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LOS ALAMOS SCIENTIFIC LABORATORY
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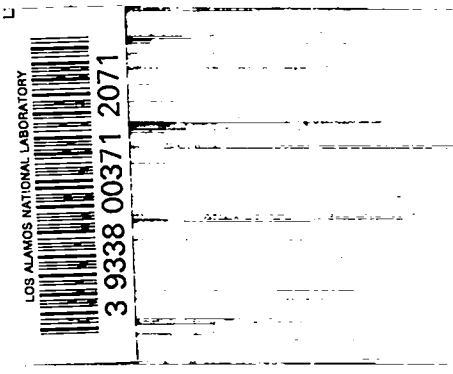
PROCESSING OF PLUTONIUM BY ION EXCHANGE - III.
THE CALCULATION OF FIXED-BED COLUMN PERFORMANCE



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PROCESSING OF PLUTONIUM BY ION EXCHANGE - III.
THE CALCULATION OF FIXED-BED COLUMN PERFORMANCE

by

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ABSTRACT

Parameters and equations are presented which permit the numerical duplication of the sorption of plutonium on nitrate-form Dowex 1x4 from 7M nitric acid. A mass-action description of the two-phase equilibria and an empirical expression for the sorption rate are coupled with the fundamental partial differential equation which describes the operation of a fixed-bed ion-exchange column to produce a system that is only numerically solvable. The calculation and experiment are in good agreement.

ACKNOWLEDGMENT

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INTRODUCTION

The sorption of plutonium by strong-base anion-exchange resin from strong nitrate solution is an excellent purification method since only a few other elements are sorbed to any significant degree. Ryan and Wheelwright[1] studied some of the kinetic and equilibrium parameters of the system and showed that 7M nitric acid is a satisfactory solvent.

Ryan[2] demonstrated that plutonium(IV) is sorbed on nitrate-form Dowex 1x4 from 7M nitric acid as $Pu(NO_3)_6^{-2}$. The equilibrium of this exchange was shown by James[3] to be described by

$$\bar{x}^* = \bar{x}_m \left\{ 1 + U - \sqrt{U(U+2)} \right\} , \qquad (1)$$

$$U = \frac{\bar{x}_m}{2c\lambda_o} , \qquad (2)$$

over the entire range of resin loading. In these equations,

$\bar{x}^*$ = equilibrium concentration of plutonium in the resin phase in millimoles per oven-dry gram

$\bar{x}_m$ = maximum concentration of plutonium in the resin phase, (half the equivalent capacity for anions)

c = total molar concentration of plutonium in the aqueous phase,

$\lambda_o = \frac{\bar{x}^*}{c}$ when $\bar{x}^* \rightarrow o$.

Ryan and Wheelwright[1] have made extended investigations of the sorption of plutonium(IV) on various anion-exchange resins from various nitrate media. They demonstrated that the rate of sorption on Dowex 1x4 from 7M nitric acid is controlled by diffusion within the resin particle and governed by an apparent diffusion coefficient which decreases with increasing degree of resin loading.

The object of the investigation was to provide a method for predicting the time-dependent concentrations in a fixed-bed anion-exchange column and its effluent. The fundamental equation which describes the fixed-bed ion-exchange column is

$$\epsilon \frac{\partial c}{\partial t} + v \frac{\partial c}{\partial z} = - \frac{\partial \bar{x}}{\partial t} \quad , \tag{3}$$

where

ϵ = fractional interstitial void space about the resin beads,

t = time in seconds,

z = distance along the column in centimeters,

v = linear flow rate of the aqueous phase in centimeters per second, and

$\bar{x}$ = nonequilibrium concentration of plutonium in the resin phase in millimoles per oven-dry gram.

Although this equation has well-known solutions[4] for the constant pattern case, the diffusion rate of plutonium in Dowex 1x4 is so slow that the necessary quasi-steady state is not established in the time of a normal processing operation. The solution of equation (3) is further

complicated by the fact that the diffusion coefficient is not constant. Therefore, a numerical approach was used to obtain a solution. This was accomplished by a straightforward simulation in two steps, with the concentration given for discrete regions of the column at discrete times; e.g.

$$c(\bar{x},t) \rightarrow c(i,j) \quad .$$

First, the fluid is moved one space point down the column,

$$c(i + 1,j) = c(i,j - 1) \quad ,$$

and second, the ion exchange between fluid and resin, $(\partial x/\partial t)\Delta t$, is allowed to proceed for an appropriate time. This technique will reproduce known analytic solutions for simpler cases.

The exchange rate, $\partial\bar{x}/\partial t$, must be given in terms of c and $\bar{x}$, and must not involve time explicitly. For diffusion into spherical particles, the only exact solution not only assumes a constant diffusion coefficient, but contains time explicitly. There are several approximations available which do not contain time explicitly. We used Vermeulen's[4] quadratic approximation,

$$\frac{\partial\bar{x}}{\partial t} = \frac{\pi^2\,\bar{D}}{2r^2}\,\frac{(\bar{x}^*)^2 - (\bar{x})^2}{\bar{x}} \quad , \tag{4}$$

where $\bar{D}$ is the diffusion coefficient and r is the average bead radius. Note that both equations (3) and (4) average the concentration over the resin bead, thus losing certain physical details of the diffusion within the resin bead.

Although Ryan and Wheelwright[1] observed $\bar{x}$ as a function of time and showed that $\bar{D}$ varied with $\bar{x}$, their values of $\bar{D}$ were averaged over the loading process and could not be used directly in equation (4). Indeed, equation (4), being an approximation to the exact solution for constant $\bar{D}$, does not necessarily hold for variable $\bar{D}$. Ryan and Wheelwright[1] suggested that increased loading raises the diffusional activation energy which indicated that $\bar{D}$ might take the form,

$$\bar{D} = \bar{D}_o e^{-k\bar{x}/\bar{x}_m} \qquad (5)$$

Batch equilibrations were conducted to obtain the form of $\partial\bar{x}/\partial t$, and with these results column behavior was computed and compared to experiment.

EXPERIMENTAL

Reagents: The resin used was Dowex 1x4 (100 - 200 mesh) NO_3^-. It was converted from the chloride to the nitrate form and its equivalent capacity for anions determined as described before.[3] The nitrate form contained 3.8 milliequivalents per oven-dry gram or about 1.5 milliequivalents per milliliter of resin bed in contact with 7M nitric acid. The impurities in the plutonium used were less than 0.01 weight percent, except for 2.6 percent iron, 0.20 percent uranium, 0.47 percent americium, and 0.05 percent aluminum.

Batch Equilibration Experiments: The rate of sorption of plutonium(IV) was followed in a round, four-liter flask with the two phases being rapidly stirred mechanically. A coarse frit at the end of a small tube allowed 1-milliliter samples of the aqueous phase to be withdrawn in about 10 seconds at a minimum of 100-second intervals.

A weighed amount of oven-dry resin, equilibrated with 7M nitric acid, and filtered "dry" with vacuum was contacted with 7M nitric acid solution of measured volume and plutonium(IV) concentration at time zero. The mixing time was less than 30 seconds.

The first experiment used 175.0 grams of resin (438 ml) and 2.00 liters of 7M nitric acid, containing 47.6 g. Pu/ℓ. The second experiment used 200.0 grams of resin (500 ml) and 1.00 liter of 7M nitric acid, containing 17.3 g. Pu/ℓ. The degree of reaction was determined by the difference between the aqueous concentration of plutonium and its initial concentration. The first sample was withdrawn after 2 minutes, and this difference was about 20 percent. Therefore, the first few data points may be in error by as much as 10 to 15 percent. The accuracy of the alpha-counting technique is probably better than 2 percent.

Column Experiment: A 7M nitric acid solution, containing 17.3 g. Pu/ℓ., was passed over a column with an inside diameter of 2.20 cm at a flow rate of 6.1 mℓ/min. The column contained 22.0 grams of oven-dry, nitrate-form resin.

RESULTS AND DISCUSSION

The results of the first batch equilibration experiment are shown in Fig. 1. The aqueous concentration was such that initially $\bar{x}^*/\bar{x}_m = 0.95$, and it reached 0.89 at 10,000 seconds. The aqueous concentration was reduced to 15 g. Pu/ℓ. This small change in $\bar{x}^*/\bar{x}_m$, due to the highly favorable equilibrium, made it possible to check equations (4) and (5) by an appropriate plot of the data.

Tangents to a plot of $\bar{x}$ versus the logarithm of t were used to calculate

$$\log \left\{ \frac{\partial \bar{x}}{\partial t} \; \frac{\bar{x}}{(\bar{x}^*)^2 - (\bar{x})^2} \right\} . \qquad (6)$$

A plot of this versus $\bar{x}/\bar{x}_m$ was linear for $\bar{x}/\bar{x}_m < 0.6$, indicating the validity of equations (4) and (5) and allowing estimates of $\bar{D}_o$ and k. Numerical integration[5] of equations (4) and (5) under these conditions was carried out, including the effect of the variation of the aqueous concentration upon $\bar{x}^*$ as given by equation (1). Results for three sets of $\bar{D}_o$ and k are compared with the experimental data in Fig. 1. Set B was used in subsequent calculations. This value of $\bar{D}_o$ agrees within expected experimental error with the datum of Ryan and Wheelwright at low resin loading.†

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†While this report was being prepared for publication, several more batch experiments were completed. These results confirm the value of $\bar{D}_o$ given in this report, but they indicate that k may be somewhat smaller.

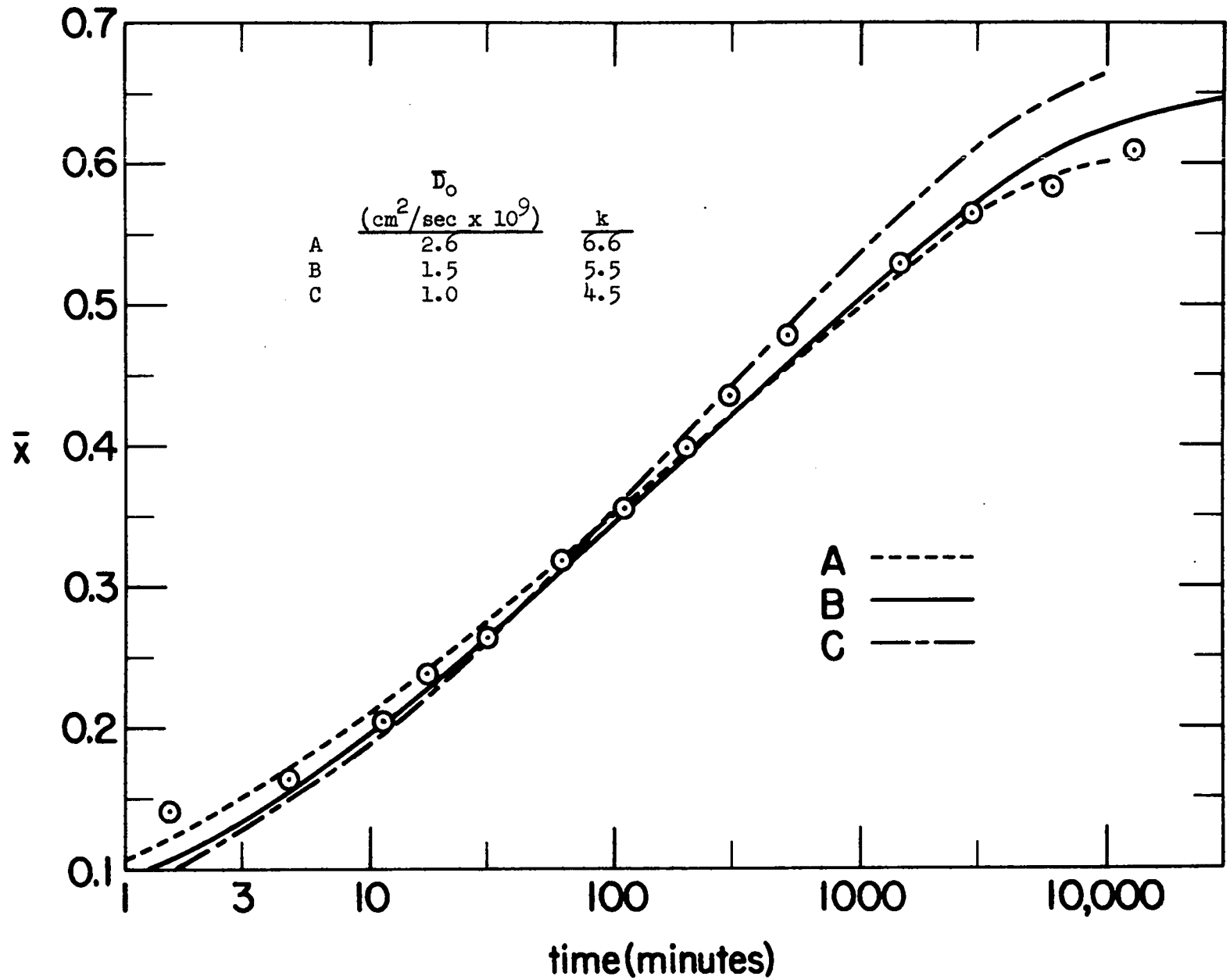

Fig. 1. Sorption of Plutonium in the First Batch Experiment

The agreement between calculation and experiment in Fig. 1 gives us a basis for computing the column behavior, but does not reveal any physical details of the diffusion process since the concentration has been averaged over the resin bead. The authors[5] have solved the diffusion into a sphere where $\bar{D}$ was an exponential function of the local concentration $\bar{x}(r)$, and it was shown that this could not be made to fit the data of Fig. 1 for any reasonable values of $\bar{D}_o$ and k. Another model, diffusion with constant coefficient followed by immediate reaction (analogous to oxidation of a metal sphere), was investigated, and it also produced a result in disagreement with experiment.

In order to check the empirical rate equation,

$$\frac{\partial \bar{x}}{\partial t} = \frac{\pi^2 \bar{D}_o}{2r^2} \frac{(\bar{x}^*)^2 - (\bar{x})^2}{\bar{x}} e^{-k \bar{x}/\bar{x}_m} \qquad (7)$$

a second batch run was made under very different conditions. The proportions of solution and resin were chosen such that the solution would become virtually depleted of plutonium, as occurs at the wave front in a column. Equilibrium was reached in approximately 300 seconds with $\bar{x}^*/\bar{x}_m = 0.14$. The experimental results and calculation are shown in Fig. 2. The experimental data were corrected to discount 4.1% of the plutonium which remained as Pu^{+3}, which does not take part in the exchange reaction.

The breakthrough concentration data for a column raffinate was computed[5] using equations (1) - (3) and (7) and is compared with

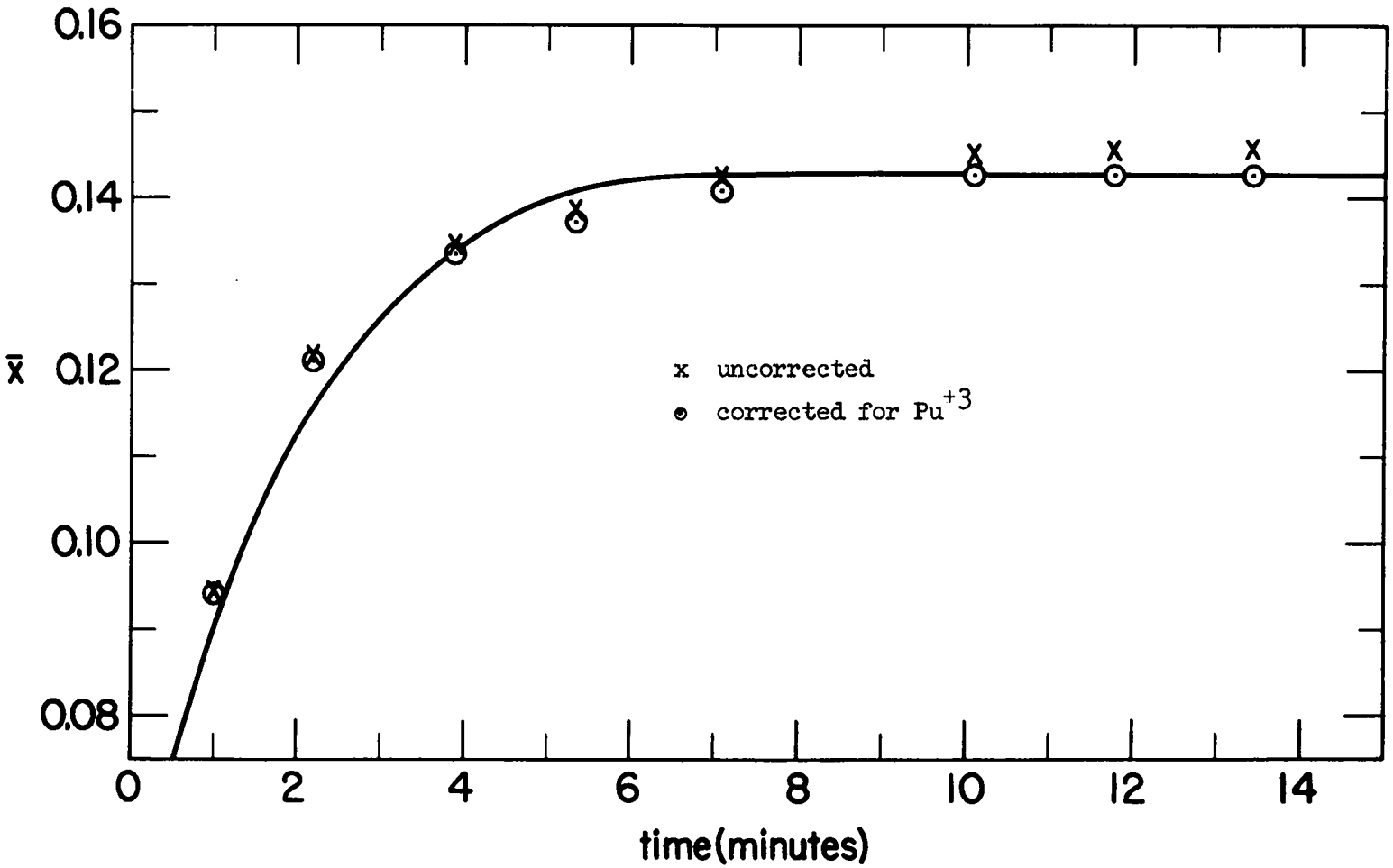

Fig. 2. Sorption of Plutonium in the Second Batch Experiment.

experiment in Fig. 3. The disagreement of about 11% could be due to uncertainties in $\bar{x}_m$, or to nonuniformities in flow over the column cross section. For the latter, any deviations would lead to the early breakthrough.

Equations (1) - (3) and (7) provide a means for calculating loading profiles and breakthrough curves from column and resin dimensions, flow rate, and feed concentration. It was shown by Ryan and Wheelwright[1] that the sorption rate is a function of the degree of cross-linkage of the resin. Therefore, equation (7) may not apply to other resins.

The next paper in this series[6] extends these calculations to the behavior of weakly sorbed impurities in their separation from plutonium by anion exchange. Future papers will discuss the sorption of plutoniun on Dowex 1x4 from mixed nitric acid-aluminum nitrate solvents.

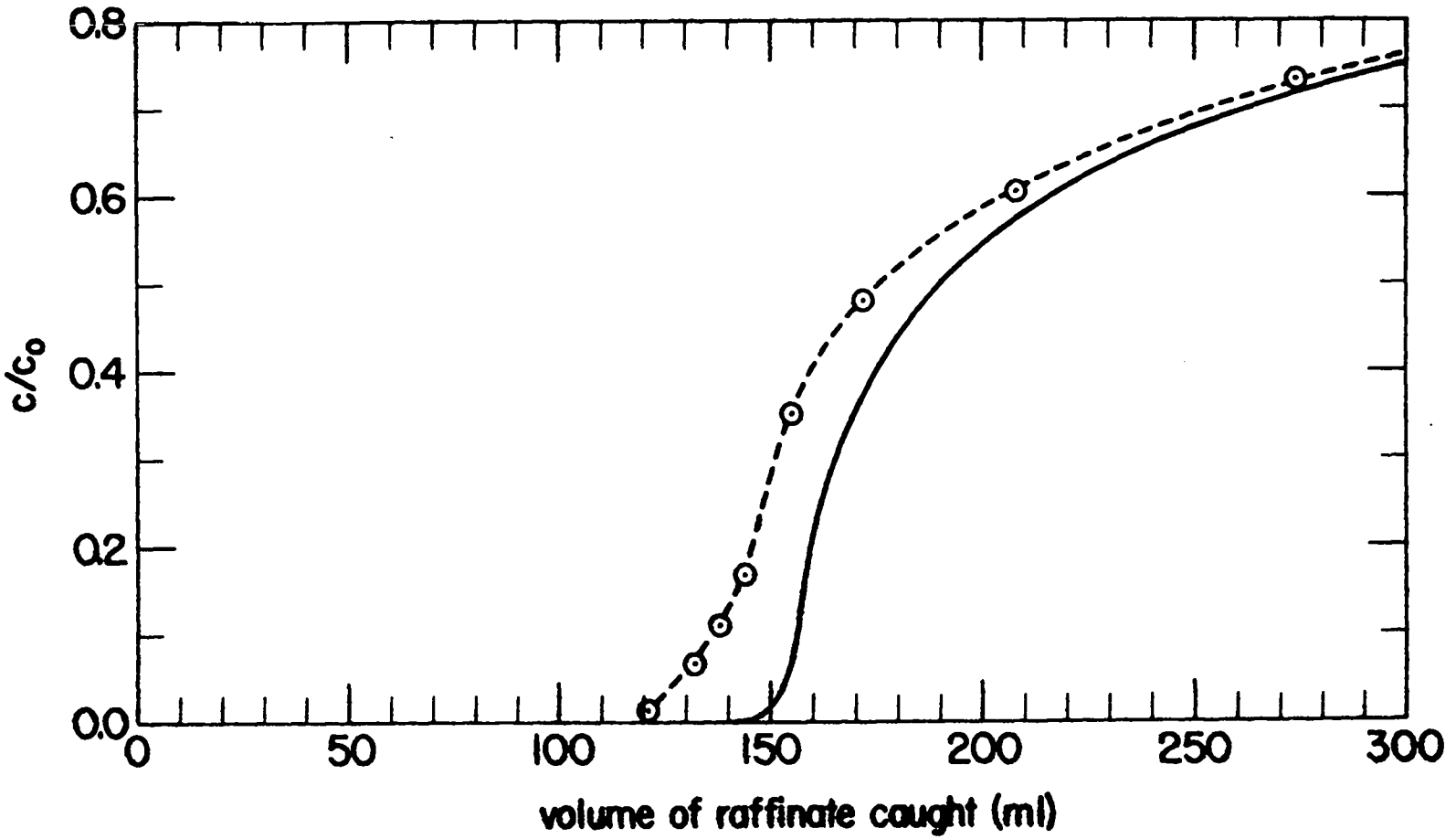

Fig. 3. Breakthrough Curve

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