

## Extraction of Tc(VII) by Trilaurylammonium Nitrate in Xylene

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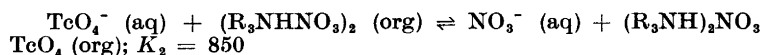
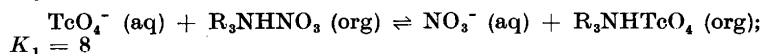
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The distribution of  $^{99}\text{TcO}_4^-$  between solutions of trilaurylammonium nitrate ( $\text{R}_3\text{NHNO}_3$ ) in *o*-xylene and aqueous solutions of  $\text{HNO}_3$  and  $\text{LiNO}_3$  has been measured at 25°C. In 1 M ( $\text{H,Li}$ ) $\text{NO}_3$  and 0.015 M  $\text{R}_3\text{NHNO}_3$  the overall equilibrium constant for the ionic exchange reaction

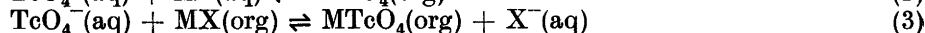
$\text{TcO}_4^- (\text{aq}) + (\text{R}_3\text{NHNO}_3)_n (\text{org}) \rightleftharpoons \text{NO}_3^- (\text{aq}) + (\text{R}_3\text{NH})_n (\text{NO}_3)_{n-1} \text{TcO}_4 (\text{org})$  is  $\log K = 2.20$ , where

$$K = \frac{(\text{total conc. of Tc in org phase}) \times (\text{total conc. of } \text{NO}_3^- \text{ in aq phase})}{(\text{total conc. of Tc in aq phase}) \times (\text{total conc. of } \text{NO}_3^- \text{ in org phase})}$$

Experiments, in which the total nitrate concentration in either phase was varied, support the ion exchange reaction even if  $K$  is somewhat dependent on the concentration. The influence on  $K$  of the amine nitrate concentration in the organic phase below 1 % can be explained by the following two reactions:



Tc(VII) can be extracted by the following three types of reactions:



In the first type of reaction solvents like cyclohexanol and tri-butyl-phosphate (TBP) which contain a donor group have been used.<sup>1-4</sup> In the second case large cations,<sup>5</sup> such as  $\text{Bu}_4\text{N}^+$ ,  $(\text{C}_6\text{H}_5)_4\text{P}^+$ , and  $(\text{C}_6\text{H}_5)_4\text{As}^+$ , with hydrophobic groups can be used together with organic solvents like chloroform. With less hydrophobic cations (*e.g.*  $\text{Na}^+$ ) extraction can still

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be obtained if the organic phase (*e.g.* cyclohexanol,<sup>1</sup> see below) has sufficient solvation power. In the third case the cation  $M^+$  has such large hydrophobic groups (*e.g.* trilaurylammonium ions) that it is not soluble in the aqueous phase.<sup>1,4,6</sup> The extraction will then take place through an ion exchange reaction.

The purpose of this work was to study the ion-exchange mechanism with solutions of trilaurylammonium nitrate in *o*-xylene as the polymerization of this extractant had been investigated by Högfeldt.<sup>7</sup> We wished to see if the polymerization of  $R_3NHNO_3$  would have any effect on a simple anion extraction. Our investigation would also form a basis for a discussion of some previous work on the extraction of Tc(VII) by Boyd and Larson.<sup>1</sup>

### EXPERIMENTAL

*Materials.* The trilaurylamine (TLA) was purchased from Rhône-Poulenc. Analysis by Mr. Å. Hultgren at the Swedish Atomic Energy Company has shown that the material is at least 99 % pure. This was confirmed by two phase potentiometric titrations by Högfeldt and his co-workers. Solutions of the amine in *o*-xylene were shaken with dilute nitric acid in order to convert the amine into the nitrate salt without any excess of  $HNO_3$ . The ammonium pertechnetate, obtained from Radiochemical Centre, Amersham, contained the  $\beta$ -emitting (0.29 MeV)  $^{99}Tc$  with the half-life of  $2.12 \times 10^6$  years. The concentration of pertechnetate was originally 0.0348 M and was brought by dilution to the final concentration of 0.000348 M. The *o*-xylene (Fluka AG Buchs SG) was used without purification as gas chromatographic analysis by Mr. G. Lindgren showed that this product contained less than 1 % of other similar hydrocarbons (mostly *m*- and *p*-xylene). All other reagents were of analytical grade.

*Procedure.* Equal volumes of the aqueous and amine nitrate solutions were shaken together for 2 h. The distribution ratio was determined by measuring the radioactivity of aliquots taken from both phases. A liquid counter tube M2-H of the 20th Century Electronics was used for this purpose. A correction factor  $A$ , due to the difference of absorption of the  $\beta$ -particles in the two phases, had to be introduced. This value was obtained by plotting the counts per min (cpm) of the organic phase *versus* the cpm of the aqueous phase, in which case the slope gives the values of  $1/A$ . The absorption coeffi-

Table 1. Distribution of  $^{99}Tc$  between 0.015 M  $R_3NHNO_3$  in xylene and aqueous solutions of  $HNO_3$ . Initial concentration of  $TcO_4^-$  in the aqueous phase 0.000348 M.  $[NO_3^-] = [H^+]$ .

Initial [ $HNO_3$ ] M	Measured [ $H^+$ ] M	$\log q$	$\log K$
0.001	0.0036	2.138	1.60
0.001	0.0041	2.193	1.73
0.002	0.0042	2.127	1.64
0.002	0.0047	2.133	1.71
0.005	0.0055	2.114	1.69
0.005	0.0065	2.113	1.79
0.01	0.0100	2.103	1.92
0.01	0.0106	1.968	1.81
0.02	0.02	1.910	2.04
0.05	0.05	1.576	2.10
0.10	0.10	1.282	2.10
0.20	—	1.028	2.15
0.50	—	0.622	2.14
0.90	—	0.263	2.04

Table 2. Distribution of  $^{99}\text{Tc}$  between 0.015 M  $\text{R}_3\text{NHNO}_3$  in xylene and aqueous solutions of  $\text{LiNO}_3$ . Initial concentration of  $\text{TcO}_4^-$  in the aqueous phase 0.000348 M.  $[\text{Li}^+] + [\text{H}^+] \simeq [\text{NO}_3^-]$ .

Initial [LiNO <sub>3</sub> ] M	Measured [H <sup>+</sup> ] M	log $q$	log $K$
0.001	0.0038	2.117	1.75
0.002	0.0036	2.123	1.82
0.005	0.0032	2.146	1.98
0.01	0.0029	1.958	1.98
0.02	0.0024	1.787	2.04
0.05	0.0018	1.464	2.06
0.10	0.0013	1.292	2.16
0.20	(0.0012)	0.995	2.16
0.50	(0.0009)	0.645	2.20
0.90	0.0005	0.418	2.21

cient was found to be  $A = 0.804$ , and the distribution ratios were calculated as being  $q = A$  (cpm)org./ (cpm)aq. The hydrogen ion concentrations in the aqueous phase were calculated from emf measurements after introducing corrections for the variations in the ionic media. All experiments were carried out at  $25 \pm 0.1^\circ\text{C}$ .

#### THE EXPERIMENTAL RESULTS

Four sets of experiments were carried out; both the concentration of the triaurylammonium nitrate in *o*-xylene and that of the nitrate ion in the aqueous solution were varied. The aqueous phase consisted of (a) 0.001 to 0.90 M nitric acid, (b) 0.001 to 0.90 M lithium nitrate, or (c) 0.99 M of a mixture of both (Tables 1–3). In the three series of experiments in which the aqueous solution was varied, the initial amine nitrate concentration was constant, 0.015 M. In the fourth series (Table 4) the TLA concentration was varied — between 0.0015 and 0.3 M — whereas the initial aqueous solution was 0.09 M  $\text{LiNO}_3$ . The initial concentration of the pertechnetate in the aqueous phase was

Table 3. Distribution of  $^{99}\text{Tc}$  between 0.015 M  $\text{R}_3\text{NHNO}_3$  in xylene and aqueous solutions of 0.99 M (H,Li)NO<sub>3</sub>. Initial concentration of  $\text{TcO}_4^-$  in the aqueous phase 0.000348 M.  $[\text{NO}_3^-] \simeq [\text{Li}^+] + [\text{H}^+]$

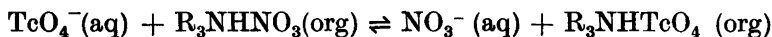
Initial [H <sup>+</sup> ] M	[Li <sup>+</sup> ] M	Measured [H <sup>+</sup> ] M	log $q$	log $K$
0.001	0.989	0.0005	0.351	2.17
0.002	0.988	0.0013	0.383	2.20
0.005	0.985	0.0040	0.387	2.21
0.01	0.98	0.01	0.377	2.20
0.02	0.97	0.02	0.377	2.20
0.05	0.94	0.05	0.365	2.19
0.10	0.89	0.10	0.378	2.20
0.20	0.79	—	0.370	2.19
0.50	0.49	—	0.332	2.15
0.90	0.09	—	0.273	2.02

Table 4. Distribution of  $^{99}\text{Tc}$  between  $\text{R}_3\text{NHNO}_3$  in xylene and aqueous solutions of 0.09 M  $\text{LiNO}_3$ . Initial concentration of  $\text{TcO}_4^-$  in the aqueous phase 0.000348 M.  $[\text{NO}_3^-] \approx [\text{Li}^+] + [\text{H}^+]$

Initial [ $\text{R}_3\text{NHNO}_3$ ] M	%	Measured [ $\text{H}^+$ ] M	$\log q$	$\log K$	Calculated [ $\text{R}_3\text{NHN}_3\text{O}$ ] <sub>org</sub> M
0.300	20	0.00200	2.452	1.94	0.0298
0.225	15	0.00195	2.450	2.07	0.0283
0.150	10	0.00190	2.421	2.21	0.0256
0.075	5	0.00182	2.169	2.27	0.0205
0.030	2	0.00162	1.784	2.29	0.0134
0.015	1	0.00135	1.318	2.15	0.0090
0.010	0.67	0.00120	1.079	2.11	0.0068
0.0050	0.33	0.00094	0.617	2.00	0.00397
0.0030	0.2	0.00074	0.276	1.93	0.00256
0.0015	0.1	0.00051	-0.191	1.84	0.00138

throughout 0.000348 M. The results of the experiments are shown in Tables 1–4 and in Fig. 1.

The expression for  $K$  in Fig. 1 is based on the overall equation of anion-exchange equilibrium:



Disregarding the fact that  $\text{R}_3\text{NHNO}_3$  is partly polymerized we calculated  $K$  from the total conc. of  $\text{NO}_3^-$  and  $\text{TcO}_4^-$  in the organic phase. Thus,  $K = q[\text{NO}_3^-]_{\text{org}} / [\text{R}_3\text{NHNO}_3]_{\text{tot,org}}^{-1}$ .

The influence of the amine concentration on  $K$

From Fig. 1 it may be seen that  $K$  varies somewhat with the total concentration of the amine nitrate in the xylene phase. Except for 15% and 20% TLA the variation can be explained if the following three reactions are considered

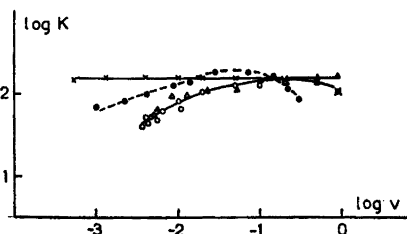


Fig. 1. Values of  $K = q[\text{NO}_3^-]_{\text{org}} / [\text{R}_3\text{NHNO}_3]_{\text{tot,org}}^{-1}$  as a function of  $v$ . Symbols: O: var.  $\text{HNO}_3$ ,  $v = [\text{HNO}_3]$  (Table 1);  $\blacktriangle$ : var.  $\text{LiNO}_3$ ,  $v = [\text{NO}_3^-]$  (Table 2);  $\times$ : 0.99 M  $(\text{H}_2\text{Li})\text{NO}_3$ ,  $v = [\text{H}^+]$  (Table 3);  $\bullet$ : var.  $\text{R}_3\text{NHNO}_3$ ,  $v = [\text{R}_3\text{NHNO}_3]_{\text{tot,org}}$  (Table 4).

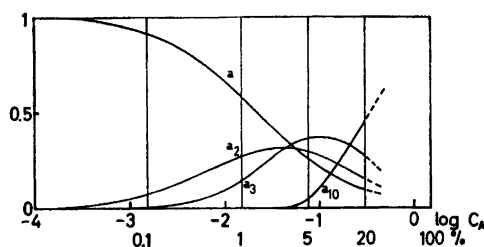
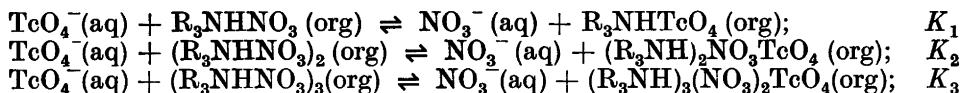


Fig. 2. Fractions of TLA nitrate in the monomeric ( $a$ ), dimeric ( $a_2$ ), trimeric ( $a_3$ ) and decameric ( $a_{10}$ ) forms as a function of the total amine concentration in the *o*-xylene phase,  $C_A = a + 2a_2 + 3a_3 + 10a_{10}$ . Above 20% further polymerization occurs.



The choice of these three reactions is based on results by Högfeltd<sup>7</sup> who investigated the polymerization of TLA nitrate in *o*-xylene by a two-phase titration technique. He found that between 0.1 and 1 % TLA mainly monomers, dimers and trimers are present as shown in Fig. 2. The dimerization constant  $K_D = [(\text{R}_3\text{NHNO}_3)_2]_{\text{org}} [\text{R}_3\text{NHNO}_3]_{\text{org}}^{-2}$  was found to be  $10^{1.43}$  and the trimerization constant  $K_T = [(\text{R}_3\text{NHNO}_3)_3]_{\text{org}} [\text{R}_3\text{NHNO}_3]_{\text{org}}^{-3} = 10^{3.03}$ . As only small amounts of  $\text{TcO}_4^-$  are used, it is rather reasonable to assume that no polymeric species such as  $(\text{R}_3\text{NHTcO}_4)_2$  are formed. The expression for the net distribution ratio of <sup>99</sup>Tc is thus:

$$q = \frac{[\text{R}_3\text{NHTcO}_4]_{\text{org}} + [(\text{R}_3\text{NH})_2\text{NO}_3\text{TcO}_4]_{\text{org}} + [(\text{R}_3\text{NH})_3(\text{NO}_3)_2\text{TcO}_4]_{\text{org}}}{[\text{TcO}_4^-]}$$

or

$$q[\text{NO}_3^-][\text{R}_3\text{NHNO}_3]_{\text{org}}^{-1} = K_1 + K_2K_D[\text{R}_3\text{NHNO}_3]_{\text{org}} + K_3K_T[\text{R}_3\text{NHNO}_3]_{\text{org}}^2$$

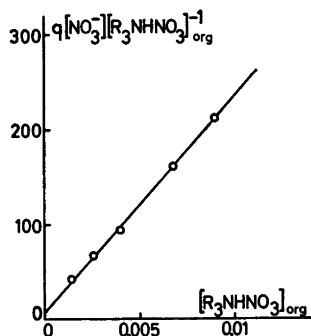


Fig. 3. Determination of  $K_1$  and  $K_2$  (see text) for the exchange reaction between  $\text{TcO}_4^-$  and  $\text{NO}_3^-$  in the monomeric and dimeric forms of TLA nitrate in *o*-xylene.  $K_1 = 8$  is the intercept and  $K_2K_D = 22\,600$  is the slope of the straight line.

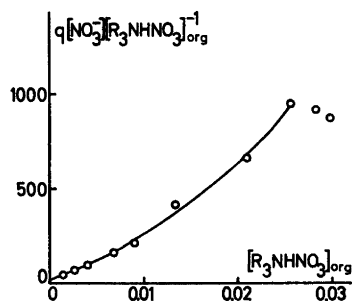


Fig. 4. The same variables as in Fig. 3, but showing also the results for 2 % to 20 % TLA nitrate. The deviation from the straight line in Fig. 3 for 2 %, 5 % and 10 % TLA can be explained by the reaction with the trimer ( $K_3 \sim 475$ ).

From the plot in Fig. 3 (0.1 to 1 % TLA) we obtained  $K_1 = 8$  and  $K_2 = 850$ . From Fig. 4 it may be seen that also the values of 2 %, 5 % and 10 % TLA fit to a smooth curve, but the values for 15 % and 20 % deviate considerably, probably because the exchange constant  $K_n$  does not increase enough to compensate for the decrease in reacting molecules due to further polymerization.

The relative constancy in  $K$  is thus explained by the large  $K_2$  value. However, because  $K_2 > K_1^2$ ,  $K$  will increase somewhat with the concentration of TLA nitrate.

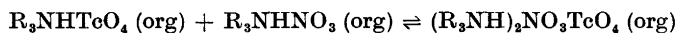
With the two equilibria for  $\text{HNO}_3$  determined by Högfeldt <sup>7</sup>



we can determine the constants for the following two equilibria:



$$K_5 = K_1 K_4 = 10^{5.44}$$

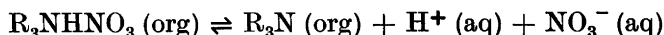


$$K_6 = K_2 K_D / K_1 = 10^{3.45}$$

The constant for the dimerization of  $\text{R}_3\text{NHNO}_3$  in *o*-xylene is thus less than for the addition of  $\text{R}_3\text{NHNO}_3$  and  $\text{R}_3\text{NHTeO}_4$ .  $K_5$  was calculated from data for two media since  $K_4$  was determined for 1 M  $(\text{Na}, \text{H})\text{NO}_3$  and  $K_1$  for 0.09 M  $\text{LiNO}_3$ .

### The influence of nitrate ion concentration on $K$

It may be seen from Fig. 1 that  $K$  decreases with  $[\text{NO}_3^-]$  at constant TLA (1 %) in range 0.1 to 0.004 M, irrespective of if the counterion is  $\text{H}^+$  or  $\text{Li}^+$ . It is not plausible that this effect is due to differences in aqueous electrolyte activities of the  $\text{TeO}_4^-$  and  $\text{NO}_3^-$  ions at such low ionic concentrations. Furthermore, our measurements show that the decrease in  $K$  is not caused by the hydrolysis of the amine nitrate:



It may be seen from Fig. 5 that the total amine nitrate concentration decreases only from 0.015 to 0.011 M when the  $[\text{NO}_3^-]$  is decreased from 1 M to 0.004 M. According to Table 4 and Fig. 1 (filled circles) this should cause only a minor decrease in  $K$ . It may also be seen from Fig. 5 that the formation of  $\text{R}_3\text{N}$  is less for  $\text{HNO}_3$  than for  $\text{LiNO}_3$ , while the decrease in  $K$  (Fig. 1) seems only to

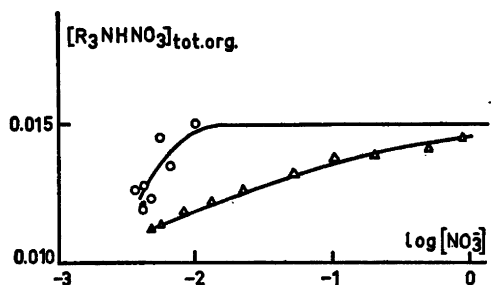


Fig. 5. The formation of  $\text{R}_3\text{N}$  in the organic phase at low nitrate ion concentration in the aqueous phase. The initial total concentration of  $\text{R}_3\text{NHNO}_3$  in the aqueous phase was 0.015 M. The circles refer to  $[\text{H}^+] = [\text{NO}_3^-]$  (Table 1) and the triangles to  $[\text{H}^+] + [\text{Li}^+] = [\text{NO}_3^-]$  (Table 2).

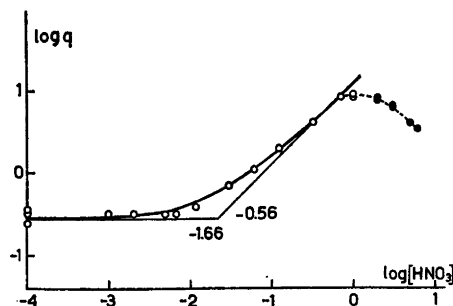


Fig. 6. Data of Boyd and Larson <sup>1</sup> for 1 M  $\text{NO}_3^-$  plotted as  $\log q$  versus  $\log [\text{HNO}_3]$ . The normalized curve  $Y = \log (1 + v)$ ;  $X = \log v$  is fitted to the data below 0.7 M  $\text{HNO}_3$ . The intercept of the asymptotes is  $\log q = -0.56$ ;  $\log [\text{H}^+] = -1.66$ . The extraction constants for  $\text{NaTeO}_4$  and  $\text{HTeO}_4$  are calculated from this point (see text).

be dependent on the nitrate ion concentration. We must therefore admit that for the moment we cannot explain the decrease in  $K$  with the nitrate ion concentration.

The curves in Fig. 5 are qualitatively in agreement with the equilibrium above for the hydrolysis. The measurements are, however, not at all suitable for the determination of an equilibrium constant, as  $[R_3N]$  is calculated from the difference in added  $HNO_3$  or  $LiNO_3$  and measured  $[H^+]$ , assuming that the amine nitrate contained neither an excess of  $HNO_3$  nor any small amounts of  $R_3N$ . From two-phase titrations using 1 M  $NaNO_3$ , Högfeldt<sup>7</sup> had determined a hydrolysis constant of  $10^{-4.54}$

#### The influence of nitric acid on $K$

As may be seen from Fig. 1 the exchange of  $H^+$  for  $Li^+$  at constant  $[NO_3^-] = 0.99$  M (Table 3) has no effect on  $K$  except for 0.5 and 0.9 M  $H^+$ . This shows that we are dealing with an ion exchange reaction and not the extraction of  $HTcO_4$ . A typical example of such a reaction (case 1 in the introduction) is shown in Fig. 6, where we have plotted data of Boyd and Larson.<sup>1</sup> Their data are explained by the distribution ratio

$$q = \frac{[HTcO_4]_{org} + [NaTcO_4]_{org}}{[TcO_4^-]}$$

or with  $[HTcO_4]_{org} = K_H [H^+] [TcO_4^-]$  and  $[NaTcO_4]_{org} = K_{Na} [Na^+] [TcO_4^-]$

$$q = K_H [H^+] + K_{Na} [Na^+]$$

and as they worked at constant  $[NO_3^-] = 1$  M

$$[H^+] + [Na^+] = 1$$

and

$$q = K_{Na} + [H^+] (K_H - K_{Na})$$

Using the normalized curve  $Y = \log(1 + v)$ ;  $X = \log v$ , it was possible to determine

$$\log K_{Na} = -0.56 \text{ and } \log(K_H - K_{Na}) = 1.66$$

or

$$K_{Na} = 0.275 \text{ and } K_H = 45.9$$

It seems that it is possible to neglect any dissociation of  $HTcO_4$  in the cyclohexanol phase or the formation of  $HTcO_4$  in the aqueous phase.

Both in the case of the TLA nitrate extraction of  $TcO_4^-$  and the cyclohexanol extraction of  $HTcO_4$  a decrease in  $K$  or  $q$  is observed at  $HNO_3$  concentration above 0.5 to 1 M. We know that (excess)  $HNO_3$  enters into the organic phase. This seems to push out the  $TcO_4^-$  or  $HTcO_4$ . The same result was obtained by Kertes and Beck<sup>4,8</sup> for tri-isooctylamine- $CCl_4$  extraction of  $TcO_4^-$  and  $ReO_4^-$ . They found that the decrease in  $q$  was proportional to the excess acid. This may be looked upon as an exchange of  $HNO_3$  for  $HTcO_4$  or  $HReO_4$ .

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