

Kinetics of Sm^{3+} extraction by BTMPPA using single drop technique

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ABSTRACT

The rate of Sm(III) extraction from acidic nitrate-acetate medium by bis(2,4,4-trimethylpentyl)phosphoric acid (Cyanex 272, BTMPPA, H_2A_2) in toluene has been measured by the single drop technique. The rate of mass transfer per unit area is found to be proportional to $[\text{Sm}^{3+}]$, $[\text{H}_2\text{A}_2]_{(o)}$, $[\text{H}^+]_{(i)}$ at the interface. The extraction rate constant, k_F , has been determined to be $10^{-7.15}$ m/s. The rate expression can be written as;

$$F_{\text{Sm}} = 10^{-7.15} [\text{Sm}^{3+}] [\text{H}_2\text{A}_2]_{(o)} [\text{H}^+]_{(i)} \text{ kmol/m}^2\text{s}$$

Analysis of the rate expression suggests that the formation of $[\text{Sm}(\text{HA}_2)]^{2+}$ at interface from Sm^{3+} and HA_2^- is the rate-determining step for the extraction of Sm(III).

1. INTRODUCTION

The wide noble applications of lanthanides are well known and separation of these elements is still a key issue to the researcher due to its similar chemical properties. It was shown that investigation of individual elements is necessary to evaluate the details behavior of each element (El-Henfy and El-Dessouky, 2006).

Simple single drop technique which can be easily modified was found very suitable to establish the reaction mechanism for solvent extraction in the earlier investigations (Biswas et al., 1996, 1997; Biswas and Begum, 2000; Biswas and Begum, 2001). Extraction mechanism of solvent extraction shows the interest to the academician and industrialist since its the prime consideration for setting up the perfect direction of a process. In the previous study for the extraction of La(III) by BTMPPA, it has been shown that extraction mechanism depend on

the time of extraction (Saleh et al. 2002a,b; Bari et al. 2006). But equilibrium study is able to reveal the extraction mechanism at the equilibrium condition only. Therefore study of kinetics of Sm(III) extraction by BTMPPA is studied to find out the extraction mechanism which would be useful in the processing industries.

2. EXPERIMENTAL

Samarium oxide (99.9% purity) was obtained from Sigma. Stock solution of samarium (10 g /L) was prepared from its pure oxide. Commercial grade bis-(2,4,4-trimethylpentyl)phosphinic acid was kindly supplied by Cytec Industries Inc., Canada. Its purity as determined by the potentiometric titration method was 92 %. It was purified to about 99.5% by the middle phase micro-emulsion method (Hu et al., 1995). For the preparation of the stock solution of BTMPPA, 582.91 g of chemically pure BTMPPA was placed into a 1 L volumetric flask and was made up to the mark with toluene so that the solution was 1 M in dimeric BTMPPA.

A double-beam spectrophotometer (Model, U2000, Hitachi) with 1.0 cm corex cuvette was used for all absorbance measurements. A pH meter (Model EA940, Orion) equipped with a combination glass electrode, was used to determine the pH of the aqueous solution and to perform the potentiometric titration. A wrist-action flask shaker (Model SFI, Stuart Scientific) was used for the stripping. The Sm(III) content in the collected drops was estimated by stripping with 5 mL of 2 M HNO₃. For a particular height of the column, the time of contact of the organic drop with the aqueous phase was calculated by averaging the rise time required for at least 10 drops. The experiments were conducted at ambient temperature.

The design of the single drop apparatus and procedure for kinetic work were given in Figure 1 (Saleh et al., 2002b; Biswas et al., 1996; Hughes et al., 1976). The amount of samarium transfer per unit area per second or flux F , during extraction can be calculated from the following equation Eq. (1) (Biswas et al., 96, 97; Saleh et al., 2002b).

$$F_{\text{Sm}} = \frac{[\text{Sm}]_{(o)} \times V_t^{1/3}}{(67.05 \times 10^5) \times N^{1/3} \times t} \text{ kmol/m}^2\text{s} \quad (1)$$

The following Eq. (2) can be derived and also in logarithmic form of the equation can be used for the evaluation of a , b , c and k_F as described in the studies of kinetics of lanthanum(III) extraction (Saleh, et al. 2002b).

$$F_{Sm} = a_{Sm}^{3+} / t.A = k_F [Sm^{3+}]^a [H^+]^b [H_2A_2]^c, (o) \quad (2)$$

At constant concentrations of Sm^{3+} , H^+ and H_2A_2 of (sm), (h) and (h_2a_2), respectively, the data on the effects of temperature on the rate of extraction can be treated by the Arrhenius equation from which the value of apparent activation energy, E_a , can be calculated and by the specific rate theory from which the value of ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger can be calculated (Bari et al. 2006; Saleh et al., 2002b; Maron and Frutton, 1975).

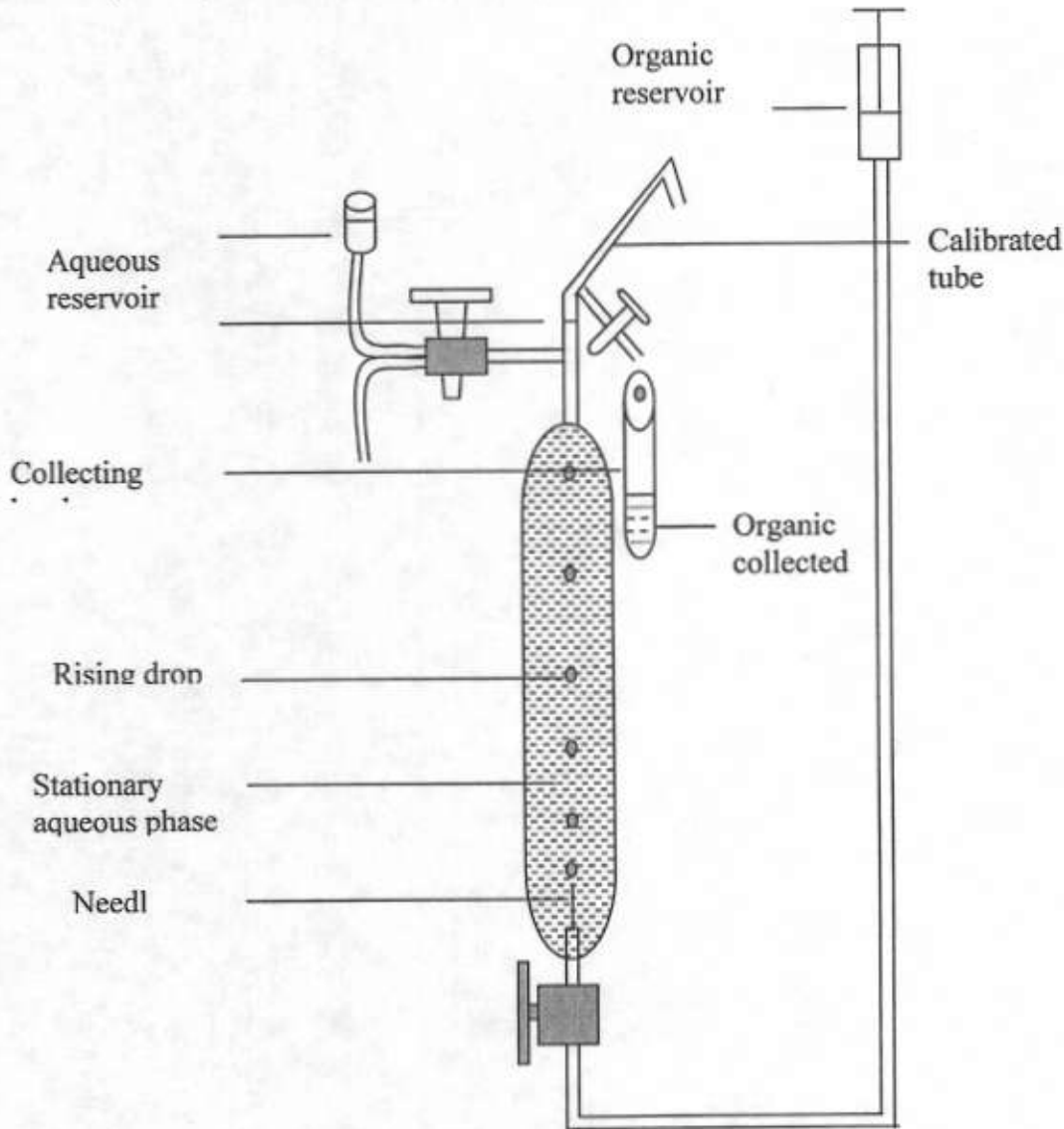


Fig. 1. Single drop apparatus (Rising) (Whewell *et. al*, 1975; Farbu *et. al*,1974).

3. RESULTS AND DISCUSSION

The common end effect problem due to the mass transfer during drop formation and coalescence in the single drop technique can be overcome after determining the mass transfer rates during the rising of a single drop of the organic phase through the aqueous phase

contained in the column of different heights. The Farbu plot, i.e., the mass transfer during drop rise time versus the drop rise time is shown in Figure 2. It is seen that mass transfer during drop rise is proportional to the drop rise time. However, the straight lines did not pass through the origin, intercepts of the time axis of 1.5 was obtained instead. This is equivalent to the amount of mass transfer during drop formation and coalescence. Therefore, in subsequent experiments, a column of 70 cm was used and 1.5 second was added to the drop rise time in calculating the fluxes for Sm(III) extraction.

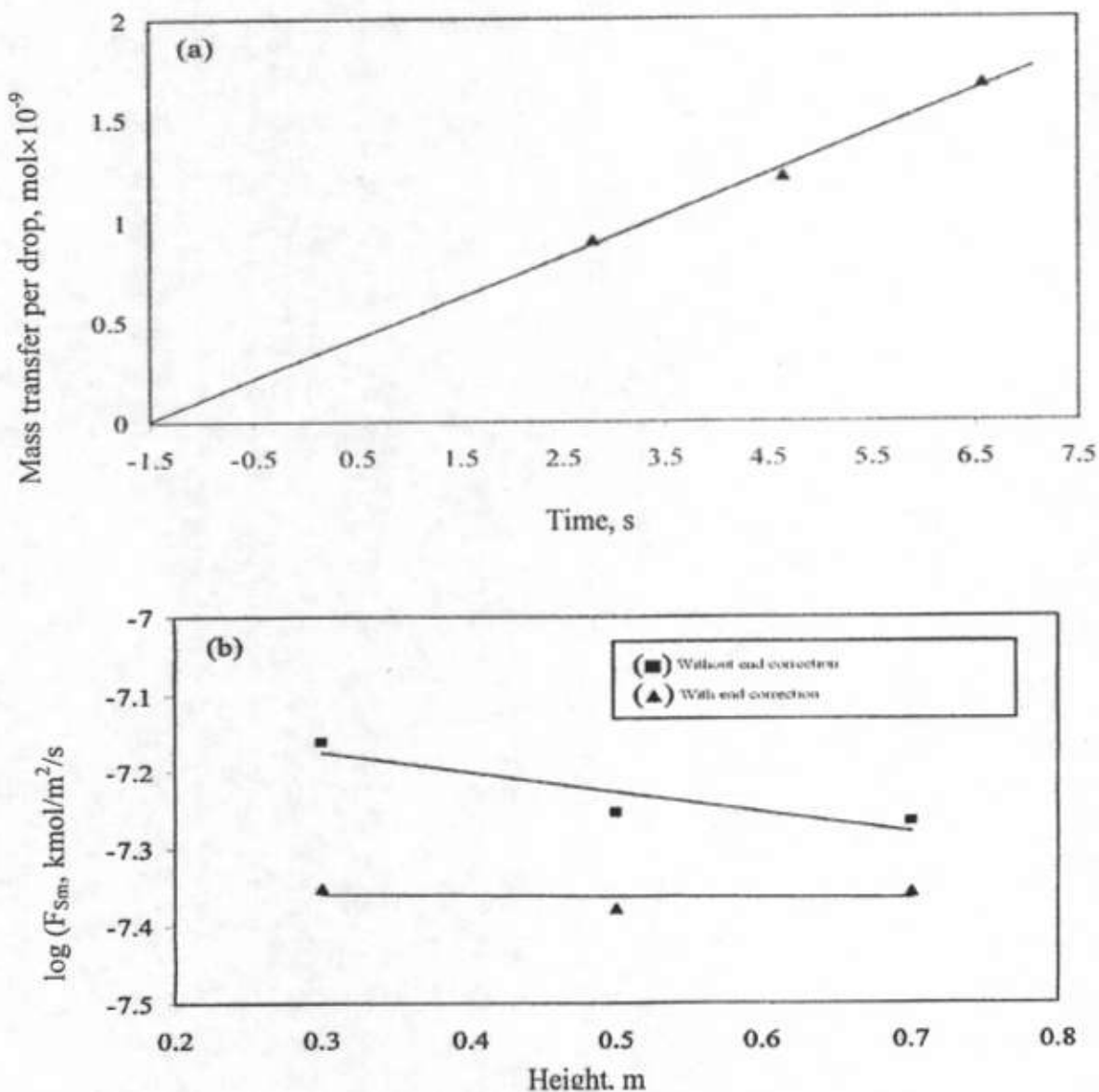


Fig. 2 (a) Mass transfer versus drop rise time plot (b) log (Flux) vs column height plot, for the extraction of samarium(III), [Sm(III)] = 0.655 mM; [H₂A₂] = 0.05 M; pH = 3.5; [NO₃⁻] = 0.1; M; [Ac⁻] = 0.25 M

The dependence of flux on Sm(III) concentration is given in Figure 2. The experimental points for a particular BTMPPA system fall on straight lines in all cases. The results suggest that the rate of extraction is directly proportional to the aqueous phase gadolinium concentration. The reaction order of one with respect to metal ion concentration was found for the extraction of lanthanum(III) from nitrate-acetato medium by BTMPPA in toluene (Saleh et al., 2002b).

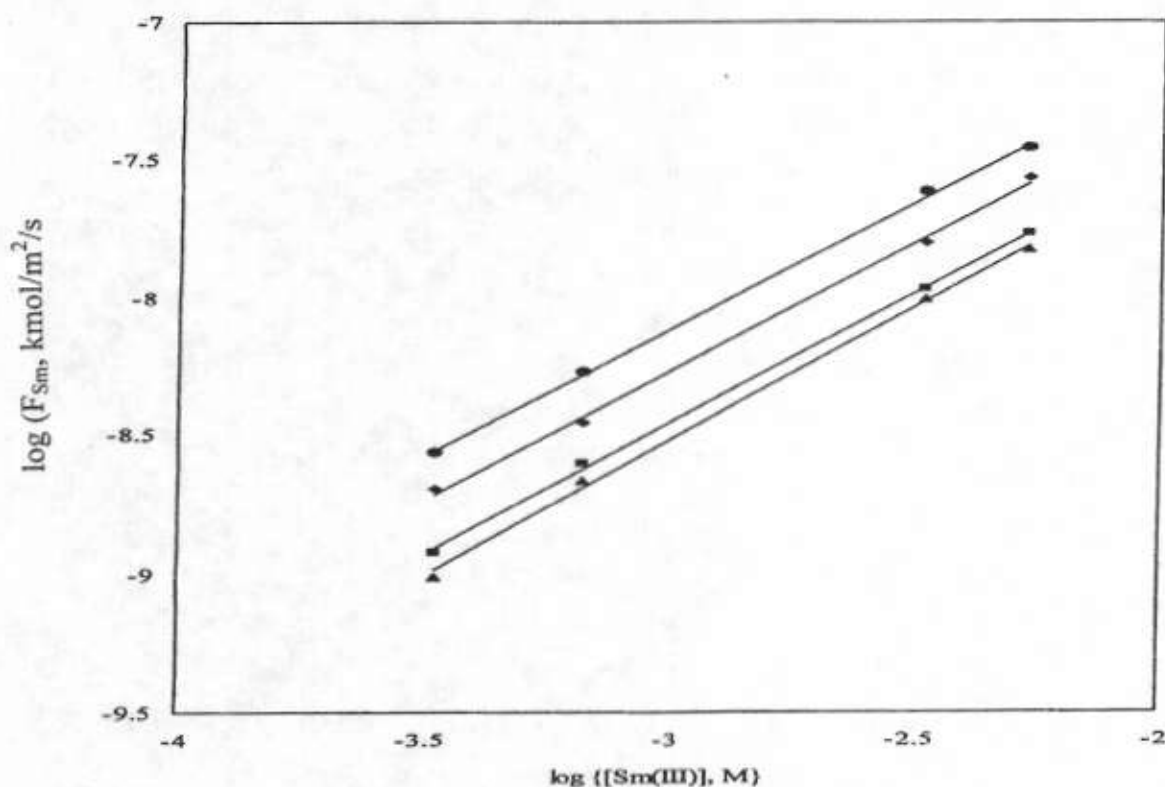


Fig.3 Dependence of extraction flux on samarium concentration in the aqueous phase, $[\text{NO}_3^-] = 0.1 \text{ M}$; $[\text{Ac}^-] = 0.25 \text{ M}$; $\text{pH} = 3.5$; (\blacktriangle), $[\text{H}_2\text{A}_2] = 0.005 \text{ M}$, $s = 0.97$, $I = -5.61$; (\blacksquare), $[\text{H}_2\text{A}_2] = 0.01 \text{ M}$, $s = 0.94$, $I = -5.63$; (\blacklozenge), $[\text{H}_2\text{A}_2] = 0.02 \text{ M}$, $s = 0.93$, $I = -5.47$; (\bullet), $[\text{H}_2\text{A}_2] = 0.05 \text{ M}$, $s = 0.92$, $I = 5.35$.

Variation of flux with aqueous pH at three H_2A_2 concentrations is shown in Figure 4. In each case, the experimental points fall on straight lines up to about pH 2.5. Similar to the extraction of La(III) (Bari et al. 2006; Saleh et al., 2002b), the theoretical lines were obtained from the equation;

$$\log F_{Sm} = \log (k_F(sm)^a (h_2a_2)_{(o)}^c) - bpH \quad (3)$$

In this case, it is found that only at below pH 2.53, experimental points are very close to the theoretical lines. Above pH 2.5, however, experimental points deviated from the straight lines due to the fact that the interfacial pH changed from the bulk pH (Hughes and Biswas, 1993). So it can be concluded that rate is inversely proportional to the hydrogen ion concentration at the interface rather than its bulk concentration. This phenomenon is common in the extractions with acidic extractants (Saleh et al., 2002a,b; Biswas et al., 1996,1997).

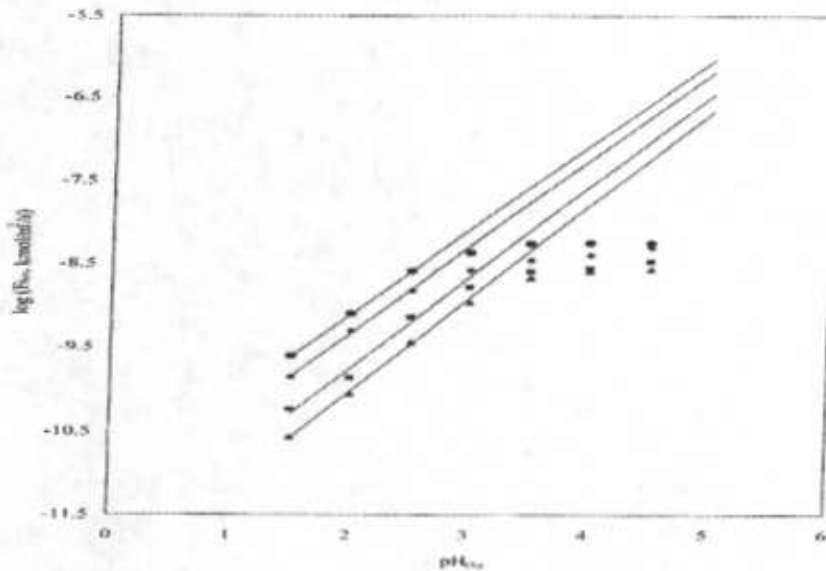


Fig.4 Dependence on extraction flux of erbium on hydrogen ion concentration in the aqueous phase, $[Sm(III)] = 0.665 \text{ mM}$; $[NO_3^-] = 0.10 \text{ M}$; $[Ac^-] = 0.25 \text{ M}$; (\blacktriangle), $[H_2A_2] = 0.005 \text{ M}$, $I = -12.26$; (\blacksquare), $[H_2A_2] = 0.01 \text{ M}$, $I = -11.95$; (\blacklozenge), $[H_2A_2] = 0.10 \text{ M}$, $I = -11.41$; (\bullet), $[H_2A_2] = 0.02 \text{ M}$, $I = -11.14$. The solid lines are: $\log F_{Sm} = \log (k_F(sm)^a (h_2a_2)_{(o)}^c) - bpH$ and points are experimental

The effect of extractant concentration on the extraction flux of Sm(III) was carried out and the experimental flux was plotted against BTMPPA in their logarithm(Fig.5).

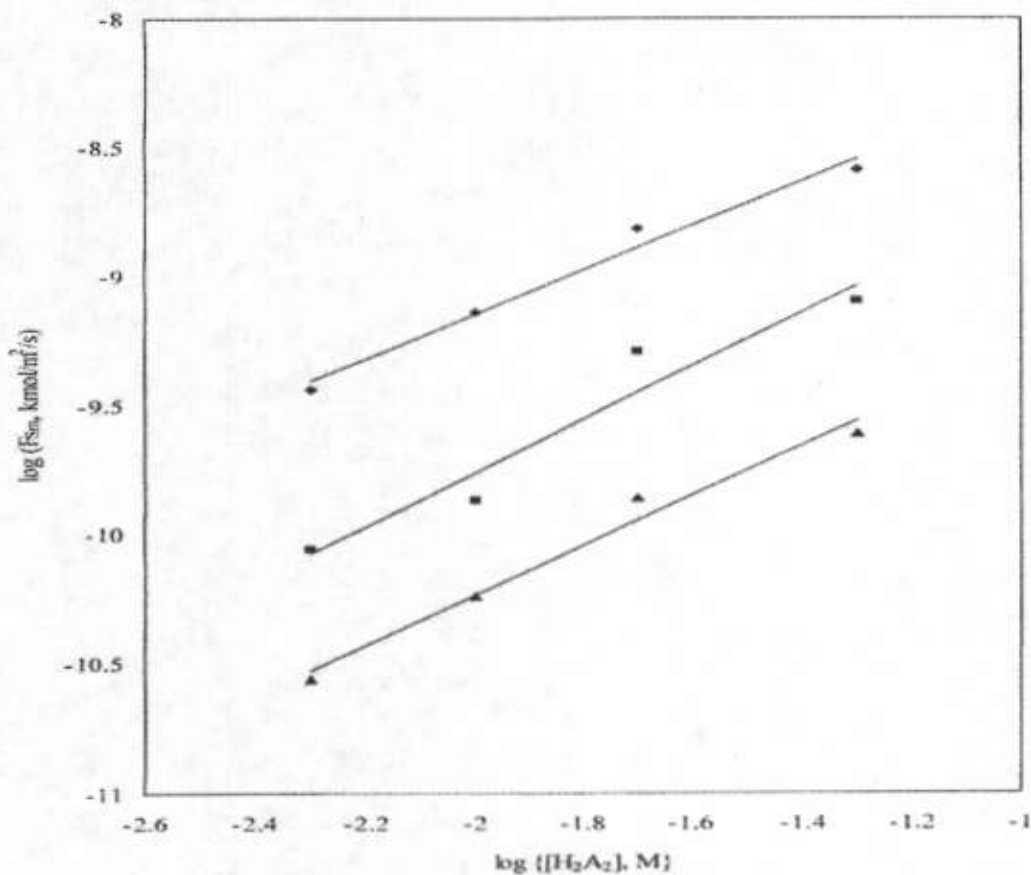


Fig. 5 Dependence of extraction flux of Sm(III) on extractant concentration in the organic phase, [Er(III)] = 0.665 mM; [NO₃⁻] = 0.1 M; [Ac⁻] = 0.25 M; (▲), pH_(b) = 1.5, s = 0.97, I = -8.30; (■), pH_(b) = 2.0, s = 1.04, I = -7.68 and (◆), pH_(b) = 2.5, s = 0.87, I = -7.42

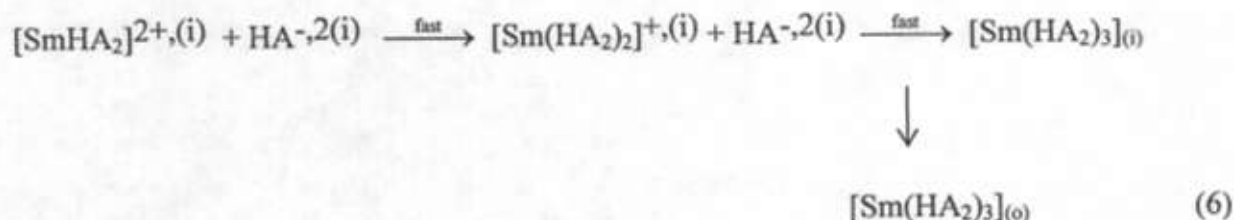
The slope of unity indicates that the rate of Sm(III) extraction from aqueous to organic phase is directly proportional to BTMPPA concentration in the organic phase.

The rate constants, k_F were calculated from the intercepts of the plots in Figures 3-5. The mean values of $\log k_F$ for the extraction of Sm(III) is -7.15.

From the results obtained in the present investigations, the rate of flux of mass transfer of Sm(III) from aqueous phase to the toluene phase containing BTMPPA at a constant temperature can be represented by the following empirical equation:

$$F_{Sm} = 10^{-7.15} [Sm^{3+}] [H_2A_2]_{(o)} [H^+]_{(o)}^{-1} \text{ kmol/m}^2\text{s} \quad (4)$$

After analyzing the rate expression equation as done in the earlier work, it was found that Sm(III) is extracted according to the following equation steps: (Bari et al.,2006; Saleh et al., 2002a, 2002b).



The step represented by Eq.(5) is the slowest or rate-determining step. Thus, the formation of 1:1 complex of Sm³⁺ with HA^{-,2} (dimeric anion) at the interface is rate-determining.

4. CONCLUSIONS

The following conclusions were drawn

1. At a constant temperature, the rate or flux expression can be written as:

$$F = 10^{-7.15} [\text{Sm}^{3+}] [\text{H}_2\text{A}_2]_{(o)} [\text{H}^+]_{(i)}^{-1}$$

2. It was observed that the interfacial pH changed from the bulk and the reaction occurred at the interface. Therefore flux is proportional to hydrogen ion concentration at interface.

3. From the value of E_a, it can be concluded that reaction of dimeric anion (HA₂⁻) with the Sm³⁺ at the interface is the rate determining step.

4. The negative entropy of activation proves that the rate-determining step occurs via the S_N2 mechanism.

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