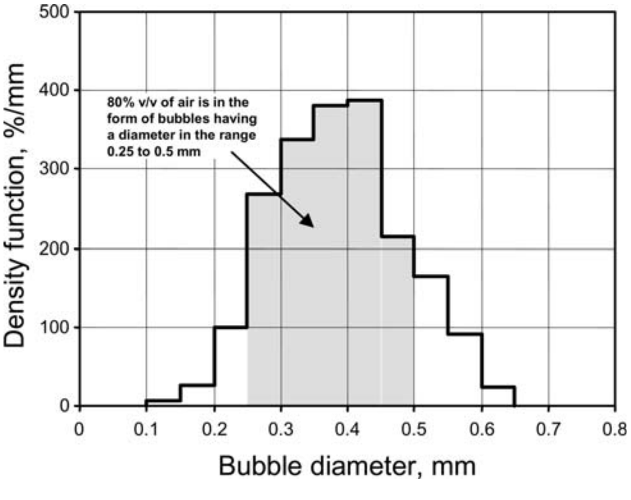

*Figure 6.* Bubble-diameter density function obtained from a sample of 585 bubbles. $Q_g = 6.1 \times 10^{-5}\ m^3/min$; 0.4% v/v ethanol; pH 4; $[Pb^{2+}]_o = 1 \times 10^{-4}$ M; [SDS] = $4 \times 10^{-4}$ M; $3 \times 10^{-3}$ M $NaNO_3$. The area under the curve represents the 100 percent volume of gas.

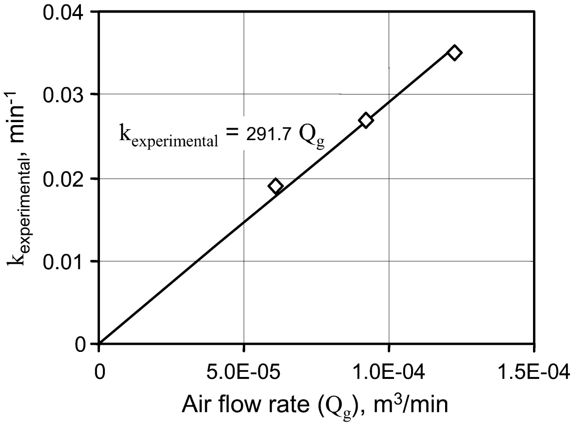

***Figure 7.*** Linear relationship between the flotation rate constant and air flow rate ($R^2 = 0.997$) for experimental results in Fig. 5.

The bubble surface rate ($A_b$) that is required in Eq. (7), was obtained by multiplying the volumetric air flow rate ($Q_g$) by the specific bubble surface area ($A_v$); this latter is defined as the bubble surface area per unit volume of gas. A value of 16630 m$^2$/m$^3$ was obtained with Eq. (8) for a sample of 585 bubbles collected in 4 digital photographs that were processed with the help of an image analyzer. The bubble-diameter density function of the above sample is presented in Fig. 6.

$$A_v = \frac{\sum_{i=1}^{585} \pi d_i^2}{\sum_{i=1}^{585} \pi/6 d_i^3}, \quad \mathrm{m^2/m^3} \tag{8}$$

## The Flotation Rate Constant

Figure 5 shows that Pb$^{2+}$ removal rate increases as the air flow rate is increased. Global rate constants are obtained adjusting the experimental data to Eq. (6). These values (termed $k_{experimental}$) were plotted against air flow rate, and a straight line that goes through the origin was obtained (Figure 7).

The rate constants predicted by the model [Eq. (7)], and those obtained by fitting the experimental data to the rate equation area presented in Table 1 and Fig. 8.

It is observe in Table 1 and Fig. 8 that values of rate constants are fairly similar and that there appears to be a constant deviation between both values. It is worth noting that such a difference vanishes if, for example, the value of *a* (the slope of the adsorption isotherm) decreases 33%. This would

***Table 1.*** Comparison between the rate constant of the model ($k_{model}$) [Eq. (7)] and that obtained by fitting the experimental data to Eq. (6) ($k_{experimental}$)

| $Q_g$ ($m^3/min$) | $A_b$ ($m^2/min$) | $k_{model}$ ($min^{-1}$) | $k_{experimental}$ ($min^{-1}$) |
|---|---|---|---|
| 6.10E − 05 | 1.01 | 0.029 | 0.019 |
| 9.15E − 05 | 1.52 | 0.044 | 0.027 |
| 1.22E − 04 | 2.03 | 0.058 | 0.035 |

$A_v = 16630\,m^2/m^3$; $a = 2.86E-05\,m$; $V = 1.0E-03\,m^3$.

mean that under the experimental conditions imposed in this work, the adsorption density of SDS is smaller than that measured by Liu and Doyle (2001b), due to the presence of ethyl alcohol, which also adsorbs at the air-liquid interface, thus competing with SDS for adsorption sites. Nevertheless, the model provides a fairly good approximation to the actual experimental results.

## CONCLUSIONS

A kinetic model for the batch-flotation of $Pb^{2+}$ with sodium dodecylsulfate is proposed. The model shows the kinetics of the metal ion removal from the aqueous solution directly depends on the bubble surface rate that is passed through the solution.

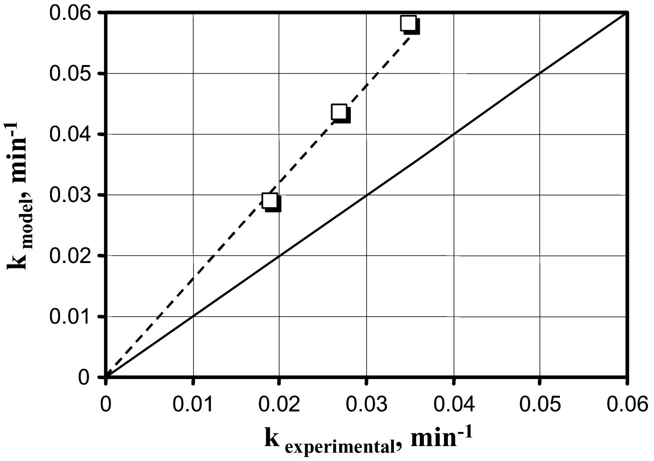

***Figure 8.*** Comparison between rate constants obtained with the model equation [Eq. (7)] and that fitted to the experimental data [Eq. (6)].

The rate constant values estimated with the experimental results obtained in the flotation of $Pb^{2+}$ ($1 \times 10^{-4}$ M) with sodium dodecylsulfate ($4 \times 10^{-4}$ M) with air ($Q_g = 6.1 \times 10^{-5}$ to $12.2 \times 10^{-5}\,m^3/min$), in the presence of ethyl alcohol as frother (0.04% v/v), are similar to those obtained with the model.

## APPENDIX

### Estimation of the Slope (*a*) of SDS Adsorption Isotherm in the Presence of $Pb^{2+}$

Adsorption of SDS at the air-water interface has been measured by Liu and Doyle (2001b) in the presence of stoichiometric amounts of $Pb^{2+}$ (i.e., molar ratios $[Pb^{2+}]/[SDS]$ of 1:2). The experimental results obtained (See Figure A.1) were fitted by the referred authors to a straight line:

$$\gamma = -70.904[SDS] + 0.0697 \quad R^2 = 0.9905 \tag{A.1}$$

where $\gamma$ is the surface tension (N/m) and [SDS] is the sodium dodecylsulfate concentration (mol/L).

The adsorption density is obtained from the Gibbs adsorption isotherm, namely:

$$\Gamma_{SDS} = -\frac{1}{RT}\frac{d\gamma}{d\ln a_{SDS}} \cong -1.753 \times 10^{-4}\frac{d\gamma}{d\log[SDS]} \tag{A.2}$$

with T = 298 K and R = 8.3145 m N/mol K.

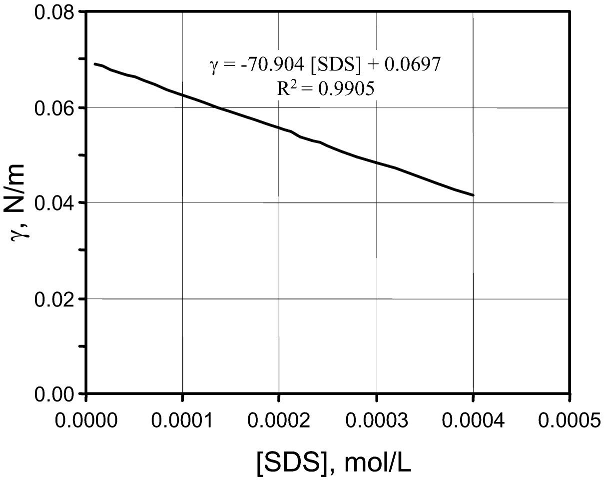

***Figure A1.*** Regression equation for the surface tension data of the SDS-$Pb^{2+}$ system at pH 4 reported by Liu and Doyle (2001b).

Expressing [SDS] in Eq. (A.1) as $10^{\log[\mathrm{SDS}]}$ and obtaining the derivative with respect to log[SDS], Eq. (A.1) becomes:

$$\frac{d\gamma}{d\log[SDS]} = -70.904 \times \ln(10) \times [SDS] \tag{A.3}$$

Combining Eq. (A.3) and (A.2), an expression for the adsorption isotherm is obtained:

$$\Gamma_{SDS} = 2.86 \times 10^{-2}[SDS] \tag{A.4}$$

with $a = 0.0286\,\mathrm{L/m^2} = 2.86 \times 10^{-5}\,\mathrm{m}$.

## ACKNOWLEDGEMENTS

The authors thank CONACYT for the financial support received through research grant 37107-U. Mr. González-Anaya (M.Sc.) is gratefully thanked for his help in the laboratory.

## REFERENCES

1. Nicol, S.K., Galvin, K.P., and Engel, M.D. (1992) Ion flotation-potential applications to mineral processing. *Minerals Engineering*, 5 (10–12): 1259–1275.
2. Liu, Z. and Doyle, F.M. (2001b) A thermodynamic approach to ion flotation. II. Metal ion selectivity in the SDS-Cu-Ca and SDS-Cu-Pb systems. Colloids and surfaces. *A Physicochemical and Engineering Aspects*, 178: 93–103.
3. Sebba, F. (1959) Concentration by ion flotation. *Nature*, 184: 1062–1063.
4. Grieves, R.B. and Keyle, R.N. (1982) Models for interactions between ionic surfactants and non surface—active ions in foam fractionation processes. *Sep. Sci. Technol.*, 17 (3): 465.
5. Xu, M., Finch, J.A., and Uribe-Salas, A. (1991) Maximum gas and bubble surface rates in flotation columns. *International Journal of Mineral Processing*, 32: 233–250.
6. Gorain, B.K., Franzidis, J.P., and Manlapig, E.V. (1997) Studies on impeller type, impeller speed and air flow rate in an industrial scale flotation cell. Part 4. Effect of bubble surface area flux on flotation performance. *Minerals Engineering*, 10 (4): 367–379.
7. Scorzelli, I.B., Fragomeni, A.L., and Torem, M.L. (1999) Removal of cadmium from a liquid effluent by ion flotation. *Minerals Engineering*, 12 (8): 905–917.
8. Kelly, E.G. and Spottiswood, D.J. (1982) *Introduction to Mineral Processing*; John Wiley & Sons: New York, 491.
9. Dobby, G.S., Yianatos, J.B., and Finch, J.A. (1988) Estimation of bubble diameter in flotation columns from drift flux analysis. *Can. Met. Quart.*, 27 (2): 85–90.

10. Liu, Z. and Doyle, F.M. (2001a) A thermodynamic approach to ion flotation. I. Kinetics of cupric ion flotation with alkylsulfates. Colloids and surfaces. *A Physicochemical and Engineering Aspects*, 178: 79–92.
11. Sun, Z.X. and Skold, R.O. (2001) A multi-parameter titration method for the determination of formation pH for metal hydroxides. *Minerals Engineering*, 14 (11): 1429–1443.