Indian Journal of Chemical Technology
Vol. 3, November 1996, pp. 373-374

Note

Liquid-liquid extraction of thorium(IV) with binary mixture of PC88A and TOPO from aqueous $HClO_4$ media

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Received 4 March 1996; accepted 1 July 1996

The extraction of thorium(IV) with PC88A is very high from low $HClO_4$ concentration. It gradually decreases with increase in acidity. The addition of synergist TOPO to PC88A in kerosene improves the extraction of thorium(IV) from 0.2-1.6 M $HClO_4$ solution. The study with different diluents shows maximum distribution ratios obtained in case of kerosene.

Synergistic extraction of thorium(IV) using organo-phosphorus extractants has been studied by several workers[1,2]. The present work aims at investigating the synergistic extraction behaviour of thorium(IV) with the binary mixture of 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC88A) and tri-*n*-octyl phosphine oxide (TOPO) in kerosene from $HClO_4$ medium. The effect of various diluents on the synergistic extraction system has been investigated.

Experimental procedure

The commercial extractants, PC88A (Daihachi Chemical Industries, Japan) and TOPO (Merck) were used as received. Commercially available kerosene was used as diluent. All other chemicals used were of AR grade. Stock solution of thorium(IV) ($\sim 10^{-3}$ M) was prepared by dissolving thorium nitrate, $Th(NO_3)_4.5H_2O$ (LOBA) in distilled water. One millilitre of concentrated $HClO_4$ was added to 100 mL of the stock soution to suppress hydrolysis. Equilibration of equal volumes of organic phase and aqueous phase was done for 10 min. Phases were allowed to settle for 20 min. Then the aqueous phase was disengaged and analysed spectrophotometrically by Arsenazo(III) method[3]. The distribution ratio (D) was calculated from the ratio of Th(IV) concentration in the organic phase and in the aqueous phase.

Results and discussion

Extraction of PC 88A—The extraction of thorium(IV) with 0.015 M PC88A [$(RH)_2$] in kerosene has been carried out in the aqueous $HClO_4$ (0.1-1.6 M). Being a cation exchanger, PC88A extracts thorium(IV) less efficiently from higher acid concentration (1.6 M $HClO_4$). The distribution ratios are very high at 0.1 M and 0.2 M $HClO_4$. This decreases to only 0.4 at 1.6 M. In the investigated concentration range (9.3×10^{-3} - 3.1×10^{-2} M) of PC88A, the extraction of thorium(IV) increases gradually with increase in PC88A molarity.

In order to establish the stoichiometric composition of the extracted thorium(IV) species with PC88A in $HClO_4$ media, log D values are plotted against log [$HClO_4$] and log [PC88A]. The slopes of -2.9 and 3.0 obtained respectively suggest the following extraction mechanism for the extraction of thorium(IV) with PC88A. In this case one perchlorate ion is incorporated in the extracted thorium complex[4].

$$ThClO_{4(aq)}^{3+} + 3(RH)_{2(org)} \rightleftharpoons ThClO_4R_3.3RH_{(org)} + 3H_{(aq)}^{+}$$

Extraction by TOPO — The distribution ratio of thorium(IV) has been determined as a function of aqueous phase $HClO_4$ concentration ranging from 0.2-1.6 M for 0.008 TOPO in kerosene. The extraction decreases with increase in acid concentration. The effect of TOPO molarities (0.0015-0.04 M) on the extraction of thorium(IV) has been studied by keeping $HClO_4$ concentration fixed at 1 M. Distribution ratio becomes very high ($D = 148$) with 0.04 M TOPO. The extracted species is proposed to be $Th(ClO_4)_4.3TOPO$ as a slope of 3.0 is obtained from the plot of log D vs log [TOPO].

Extraction by mixture of PC88A and TOPO — With the binary mixture of 9.3×10^{-3} M PC88A and 0.006 M TOPO the extraction of thorium(IV) decreases gradually with varying range of $HClO_4$ molarity (0.2-1.6 M). Synergistic effect is observed which decreases with increase in acidity. The data are presented in Table 1. The effect of extractant concentrations on the synergistic extraction has been studied in order to know the composition of the adduct species. With 1M $HClO_4$, the variation of TOPO (0.001-0.01 M) in the mixture of 9.3×10^{-3} M PC88A and TOPO and variation of PC88A (3.1×10^{-3} to 1.5×10^{-2} M) in the mixture of 0.002 M TOPO and PC88A, results in a regular increase in the extraction of thorium(IV)

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Table 1—Effect of $HClO_4$ concentration on the extraction of Th(IV) with 9.3×10^{-3} M PC88A (D_1), 0.006 M TOPO (D_2) and their binary mixture (D_{mix}) in kerosene

$[HClO_4]$, M	D_1	D_2	D_{mix}
0.2	—	0.5	—
0.4	9.71	0.4	—
0.6	2.02	0.3	20.9
0.8	0.74	—	10.6
1.0	0.29	0.25	5.5
1.2	0.17	0.28	4.0
1.4	—	0.27	2.9
1.6	0.14	0.26	2.5

with increase in extractant concentration. Slopes of 1.4 and 2.1 obtained from the plots of log D_{mix} vs. log [TOPO] and log D_{mix} vs. log [PC88A], respectively provide the evidence in favour of the formation of the synergic adduct species, $Th(ClO_4)_2R_2.TOPO$ in the organic phase.

Effect of diluents — Individual extractant solutions (9.3×10^{-3} M PC88A and 0.002 M TOPO) and the binary mixture of both PC88A and TOPO have been prepared in various diluents. The distribution ratios of thorium(IV) are determined at 1 M $HClO_4$ (Table 2). From the above data it is evident that the distribution ratios of thorium(IV) are high when kerosene is used as organic phase diluent.

Table 2—Effect of diluents on the extraction of Th(IV) with PC88A (D_1), TOPO (D_2) and their mixture (D_{mix})

Diluents	D_1	D_2	D_{mix}
Kerosene	0.29	—	1.11
Toluene	0.07	0.05	0.58
Xylene	0.04	0.04	0.42
Benzene	0.06	0.01	0.68

Acknowledgement

One of the authors (S M) is thankful to CSIR, New Delhi for the award of a Senior Research Fellowship.

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