Table 3. Mean amplitudes of vibration (u in Å) and linear shrinkage effects (δ in Å) for tetrolyl chloride, $CH_3CCCOCl$.

Distance	(R, Å)	0 K	298 K
$u(C_1=O)$	(1.192)	0.039	0.039
$u(C_1-Cl)$	(1.789)	0.045	0.047
$u(C_1-C_2)$	(1.426)	0.048	0.049
$u(C_2\equiv C_3)$	(1.207)	0.036	0.036
$u(C_3-C_4)$	(1.458)	0.049	0.051
$u(C_4-H)$	(1.110)	0.078	0.078
$u(C_1\cdots C_3)$	(2.633)	0.051	0.053
$u(C_1\cdots C_4)$	(4.091)	0.062	0.066
$u(C_1\cdots H)$	(4.582)	{0.135 {0.134	{0.154 {0.151
$u(C_2\cdots C_4)$	(2.665)	0.053	0.055
$u(C_2\cdots O)$	(2.346)	0.055	0.059
$u(C_2\cdots Cl)$	(2.683)	0.058	0.069
$u(C_2\cdots H)$	(3.210)	{0.125 {0.123	{0.132 {0.129
$u(C_3\cdots O)$	(3.484)	0.059	0.067
$u(C_3\cdots Cl)$	(3.710)	0.068	0.101
$u(C_3\cdots H)$	(2.106)	0.109	0.110
$u(C_4\cdots O)$	(4.903)	0.071	0.092
$u(C_4\cdots Cl)$	(5.057)	0.081	0.143
$u(O\cdots Cl)$	(2.602)	0.053	0.060
$u(O\cdots H)$	(5.181)	0.156	0.207
$u(O\cdots H)$	(5.461)	0.143	–
$u(Cl\cdots H)$	(5.349)	0.181	–
$u(Cl\cdots H)$	(5.814)	0.122	0.143
$u(H\cdots H)$	(1.813)	0.128	0.128
$\delta(C_1\cdots C_3)$	(2.633)	0.007	0.012
$\delta(C_1\cdots C_4)$	(4.091)	0.015	0.030
$\delta(C_2\cdots C_4)$	(2.665)	0.008	0.012

values deduced from structurally related molecules.[3,5,10]

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Aqueous Chemistry of Protactinium(IV). 3. Solvent Extraction of Pa(IV) Perchlorate by Trioctyl Phosphine Oxide

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In studying the aqueous chemistry of Pa(IV)[1,2] it was found that a pH independent extraction method would be of value. An investigation of the extraction of Pa(IV) from perchlorate solutions by neutral adduct forming agents was therefore undertaken. The neutral organophosphorus compounds, which are among the strongest adduct forming molecules,[3] were selected for this investigation. Because the commonly used TBP (tributylphosphate) showed unsatisfactory extraction power, the more basic TOPO (trioctyl phosphine oxide) was chosen for a more detailed study.

Chemicals. Stock solutions of ^{233}Pa (in 7 M $HClO_4$), $(Na,H)ClO_4$, Zn(Hg) and 1.92 M $Cr(ClO_4)_3$ were prepared as described earlier.[1] The isotopes ^{51}Cr and ^{65}Zn were supplied from AB Atomenergi, Studsvik, Sweden, and Institutt for Atomenergi, Kjeller, Norway, respectively. The ^{24}Na was obtained by 1.8 h neutron irradiation (AB Atomenergi, Studsvik, Sweden) of 30 mg Na_2CO_3 at a neutron flux of 2.5×10^{12} n s^{-1} cm^{-2}. Stock solutions of ^{51}Cr (9 mCi/ml) in 0.1 $HClO_4$, ^{65}Zn (0.2 mCi/ml) in 1 M $HClO_4$, and ^{24}Na (0.4 mCi/ml)

in 1 M HClO$_4$ were prepared. The radiochemical purity of the gamma spectra was checked using a high resolution Ge(Li)-detector equipped with a multichannel analyzer. Commercial TBP solution (99 %) was purified [4] by distillation together with 0.1 M NaOH, washing with water and drying under vacuum. Later, TBP from another source (British Drug House, p.a.) was used without purification. The IR-spectra of the two TBP batches were measured with a Perkin-Elmer 337 grating IR spectrophotometer in the range 2.5 to 25.0 μ, and were found to be identical. A stock stolution of TOPO was made by successively washing a 1 M TOPO (Eastman Kodak) solution in benzene with equal volumes of first 0.1 NaOH + 0.9 NaClO$_4$ and then (0.1 H, 0.9 Na)ClO$_4$. The purified TOPO solution was slightly yellow. The chemicals used were of p.a. quality, if not otherwise stated.

Extraction technique. The extraction runs were made in an oxygen-free nitrogen atmosphere in a small glass vessel thermostated to ± 0.05 °C. Mixtures composed of 15 ml (Na, H)ClO$_4$ (of various molarities) + 0.1 ml 1.92 M Cr(ClO$_4$)$_3$ + 15 ml benzene were reduced either with 3 − 6 ml Zn(Hg) or electrolytically between a mercury cathode and a platinum anode. After complete reduction one drop of the ^{233}Pa stock solution (or ^{51}Cr or ^{65}Zn) and 0.005 − 1.6 ml 1 M TOPO in benzene was added. Separate electrolytic reduction experiments using ^{51}Cr as a tracer showed that chromium could be completely removed from the solution by amalgamation (or deposition) at the cathode, but the process was rather slow under the conditions used (∼ 20 mA, 20 V).

The ph (= − log[H$^+$]) was adjusted if necessary with 1 M NaOH or 1 M HClO$_4$ and the distribution system was stirred for 10 min, which was sufficient to establish equilibrium. In the beginning of some experiments, the organic phase was somewhat opaque after the addition of TOPO but this was found to have no effect on the distribution of Pa. The gamma activities, from equal samples of each phase (80 − 100 keV for ^{233}Pa and ^{51}Cr, above 1 MeV for ^{65}Zn and ^{24}Na), were measured with a NaI(Tl) crystal. The total number of disintegrations registered of each couple of phases was about 200 000. The number of disintegrations registered of the least active phase examined (which was at least twice as active as the background) was more than 2000, giving a radiometric accuracy in the logarithm of the distribution factor D_{Pa} of ± 0.01.

Results. The extraction using TOPO in benzene of ^{233}Pa(IV) from aqueous solutions of (Na, H, 0.01 M Cr^{2+})Cl$_4$O was studied at different concentrations of perchlorate (Figs. 1 and 2), of TOPO (Fig. 2) and of hydrogen ions (Fig. 3). Because the reduction procedure introduced Cr^{2+} and in some cases Zn^{2+} (less than 0.01 M), it was necessary to investigate whether these species affected the extraction of Pa(IV). The distributions of ^{65}Zn and ^{51}Cr

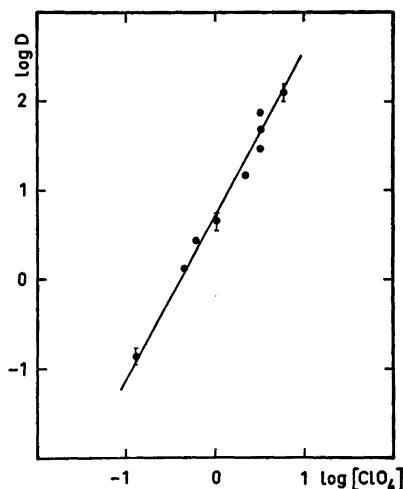*Fig. 1.* The distribution of ^{233}Pa(IV) between 10$^{-1.93}$ M TOPO in benzene and perchlorate media of various concentrations at ph 1 and 25 °C. The points marked with error limits are average values from at least 5 experiments.
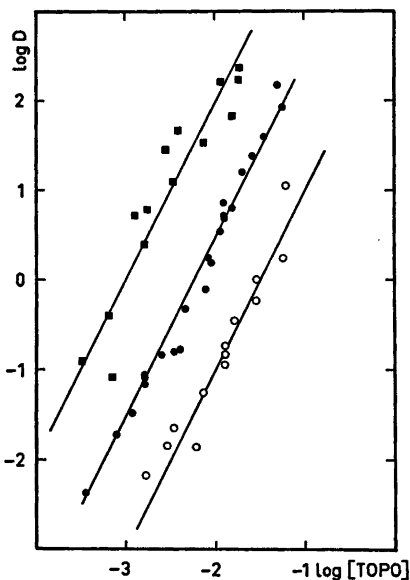

Fig. 2. The influence, at 25 °C, of the TOPO concentration on the distribution of ^{233}Pa(IV) between benzene and perchlorate media for different perchlorate concentrations at ph 1. ■ [ClO$_4^-$] = 5.93 M; ● [ClO$_4^-$] = 1.03 M; ○ [ClO$_4^-$] = 0.13 M.
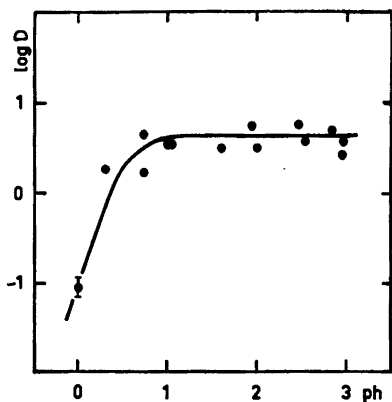
Fig. 3. The p*h* dependence of the distribution of ^{233}Pa(IV) between $10^{-1.93}$ M TOPO in benzene and 1.03 M perchlorate solution at 25 °C.

were found to be very low; about $10^{4.9}$ and $10^{3.7}$ times lower distribution values than for Pa(IV), respectively. The amount of TOPO complexed with Zn and Cr could thus be neglected. As extraction of perchloric acid reduces the free TOPO concentration, the ratio $[TOPO]_o/[HClO_4]_o$ (index o refers to the organic phase) was determined (in separate experiments) by titration of the aqueous and organic phases with 0.01 M NaOH. The extraction of $HClO_4$ (at p*h* 1) was investigated at high concentrations of TOPO (0.01 – 0.07 M) and perchlorate (1 and 6 M) and was found to be proportional to the perchlorate concentration and to the square of the TOPO concentration (if $[TOPO]_o/[HClO_4]_o > 2$). This is in agreement with the known extraction behaviour; $HClO_4$ is extracted [5] as an ion pair with the proton solvated with two TOPO molecules (if $[TOPO]_o/[HClO_4]_o < 2$). The ratio $[TOPO]_o/[HClO_4]_o$ (which is proportional to $[ClO_4]^{-1}$ and $[TOPO]^{-1}$) was found to be about 5 for 0.01 M TOPO ($[ClO_4] = 6$ M) and 10 for 0.072 M TOPO ($[ClO_4] = 1$ M).

The extraction of $NaClO_4$ was studied using the isotope ^{24}Na. The highest distribution $(D = 10^{-2.89})$ of $NaClO_4$ was found at the highest investigated concentrations of TOPO (0.072 M) and perchlorate (6 M). The ratio $[TOPO]_o/[NaClO_4]_o$ was thus ≥ 100 for all the distribution experiments of Pa(IV) and hence the extraction of $NaClO_4$ was neglected. Neither the concentration of ^{233}Pa ($10^{-11} – 10^{-10}$ M) nor the presence of less than 10^{-3} M sulphate or less than 10^{-2} M chloride affected the distribution. The sizes of the dots in the figures correspond approximately to the uncertainties.

The *perchlorate dependence* of the distribution of Pa(IV) was studied in the range from 0.13 to 5.93 M ClO_4. The ionic strength could not be kept constant but varied with the perchlorate

concentration, because no weaker complexing anion to Pa(IV) than ClO_4 could be added. The influence of the perchlorate concentration was, however, much stronger than could be expected from the change in ionic strength. The function log $D = f(\log [ClO_4])$ had a slope of 2; see Fig. 1. The *TOPO dependence* was studied at p*h* 1 (see Fig. 2) and 0 at different perchlorate concentrations. The slopes ∂ log D/∂ log [TOPO] were constant and equal to $+ 2$ over the perchlorate concentration range investigated both at p*h* 1 (0.13 – 5.93 ClO_4) and at p*h* 0 (1 M $HClO_4$). The TOPO dependence of the distributions of Zn(II) and Cr(II) at p*h* 1 (1.03 M ClO_4) was found to be similar to that for Pa(IV), but the distributions were much lower. The *p*h *dependence* was investigated at 1.03 M perchlorate and $10^{-1.93}$ M TOPO concentrations, see Fig. 3. The distribution of protactinium $(D = [Pa]_o/[Pa])$ at 25 °C was found to be constant from p*h* 1 up to at least 3. The useful p*h* range for extraction was limited by the rapid decrease in D at lower p*h* than 1 and the formation of Cr(II) hydroxides at higher p*h* than about 4 – 5. The *temperature dependence* was rather strong and showed a decreasing distribution of Pa(IV) with increasing temperature; log $D = 1.22 \pm 0.15$ (10 °C), log $D = 0.68 \pm 0.07$ (25 °C), log $D = -0.25 \pm 0.07$ (45 °C). The temperature dependence was studied at p*h* 1 and at constant perchlorate (1.03 M) and TOPO ($10^{-1.93}$ M) concentrations.

Discussion. In evaluating the distribution data for Pa(IV) it is important to bear in mind that the free TOPO concentration in the organic phase may be lowered due to complexation with Na^+, H^+, Pa(IV), Zn(II), Cr(II) and H_2O. TOPO is known to be complexed with water both due to the solubility of water in benzene and as a result of the extraction of water, which occurs with one TOPO molecule solvating each water aggregate.[5] The complexation with water is here assumed to be constant (at least for constant ionic strength). Of the remaining species only H^+ was found to have any influence on the free TOPO concentration, and this only when the ClO_4 concentration was high. For 0.1 M $HClO_4$, the influence of the H^+ concentration was negligible. For 1 M ClO_4 and $[TOPO] \leq 10^{-1.93}$ M, the influence of H^+ was negligible at ph ≥ 1 which is reflected by the constant distribution of Pa(IV) and further confirmed by the value of the ratio $[TOPO]_o/[HClO_4]_o = 10$ determined for $[TOPO] = 10^{-1.72}$. A small correction of the log D (6 M ClO_4) values may be relevant for the highest TOPO concentrations used, but as the correction is of the same magnitude as the error in log D it does not change the stoichiometric conclusions drawn below. Uncorrected log D values are shown in the figures.

From the zero protactinium concentration dependence $(\partial$ log D/∂ log [Pa] = 0) and from the strong perchlorate dependence $(\partial$ log D/∂ log $[ClO_4] = 2)$ of the distribution of Pa(IV), it

is likely that Pa(IV) is distributed in the form of monomeric aggregates of ion pairs. If the degree of complexation between TOPO and water is constant (or nearly constant), and the influence of the ionic strength on the distribution of Pa(IV) is small for the investigated perchlorate concentration range, then the ion pair must consist of two perchlorate and one Pa(IV) ion, which latter from the electro-neutrality criterium must be a doubly charged cation. Two cations, PaO^{2+} or $Pa(OH)_2^{2+}$, are possible, which conclusion is in agreement with observations from other perchlorate media extraction systems.[1,2]

From the TOPO dependence of the distribution ($\partial \log D/\partial \log [\text{TOPO}] = 2$) one concludes that the ion pair of Pa(IV) is solvated with two TOPO molecules. The extraction of Pa(IV) may then be formulated as $M^{2+} + 2ClO_4^- + 2TOPO(\text{org}) \rightleftharpoons [M^{2+}(TOPO)_2][ClO_4^-]_2(\text{org})$. The possible participation of water in the extraction mechanism has not been studied due to experimental difficulties in determining the water content in the extracted complex when working at trace concentrations of Pa, and in evaluating the influence of the water activity on the extraction (one of the difficulties arises from the fact that TOPO itself extracts water). One notes that the number of TOPO solvates is still two at low acidities (1 M $HClO_4$), which indicates that the extraction mechanism is uncharged although dehydrolyzation of Pa(IV) is expected.[6]

The distribution of Cr(II) and Zn(II) was found, from a preliminary investigation, like Pa(IV), to be dependent on the second power of the TOPO concentration. The extraction of the divalent ions with TOPO seems therefore to be similar to their extraction with TBP;[7]

$M^{2+} + 2ClO_4^- + mH_2O + 2TBP(\text{org}) \rightleftharpoons [M^2(H_2O)_m(TBP)_2][ClO_4^-]_2(\text{org}).$
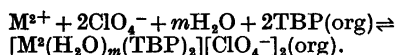
The extraction constant for Pa(IV) has been calculated to be log $K_D = 4.41 \pm 0.10$ (the total TOPO concentration is used in the calculations, not free TOPO concentration). The thermodynamic constants corresponding to K_D, obtained from the temperature data, were $\Delta H° = -72 \pm 9$ kJ mol^{-1} and $\Delta S° = -157 \pm 31$ J K^{-1} mol^{-1}.

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A High Temperature Iron Telluride with Rhombohedral Structure

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A high temperature iron-tellurium phase has been found by DTA and X-ray high temperature investigations. This phase melts incongruently at about 920 °C, and transforms eutectoidally at 805 °C into the $Fe_2As-PbO$ type phase with tetragonal structure and the phase with the hexagonal NiAs-Cd(OH)$_2$ type structure. The high temperature phase exists in a rather broad range of homogeneity from about $FeTe_{0.80}$ to $FeTe_{0.93}$ at 845 °C. This temperature corresponds to the peritectoid decomposition of the $Fe_2As-PbO$ type phase. The corresponding composition of this phase is between $FeTe_{0.75}$ and $FeTe_{0.80}$. By the peritectoid decomposition metallic iron and the high temperature phase are formed.

The X-ray high temperature patterns could be indexed according to a rhombohedral unit cell and the data are given in Table 1.

The lattice constants of $FeTe_{0.90}$ were calculated for the temperatures 835 and 870° C, and of a metal rich sample, $FeTe_{0.75}$ at 850 °C. The latter is a two phase sample in which metallic iron exists in equilibrium with the high temperature phase of approximate composition $FeTe_{0.80}$. The following lattice constants refer to hexagonal setting:

$FeTe_{0.90}$, 835 °C:
$a = 4.013 \pm 0.003$ Å, $c = 20.96 \pm 0.02$ Å
$FeTe_{0.90}$, 870 °C: