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Modeling of the Permeation of Thorium through Liquid Emulsion Membrane

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Abstract: A general permeation model for the separation of thorium by liquid emulsion membrane (LEM), using theonyletrichloroacetone HTTA as a carrier is presented. The internal mass transfer in the W/O emulsion drop, the external mass transfer around the drop, the rates of formation, and the decomposition of the complex at the external aqueous-organic interface were considered. Further, the leakage of the internal aqueous phase to the external phase due to the membrane break-up is also taken into account. The batch extraction of thorium using HTTA as a carrier was carried out under various experimental conditions. It is found that the extraction rates can be satisfactorily simulated by the proposed model.

Keywords: Liquid emulsion membrane, thorium extraction permeation, LEM modelling

INTRODUCTION

The concept of a permeable barrier for use in solvent extraction was first proposed by Li (1) in 1968 in the form of a liquid emulsion membrane. Ho and Li (2) provided a good review of this technology. Liquid Emulsion Membrane (LEM) is formed by first capsulation of the aqueous receiving phase or the stripping phase within a hydrophobic liquid membrane. The formed emulsion is further dispersed within the continuous external aqueous feed phase. Mass transfer occurs between the external phase and the internal phase. Once this mass transfer is complete, settling is used to separate out the

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external phase followed by breakage of the internal emulsion system. The operation can be completed within the mixer settler type units or in continuous counter current columns (3, 4). In a previous work, the recovery of uranium and thorium from an acidic solution has been carried out by using TOPO in cyclohexane, as a carrier, span 80, as a surfactant and sodium citrate as a stripping agent (5, 6). A method for the separation of trace Th-234 from its parent U in macro-amounts was developed using HDEHP in cyclohexane as a carrier, polyethylene glycol dioleate as a surfactant, and HCl as a stripping agent (7).

The present work is directed mainly to investigate the possible recovery of thorium from nitrate medium using LEM technique. Teramoto et al. (8) proposed a general mass transfer model for the extraction of weak bases and weak acids by LEM in which the diffusion in the W/O emulsion drops, the external mass transfer, and both the chemical and phase equilibria were taken into account. This study was carried out using HTTA as a carrier to extract thorium from an acidic solution based on the proposed mass transfer model of Teramoto 1983 (8) and the Chan and Lee model 1986 (9). The permeation rate of thorium through the membrane can be quantitatively explained by the proposed model.

THEORY

It is assumed that the mass transfer resistance in the internal aqueous phase is neglected because of the very small size of the internal droplet and also that a mono-basic acid such as hydrochloric acid and nitric acid is used as the internal stripping agents. The elementary steps of thorium permeation through the liquid membrane are as follows.

1. Diffusion of thorium and hydrogen ions through the stagnant film of the external aqueous phase.
2. A complex formation between Th^{4+} and the chelating agent, at the external interface of the O/W emulsion drop.
3. Diffusion of the complex and the chelating agent in the peripheral oil layer of the emulsion drop.
4. Diffusion of the complex and the chelating agent through the interstitial oil membrane phase.
5. Stripping of thorium at the interface between the oil membrane phase and the internal aqueous phase droplets containing nitric acid.

It has been found that the reaction between Th^{4+} and HTTA occurs at the organic–aqueous interface, and also that the forward and the reverse reaction rates are represented as follows:

$$A^{4+} + 2HB \longrightarrow AB_2 + 2H^+$$

EXPERIMENTAL

The LEM used was generally prepared by mixing 25 cm^3 of the organic, HTTA with span 80 as a surfactant in toluene. To this mixture 25 cm^3 of the stripping aqueous phase solution, was added. The emulsification was performed with an ultra high-speed homogenizer IKA, Ultra-Turrax T25, (USA). The rate of emulsion stratification, without contacting the feed solution, was 0.1% per hour.

The water in oil (W/O) emulsion was then poured into the external aqueous phase containing Th. The LEM system was stirred with a magnetic stirrer of the type Cole palmer (USA) of variable speed ranging from 100 to 1400 rpm. Samples were withdrawn from the external phase, and the thorium concentration was analyzed by UV-visible spectrophotometer (10). The fraction of leakage F, which is defined as the ratio of the volume of the internal phase, which leaks to the external phase to the initial volume of the internal phase, was calculated by:

$$F = 1 - \Phi\,[C_{ex}]/\ \Phi\phi\ [C_{in,o}] \qquad (1)$$

The drop size distributions of the W/O emulsion was measured by a photographic method. Unless otherwise stated the concentration of span 80 was 4% v/v, the stirring speed 350 rpm, the temperature was 298 K, and the initial concentration of thorium in phase III was zero.

RESULTS AND DISCUSSION

LEM Stability

Different surfactants were tested for investigation the stability of prepared membrane. The volumetric rate of leakage v_b of the internal aqueous phase III to the external aqueous phase I due to the membrane break-up was obtained by plotting F (fraction of leakage) against time t as shown in Fig. 1. Considerable leakage was observed when the emulsion was dispersed at the start of the extraction when using span 85 and Arlacel A, and F increased linearly with time. The value of v_b was calculated as a product of the slope and the volume of the internal aqueous phase as shown in Table 1 (8). The results revealed that span 80 is the best stabilizing agent and span 80 of concentration to be used for preparing a stable LEM, Fig. 2.

Effect of Hydrogen Ion Concentration in the Feed Solution on the Permeation Rate

The effect of the hydrogen ion concentration of the external phase is closely connected with the forward reaction rate and the distribution ratio of

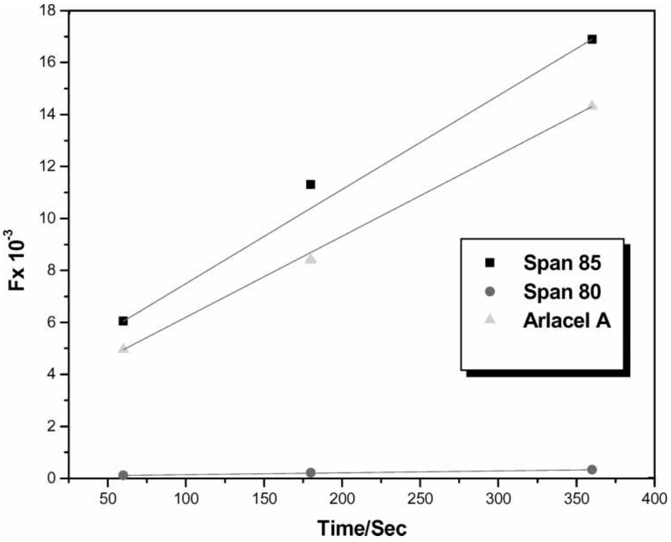

Figure 1. Determination of v_b with different surfactants with concentration 4%.

thorium. In this study, the hydrogen ion concentration was varied in the range from 0.01 to 0.1 M to investigate the effect of the reaction rate on the extraction rate and how the rate-determining step changes with the hydrogen ion concentration. The effect of initial hydrogen ion concentration is shown in Fig. 3. As anticipated from Eq. (3) the higher the $H_{I,o}$, the lower the extraction or the permeation rate. Under the condition of higher $H_{I,o}$, the rate of the complex formation at the interface of the drop is slow and this step is the determining rate. On the other hand, when $H_{I,o}$ is low, the reaction rate is fast and $H_{I,o}$ has little influence on the rate.

Effect of HTTA Concentration

As shown in Fig. 4 the effect of HTTA concentration on the distribution coefficient of Th (IV) and from log-log curve, we can confirm the mechanism of

Table 1. Effect of surfactant type and concentration on the stability of LEM

Types of surfactant	$v_b \times 10^{-5}$ ml/Sec	Surfactant Conc. [Span 80]	$v_b \times 10^{-5}$ ml/Sec
Span 85	18	0.8%	10
Span 80	0.036	2.0%	3.5
Arlacel A	15	4.0%	0.036

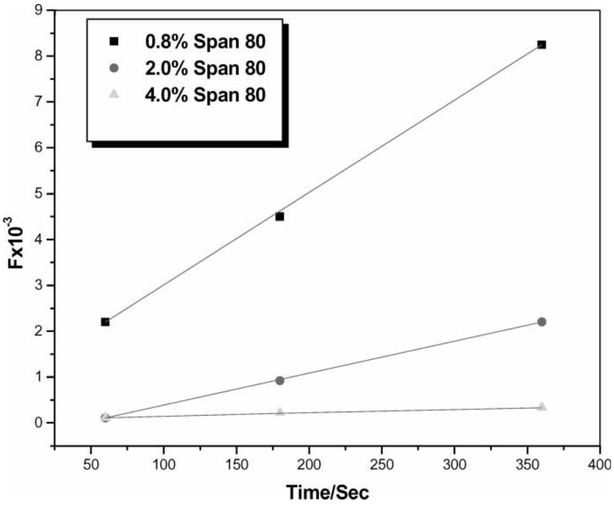

Figure 2. Determination of v_b with different span 80 concentrations.

HTTA with Thorium, the slope of the log-log curve is 2.0, which means that the HTTA contributes in the reaction as follows:

$$Th^{4+} + 2HB \longrightarrow ThB_2 + 2H^+$$
$$A + 2B \longrightarrow C + 2H$$

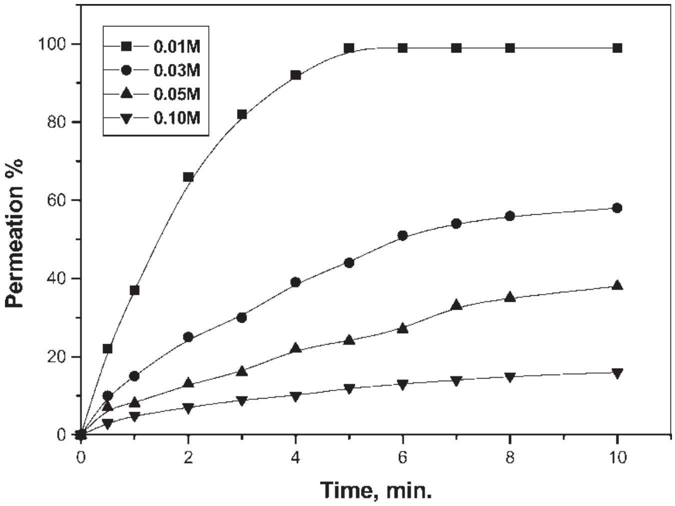

Figure 3. Effect of initial hydrogen ion concentration in the external phase on the permeation rate of Th.

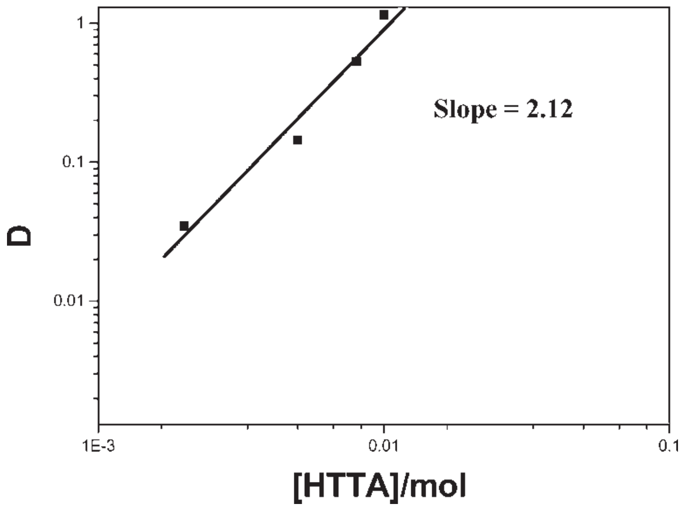

Figure 4. Log log relation between HTTA concentration and distribution coefficient.

When we adapted the multilayer shell model in which the W/O emulsion drop consists of multilayer shells each of which contains the oil membrane phase and the internal droplet. The mass transfer of the carrier and the complex occurs between adjacent shells and the concentrations of the chemical species are uniform in each shell. The reaction between thorium ion and HTTA and its equilibrium are expressed by the following equations (8).

$$K_{ex} = [ThB_2][H^+]^2/[Th^{4+}][HB]^2 = (CH^2/AB^2) \tag{2}$$

$$r_f = k_f(AB/H - CH/K_{ex}B) \tag{3}$$

Effect of the Addition of Anionic Surfactant to the External Phase

As described before, it was deduced that the reaction at the interface between the external aqueous phase and the W/O emulsion drops are rate determining when HI,0 is considerably high. Therefore under this condition, the rate of the extraction may be increased by increasing the rate of the interfacial reaction. It was anticipated that an anionic surfactant added to the external aqueous phase is adsorbed at the aqueous-organic interface and the interface has a negative charge. Then the interface attracts Th^{+4} ions by the electric force resulting in a much higher thorium concentration at the interface than in the bulk. Hydrogen ion may also be concentrated at the interface. However the Th^{+4} ion is more concentrated at the interface than the univalent hydrogen ion. Thus the concentration ratio $[Th^{+4}]/[H^+]$ at the interface is higher than in the bulk liquid. Because the interfacial reaction is proportional to

$[Th^{+4}]/[H^{+}]$ as indicated in Eq. (3), the extraction rate increases by adding anionic surfactants to the feed solution. As shown in Fig. 4 the permeation rate was remarkably enhanced by the addition of a very small amount of sodium dodecyle sulfate (Figure 5).

ESTIMATION OF PARAMETERS

A general permeation model for the permeation of thorium by a liquid emulsion membrane using HTTA as carrier is presented. The external mass transfer around the drop k_A, the rate of formation and decomposition of the complex at the aqueous/organic interface k_f, and the internal mass transfer of carrier and complex in the W/O emulsion drop k_B and k_C respectively, were calculated.

To better understand the transfer mechanism, the transfer sequence needs to be examined in more detail. There are actually five steps involved, and each step has a specific mass transfer coefficient. If the transfer is from the external phase to the internal phase as shown in Fig. 6, the first step is the mass transfer from the external phase to the interface between the external and the membrane phase. This is represented by the mass transfer coefficient k_A. The second step is the transfer across this interface, which can be represented by km. The third step is diffusion through the membrane phase represented by the mass transfer coefficient k_C or k_B. The fourth step is the transfer across the interface between the membrane and the internal phase represented by the

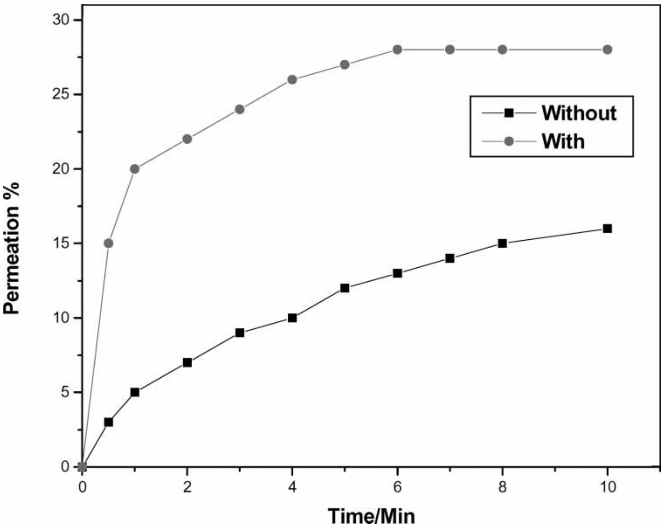

Figure 5. Effect of the additon of anionic surfactant on the extraction rate.

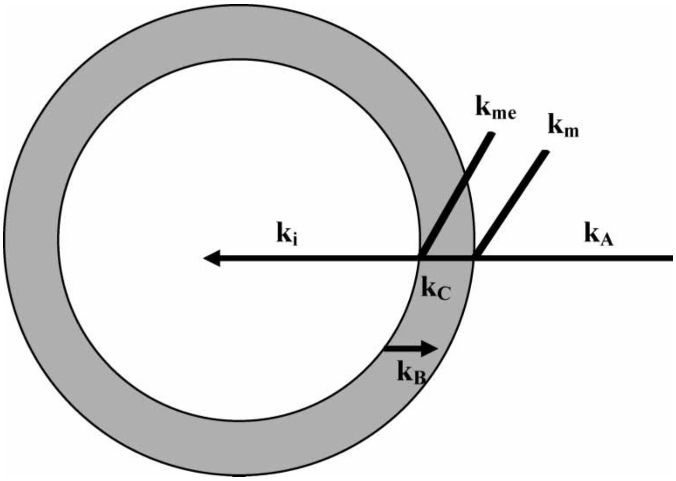

Figure 6. Permeation model based on Teramoto et al.

mass transfer coefficient k_{me}. The last step is the diffusion into the internal phase represented by k_i (8).

This mass transfer analysis is built on an immobilized hollow spherical emulsion globule model (Chan and Lee, 1986) that assumed a couple countercurrent transport mechanism. As shown in Fig. 7 the basic steps of metal permeation through the liquid membrane including the following

i. the metal ion diffuses from the external aqueous phase to boundary of the membrane phase;
ii. the metal ion forms a complex with carrier on the external interface;
iii. the complex diffuses to the center of the emulsion globule;

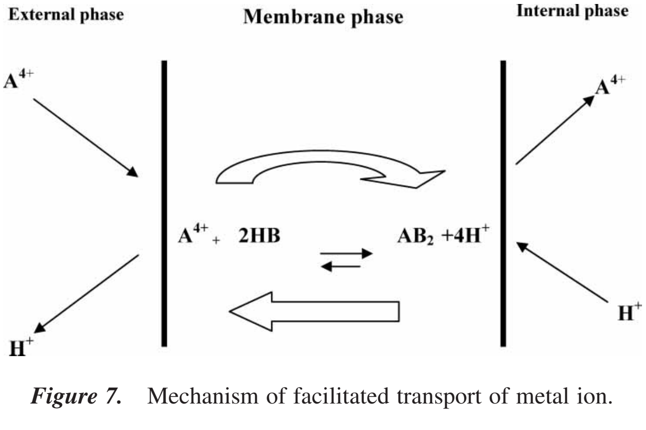

Figure 7. Mechanism of facilitated transport of metal ion.

iv. a stripping reaction occurs when the complex diffuses toward the internal aqueous phase and the metal ion is released to the internal aqueous phase;
v. the carrier diffuses from the internal interface to the external interface and forms a complex again with the metal ion.

In order to simplify the mathematics of model development the following assumptions are made:

i. an ideal batch system is under complete mixing and constant temperature operation;
ii. the carrier and the solvent are insoluble in water;
iii. the physical and the transport properties are constant during the permeation process;
iv. the droplets dispersed in the external phase as the emulsion globules are immobile and are uniformly distributed.

The values of k_A (the mass transfer around the drop) and k_f (the rate of formation of complex at the aqueous/organic interface) were obtained as follows, the rate determining step of thorium extraction changes depending on the experimental conditions that, $A_{I,o}$ (initial metal ion concentration in the outer phase) is low compared with B_o (initial concentration of carrier), the rate is limited by diffusion of thorium through the external aqueous stagnant film if H_I (hydrogen ion concentration in the outer phase) is sufficiently low and by the reaction at the interface of the emulsion drop if H_I is high, when the reverse reaction is ignored (Table 2). The extraction rate is expressed as follows

$$\begin{aligned} V_I dA_I/dt &= k_A S(A_I - A_{I,i}) = k_f S A_{I,i} B_i/H_I \\ &= A_I S/1/k_A + H_I/k_f B_o = K_A S A_I \end{aligned} \tag{4}$$

Integration of equation (4) gives

$$\ln A_I/A_{I,o} = \ln y = -\{K_A a_o/(1-\Phi)\}t = -\{3K_A\Phi/(1-\Phi)R\}t \tag{5}$$

Table 2. The values of various physical parameters

Parameters	Thorium
k_A	0.039 cm/sec.
k_B	1.86×10^{-3} cm/sec.
k_C	6.85×10^{-4} cm/sec.
D_C	1.37×10^{-7} cm^2/sec.
D_B	2.01×10^{-6} cm^2/sec.
k_f	4.08×10^{-3} cm/sec.
δ	10.8 μm

Where:

$$1/K_A = 1/K_A + H_I/k_f B_o \tag{6}$$

Experiments were carried out at various hydrogen ion concentrations with other conditions kept constant. As shown in Fig. 8, the plot of ln y vs t gives straight lines and K_A's are calculated from their slopes. Figure 9 indicates that the plot of $1/K_A$ against H_I also gives straight lines in accordance with eq. (6). The values of k_A and k_f can be calculated from their intercept and slope, respectively.

It was impossible to determine k_B or k_C in the W/O/W multiphase system, however, a rough estimate was made by the extraction experiment using an agitation vessel 7 cm and 14 cm height equipped with a magnetic stirrer. 200 cm^3 of the aqueous thorium solution was first introduced into the vessel. Then 50 cm^3 of the W/O emulsion phase was carefully poured over the aqueous phase so as not to disturb the interface. Stirring in the emulsion phase was started at 100 rpm and samples were taken from the aqueous phase for analysis. Under the condition that $A_{I,o}$ was sufficiently high and $H_{I,o}$ was considerably low, the resistance of the aqueous stagnant film diffusion and the interfacial reaction could be neglected. It was anticipated that, the diffusion rate of the complex in the emulsion phase would be fast due to the convection caused by agitation. The experimental results are shown in Fig. 9.

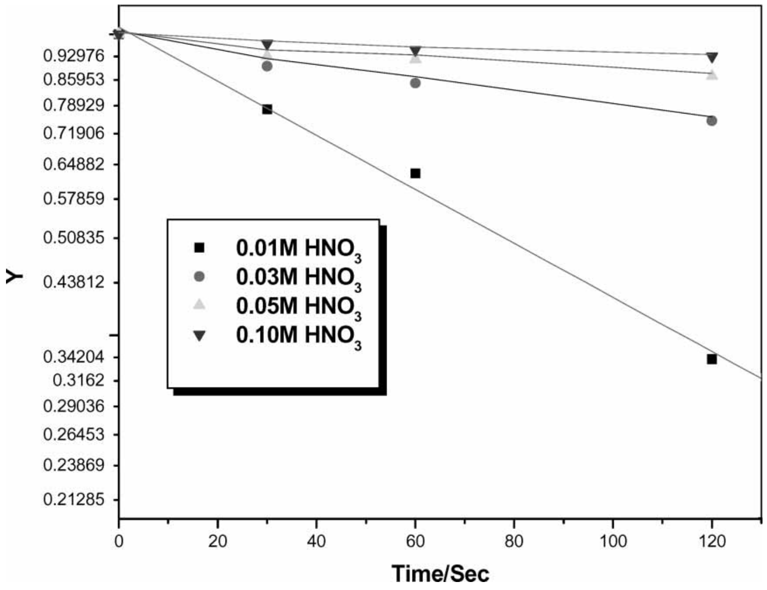

Figure 8. Determination of K_As.

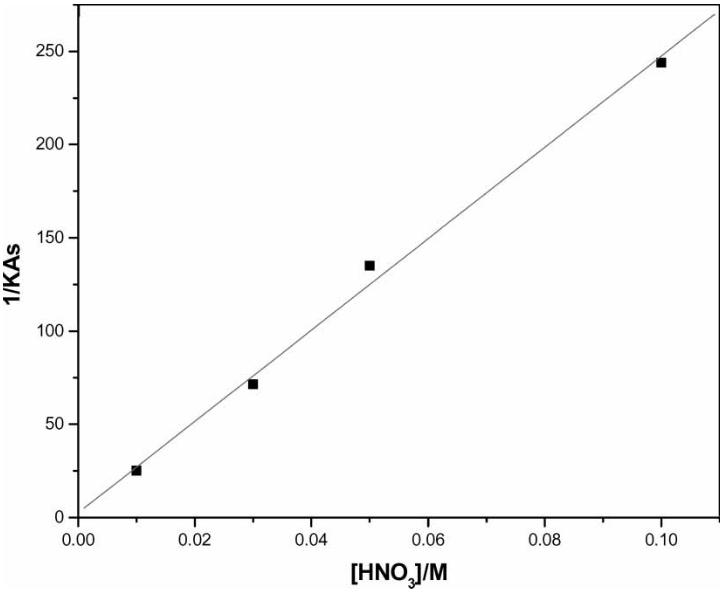

Figure 9. Determination of k_A and k_f.

Thorium concentration in the aqueous phase decreased linearly with time, suggesting that, the rate of the extraction was independent of thorium concentration. This means that, on the aqueous side of the oil layer almost the entire carrier was consumed by complexation with thorium. Thus the extraction rate is expressed by:

$$-V_I dA_I/dt = k_B S(B_o - B_i)/2 = k_B S(B_o - 0)/2 \tag{7}$$

From Eq. (7) and the data shown in Fig. 7 the value of k_B was calculated and also the values of k_C was estimated using the relation,

$$k_C = k_B(D_C/D_B) \tag{8}$$

The diffusion coefficient of carrier (B) and complex (C) estimated by Wilke–Chang is given in Eqs (9) and (10) and shown in Figs. 10 and 11.

$$A_I/A_{I,o} = S(2\Phi D_C)^{0.5}(B_o H_{III,o} t)^{0.5}/3A_{I,o}V_I \tag{9}$$

$$D_B = 7.4 \times 10^{-8}(\acute{\oslash} M)^{0.5} Tk/\mu V_B^{0.6} \tag{10}$$

Then the oil layer thickness calculated from $\delta = D_B/k_B$ was 18.5 μm.

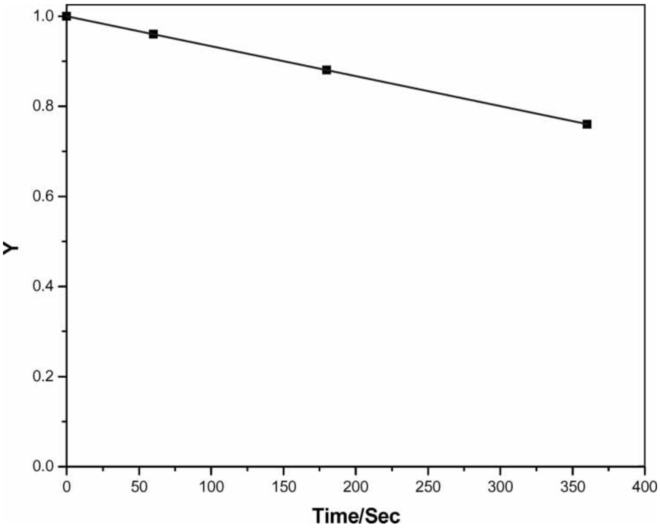

Figure 10. Determination of k_B.

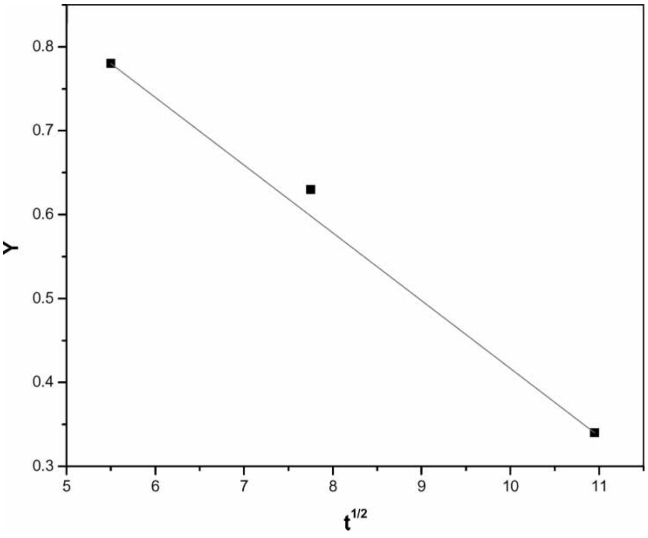

Figure 11. Determination of D_c.

CONCLUSION

Experimental data on the batch extraction of thorium by a liquid emulsion membrane using a chelating agent HTTA as carrier were analyzed on the basis of a general permeation model in which the diffusion in the W/O emulsion drop, the external mass transfer around the drop, the rate of the formation, as well as the decomposition of the complex at the aqueous-organic interface, the membrane thickness, and the leakage of the internal phase to the external phase due to the membrane breakup were taken into account.

The verification of the results by using an anionic surfactant revealed that the reaction at the organic – aqueous interface is the rate-determining step at a slightly high hydrogen ion concentration in the external aqueous phase and also the present model used in this study gives a better understanding and conforming to the experimental results.

ABBREVIATIONS

A	concentration of metal ions, M
B	carrier concentration, M
C	concentration of complex, M
D	molecular diffusivity, cm^2/s
F	fraction of volume of internal aqueous phase which leaks to outer phase due to membrane break-up
H	concentration of hydrogen ion, M
K_A	overall mass transfer coefficient, cm/s
K_A	mass transfer coefficient of metal ions under investigation through the outer aqueous phase, cm/s
K_B, k_C	mass transfer coefficients of carrier and complex through the oil layer around W/O emulsion drop, respectively, cm/s
k_f, k_r	Forward and reverse reaction rate constants, cm/s
K_{ex}	extraction constant
r_f	rate of extraction
R	radius of W/O emulsion drop
S	total interfacial area between outer phase and W/O emulsion drops, cm^2
t	time, s
V	volume, cm^3
v_b	volumetric rate of leakage from the internal aqueous phase to the outer aqueous phase. cm^3/s
ϕ	volume fraction of W/O emulsion in W/O/W multiphase emulsion
Φ	volume fraction of the internal aqueous phase in W/O emulsion drop
D_e	diffusion coefficient of metal ions in the outer phase, cm^2/s
D_C	diffusion coefficient of complex in the membrane phase, cm^2/s
M’	Molecular weight of solvent
T_k	absolute temperature

V_B	molecular volume $cm^3/mole$
μ	viscosity of solvent
I	phase I (external aqueous phase)
II	phase II (organic membrane phase)
III	phase III (internal aqueous phase)
i	Interface between external aqueous phase and W/O emulsion drop
O	Intial value

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