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Verification of a Stochastic Model for a Frothless Solvent Ion Flotation Using Thulium and Americium

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Abstract

A stochastic model for a frothless solvent ion flotation from aqueous solutions is presented. The model takes into consideration both adsorption and desorption of ions onto bubbles passing through the aqueous solutions to the organic phase. Theoretical predictions of the stochastic model compare very well with the experimental results of "flotoextraction" of thulium and americium from citrate aqueous solutions.

INTRODUCTION

In recent years a growing interest in ion flotation, initiated by Sebba in 1959 (*1*), has been observed. This interest has been manifested in a series of papers on the application of ion flotation to the separation of valuable species from dilute aqueous solutions, and on the effects of various agents on this process (*2–8*).

Ion flotation is based on the adsorption of ionic surface-active substances at the solution–air interface. The surfactants (collectors) react with metal ions to form more or less stable complexes which adsorb at the phase boundary or flocculate to form aggregates that subsequently attach to air bubbles passing through the aqueous solution. The bubbles transport the adsorbed and attached species to the surface, either to the layer of froth or, in the case of "flotoextraction" (solvent extraction), to the layer of organic solvent covering the surface of the aqueous solution. In spite of its simplicity, ion flotation is an extremely complicated process. It depends on numerous factors such as the character of ions undergoing flotation, the physicochemical properties of the collectors, the concentration of hydrogen and other ions, and the presence of other substances (*2*, *4*, *5*, *8*).

In this paper an attempt is undertaken to describe flotoextraction (i.e., flotation with the use of an organic solvent) of Tm and Am in a mathematical way in order to determine some parameters characteristic of the frothless ion flotation. A probabilistic model of the flotoextraction process is suggested. In contrast to the model presented in other papers (*9*, *10*), the present model takes into account the adsorption and desorption of ions from air bubbles during flotation.

DEVELOPMENT OF THE STOCHASTIC MODEL

The rate of flotoextraction (its intensity) is an important technological parameter of this process. It reflects not only the efficiency of flotoextraction with respect to time but also the influence of the changes in physicochemical conditions of the system under investigation. When the bubbles of air flow through the aqueous solution, an adsorption of the collector ions (which bind the metal ions) takes place on the surface of the bubbles. At the same time an adsorption of the collector–metallic ion complexes, which sometimes are formed in the aqueous solution, is also observed.

Metal ions complexed with the collector on the surface of air bubbles may escape (desorb) from this surface in the form of free ions or as undissociated collector complexes; in the later stages of the process the same species may be re-adsorbed on the air bubbles and transported to the organic phase.

The frequency of these adsorption–desorption phenomena and their random nature permit the treatment of this process as a stochastic one. In order to derive an equation describing the kinetics of the frothless ion flotation, the following conditions are assumed: the organic phase covering the aqueous solution with a layer of a suitable thickness is not soluble in the water phase, and is a good solvent for the collector and its complexes with the metallic ions undergoing flotation; in the probabilistic model of the frothless ion flotation process it is assumed that the number of ions transported in the form of collector complexes by air bubbles to the solvent layer is a random variable dependent on the time parameter t.

Let N be a number of ions in the aqueous solution undergoing flotation in the flotation apparatus at the time $t = 0$. Because of the random character of the transport of ions in the form of ion–collector complexes by air bubbles to the layer of the organic solvent, the number $n(t)$ of ions will be treated as a random variable at time $t > 0$. When t changes, a computable stochastic process $(n(t))$ with a continuous parameter t is obtained.

Let us introduce a function of the transition probability in the form

$$P_{jk}(t, t + \Delta t) = P_r\{n(t + \Delta t) = k \mid n(t) = j\}$$

Transition function $P_{jk}(t, t + \Delta t)$ denotes conditional probability of ions gathered in the surface layer on the air bubbles such that in time $(t + \Delta t)$ there are $n(t + \Delta t) = k$ of ions if in time t there were $n(t) = j$ of them. We assume that the process $(n(t))$ is homogeneous in time, i.e., that the probabilities $P_{jk}(t, t + \Delta t)$ depend on the difference Δt, and hence

$$P_{jk}(t, t + \Delta t) = P_{jk}(\Delta t)$$

Conditional probability of the change in the number of ions during the process in the time Δt is a function of Δt, j, and k.

We assume that in the small interval $(t, t + \Delta t)$ the probability of both an increment and a decrement of $n(t)$ by a unit in the surface layer of air bubbles is proportional to some exact component of a higher order $o(\Delta t)$. This probability is equal to $\lambda(j)\Delta t + o(\Delta t)$, $\lambda(j) > 0$, and to $\mu(j)\Delta t + o(\Delta t)$, $\mu(j) > 0$.

If no change has taken place in the interval $(t, t + \Delta t)$, the probability is equal to $1 - \lambda(j)\Delta t - \mu(j)\Delta t + o(\Delta t)$.

The conditions of the transition function for the process $(n(t))$ may be briefly written as

$$P_{jk}(\Delta t) = \begin{cases} \lambda(j)\Delta t + o(\Delta t) & \text{for } k = j + 1 \\ \mu(j)\Delta t + o(\Delta t) & \text{for } k = j - 1 \\ 1 - \lambda(j)\Delta t - \mu(j)\Delta t + o(\Delta t) & \text{for } k = j \\ o(\Delta t) & \text{for } k \neq j - 1, j + 1 \end{cases} \tag{1}$$

Thus the specified process is a particular case of the computable Markow process, i.e., the process of birth and death. We assume that $n(0) = 0$ for $t = 0$, and thus the probability $P_{jk}(t)$ may be presented as: $P_{ok}(t) = P_k(t)$.

The probability $P_k(t)$ satisfies the following set of equations of Kolmogorov-Feller:

$$\frac{d}{dt}P_k(t) = -[\lambda(k) + \mu(k)]P_k(t) + \lambda(k-1)P_{k-1}(t) + \mu(k+1)P_{k+1}(t) \tag{2}$$

Functions $\lambda(k)$ and $\mu(k)$ characterize the intensity of the ion flotation process. Bearing in mind the applicability of the model, we assume that the functions $\lambda(k)$ and $\mu(k)$ have the forms

$$\begin{aligned} \lambda(k) &= \alpha(N-k) \\ \mu(k) &= \mu k \end{aligned} \tag{3}$$

where $\alpha > 0$ and $\mu > 0$ are constant values characterizing the process. For an efficient process, the coefficients of intensity α should be sufficiently large, whereas μ should be sufficiently small. If $\mu = 0$, we deal with a process in which the phenomenon of the liberation of ions from the adsorption layer on the air bubbles does not occur (*9*).

The specified function of intensity given in Eq. (3) determines the conditional probability $P_k(t)$ of the ion flotoextraction process. The smaller the value of the function $\lambda(k)$, the greater number of ions bound to the adsorption layer and transported by the bubbles to the organic phase. Taking into account the function of intensity (*3*), the basic set of Eq. (3) will have the form

$$\begin{aligned} \frac{d}{dt}P_k(t) = {} & -[\alpha(N-k) + \mu(k)]P_k(t) + \alpha[N-(k-1)]P_{k-1}(t) \\ & + \mu(k+1)P_{k+1}(t) \end{aligned} \tag{4}$$

which together with the initial condition

$$\lim_{t\to 0} P_k(t) = P_k(0) = \begin{cases} 1 & \text{for } k = 0 \\ 0 & \text{for } k = 1, 2, 3, \ldots, N \end{cases} \tag{5}$$

has a single solution $P_k(t)$.

To solve the set of Eqs. (4), a generating function of the process under investigation is applied:

$$G(t, z) = \sum_{k=0}^{N} z^k P_k(t) \tag{6}$$

then, considering that

$$\frac{\partial G(t, z)}{\partial z} = \sum_{k=0}^{N} k z^{k-1} P_k(t)$$

if both sides of the kth equation of the set (4) are multiplied by z^k, and both sides are added in the relation for k, the following equation for the generating function (6) is obtained:

$$\frac{\partial G(t, z)}{\partial t} + (\alpha z + \mu)(z - 1)\frac{\partial G(t, z)}{\partial z} = N(z - 1)(G(t, z) \tag{7}$$

Using the assumption (5) and the equality (6), the initial condition for Eq. (7) has been determined:

$$G(0, z) = \sum_{k=0}^{N} z^k P_k(0) = 1 \tag{8}$$

Equations for the characteristics for Eq. (7) to determine functions $G = G(t, z)$ have the form

$$\frac{dt}{1} = \frac{dz}{(\alpha z + \mu)(z - 1)} = \frac{dG}{N(z - 1)G} \tag{9}$$

Hence two first integrals, linearly independent, are obtained:

$$\frac{(z - 1)}{\alpha z + \mu} e^{-(\alpha+\mu)} = C_1$$

$$(\alpha z + \mu)G^{-1/N} = C_2$$

The particular integral of Eq. (7) satisfying the condition (8) is determined from the general integral

$$G(t, z) = (\alpha z + \mu)^N \varphi\left(\frac{z - 1}{z + \mu} e^{-t(\alpha+\mu)}\right)$$

Having determined an arbitrary function, the final expression of the generating function is obtained in the form:

$$G(t, z) = \frac{1}{(\alpha + \mu)^N}[\alpha z + \mu - \alpha(z - 1)e^{-t(\alpha+\mu)}]^N \tag{10}$$

When the generating function is known, it is possible to determine the probability $P_k(t)$ for every distribution time.

Taking into consideration

$$P_0(t) = G(t, 0)$$

$$P_k(t) = \frac{1}{k!}\frac{\partial^k G(t, z)}{\partial z^k}\bigg|_{z=0} \tag{11}$$

the following formula is obtained by the application of (10):

$$P_k(t) = \binom{N}{k}\frac{k}{(\alpha+\mu)^N}[\mu + \alpha e^{-t(\alpha+\mu)}]^{N-k}[1 - e^{-t(\alpha+\mu)}]^N$$
$$\text{for } 0 \leqslant k \leqslant N \tag{12}$$

to determine the distribution of the probability $P_k(t)$ of the random variable $n(t)$.

The mean value of the random variable $n(t)$ is calculated by means of the generating function (10) on the basis of the relation

$$E\{n(t)\} = m(t) = \left.\frac{\partial G(t, z)}{\partial z}\right|_{z=1} \tag{13}$$

and the following is obtained

$$m(t) = \frac{N\alpha}{(\alpha+\mu)}[1 - e^{-t(\alpha+\mu)}] \tag{14}$$

This formula gives the mean value of the random variable $n(t)$ of ions present in the layer of an organic solvent in the given time t of the flotoextraction process. Then, subsequently, the dispersion of the random variable $n(t)$ is calculated by means of

$$D^2\{n(t)\} = \left[\frac{\partial^2 G(t, z)}{\partial z^2} + \frac{\partial G(t, z)}{\partial z} - \left(\frac{\partial G(t, z)}{\partial z}\right)^2\right]_{z=1} \tag{15}$$

and the following dependence is obtained

$$D^2\{n(t)\} = \frac{N\alpha}{(\alpha+\mu)^2}[1 - e^{-t(\alpha+\mu)}][\mu + \alpha e^{-t(\alpha+\mu)}] \tag{16}$$

Using the expression (14), the asymptotic values of the average number of ions present in the layer of an organic solvent at high values of the parameter t (at $t \to \infty$) permit determination of the relation between the constants α and μ. Thus we obtain

$$d = \lim_{t\to\infty}[m(t)] = \frac{N\alpha}{\alpha+\mu} \tag{17}$$

which is an equation of the horizontal asymptote for the function $m(t)$. To determine the degree of the dispersion of the random variable value $n(t)$ around the mean value (expected at the given time t of the flotoextraction process), a variability coefficient defined by formula (18) is introduced:

$$\delta(t) = \frac{\sqrt{D^2\{n(t)\}}}{m(t)} = \sqrt{\frac{\mu + \alpha \exp[-t(\alpha + \mu)]}{N\alpha(1 - \exp[-t(\alpha + \mu)])}} \tag{18}$$

EXPERIMENTAL RESULTS

Theoretical predictions of the stochastic model of the frothless ion flotation have been compared with the experimental results of Tm and Am flotation (*11*, *12*). With citric acid, these elements form complex compounds whose compositions and structures depend considerably on the concentration of citric acid and pH of the solution. Transplutonium and lanthanum ions can be floated as citrate complexes using a cationic collector, cetylpyridinium bromide (*12*).

Figure 1 shows the recovery of Tm obtained in flotoextraction, in relation to pH, at different concentrations of citric acid; the results for Am flotation using 0.01 mole/liter citric acid solution are also given. The data show clearly the effect of the concentration of citric acid and that of the pH of the solution on the recovery of flotoextraction. Optimum conditions for Am and Tm flotoextraction are obtained at pH ~10.5, and the recovery of flotation decreases with the increasing concentration of citric acid.

The efficiency of ion flotoextraction depends on time of the process, as

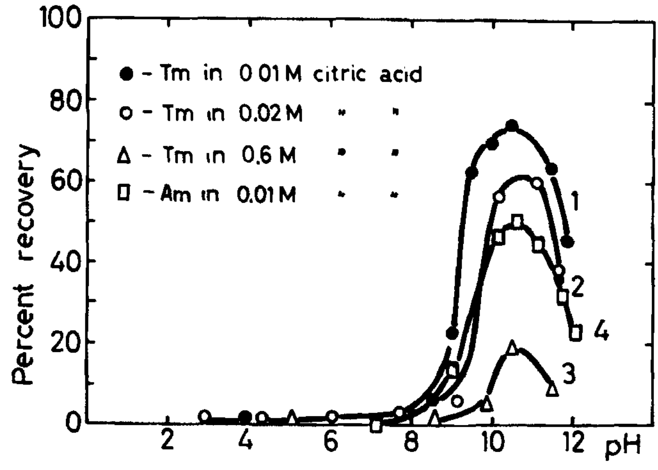

FIG. 1. Recovery of Tm obtained by flotoextraction in relation to pH.

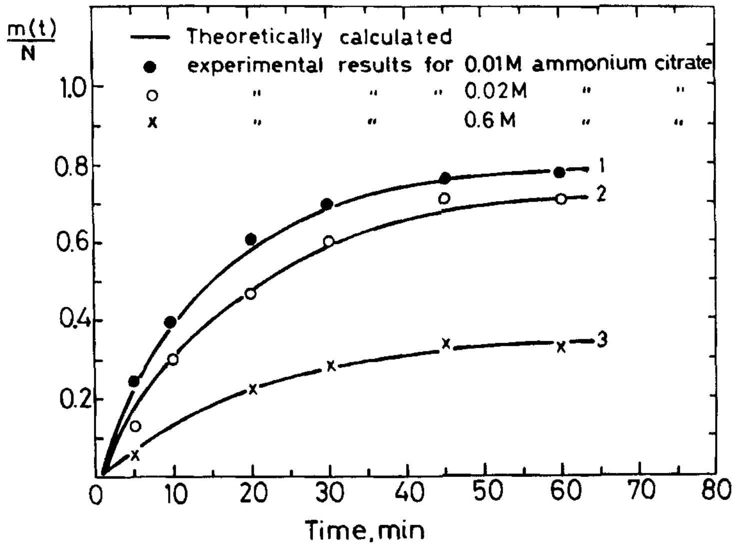

FIG. 2. Time dependence of recovery of Tm by flotoextraction from ammonium citrate solutions at pH 10.5

seen in Fig. 2, giving the recovery of Tm from the 0.01, 0.02, and 0.6 mole/liter solutions of ammonium citrate at pH 10.5.

Using the above experimental results, the values of the intensity coefficients α and μ for the flotoextraction process of Tm have been calculated from the formulas (14) and (17) (Table 1). These coefficients have been subsequently used to calculate the theoretical recoveries of flotoextraction by means of the formula (14). Theoretical recoveries are presented in Fig. 2 by continuous lines.

Similar experiments have been carried out for americium, and the results are shown in Fig. 3 as points representing the dependence of the recovery

TABLE 1

Concentration of citric acid (mole/liter)	Coefficients for flotoextraction of Tm				
	α	μ	ε	η	$\bar{D}$
0.01	0.05	0.0125	0.80	0.20	4.0
0.02	0.04	0.016	0.71	0.29	2.45
0.6	0.0125	0.0251	0.33	0.67	0.49

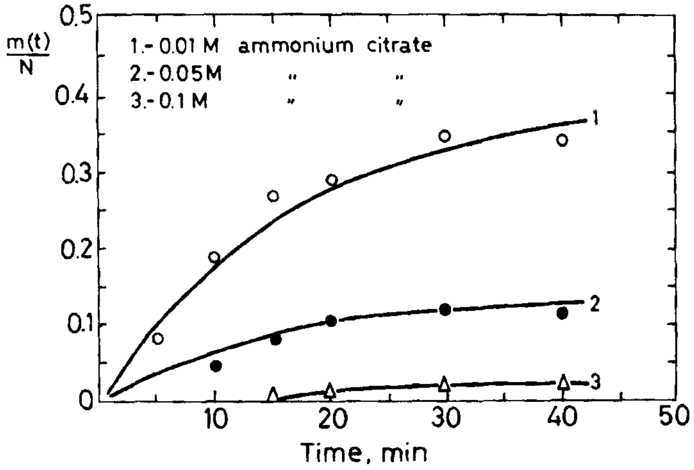

FIG. 3. Time dependence of recovery of Am by flotoextraction from ammonium citrate solutions at pH 10.5.

TABLE 2

Concentration of citric acid (mole/liter)	Coefficients for flotoextraction of Am				
	α	μ	ε	η	$\bar{D}$
0101	0.02	0.037	0.35	0.65	0.54
0.05	0.01	0.066	0.13	0.87	0.16
0.1	—	—	—	—	—

of Am on time in flotoextraction from the 0.01, 0.05, and 0.1 mole/liter solutions of ammonium citrate at pH 10.5. Continuous lines in Fig. 3 denote the theoretical recovery calculated in an analogous manner to that of Tm by means of formula (14). The values α and μ are presented in Table 2.

The data given in Figs. 2 and 3 show good agreement between experiments and theoretical results.

Knowledge of the values of the coefficients α and μ permits us to determine the degree of flotability or nonflotability and to calculate the flotoextraction coefficients. The degree of flotability is

$$\varepsilon = \frac{\alpha}{\alpha + \mu} \tag{19}$$

The degree of nonflotability η has the form:

$$\eta = \frac{\mu}{\alpha + \mu} \tag{20}$$

The coefficient of flotoextraction $\bar{D}$ characterizes the partition of the substance undergoing flotation into aqueous and organic phases. This coefficient is equal to the ratio of the process intensity coefficients α and μ:

$$\bar{D} = \alpha/\mu \tag{21}$$

The values of these parameters are presented in Tables 1 and 2. The dependence of the coefficients ε and η on the concentration of ammonium citrate for Tm and Am is presented in the form of graphs in Figs. 4 (for Tm) and 5 (for Am).

DISCUSSION

The mathematical model of the process of flotoextraction developed above may be used for the determination (by means of formula 14) of the number $m(t)$ of ions or molecules separated by flotation up to the time t.

The coefficient α determines the efficiency of the flotoextraction process. The coefficient μ characterizes the intensity of the liberation (desorption) of components undergoing flotation from the surface layer of air bubbles during their flow through the aqueous solution. For an efficient process, the coefficient α should have a relatively high value in comparison with that of the coefficient μ (Tables 1 and 2). When $\mu = 0$, the formulas given in Ref. *9* are valid. The experimental results may be used for the determination of the values of the coefficients α and μ by means of formulas (14) and (17), and by utilizing the value of the angular coefficient of the tangent (passing through the beginning of the system of coordinates) to the curve illustrating the experimental flotoextraction process. In this case, the angular coefficient with respect to the abscissa axis is calculated by differentiating the function $m(t)$ known from formula (14), i.e.,

$$\frac{1}{N}\frac{\partial m(t)}{\partial t}\bigg|_{t=0} = \alpha$$

The probability distribution of the value $P_k(t)$ of the random variable $n(t)$ is known from formula (12). Using formula (16), it is possible to establish the dispersion of the random variable $n(t)$ by determining the number of ions transported by air bubbles to the layer of the organic solvent at any given time t of the process. The variability coefficient $\delta(t)$, defined by

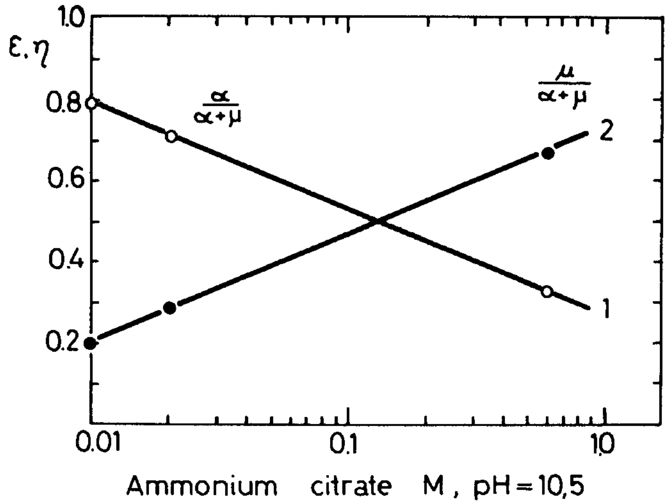

Fig. 4. Dependence of the floatability ε and nonfloatability η coefficients for Tm on the concentration of ammonium citrate.

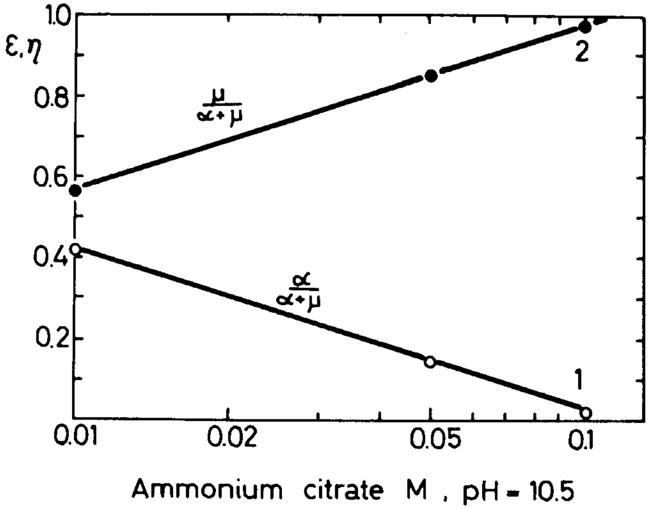

Fig. 5. Dependence of the floatability ε and nonfloatability η coefficients for Am on the concentration of ammonium citrate.

formula (18), gives the degree of the dispersion of the random variable $n(t)$ around the mean number of ions or molecules passing to the solvent layer in the given time t of the process. Verification of the assumed hypothesis concerning the kinetics of the frothless flotation carried out by comparing the results of Tm and Am flotation shows excellent agreement of the experimental and theoretical data (Figs. 2 and 3).

Using a certain combination of the coefficients α and μ, it is possible to determine the degree of flotability (19) or nonflotability (20) and to calculate the flotoextraction coefficient given by formula (21).

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