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Tributyl Phosphate Extraction of Uranium(VI) Trichloroacetate

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LEGAL NOTICE

ABSTRACT

Uranium(VI) is strongly extracted by 40% tributyl phosphate in hexane from aqueous sodium trichloroacetate. The extraction is suppressed sharply by addition of trichloroacetic acid. Typical values of the U(VI) distribution coefficient (organic/aqueous) are 838 at 0.01 M trichloroacetic acid -0.29 M sodium trichloroacetate and 5.1 at 0.30 M trichloroacetic acid. A spectrophotometric method is described for determination of distribution coefficients without separate measurement of extinction coefficients.

INTRODUCTION

Trichloroacetate ion is a very weak base, a property which suggests its use for promoting the extraction of easily hydrolyzed metal ions. It has, however, received relatively little study in liquid-liquid extraction systems. In this report, we present measurements of the distribution of U(VI) between 40% tributyl phosphate in hexane and (1) 0.01 - 1.0 M trichloroacetic acid and (2) trichloroacetic acid - sodium trichloroacetate mixtures with trichloroacetate molarities of 0.025, 0.10, and 0.30.

EXPERIMENTAL

Materials

Reagent grade trichloroacetic acid was recrystallized twice from benzene and dried over concentrated sulfuric acid in a vacuum desiccator. The tributyl phosphate was prepared from technical grade material by scrubbing with dilute aqueous sodium hydroxide and distilling the resulting material under reduced pressure. Other materials were of reagent grade or equivalent and were used without further purification.

Procedure

A sample of 40 volume percent tributyl phosphate (TBP) was presaturated with a trichloroacetate solution of known composition. Equal volumes of the TBP and of a concentrated $UO_2(ClO_4)_2$ stock solution were added to each of two mixing cylinders. Widely different volumes of the trichloroacetate solution were added then so that, in a typical case, one cylinder contained 100 ml of aqueous phase, 1 ml of organic phase, and 0.05 millimole of $UO_2(ClO_4)_2$, and the other cylinder contained 3 ml of aqueous phase, 1 ml of organic phase, and 0.05 millimole of $UO_2(ClO_4)_2$. Equilibrium was established by end-over-end stirring for at least two hours at room temperature.

The optical density of each organic phase was measured at 4230 Å using a Cary Model 14 spectrophotometer. The distribution coefficient, D, is given by

$$D = \frac{A_1V_1 - A_2V_2}{V_o\ (A_2 - A_1)} \qquad (1)$$

in which V_o is the volume of the organic phase, and A_1 and A_2 are the absorbances (i.e. optical densities) measured with samples from the cylinders with aqueous phase volumes of V_1 and V_2, respectively. For Eq. (1) to hold, both the distribution coefficient and the extinction coefficient must be independent of the amount of U(VI) present. This was found to be true over the low U(VI) concentration range employed in these measurements. The derivation of Eq. (1) is given in the next section.

Derivation of Equation (1)

Consider two extractions carried out with V_o ml of organic phase and n millimoles of extractable ion, but with two different volumes of aqueous phases, V_1 and V_2, which are identical in composition except for the small amounts of extractable ion present at equilibrium. The absorbances of the organic phases at equilibrium are denoted by A_1 and A_2; the concentrations of the colored ion in the organic phases will be $A_1/\epsilon \ell$ where ϵ is the extinction coefficient and ℓ is the path length of the spectrometer cell. The distribution coefficient is given by

$$D = \frac{A_1/\epsilon\ell}{(n - V_o A_1/\epsilon\ell)/V_1} = \frac{A_2/\epsilon\ell}{(n - V_o A_2/\epsilon\ell)/V_2}$$

The last equality is solved for $n\epsilon\ell$.

$$\frac{V_1A_1}{n\epsilon\ell - V_oA_1} = \frac{V_2A_2}{n\epsilon\ell - V_oA_2}$$

$$n\epsilon\ell = \frac{V_oA_1A_2(V_1 - V_2)}{V_1A_1 - V_2A_2}$$

This value is substituted into the expression for D.

$$D = \frac{V_1A_1}{n\epsilon\ell - V_oA_1} = \frac{V_1A_1(V_1A_1 - V_2A_2)}{V_oA_1A_2(V_1 - V_2) - V_oA_1(V_1A_1 - V_2A_2)}$$

$$= \frac{V_1A_1 - V_2A_2}{V_o(A_2 - A_1)}$$

RESULTS

The distribution coefficients for U(VI) obtained in this study are tabulated in Table 1 and displayed in Fig. 1.

The distribution of trichloroacetic acid was measured by mixing known amounts of acid, water, and 40% tributyl phosphate and titrating the acid remaining in the aqueous phase. A distribution coefficient of 13.2 ± 1.0 was obtained at equilibrium acid concentrations of 0.014, 0.040, and 0.058 M. No trend with concentration was indicated.

TABLE 1

Distribution of U(VI) between 40 volume percent tributyl phosphate (in hexane) and aqueous trichloroacetate media.

Molarity Trichloroacetic Acid	Molarity Sodium Trichloroacetate	D (Organic/aqueous)
0.010	0	15.5, 13.8, 12.6
0.025	0	23.2, 25.5, 23.3
0.075	0	16.8
0.076	0	18.9
0.100	0	15.2, 15.3
0.150	0	12.2
0.303	0	5.1
1.009	0	4.3
0.00018	0.098	1998
0.00091	0.025	293
0.0097	0.290	838
0.0098	0.090	268
0.048	0.251	73.7
0.049	0.050	47.4
0.150	0.149	15.8

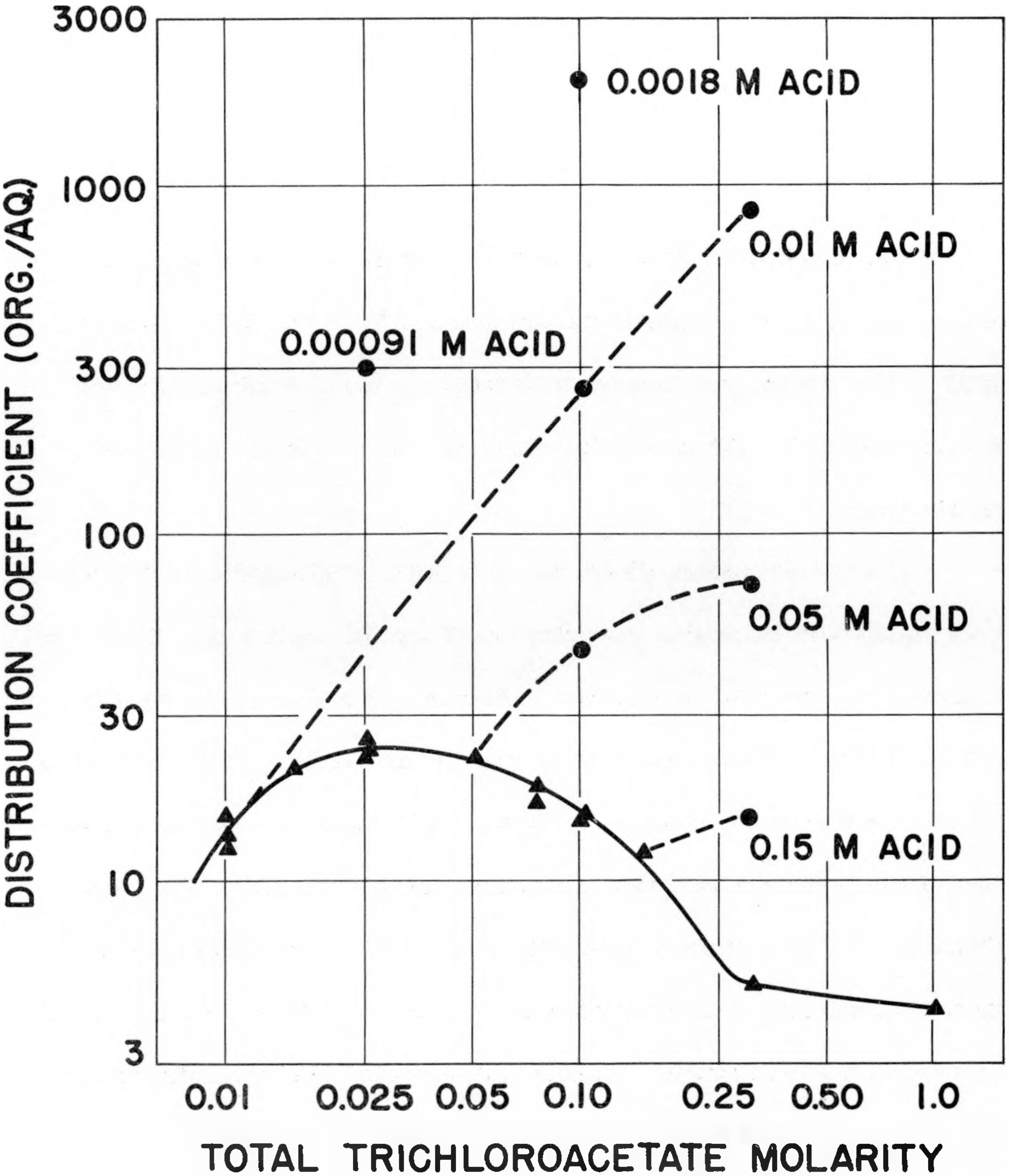

Fig. 1. — Distribution of U(VI) between 40 volume percent tributyl phosphate (in hexane) and aqueous trichloroacetic acid (▲) or aqueous sodium trichloroacetate-trichloroacetic acid mixtures (●).

DISCUSSION

The principal result of this study is the demonstration that trichloroacetate ion effectively promotes the extraction of U(VI) into tributyl phosphate (TBP). The extraction is suppressed strongly by acid. Solutions of uranyl trichloroacetate in TBP are highly colored and convenient for spectrophotometric study.

At low acid concentrations, the distribution coefficient for U(VI) rises very rapidly with increasing concentration of trichloroacetate ion. The most informative measure of the increase is the derivative $d \log D/d \log (TCA)$ in which (TCA) is the concentration of trichloroacetate ion. This derivative is expected to assume the value of 2 if the uranyl trichloroacetate is completely dissociated in the aqueous phase and undissociated in the TBP. The values obtained in the present study depend strongly on the acid concentration but appear to approach 2 at moderately low trichloroacetate concentrations and very low acid concentrations. At high trichloroacetic acid concentrations, the value becomes less than one, probably as a result of two effects; namely, competitive extraction of trichloroacetic acid and formation of trichloroacetate complexes of U(VI) in the aqueous phase.

Some qualitative support for occurrence of competitive extraction of acid is provided by the measurements of acid distribution. A distribution coefficient of about 13 was found for aqueous phase concentrations in the range 0.014 to 0.058 M. The TBP is initially 1.5 M in 40 volume percent TBP in hexane. Hence, it is reasonable to suppose that much of the TBP is tied up and not available for interaction with U(VI) at acid concentrations above a few hundredths molar. Many more measurements would be required to provide an adequate basis for quantitative description of the competitive extraction.