REACTION STOICHIOMETRY FOR COEXTRACTION OF TECHNETIUM(VII) WITH URANIUM(VI) BY CMPO

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The coextraction equilibrium of technetium(VII) and uranium(VI) from nitric acid solution was studied in a system involving n-octyl(phenyl)-N,N-diisobutylcarbamoylmethyl phosphine oxide (CMPO) in decalin. Stoichiometry of technetium, uranium and CMPO in the Tc–U–CMPO complex was obtained from the distribution data by slope analysis. The results indicated that the enhanced extraction of technetium was caused by the formation of UO2NO3TcO4·nCMPO (where n = 2 and/or 3). It was found that this coextraction of technetium with uranium was well explained by using ion exchange reaction between UO2(NO3)2·2CMPO complex and TeO4−.

It is well known that the extraction of technetium by TBP is enhanced by the presence of uranyl ions. In a similar way, the present authors reported that the enhancing effect in the CMPO system was remarkable at low nitric acid concentration (Fig. 1).11 The coextraction behavior of technetium and uranium by CMPO, TBP and CMPO + TBP was also explained qualitatively.

In the mixed CMPO–TBP system, technetium in the absence of uranium was extracted by the following reactions:12

\[
\begin{align*}
H^+_{(aq)} + TcO_4^{-}_{(aq)} + 2CMPO_{(org)} & \Leftrightarrow HTcO_4^- \cdot 2CMPO_{(org)}, \quad (1) \\
H^+_{(aq)} + TcO_4^{-}_{(aq)} + 3TBP_{(org)} & \Leftrightarrow HTcO_4^- \cdot 3TBP_{(org)}; \quad (2) \\
H^+_{(aq)} + TcO_4^{-}_{(aq)} + CMPO_{(org)} + 2TBP_{(org)} & \Leftrightarrow HTcO_4^- \cdot CMPO \cdot 2TBP_{(org)}. \quad (3)
\end{align*}
\]

These reactions could occur even in the presence of uranium. However, the enhancing effect of TBP was found to be negligible in the present experimental conditions.11 Therefore, equilibria (2) and (3) can be neglected in the present study.
In the present coextraction system, the following reactions, which are discussed later, are considered to be important:

**U–CMPO system**

\[
\text{UO}_2^{2+} + 2\text{NO}_3^{-} + n\text{CMPO}_{\text{org}} \leftrightarrow \text{UO}_2(\text{NO}_3)_2 \cdot n\text{CMPO}_{\text{org}},
\]  

(4)

**Tc–U–CMPO system**

\[
\text{UO}_2(\text{NO}_3)_2 \cdot n\text{CMPO}_{\text{org}} + \text{TcO}_4^{-} \leftrightarrow \\
\leftrightarrow \text{UO}_2 \cdot \text{NO}_3 \cdot \text{TcO}_4 \cdot n\text{CMPO}_{\text{org}} + \text{NO}_3^{-}
\]  

(5)