

## EXTRACTION OF ZIRCONIUM(IV) FROM HCl SOLUTIONS BY MIXTURES OF ALIQUAT-336 AND ALAMINE-336 WITH TBP

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(Received April 10, 1989)

Synergism has been observed in the extraction of zirconium(IV) by mixtures of Aliquat 336 or Alamine 336 with a neutral donor TBP from aq. HCl solutions. Although the extractant dependency for Zr(IV) is found to be nearly second power with respect to TBP alone, monosolvate is found to be formed for extraction by its mixture with Aliquat 336 or Alamine 336. Quantitative extraction is observed with mixtures at a lower acidity than that with individual extractants. The species formed is tentatively assigned to be  $Q_2 ZrCl_6 \cdot TBP$ , where  $Q = R_3 \ddot{N}(CH_3)$  for Aliquat 336 and  $R_3 \ddot{N}H$  for Alamine 336.

### Introduction

Extraction of Zr(IV) by  $TBP^{1-3}$  and its mixtures with sulfoxides<sup>4,5</sup> has largely been investigated mainly from mineral acid media. Sato and coworkers<sup>6,7</sup> have studied the extraction of Zr(IV) from strong aqueous HCl solutions by various tertiary amines and quaternary ammonium chloride (Aliquat 336). Mixture of liquid anion exchanger (Aliquat 336) and a neutral donor, has been found to produce considerable synergism in lanthanide and actinide extractions from chloride and nitrate media.<sup>8</sup> Hence it is of interest to study the case of synergism or antagonism as the case may be in case of extraction of Zr(IV) by mixtures of cationic extractant (Aliquat 336 or Alamine 336) and a neutral donor from mineral acid media. Our previous work<sup>9</sup> in the extraction of Zr(IV) by mixtures of Alamine 336 or Aliquat 336 and a neutral donor DOSO from aq. HCl solutions has shown considerable synergism in the extraction process. A number of investigations on synergistic extraction of different base

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metals by mixtures of several other cationic extractants and neutral donors or chelating extractants<sup>10,11</sup> have also been made in recent years and a critical review on synergistic extraction of zirconium(IV) and hafnium(IV) has also appeared.<sup>12</sup> In this report we present extraction behaviour of Zr(IV) from aq. HCl solutions by mixtures of a cationic extractant Aliquat 336 or Alamine 336 and TBP.

### Experimental

Aliquat 336 (tricaprylmethylammonium chloride) (Aldrich Chemical Co. Inc.) was purified by washing several times with aqueous 0.1M NaCl solution, followed by washing with n-hexane, and was then diluted with benzene. Alamine 336 (tricaprylamine) (Henkel Corp., USA), TBP (E. Merck) were used as such in the diluent benzene.  $ZrOCl_2 \cdot 8H_2O$  (E. Merck) was prepared and standardized by a reported method.<sup>13</sup>

<sup>95</sup>Zr tracer was obtained from Bhabha Atomic Research Centre, Bombay (India) in the form of oxalate complex. The tracer solution was repeatedly evaporated with conc. HCl to ensure complete transfer into chloro complex from its original oxalate form. The <sup>95</sup>Zr-<sup>95</sup>Nb tracer in its chloride form was added to inactive 0.001M  $ZrOCl_2 \cdot 8H_2O$  carrier. This concentration of Zr(IV) was maintained throughout the experiment. Since the gamma counting was undertaken using a high purity Ge detector coupled with a multi-channel analyzer ND 65, it was not necessary to separate <sup>95</sup>Nb from its parent <sup>95</sup>Zr, because the major gamma-ray peaks arising from different gamma-ray transitions in the <sup>95</sup>Zr-<sup>95</sup>Nb mixture could easily be resolved by the above detector. The measurement of distribution ratio<sup>14,15</sup> and the procedure for extraction process are the same as reported.<sup>4</sup> Centrifugation was necessary for better phase separation.

### Results and discussion

Studies on the extraction of zirconium(IV) by 5% (v/v) Aliquat 336, or 5% (v/v) Alamine 336 and 1% (v/v) TBP, and their mixtures (Fig. 1) indicate that under otherwise identical conditions extractions by Aliquat 336 alone or its mixtures with TBP are better than extractions by Alamine 336 alone or its mixtures with TBP. SATO and co-workers<sup>6,7</sup> have shown similar increased extraction efficiency of quaternary ammonium compounds over tertiary amines in the extraction of zirconium(IV) from aq. HCl solution. Our previous work<sup>9</sup> has also shown that extraction by Aliquat 336 alone or its mixtures with DOSO is always greater than that by Alamine 336 or its mixtures with DOSO (dioctyl sulfoxide). Our present observations indicate that 1% TBP extracts more than either 5% Aliquat 336 or Alamine 336. With the mixtures of 5% Aliquat 336 or 5% Alamine 336 and 1% TBP, extraction is always higher than

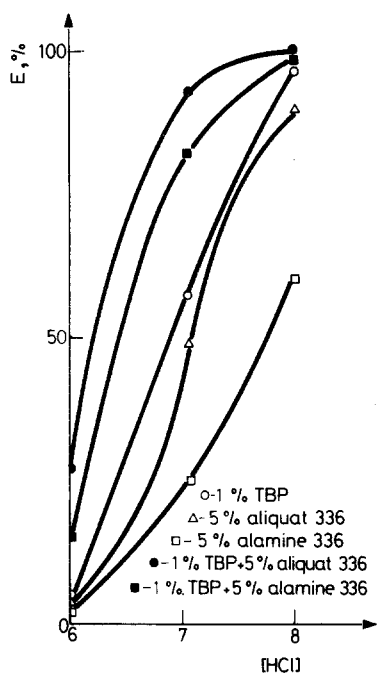


Fig. 1. Extraction of zirconium(IV) from aq. HCl solutions by 5% (v/v) Aliquat 336 or 5% (v/v) Alamine 336, 1% (v/v) TBP and their mixtures

that by the individual components. Quantitative extraction has been achieved at and above 8M HCl which is not the case with either of the extractants alone under similar conditions.

Synergism has been observed in the extraction by mixtures of extractants. The extent of synergism is computed in Table 1. Effect of variation of percentage concentration of Alamine 336, Aliquat 336 or TBP in their mixtures on extraction has been studied.

The species extracted by TBP in the extraction of zirconium(IV) from HCl solutions is reported to be disolvate in TBP,<sup>1,2</sup> and the species is reported to be  $ZrCl_4 \cdot 2TBP$ .<sup>4</sup> In the present investigations the plot of  $\log D$  vs.  $\log [\% TBP]$  for both TBP alone and its mixtures with 5% (v/v) Aliquat 336 or 5% (v/v) Alamine 336 in the extraction of zirconium(IV) from 6M and 7M HCl (Figs 2 and 3) are found to be nearly 2 and 1, respectively, indicating the species to be the disolvate in pure TBP and monosolvate in the mixtures.

A large number of investigations<sup>6,7,16,17</sup> in the extraction of different metal ions by amines or quaternary ammonium compounds from chloride media indicate that no

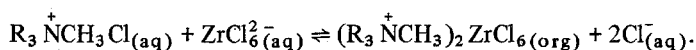
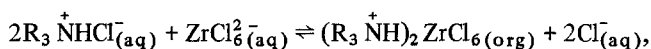
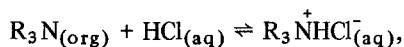
Table 1  
Extraction of Zr(IV) from 6M HCl

TBP, %	Aliquat 336, %			
	0	5		
	D	D	ΣD	ΔD
0	—	0.04	—	—
1	0.05	0.36	0.09	0.27
2	0.13	0.61	0.17	0.44
3	0.26	0.93	0.30	0.63
4	0.31	1.03	0.35	0.68
5	0.78	1.51	0.82	0.69

	Alamine 336, %			
	0	5		
	D	D	ΣD	ΔD
0	—	0.02	—	—
1	0.05	0.19	0.07	0.12
2	0.13	0.28	0.15	0.13
3	0.26	0.48	0.28	0.20
5	0.78	1.10	0.80	0.30

conclusive result could be obtained from the plot of log D vs. log [amine] or [quaternary ammonium salts]; since the concentration of chloride ion greatly influences the slope of the curve.<sup>18</sup> In the present experiments, the slopes are very low for knowing the species formed involving Alamine 336 or Aliquat 336 in the extraction process. Though at lower acidities different polymeric forms of zirconium are predominant, polymerization decreases with increasing acidities and decreasing zirconium(IV) concentration.<sup>19</sup> Under the present experimental conditions, the species  $ZrCl_6^{2-}$  can be thought<sup>20</sup> to be present and are extractable from the aq. HCl solution. On the basis of various reports<sup>6,7,16,20</sup> and theoretical evidence, the following mechanism can be proposed for the extraction process:



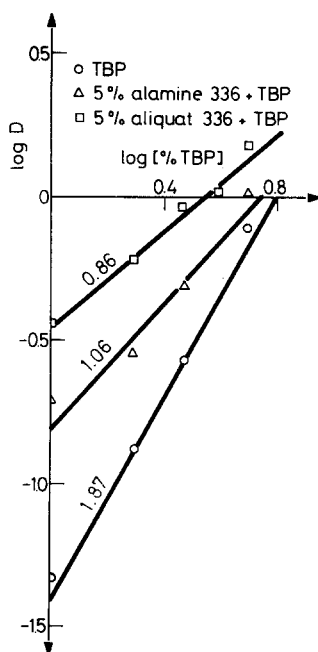


Fig. 2. Plot of log D vs. log [% TBP] for extraction of Zirconium(IV) from 6M HCl, by TBP and its mixtures with 5% (v/v) Aliquat 336 and 5% (v/v) Alamine 336

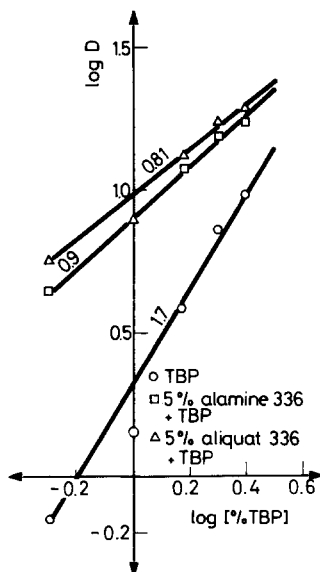


Fig. 3. Plot of log D vs. log [% TBP] for extraction of zirconium(IV) from 7M HCl, by TBP and its mixtures with 5% (v/v) Aliquat 336 and 5% (v/v) Alamine 336

The species extracted may be tentatively suggested to be  $Q_2ZrCl_6 \cdot TBP$ , where  $Q = R_3NH$  for Alamine 336 and  $R_3N^+CH_3$  for Aliquat 336 for the extraction of zirconium(IV) by mixtures of TBP and Aliquat 336 or Alamine 336 from aqueous HCl solutions.

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Thanks are due to M/s Henkel Corp., USA, for gift sample of Alamine 336 and Council of Scientific and Industrial Research (CSIR), New Delhi for supporting this work through a grant.

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