

1 with approximate individual values in parenthesis.

Conclusion. Calculations of partial molal volumes by adding the partial molal volumes of the groups comprising the molecule or ion, agree well with the experimental values for the carboxyl series, Table 2. The additivity relations thus established make possible a simplified treatment of solute solvent interactions, reducing the effective number of systems. It would mean that investigations of microscopic relations in solution may be concentrated to one or two of the groups of the molecule. The search for realistic models for statistical simulation calculations would also be simplified.

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Aqueous Chemistry of Protactinium(IV). 4. Complex Formation between Pa(IV) and EDTA

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In studying the aqueous chemistry of Pa(IV) it was concluded¹ that Pa(IV) exists as a doubly charged cation PaO^{2+} (or $\text{Pa}(\text{OH})_2^{2+}$). To obtain further information on this species, complex formation with ethylenediaminetetraacetic acid (EDTA) was investigated. To study the complexation with EDTA, the liquid-liquid distribution system $^{233}\text{Pa}(\text{IV})$ -acetylacetonone in benzene-1 M $(\text{Na},\text{H})\text{ClO}_4$ was chosen since this system had been used previously.² The influence of EDTA (added to the aqueous phase

of the extraction system) on the distribution of Pa(IV) will then provide information on Pa(IV)-EDTA complexes.

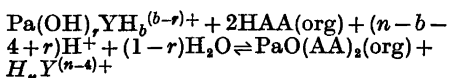
Experimental. The extraction technique and the preparation of most chemicals have been previously described.^{2,3} The distribution system, 2.16 M acetylacetonone in benzene-1 M $(\text{Na},\text{H},0.01 \text{ Cr}^{3+})\text{ClO}_4$ was reduced electrolytically in an atmosphere of argon gas before addition of ^{233}Pa and EDTA (EDTA was always added after the ^{233}Pa). EDTA (Merck, *p.a.*) was added as a 10^{-2} M solution in 1 M NaClO_4 . The system was stirred during electrolysis until the D -values ($D = [\text{Pa}]_{\text{org}}/[\text{Pa}]$) were constant, which usually occurred within 15 min.

The extraction system was found to be independent of the Cr^{2+} concentration for concentrations up to at least 0.02 M, at pH ($= -\log [\text{H}^+]$) = 1. Moreover, the degree of complexation between Cr^{2+} and EDTA was calculated using literature data⁴ and was found negligible for the pH range examined.

Evaluation of the species involved in the extraction. In order to derive the ionic forms of the complexes formed in the reactions between Pa(IV) and EDTA the following general reaction is considered: $\text{PaO}^{2+} + \text{H}_n\text{Y}^{(n-4)+} \rightleftharpoons \text{Pa}(\text{OH})_r\text{YH}_b^{(b-r)+} + (n-b-2+r)\text{H}^+ + (1-r)\text{H}_2\text{O}$; $b = 0, 1, 2$; $n = 0, 1, \dots, 6$.

Here Pa(IV) is denoted with PaO^{2+} but a similar reaction may be set up with $\text{Pa}(\text{OH})_2^{2+}$. Since EDTA, denoted by H_nY , is expected to have a maximum of 6 chelate positions, of which at least 4 are assumed to be occupied by Pa(IV) in the complex $\text{Pa}(\text{OH})_r\text{YH}_b^{(b-r)+}$, b can have the values 0, 1 or 2. In the above equation provision is made for a change in the extent of hydrolysis of the central atom.

The number of protons participating in the reaction may be derived from the experimentally determined pH dependence of the extraction reaction. The extraction reaction formula is obtained by combination of the above reaction formula and the extraction reaction formula valid for Pa(IV) in the absence of EDTA: $\text{PaO}^{2+} + 2\text{HAA}(\text{org}) \rightleftharpoons \text{PaO}(\text{AA})_2(\text{org}) + 2\text{H}^+$, (HAA = acetylacetonone); equilibrium constant K_D . The following overall extraction reaction is thus obtained:



This reaction mechanism was studied experimentally under conditions where the Pa-EDTA complex was the dominating protactinium species. The observed dependence of the distribution ratio on the concentrations of HAA ($\partial \log D / \partial \log [\text{HAA}] = 2$) and EDTA ($\partial \log D / \partial \log [\text{EDTA}] = -1$) verifies the proposed extraction mechanism.

From the limiting pH -dependence $\partial \log D / \partial \log \text{pH} = -2$ (see Fig. 1), one concludes that the average number of protons ($n-b-4+r$)

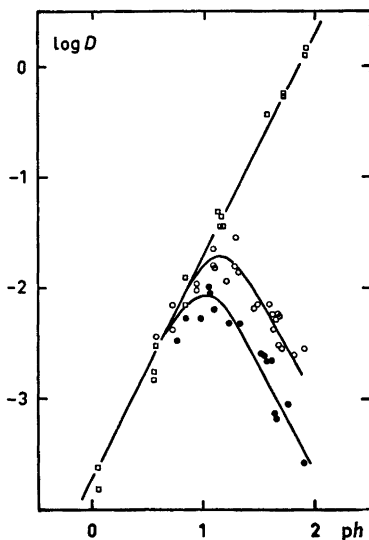


Fig. 1. Distribution of $^{233}\text{Pa(IV)}$, at 25 °C, between 2.16 M acetylacetone in benzene and dilute solutions of EDTA in 1 M (Na,H)ClO₄ as a function of pH (= -log [H⁺]). The line and curves are calculated from estimated stability constants. □, [EDTA]=0 M; ○, [EDTA]=10^{-3.92} M; ●, [EDTA]=10^{-3.25} M.

involved in the extraction reaction is equal to 2. Thus $r=6+b-n$. The values of n are obtained by considering the presence of three EDTA species H₃Y⁻, H₄Y, and H₅Y⁺ ($n=3, 4$, and 5) in the appropriate pH range (1.2–1.7) according to the reported protonisation constants⁵ for EDTA; H_{*n*}Y^{(*n*-5)+} + H⁺ ⇌ H_{*n*}Y^{(*n*-4)+}, $K_1=10^{8.85}$, $K_2=10^{8.26}$, $K_3=10^{2.3}$, $K_4=10^{2.3}$, $K_5=10^{1.4}$, and $K_6=10^{-0.12}$. Formally, r -values ranging from 1 to 5 are obtained. However, Pa(IV) is not expected to be further hydrolyzed due to the complexation with EDTA and hence r -values greater than 2 are not considered. Of the remaining two possible values, r equal to 1 or 2, one concludes that, on the average, $r=2$ must be the most probable value since the value $r=1$ is limited to a reaction ($n=5, b=0$) with only one EDTA species, H₅Y⁺, which furthermore represents only a minor portion of the EDTA species. Since only the average number ($n-b-4+r$) of protons participating in the reaction is known, one cannot exclude reactions other than those outlined above. However, one may expect the following species to be the main ones in the extraction system M²⁺, M(AA)₂(org), MY²⁻ and MYH⁻, where M²⁺=Pa(OH)₂²⁺ or PaO²⁺.

Calculation of formation constants. Having evaluated the main species of the extraction system one can write the distribution constant $D=[\text{Pa(IV)(org)}]/[\text{Pa(IV)}]$ as

$$D = \frac{[\text{M(AA)}_2\text{(org)}]}{[\text{M}^{2+}] + [\text{MY}^{2-}] + [\text{MYH}^-]}$$

The distribution of Pa(IV) in the absence of EDTA, given by D_0 , may be obtained from the extraction constant K_D :

$$K_D = \frac{[\text{M(AA)}_2\text{(org)}][\text{H}^+]^2}{[\text{M}^{2+}][\text{HAA}(\text{org})]^2} = \frac{D_0[\text{H}^+]^2}{[\text{HAA}(\text{org})]^2}$$

The value of K_D , calculated from the straight line in Fig. 1 was found to be 10^{-4.32 ± 0.10}. This value is slightly different from that reported before,³ i.e. 10^{-4.13 ± 0.05}. The small difference is probably due to the more acidic media in the present investigation and to only one HAA concentration being used. The former value was used in the calculation below. As Pa(IV) is present in trace concentrations ([Pa] ≈ 10⁻¹⁰ M), the amount of EDTA complexes with Pa(IV) can be neglected. The concentrations of H_{*n*}Y^{(*n*-4)+} may then be calculated from the total concentration of EDTA and H⁺.

Knowing the main Pa-EDTA species, the concentrations of Y⁴⁻ and H⁺ and their effect on the distribution of Pa(IV), it is possible to calculate the complex formation constants K_1 and K_1^* for the reactions M²⁺ + Y⁴⁻ ⇌ MY²⁻ and M²⁺ + Y⁴⁻ + H⁺ ⇌ MYH⁻, respectively. The following equation may be derived $D_0/D - 1 = [\text{Y}^{4-}]/(K_1 + K_1^*[\text{H}^+])$. The values of ($K_1 + K_1^*[\text{H}^+]$) were calculated for each experimental point ($D, [\text{H}^+]$) and the regression of ($K_1 + K_1^*[\text{H}^+]$) as a function of $[\text{H}^+]$ was calculated using the weighted least squares method. The values obtained were $K_1=10^{19.0 ± 0.3}$ and $K_1^*=10^{20.5 ± 0.3}$. (Since the accuracy of the ($K_1 + K_1^*[\text{H}^+]$) values is proportional to ($D_0/D - 1$) the error square sum was weighted with this factor). The calculated functions $\log D=f(\text{pH})$ for [EDTA]=10^{-3.92} M and 10^{-3.25} M are shown together with experimental data in Fig. 1. Due to the large uncertainty in the K_1^* value, calculations were also carried out with $K_1^*=0$ (i.e. the MHY⁻ complex was neglected). The value $K_1=10^{19.2 ± 0.1}$ was then obtained.

Discussion. The present investigation shows that PaO²⁺ (or Pa(OH)₂²⁺) is the dominating Pa(IV) species also under rather acidic conditions, pH 0–2 (Fig. 1). In the presence of EDTA the species PaOY²⁻ (or Pa(OH)₂Y²⁻) and possibly also PaOYH⁻ (or Pa(OH)₂YH⁻) are formed. The formation constant $K_1=10^{19.2 ± 0.1}$ for PaOY²⁻ (or Pa(OH)₂Y²⁻) may be compared to the corresponding constant⁶ $K=10^{22.1 ± 0.1}$ for the complex Pa(OH)₂Y⁻ of Pa(V) and EDTA ($\mu=1, 20^\circ\text{C}$, chloride media). The complexation is as expected stronger with the higher charged Pa(V) ion. However, in comparison with other divalent cations⁷ (e.g. UO₂²⁺, VO²⁺, TiO²⁺, PuO²⁺, the first transition series V²⁺–Zn²⁺, and Group IIA Be²⁺–Ba²⁺) the complexation between Pa(IV) and EDTA is strong.

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