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KINETICS MEASUREMENTS IN LIQUID-LIQUID EXCHANGE APPLIED TO ISOTOPIC SEPARATION

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ABSTRACT

A method using calibrated drops, freely falling through a stationary continuous phase, is commonly used to study the kinetics of heat or mass transfer. This technique has been applied to uranium isotopic transfer between free ions dissolved in an aqueous phase and the corresponding complexes of an organic phase.

In this report, results are presented for experiments in which an aqueous hydrochloric acid solution of U(IV) of naturally occurring isotope composition and an organophosphorous extractant, diluted in aromatics, containing a U(IV) complex at ^{235}U atom fraction of 0.5% were used to determine isotopic mixing kinetics. The aqueous phase was fed as calibrated drops through the stationary organic phase at a velocity depending on the drop size and the physical characteristics of the contacted phases. The ^{235}U concentration of the effluent stream was determined as a function of the drop residence time.

An isotopic transfer coefficient k_A (cm/sec) was calculated. Its variation was investigated as a function of drop diameter between 0.07 to 0.4 cm. The plot of k_A vs diameter can be divided in two regions where k_A is practically constant. In the region of small drops, the activation energy of k_A was measured. The low value, 6 kcal/mole, indicates diffusional, rather than chemical transfer resistance. In the diffusion control region the isotopic

exchange kinetics are controlled by the physical characteristics of the phases. A model which was developed from this study is shown to be useful in optimizing the operation of the process.

INTRODUCTION

A method using calibrated drops, freely falling through a stationary continuous phase, is commonly used to study the kinetics of heat or mass transfer. In this study, the technique was applied to determine uranium isotope mixing kinetics between free ionic species dissolved in an aqueous phase and the corresponding complexes of an organic phase, with the two phases not in isotopic equilibrium.

These studies employed an aqueous hydrochloric solution of U(IV) at the isotopic composition

$N_O = 0.50$ atom % of ^{235}U,

and an organic solution consisting of U(IV) at the isotopic composition

$N_C = 0.72$ atom % of ^{235}U

which is bound with an organophosphorous extractant in an aromatic diluent.

A mathematical description of the process was developed under the assumption that chemical equilibrium is attained, so that ^{235}U transfer to one phase causes a corresponding transfer of ^{238}U in the opposite direction. Isotopic separation effects are not taken into account by the model, as none occurs in the system investigated.

EXPERIMENTAL

In order to obtain very small drops, only an aqueous dispersed phase was used. Preliminary experiments indicated that if k_A is the transfer rate constant to the aqueous drop, and k_0 the transfer rate constant to the organic drop, then

$$k_0 = mk_A, \qquad (1)$$

where m is the equilibrium distribution coefficient.

The aqueous phase was fed as calibrated drops which passed through the stationary phase at a velocity depending on drop size and the physical characteristics of the contacted phases. Drops were collected after 20, 50, 100, and 200 centimeters of fall.

The ^{235}U concentration of the aqueous stream was determined as a function of the residence time of the falling drop in the continuous phase. Note that the ^{235}U isotopic fraction in the continuous phase, N_C, was constant throughout the experiment because of the relatively large amount of U in this phase.

For the time interval dt, the rate of transport of ^{235}U from a drop is given by

$$\emptyset = k_A(N_t - N^*)C_A S, \tag{2}$$

where N_t is the isotopic fraction at time t, N* is its value when at equilibrium with the continuous phase, k_A is the global velocity transfer rate to the aqueous phase drop, C_A is the uranium concentration in the aqueous phase, and S denotes the area of the drop.

The rate of loss of ^{235}U from the drop is alternatively given by

$$\emptyset = VC_A(dN_t/dt), \tag{3}$$

in which V represents the volume of the drop. Substitution of Eq. (2) into Eq. (3) and the recognition that, to a very good approximation, $N^* = N_C$, yields

$$-\frac{dN_t}{(N_t - N_C)} = k_A \frac{S}{V} dt. \tag{4}$$

Upon integration, Eq. (4) becomes

$$-\ln \left[\frac{N_t - N_C}{N_o - N_C}\right] = k_A \frac{S}{V} t, \tag{5}$$

where N_o is the fraction of ^{235}U in the aqueous drop initially.

If the isotopic exchange efficiency E_i is defined as the amount of ^{235}U exchanged at time t relative to the maximum amount that can be exchanged, then

$$E_i = \frac{N_o - N_t}{N_o - N_C}, \qquad (6)$$

or

$$-\ln(1 - E_i) = k_A \frac{S}{V} t. \qquad (7)$$

For perfectly spherical drops of diameter d,

$$\frac{S}{V} = \frac{6}{d}, \qquad (8)$$

whence

$$-\ln(1 - E_i) = (6k_A/d)t. \qquad (9)$$

It should be noted that Eq. (9) does not take into consideration isotopic exchange during drop formation or coalescence. Hence, the linear relationship indicated by Eq. (9) is only valid over the time period $t_2 - t_1$ which corresponds to the approximate range

$0.2 < E_i < 0.8$.

RESULTS

The first phase of this study involved investigations of the dependence of drop velocity and of k_A on the diameters of the drops. The corresponding results are presented in Figs. 1 and 2.

The observed dependence of drop velocity on diameter is in good agreement with the relationship developed by Vignes (1). In the intermediate state, very small drops are rigid. Although circulation may occur within the drop, inducing acceleration, the surface remains stable up to a limiting diameter $d\ell$. In this state, the relationship between drop velocity, diameter, and the characteristics of the phases is given by (1)

$$v_\infty = \frac{d}{4.2}\left(\frac{g\Delta\rho}{\mu_c}\right)^{2/3}\left(\frac{\rho_c}{\mu_c}\right)^{1/3}\left(\frac{1 - g\Delta\rho d^2}{6\sigma_i}\right), \qquad (10)$$

where v_∞ is the velocity of a single drop in an infinite continuous phase, g is the acceleration due to gravity, $\Delta\rho = \rho_d - \rho_c$ is the difference between the specific gravity of the dispersed phase and

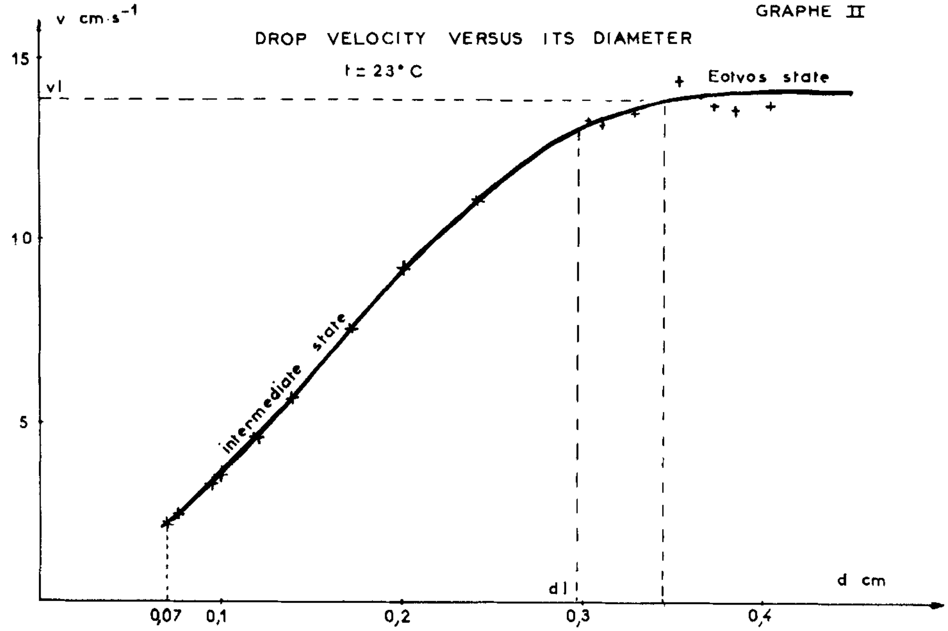

FIGURE 1. Dependence of drop velocity on drop diameter at 23°C.

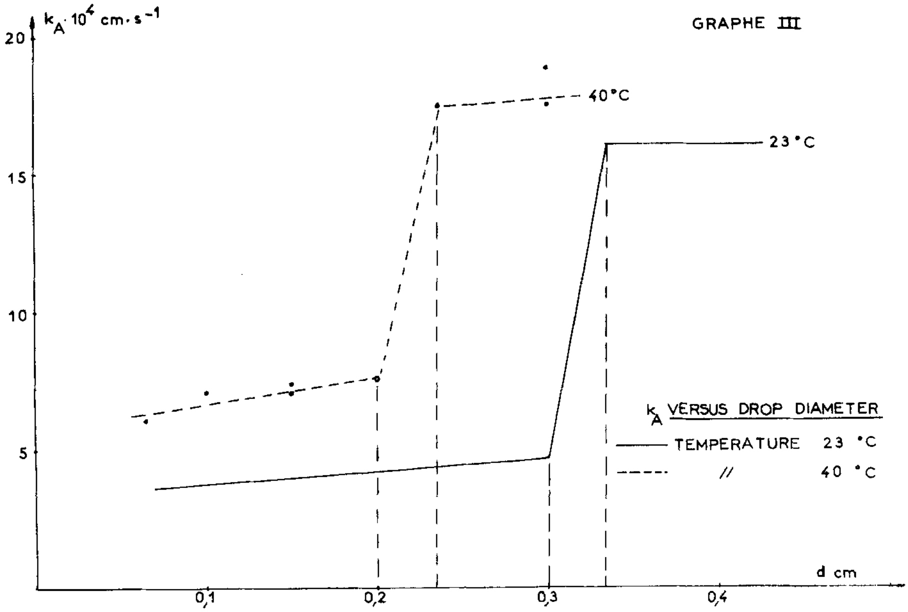

FIGURE 2. Dependence of k_A on drop diameter.

the continuous phase, μ_c is the coefficient of viscosity of the continuous phase, and σ_i represents the interfacial tension of the drop. The physical characteristics of the phases involved in this study are presented in Table 1.

<u>In the Eotvos state</u>, i.e., for drop diameters larger than $d\ell$, the drops no longer retain a spherical shape and so retard acceleration.

The dependence of k_A on drop diameter which is presented graphically in Fig. 2 displays two regions over which k_A is sensibly constant, and a "breakthrough" at the diameter $d\ell$. At 23°C, this breakthrough corresponds to a diameter of 0.3 cm; at 40°C, the same behavior was observed, except that the breakthrough occurred at a diameter of 0.2 cm.

The agreement between the behavior of k_A and the onset of the Eotvos state is very good; for the large drops, which are characterized by significant vibratory and oscillatory motions, the corresponding k_A values are a factor of three larger than those of the smaller size drops.

The activation energy characteristic of the process in smaller size drops ($d \leq 0.2$ cm) is about 6 kcal/mole over the temperature range 20 to 65°C. Moreover, at 23°C, when the concentration of organophosphorous compound in the organic phase decreases, thus

TABLE 1

Physical Characteristics of the Phases at 25°C

Continuous organic phase	Dispersed aqueous phase
$D_c = 1.2 \times 10^{-6}$ cm^2/sec	
$\rho_c = 1.054$ g/cm^3	$\rho_d = 1.43$ g/cm^3
$\mu_c = 0.038$ P	$\mu_d = 0.027$P

$\sigma_i = 12$ dyne/cm

yielding a solution of decreased viscosity, the value of k_A increases and the activation energy decreases. The low value of the activation energy and the inverse dependence of the rate constant on viscosity is indicative of a diffusion-controlled transfer process. The experimental data were therefore analyzed in terms of a diffusional transfer model.

According to double film theory,

$$\frac{1}{k_A} = \frac{1}{k'_A} + \frac{m}{k'_0} + \frac{1}{\alpha} , \tag{11}$$

where $(1/\alpha)$ represents the interfacial chemical resistance term (which is negligible in the present study), $(1/k'_A)$ denotes the resistance within the drop, $(1/k'_0)$ is the resistance outside the drop, and $m(= C_A/C_0)$ is the ratio of uranium concentration in the aqueous and organic phases. Since k_A was observed to be virtually invariant with respect to drop diameter over the range 0.07 to 0.3 cm, this suggests that the overall resistance to transfer is due mainly to the continuous phase, whence

$$\frac{1}{k_A} \sim \frac{m}{k'_0} = \frac{C_A}{C_0 k'_0} . \tag{12}$$

Equation (12) permits a determination of k'_0 from the experimental data.

A modification of the model developed by Rowe, Claxton, and Lewis (2) yields a good correlation of the experimental values:

$$Sh = C^{ste} Re^{1/2} Sc^{1/3} , \tag{13}$$

where

Sh = Sherwood number = $k'_0 d/D_c$,

Re = Reynolds number = $\rho_c v d/\mu_c$,

Sc = Schmidt number = $\mu_c/\rho_c D_c$,

and C^{ste} is an experimentally determined constant. The diffusion coefficient may be replaced by the Stokes-Einstein relationship

$D_c \mu_c / T$ = constant,

and Eq. (13) yields, at constant temperature, the result

$$k_0' = C_1^{ste} F, \tag{14}$$

where

$$F = (v/d)^{1/2} \rho_c^{1/6} / \mu_c^{5/6}, \tag{15}$$

and C_1^{ste} is an adjustable constant. In view of Eq. (10), this expression indicates that k_0' depends only weakly on drop diameter.

The extent to which Eq. (14) may be used to correlate the experimental data is shown in Table 2. It was also noted that k_0'/F remains constant when the organophosphorous and the uranium concentrations in the phases are varied.

CONCLUSIONS

The mathematical model appears to correlate the experimental data reasonably well; as a result, it is possible to use the model as a guide in determining which parameters should be optimized in order to improve the rate of transfer. Equations (10) and (14) can be combined to yield

$$k_0' \sim \frac{C_0}{C_A} \frac{\Delta\rho}{\mu_c}^{1/3},$$

which indicates that the rate of transfer is strongly dependent on the viscosity of the continuous phase and to a lesser extent on $\Delta\rho$.

Figure 3 is a graphical display of the dependence of $K_A (= k_A/d)$ on drop size. These data indicate that it is necessary to produce drops which are less than one millimeter in diameter in a spray column (or a pulsed column) in order to obtain large values of K_A. Moreover, although the use of surface

TABLE 2

Correlation of the Experimental Data with a Diffusional Model

d (cm)	v (cm/s)	$10^4 k_A$ (cm/s)	$(10^4 k_0')_{exp}$ (cm/s)	$(10^4 k_0')_{calc}$ (cm/s)
0.1	3.4	3.7	8.9	8.6
0.15	6.2	4.0	9.6	9.4
0.25	9.2	4.2	10.0	10.0
0.3	11.5	4.5	10.8	10.0

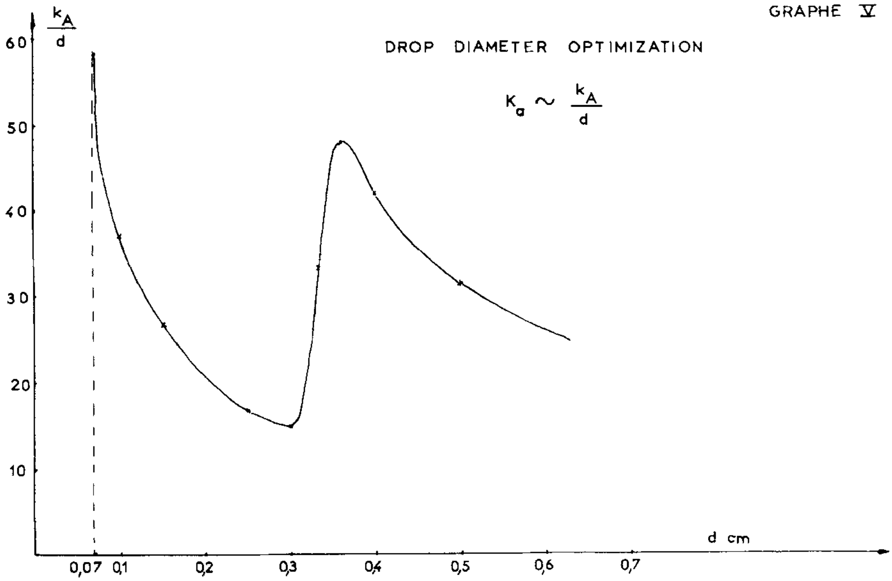

FIGURE 3. Dependence of K_A on drop diameter.

active agents does result in the formation of smaller drops, it also yields smaller values of k_A.

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