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 Protaactinium(IV). 4. Complex Formation between Pa(IV) and EDTA**

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In studying the aqueous chemistry of Pa(IV) it was concluded that Pa(IV) exists as a doubly charged cation PAO^{3+} (or PA(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 Pa(IV) - acetylacetone in benzene - 1 M (Na,H)ClO_{4} was chosen since this system had been used previously. The influence of EDTA (added to the aqueous phase of the extraction system) on the distribution of Pa(IV) - EDTA complexes.

**Experimental.** The extraction technique and the preparation of most chemicals have been previously described. The distribution system, 2.16 M acetylacetone in benzene - 1 M (Na,H-0.01 Cr^{3+})ClO_{4} was reduced electrolytically in an atmosphere of argon gas before addition of the Pa and EDTA (EDTA was always added after the Pa). EDTA (Merck, p.a.) was added as a 10^{-4} M solution in 1 M NaClO_{4}. The system was stirred during electrolysis until the D-values (D = [Pa]_{org} / [Pa]) were constant, which usually occurred within 15 min.

The extraction system was found to be independent of the Cr^{3+} concentration for concentrations up to at least 0.02 M, at pH (= - log [H^{+}]) = 1. Moreover, the degree of complexation between Cr^{3+} and EDTA was calculated using literature data 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: PaO^{4+} + H_{2}Y^{n-4}+ => Pa(OH)_{2}Y^{(b-r)+} + (n-b-2+r)H^{+} + (1-r)H_{2}O; b = 0,1,2; n = 0,1,2, ... 6.

Here Pa(IV) is denoted with PaO^{3+} but a similar reaction may be set up with Pa(OH)_{2}^{2+}. Since EDTA, denoted by H_{2}Y, 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 Pa(OH)_{2}Y^{(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 obtained by combination of the above reaction formula and the extraction reaction formula is valid for Pa(IV) in the absence of EDTA: PaO^{4+} + 2HAA(organ) => PaO(AA)_{2}(organ) + 2H^{+},

(K_{E}) the following overall extraction reaction is thus obtained:

Pa(OH)_{2}Y^{(b-r)+} + 2HAA(organ) + (n-b-4+r)H^{+} + (1-r)H_{2}O => Pa(OH)_{2}A(organ) + H_{2}Y^{(n-4)+}.

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 (\(\log D / \log [HAA] = 2\)) and EDTA (\(\log D / \log [EDTA] = -1\)) verifies the proposed extraction mechanism.

From the limiting pH-dependence \(\log D / \log pH = -2\) (see Fig. 1), one concludes that the average number of protons \((n-b-4+r)\)
Fig. 1. Distribution of $^{313}$Pa(IV), at 25 °C, between 2.16 M acetylacetone in benzene and dilute solutions of EDTA in 1 M (Na, H)ClO$_4$ as a function of pH (= – log [H$^+$]). The line and curves are calculated from stability constants. □, [EDTA] = 0 M; ○, [EDTA] = 10$^{-3.48}$ M; ●, [EDTA] = 10$^{-3.36}$ M.

The value of $K_D$, calculated from the straight line in Fig. 1 was found to be $10^{-4.38}$. This value is slightly different from that reported before, i.e. $10^{-4.18}$. 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 ($[\text{Pa}] = 10^{-10}$ M), the amount of EDTA complexes with Pa(IV) can be neglected. The concentrations of H$_2$Y$^{(n+4)}$ may then be calculated from the total concentration of EDTA and H$^+$.

Knowing the main Pa-EDTA species, the concentrations of Y$^{n+}$ and H$^+$ and their effect on the distribution of Pa(IV), it is possible to calculate the complex formation constants $K_1$ and $K_5^*$ for the reactions M$^{2+}$ + Y$^{n+}$ = M$^{2+}$Y$^n$ and M$^{2+}$ + Y$^{n+}$ + H$^+$ = MYH$^-$. The following equation may be derived $D_H/D_H^* = (K_1 + K_5^* [H^+])$. The values of $(K_1 + K_5^* [H^+])$ were calculated for each experimental point $(D_H, [H^+])$ and the regression of $(K_1 + K_5^* [H^+])$ as a function of [H$^+$] was calculated using the weighted least squares method. The values obtained were $K_1 = 10^{10.36}$ and $K_5^* = 10^{9.49}$. (Since the accuracy of the $(K_1 + K_5^* [H^+])$ values is proportional to $(D_H/D_H^* - 1)$ the error square sum was weighted with this factor). The calculated functions log $D = f(pH)$ for [EDTA] = 10$^{-3.48}$ M and 10$^{-3.36}$ M are shown together with experimental data in Fig. 1. Due to the large uncertainty in the $K_5^*$ value, calculations were carried out with $K_5^* = 0$ (i.e. the MYH$^-$ complex was neglected). The value $K_5^* = 10^{9.49}$ was then obtained.

Discussion. The present investigation shows that PaO$^{2+}$ (or Pa(OH)$_2$O$^{2+}$) is the dominating Pa(IV) species also under rather acidic conditions, pH 0–2 (Fig. 1). In the presence of EDTA the species PaOY$^-$ (or Pa(OH)$_2$Y$^-$) and possibly also PaOYH$^-$ (or Pa(OH)$_2$YH$^-$) are formed. The formation constant $K_1 = 10^{9.87}$ for PaOY$^-$ (or Pa(OH)$_2$Y$^-$) may be compared to the corresponding constant $K_5^* = 10^{9.36}$ for the complex Pa(OH)$_2$Y$^-$ of Pa(V) and EDTA ($\mu = 1$, 20 °C, chloride media). The complexation is as expected stronger with the higher charged Pa(V) ion. However, in comparison with other divalent cations (e.g. UO$^{2+}$, VO$^{2+}$, TiO$^{2+}$, PuO$^{2+}$) first transition series V$^{2+}$–Zn$^{2+}$, and Group IIA Be$^{2+}$–Ba$^{2+}$) the complexation between Pa(IV) and EDTA is strong.
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