The Synergistic Effect on the Extraction of $^{233}U(VI)$ by Di-butylphosphate (DBP) and Tri-butylphosphate (TBP) or Tri-octyl phosphineoxide (TOPO)

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The addition of a neutral organophosphorus compound (= B) such as tributylphosphate (TBP), has been found to give rise to a synergistic effect on the extraction of UO_2^{2+} by di-alkylphosphoric acid (= HA) into a non-polar organic solvent.[1-3] In other words, the distribution ratio for U is greater with the combination HA + B than the sum of the distribution ratios with HA or with B used separately. This synergistic effect may be explained by the extraction of uranyl mixed complexes of the general formula $UO_2A_2(HA)_pB_q$, where the values of p and q can vary depending on the extraction conditions used.

We now report the extraction of carrier-free $^{233}U(VI)$ from aqueous 0.10 M H_2SO_4 at 25°C into hexane or carbon tetrachloride by di-butylphosphate (= HA) in the presence of tri-butylphosphate or tri-octylphosphineoxide (= B).

As a preliminary the distribution of ^{32}P-labelled DBP (HA) between 0.10 M H_2SO_4 aqueous solution and hexane or carbon tetrachloride, was studied at 25°C in the presence of tri-butylphosphate or trioctylphosphineoxide. From the results we deduce the reactions and equilibrium constants summarized in Table 1, and with the aid of these constants, and the HALTABI computer program [4] we calculate the equilibrium concentrations of the various HA−B species, needed for treating the experimental data on the extraction of UO_2^{2+}.

From these data we deduce the reactions in Table 2. The results indicate that the synergistic effect in our systems may in some cases be described as an addition reaction:

$$UO_2A_2(HA)_2 \text{ (org)} + B \text{ (org)} \rightleftharpoons UO_2A_2(HA)_2B \text{ (org)}$$

and in other cases as a substitution reaction:

$$UO_2A_2(HA)_2 \text{ (org)} + B \text{ (org)} \rightleftharpoons UO_2A(HA)B \text{ (org)} + HA \text{ (org)}$$

or

$$UO_2A_2(HA)_2 \text{ (org)} + B \text{ (org)} \rightleftharpoons UO_2A_2B \text{ (org)} + 2\ HA \text{ (org)}$$

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Table 1. The distribution of DBP between 0.10 M H_2SO_4 and hexane or CCl_4 in the presence of TBP or TOPO.

System	*Reaction and equilibrium constant*	
DBP-hexane-0.10 M H_2SO_4	HA (aq) ⇌ HA (org)	log K_d = −2.13
	2 HA (org) ⇌ H_2A_2 (org) *	log K_2 = 6.52
DBP-TBP-hexane-0.10 M H_2SO_4	HA (org) + B (org) ⇌ HAB (org)	log K_{11} = 2.90
	HA (org) + 2 B (org) ⇌ HAB_2 (org)	log K_{12} = 3.30
	H_2A_2 (org) + B (org) ⇌ H_2A_2B (org)	log K_{21} = 1.23
DBP-TOPO-hexane-0.10 M H_2SO_4	HA (org) + B (org) ⇌ HAB (org)	log K_{11} = 4.82
DBP−CCl_4-0.10 M H_2SO_4	HA (aq) ⇌ HA (org)	log K_d = −1.33
	2 HA (org) ⇌ H_2A_2 (org)	log K_2 = 6.27
	2 HA (aq) ⇌ H_2A_2 (aq)	log K_{2aq} = 2.36
DBP-TBP-CCl_4-0.10 M H_2SO_4	HA (org) + B (org) ⇌ HAB (org)	log K_{11} = 2.63
DBP-TOPO-CCl_4-0.10 M H_2SO_4	HA (org) + B (org) ⇌ HAB (org)	log K_{11} = 4.29

* For $[HA]_{tot} > 0.1$ M, polymeric DBP species become appreciable.

Table 2. The extraction of U(VI) by DBP into hexane or CCl_4 in the presence of TBP or TOPO. The total concentration of U(VI) was less than 10^{-5} M.

System	Equilibrium constant for formation of predominating complex
DBP–hexane–0.10 M H_2SO_4	
$C_A = 1-260$ mM	$UO_2^{2+}(aq) + 4\,HA(aq) \rightleftharpoons UO_2A_2(HA)_2(org) + 2\,H^+(aq)$ $\log K = 8.35$
DBP–TBP–hexane–0.10 M H_2SO_4	
[HA] = 0.25–4 mM; $C_B = 0.02-1.5$ M	$UO_2^{2+}(aq) + 4\,HA(aq) + B(org) \rightleftharpoons UO_2A_2(HA)_2B(org) + 2\,H^+(aq)$ $\log K = 11.51$
$[HA] = 10^{-3.954}-10^{-2.978}$ M and $C_B \geq 2$ M	$UO_2^{2+}(aq) + 2\,HA(aq) + B(org) \rightleftharpoons UO_2A_2B(org) + 2\,H^+(aq)$ $\log K = 4.62$
$[HA] < 10^{-4.730}$ M and $C_B \geq 2$ M	$UO_2^{2+}(aq) + SO_4^{2-}(aq) + 2\,B(org) \rightleftharpoons UO_2SO_4B_2(org)$ $\log K = -1.22$
DBP–TOPO–hexane–0.10 M H_2SO_4	
$[HA] > 10^{-4.0}$ M and $C_B = 4.56-55$ mM	$UO_2^{2+}(aq) + 2\,HA(aq) + B(org) \rightleftharpoons UO_2A_2B(org) + 2\,H^+(aq)$ $\log K = 8.18$
$[HA] < 10^{-4.66}$ M and $C_B \geq 55$ mM	$UO_2^{2+}(aq) + SO_4^{2-}(aq) + 2\,B(org) \rightleftharpoons UO_2SO_4B_2(org)$ $\log K = 4.29$
DBP–CCl_4–0.10 M H_2SO_4	
$[HA] = 10^{-3.65}-10^{-2.40}$ M	$UO_2^{2+}(aq) + 4\,HA(aq) \rightleftharpoons UO_2A_2(HA)_2(org) + 2H^+(aq)$ $\log K = 10.71$
DBP–TBP–CCl_4–0.10 M H_2SO_4	
$[HA] = 10^{-4.20}-10^{-2.90}$ M and $C_B = 0.20-0.41$ M	$UO_2^{2+}(aq) + 4\,HA(aq) + B(org) \rightleftharpoons UO_2A_2(HA)_2B(org) + 2H^+(aq)$ $\log K = 12.79$
DBP–TOPO–CCl_4–0.10 M H_2SO_4	
$[HA] = 10^{-4}-10^{-2.8}$ M and $C_B = 0.47-4.68$ mM	$UO_2^{2+}(aq) + 3\,HA(aq) + B(org) \rightleftharpoons UO_2A_2(HA)B(org) + 2H^+(aq)$ $\log K = 11.95$
$[HA]^2[B]_{org}^{-1} > 10^{-7.4}$ M and $C_B = 29.3-58.7$ mM	$UO_2^{2+}(aq) + 2\,HA(aq) + B(org) \rightleftharpoons UO_2A_2B(org) + 2H^+(aq)$ $\log K = 8.66$
$[HA]^2[B]_{org}^{-1} < 10^{-10}$ M and $C_B = 29.3-58.7$ mM	$UO_2^{2+}(aq) + SO_4^{2-}(aq) + 2\,B(org) \rightleftharpoons UO_2SO_4B_2(org)$ $\log K = 3.49$

Whether addition or substitution predominates depends on the extraction conditions and on the neutral organophosphorus compound used. High concentrations and basic character for the neutral organophosphorus compound B seem to promote substitution, whereas a not so basic neutral organophosphorus compound like TBP, in low concentrations seems to favor addition.

A full account will be published in this journal in the near future.

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Formulation of Active Peptide Structure by Quantitative End Group Determination and Bioassay

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The determination of the structure of bradykinin has mostly relied upon an end group determination with fluoro-2,4-dinitrobenzene using chymotryptic fragments of the peptide and subsequent degradation by the Edman procedure.[1,2] In general the C-terminal amino acid has been determined after incubation with carboxypeptidase. Continuing beyond phenylalanine in position five was not advisable due to the accumulation of disturbing artefacts with the Edman technique. The enzymatic procedures involve a number of time consuming operations, which might be simplified by applying the straightforeward degradation as described by Edman.[3-6] Combined with a quantitative end group determination at the N-terminal and bioassay of the biologically active peptide, the formulation of the structure of the kinin peptides would be simplified, particularly in view of the fact that several bradykinin-like peptides have been isolated from blood plasma, which have in common the nonapeptide sequence in bradykinin at the same time as quantitative differences occur in respect to their biological activities. Since however also species differences may occur,[7] the sequence of amino acids also becomes essential for the complete formulation of the active peptide structure.

In earlier work [8,9] we have shown that the molar proportions of the 2,4-dinitrophenyl-amino acids in bradykinin may be estimated with small amounts of pure isolated peptide from bovine and human plasma. The amino acid sequence in bovine bradykinin obtained with snake venom from the total plasma has not been as yet completely determined [10] by chemical methods. In the present study we have attempted to formulate the active peptide structure by determining the unity ratio between the peptide amount deduced