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P. R. Danesi[a]; C. Cianetti[a]; E. P. Horwitz[a]; H. Diamond[a]
[a] CHEMISTRY DIVISION ARGONNE NATIONAL, ILLINOIS

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ARMOLLEX: An Apparatus for Solvent Extraction Kinetic Measurements

P. R. DANESI, C. CIANETTI, E. P. HORWITZ, and H. DIAMOND

CHEMISTRY DIVISION
ARGONNE NATIONAL LABORATORY
ARGONNE, ILLINOIS 60439

Abstract

A new forced-convection constant-interfacial-area stirred cell, suitable for studying kinetics of liquid–liquid extraction of metal cations, is described. The apparatus permits operation over a wide range of stirring conditions and continuous monitoring of concentration variations.

INTRODUCTION

Liquid–liquid extraction kinetics are often characterized by interfacial rate-determining steps (*1*). The interfacial chemical reactions are quantitatively described by their interfacial rate constants which, in the case of pseudo-first-order reactions, are expressed in cm/s units. To evaluate the interfacial rate constants, the interfacial area available for the liquid–liquid heterogeneous reaction has to be known exactly. At the same time, very efficient stirring of the two phases up to the phase boundary has to be achieved in order to avoid interfacial film diffusion processes which contribute significantly to the measured extraction kinetics.

Constant interfacial area stirred cells (*2*), also called Lewis cells, have often been used to obtain solvent extraction kinetic data in experiments where knowledge of the interfacial area for the heterogeneous process was required. Unfortunately, this kind of cell does not permit efficient stirring of the regions close to the liquid–liquid interface because of the generally low angular velocity of the stirrer paddles required to avoid vortex formation. Further, only a small fraction of the translational energy provided by the stirrers causes enough interfacial turbulence to destroy the diffusion films.

In order to overcome this disadvantage, Nitsch and Hillekamp (*2*) have developed an apparatus with cylindrical inserts containing screens at the ends closest to the interface and impellers with blades inclined 45° to the surface. This arrangement produces a very efficient forced convection and allows one to stir the aqueous and the organic phases at very high speeds without breaking the interface. The apparatus was designed to handle rather large volumes (about 1 L), and the time dependence of the concentrations of solute were determined by discontinuous withdrawal of sample volumes. However, a continuous monitoring of the concentration variations and the use of small volumes are highly desirable to reduce the amount of experimental work required to accumulate enough data to determine a reaction mechanism and to allow the use of organic reagents often available only in limited quantities. We have developed a new cell which retains the efficient hydrodynamic features described in Ref. *2*, and permits the use of small volumes (about 100 mL) and a continuous monitoring of the concentration variations. This new forced convection, constant-interfacial-area stirred cell, where concentration variations are monitored by radiometric flow counting, is called ARMOLLEX, an acronym for *AR*gonne *MO*dified *L*ewis cell for *L*iquid–liquid *EX*traction kinetic measurements.

The ARMOLLEX apparatus has been tested on two solvent extraction systems:

(*a*) Eu^{3+}, HNO_3, water–bis(2-ethylhexyl)phosphoric acid (HDEHP), *n*-dodecane
(*b*) TcO_4^-, HNO_3, water–trioctylmethylammonium nitrate, (TOMAN), *o*-xylene

previously investigated in this laboratory (*3*, *4*). System (*a*) was chosen because hydrodynamic conditions leading to a kinetic regime could be found. System (*b*) was chosen because in our apparatus it should always be diffusion controlled. The kinetic and diffusion regimes have been extensively discussed in Ref. *1*.

EXPERIMENTAL

Apparatus

Figure 1 shows the constant-interfacial-area stirred cell. Two high torque stirring motors, Cafrano Type RZR 50 having a continuously variable stirring speed from 45 to 2000 rpm, are connected to the upper and lower stirring shafts. Figure 2 shows in a schematic way the forced convection

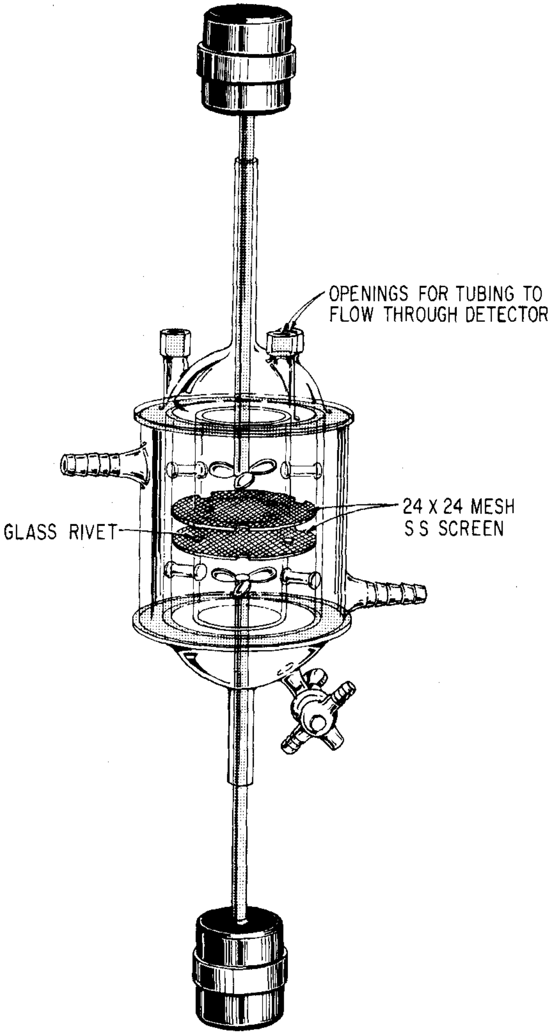

FIG. 1. ARMOLLEX cell for liquid–liquid extraction kinetic measurements.

inside the cell. Figure 3 shows the flow system, counting apparatus, and recording system used in conjunction with the stirred cell.

The flow through detector (Nuclear Enterprises Inc., San Carlos, California, Model NE 801) consists of a spiral of 0.7 mm (internal diameter) tubing whose walls emit light upon being excited by α, β, or γ activity (5). It is contained in a light-tight chamber along with a photomultiplier tube and

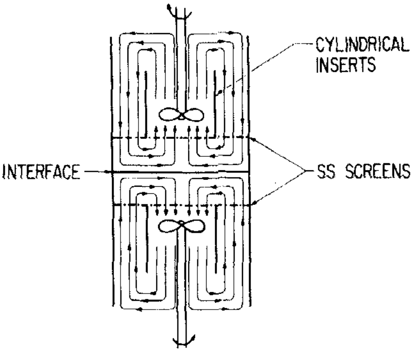

FIG. 2. Schematic illustration of forced convection inside the ARMOLLEX cell.

preamplifier. The signal is conducted out of the hood, where it is amplified, counted, and recorded as shown in Fig. 3. The volume contained in the counting loop is small (<1 mL) compared to that remaining in the cell, and the transit time and rate-meter time constants are both small compared to the time variation of the solute concentration in the aqueous phase.

Procedure

The extraction kinetic measurements have been performed in the following way: 65 mL of the aqueous electrolyte solution was introduced into the cell, the lower stirring was started, and the background signal recorded for a few minutes. Then a small aliquot of the radioisotope to be studied was added to the aqueous phase; a constant signal was obtained in a few minutes. The amount of radionuclide was chosen to give a signal that was nearly at the full recorder scale. The stirring of the aqueous phase was then interrupted and an equal volume of the extracting organic phase was slowly poured into the cell. Both the stirring motors were started and this was taken as the initial time of the kinetic experiment. The concentration vs time curve drawn by the recorder was followed for the time necessary to evaluate the rate constant of the heterogeneous process within a few percent.

Rate Data

The aqueous to organic mass transfer coefficients, k_{ao}, have been evaluated as described in Ref. *3*.

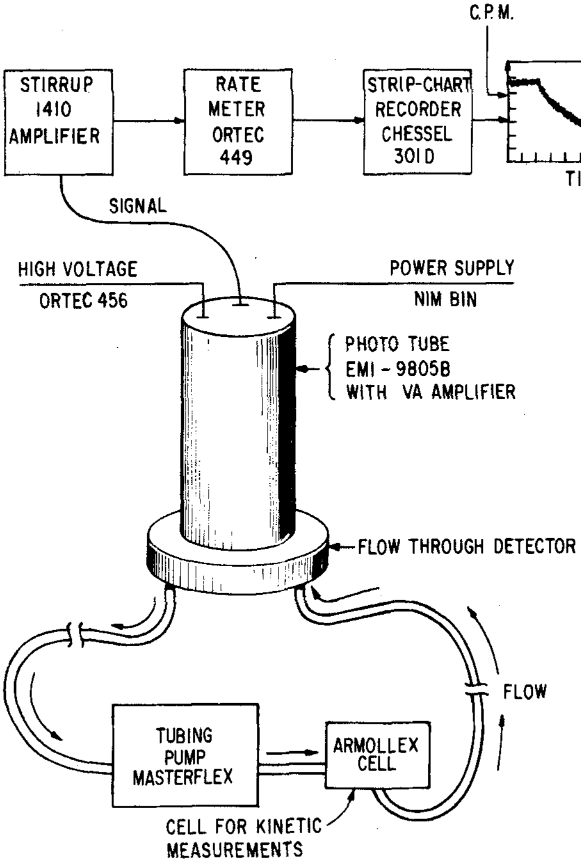

FIG. 3. Schematic illustration of flow system, counting apparatus, and recording system used with the ARMOLLEX.

Reagents

$^{152,154}Eu$ was an ANL stock; $NaNO_3$ and HNO_3 were reagent grade products. All aqueous solutions used in the Eu^{3+} extraction kinetic experiments had a constant ionic strength of 1.0 *M*, i.e., $[HNO_3] + [NaNO_3] = 1.0\ M$. The source and purification of bis(2-ethylhexyl)-phosphoric acid, HDEHP, have been described (*3*). The reagents used and the experimental conditions for the kinetics of pertechnetate (TcO_4^-) extraction by trioctylmethylammonium nitrate (TOMAN) were the same as those of Ref. *4*.

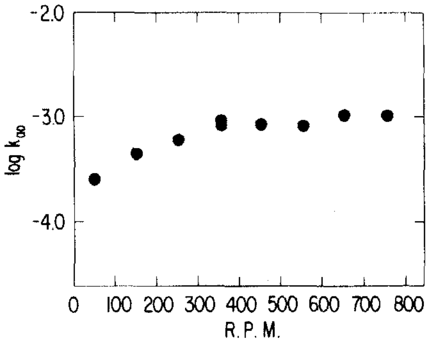

FIG. 4. Log k_{ao} vs rpm plot for the extraction of Eu^{3+} from $[HNO_3] = 0.01$ *M* + $[NaNO_3] = 0.99$ *M* into [HDEHP] = 0.02 *F* in *n*-dodecane. Aqueous and organic phases stirred at the same speed.

RESULTS

Eu^{3+} Mass Transfer Coefficients

The Eu^{3+} mass transfer coefficient refer to the overall extraction reaction (*3*):

$$Eu^{3+} + 3\overline{(HDEHP)_2} \rightleftharpoons \overline{Eu(DEHP)_3\ 3(HDEHP)} + 3H^+ \qquad (1)$$

where the bar indicates organic species. The organic diluent of HDEHP is *n*-dodecane and the aqueous electrolyte $[HNO_3] = 0.01$ *M*, $[NaNO_3] = 0.99$ *M*. The dependence of the mass transfer coefficient (k_{ao}) on the stirring speed of the propellers is shown in Fig. 4. In this set of experiments the stirring speed of both the aqueous and organic phase was varied simultaneously. The data indicate that in the range 350–750 rpm the mass transfer coefficient is independent of the stirring speed of the two phases, and thus a kinetic regime is operative. Figure 5 shows the k_{ao} data obtained by varying separately the aqueous and the organic phase stirring. The phase where the stirring rate was not varied was stirred at a constant value of 350 rpm. Again in this case it is observed that k_{ao} becomes independent of rpm at 350 rpm. The effect of the aqueous and organic stirring on k_{ao} is approximately the same. The Eu^{3+} mass transfer coefficients confirm the previous findings of Ref. *3*. They lead to the conclusion that in the ARMOLLEX apparatus a wide range of hydrodynamic conditions exist where the thickness of the diffusion films becomes small enough to make diffusional processes negligible with respect to the rate of the interfacial chemical reactions, or (alternatively) a constant

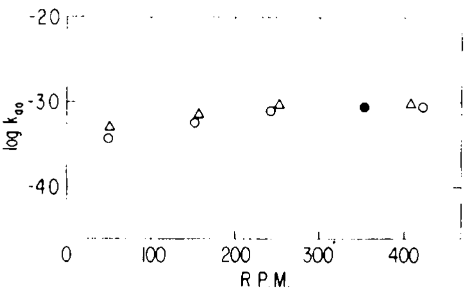

FIG. 5. Log k_{ao} vs rpm for the extraction of Eu^{3+}. The phases composition is the same as in Fig. 4. (○) Organic stirring = 350 rpm, aqueous stirring, variable; (△) organic stirring, variable, aqueous stirring = 350 rpm.

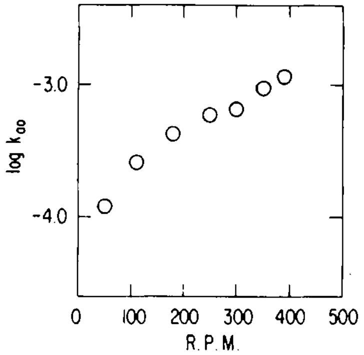

FIG. 6. Log k_{ao} vs rpm plot for the extraction of TcO_4^- from $[HNO_3]$ = 2 M into [TOMAN] = 0.01 M in *o*-xylene. Aqueous and organic phases stirred at the same speed.

thickness of the diffusion film, independent of the stirring speed, is reached at 350 rpm.

TcO_4^- Mass Transfer Coefficients

The TcO_4^- mass transfer coefficients refer to the overall extraction reaction (*4*):

$$TcO_4^- + \overline{ANO_3} \rightleftharpoons \overline{ATcO_4} + NO_3^- \qquad (2)$$

where the bar represents organic species and A = trioctylmethylammonium ion. In this case the organic diluent is *o*-xylene and the aqueous electrolyte

[HNO_3] = 2 *M*. The dependence of k_{ao} on the stirring speed of the two phases (simultaneously varied) is shown in Fig. 6. In this case, because of the lower kinematic viscosity of *o*-xylene compared to that of *n*-dodecane, the highest stirring rate obtainable in the organic phase before breaking of the interface is 400 rpm. The data of Fig. 6, showing a linear dependency of k_{ao} on rpm, are in qualitative agreement with a previously published stirring rate dependency (*4*). They lead to the conclusion that the mass transfer rate of TcO_4^- is controlled by interfacial film diffusion. This result was expected because the very rapid kinetics which characterizes ion-exchange reactions, such as (2), never allows the extraction system to become kinetically controlled, in spite of the decrease in the thickness of the diffusion film.

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