STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, XLV, 1-2, 2000

EXTRACTION OF ZIRCONIUM(IV) WITH TRITOLYLPHOSPHATE

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ABSTRACT. Solvent extraction of zirconium(IV) from chloride aqueous media by tritolylphosphate (TTP) has been investigated. The effect of certain variable such as acidity, the concentration of the extractant and the concentration of chloride anion have been examined. Based on slope analysis applied to the distribution data, a possible mechanism for the extraction of Zr(IV) has been proposed.

INTRODUCTION

During recent years we reported a lot of works on the extraction of some actinide and lantanide with acidic and neutral organophosphorus extractants [1-5]. We have studied the separation of uranium(VI) and thorium(IV) from zirconium(IV), lantanum(III), cerium(III) and other trivalent and divalent metals by solvent extraction and thin layer chromatography[6-8].

This work deal with the extraction of zirconium(IV) from acidic aqueous solutions with tritolylphosphate in benzene, in order to establish the extraction mechanism.

EXPERIMENTAL

Reagent and equipment

Zirconium chloride, tritolylphosphate and Arsenazo III were supplied by Aldrich and Ventron AG Germany. All the other reagents used were of analytical grade.

A Spekol C. Zeiss Jena (DDR) spectrophotometer was used for the determination of zirconium(IV). The acidity of the aqueous phase was determined by titration with NaOH.

Operating procedure

The partition experiment were carried out by equilibrating equal volumes (10 ml) of organic and aqueous phases in 100 ml separation fuels. Preliminary test showed that the distribution equilibrium is attained in 4 min. at room temperature (20-23^{0}C). After the phases were separated the zirconium content in the aqueous phase was determined photometrically with Arsenazo III [9].

RESULTS AND DISCUSSION

The extraction of zirconium(IV) with tritolylphosphate (TTP) in benzene was studied. The dependence of the distribution ratio on the aqueous layer acidity, the concentration of chloride anion and the concentration of the extractant in the organic phase was investigated.

Treatment of data

The extraction equilibrium of metal ion M^{m+} with an neutral organophilic extractant S can be described by the following equation:

$$M^{m+} + mA^- + z(S)_o \rightleftharpoons (M A_m S_z)_o \qquad (1)$$

where A^- is the counter anion present in the aqueous phase and "o" indicates the organic phase.

The extraction equilibrium constant is given by the relation:

$$K = \frac{[MA_m S_z]_o}{[M^{m+}][A^-]^m [S]_o^z} \qquad (2)$$

Defining the distribution ratio D as the ratio between the total concentration of the metal in the organic phase and the total concentration of the metal in the aqueous phase it follows that:

$$K = D \cdot \frac{1}{[A^-]^m [S]_o^z} \qquad (3)$$

After some simple transformations one obtains:

$$\log D = \log K + m \log [A] + z \log [S]_o \qquad (4)$$

Equation (4) can give information concerning the nature of the species involved in the extraction process. It should be mentioned that K and D are not thermodynamic constants since they ignore activity coefficient. They can serve only for comparing various extraction systems under similar conditions.

Zr(IV) – TTP – benzene system

The effect of HCl concentration on the extraction of Zr(IV) with TTP in benzene was investigated. The results ilustrated in Table 1 indicate an increase of distribution ratio; the maximum value of D is obtained at 1.0 – 1.5M HCl. If the concentration of the hydrocloric acid is greater than 1.5M the extraction of Zr(IV) decrease. This trend in the extraction behaviour of Zr(IV) has been reported by other workers too [10].

Table 1.

The effect of HCl concentration of Zr(IV) with 0.5M TTP in benzene

C_{HCl}	Distribution ratio (D)
0.10	0.50
0.50	0.85
1.00	1.41
1.50	1.53
2.00	0.85
2.50	0.72
3.00	0.54
4.00	0.20

Maintaining constant the concentration of HCl (1M) the influence of TTP on the distribution ratio of Zr(VI) was studied. The data obtained ilustrate that the extraction increase with the increasing of extractant concentration. The plot of logD against to log[TTP] was determined (Fig. 1, curve 2). The slope of 2 for the linear portion of the curve indicate that two TTP molecules are involved in the formation of the extracted species in the organic phase (Eq. 4, z = 2).

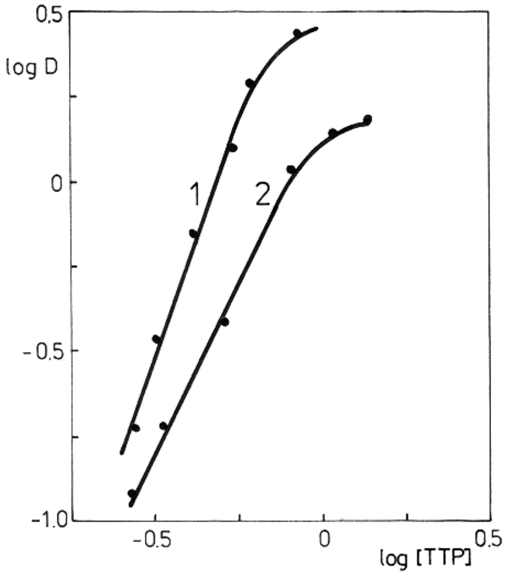

Fig. 1. The dependence of zirconium(IV) extraction with TTP concentration
C_{HCl} = 1M; C_{Zr} = 0.001M

The distrubution ratio was also determined for different concentrations of chloride ion in the aqueous phase. The variation of logD versus log[Cl^-], at constant acidity (1M) of the aqueous phase, is ilustrated in Figure 2, curve 1. The slope 3.7 of the straight line obtained suggest that four chloride anions are involved in the extraction process (Eq. 4, m = 4). At lower acidity of the aqueous phase (<1M) the slope value of 2 shows that only 2 chloride anion participate in the formation of the extracted species.

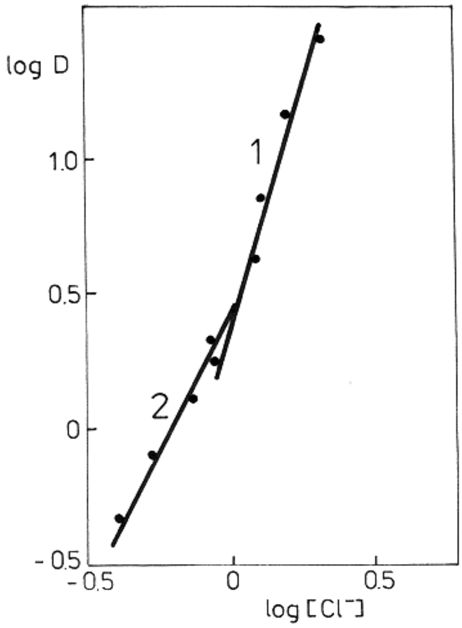

Fig. 2. The dependence of zirconium(IV) extraction with chloride ion concentration. C_{Zr} =0.001 M; C_{TTP} = 0.5 M

Final remarks

The data presented above show that the extraction of zirconium(IV) is strongly affected by the acidity of the aqueous phase. This can be understood taking into account that the acidity plays an important role in the existence of many chemical forms of Zr(IV) in aqueous phase. At high acidity zirconium(IV) exist as Zr^{4+} ion. In this case the extraction of metal can be described by the equation:

$$Zr^{4+} + 4Cl^- + 2(TTP)_o \rightleftharpoons [ZrCl_4(TTP)_2]_o$$

At moderate acidity (<2M) ZrO^{2+} species is dominating in aqueous solutions and extraction process may be represented by the following equation:

$$ZrO^{2+} + 2Cl^- + 2(TTP)_o \rightleftharpoons [ZrOCl_2(TTP)_2]_o$$

The decrease of extraction at higher acidities might be due to the formation of the less extractable acido-complex of zirconium in aqueous phase [11]

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