Determination of Small Amounts of Nitric Acid in the Presence of Large Amounts of Uranium (VI) and Extraction of Nitric Acid into TBP Solutions Highly Loaded with Uranyl Nitrate

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AND EXTRACTION OF NITRIC ACID INTO TBP SOLUTIONS

HIGHLY LOADED WITH URANYL NITRATE

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Abstract:

A new method for the determination of small amounts of nit-
ric acid in the presence of large amounts of uranium(VI) was
elaborated. The method is based on the precipitation of ura-
nium(VI) as iodate and subsequent alkalimetric titration of
the acid in the supernatant. The extraction of nitric acid
and uranium(VI) with 30% TBP in dodecane was studied at high
loading of the organic phase with uranyl nitrate and at 25,
40 and 60°C. The results are compared with available publis-
hed data on the extraction of nitric acid under similar con-
ditions.

Bestimmung kleiner Mengen von Salpetersäure bei Anwesenheit
von großen Mengen von Uran(VI); Extraktion der Salpetersäure
mit TBP in Dodekan bei hohen Beladungen der organischen Pha-
se mit Uranylnitrat

Zusammenfassung:

Eine neue Methode wurde ausgearbeitet für die Bestimmung von
kleinen Mengen von Salpetersäure bei Anwesenheit von großen
Mengen von Uran(VI). Die Methode beruht auf Fällung von Uran-
(VI) als Iodat und anschließender alkalimetrischer Titration
der Säure in der überstehenden Lösung. Die Extraktion von
Salpetersäure und Uran(VI) mit 30% TBP in Dodekan wurde bei
hohen Beladungen der organischen Phase mit Uranylnitrat un-
tersucht. Die Ergebnisse werden mit vorhandenen Literaturan-
gaben über die Extraktion von Salpetersäure unter ähnlichen
Bedingungen verglichen.

INTRODUCTION

Knowledge of distribution ratios of actinides and nitric acid in extraction systems involving tri-$\underline{n}$-butyl phosphate (TBP) and an alkane diluent is of great importance for modelling extraction or reextraction operations of the Purex process for the reprocessing of spent nuclear fuel. Data obtained at a TBP concentration of 30 vol.% are particularly interesting. Systems involving uranyl and plutonium(IV) nitrates and nitric acid have been studied very extensively, as a collection of distribution data /1/ shows, but there still are some gaps. One of them is the distribution of nitric acid at high concentrations of uranium(VI) ($\geqslant$ 0.4M) in the organic phase. Few acceptable distribution ratios at such a high loading of the organic·phase were published before 1978 /1/. In 1978, Vereshchagin and Renard /2,3/ reported distribution ratios which appeared plausible at high concentrations of nitric acid in the aqueous phase ($>$ 1M), but were unexpectedly high at lower acid concentrations. An extrapolation of data obtained at a lower loading of the organic phase with uranium(VI) /1/ to high organic uranium-(VI) concentrations lets expect distribution ratios of nitric acid lower by an order of magnitude than those given in /2,3/. The high distribution ratios found by the russian authors /2,3/ can be ascribed either to a salting-out of the acid from the aqueous phase by uranyl nitrate or, more plausibly, to an erroneous determination of small amounts of nitric acid in the presence of large amounts of uranium(VI) in the organic phase. To clear this question, we elaborated a new method for the determination of nitric acid at high concentrations of uranium(VI) and measured the distribution of nitric acid. The distribution of uranium(VI) was measured simultaneously. We varied the concentration of nitric acid in a range relevant to the Purex process and also studied the effect of the temperature.

EXPERIMENTAL

TBP, nitric acid, uranyl nitrate, potassium iodate (all Merck, reagent grade), n-dodecane (Fluka, olefine free) and 2-ethylhexanol (Fluka, pure) were used as received.

To measure distribution ratios, we stirred mechanically an aqueous solution containing uranyl nitrate and nitric acid with a 30 vol.% solution of TBP in n-dodecane in a thermostated vessel. After a ~20 min stirring the phases were separated by gravitation (standing time ~20 min), aliquots of them were cooled to $25^{\circ}C$ and samples for the analysis were taken. The determination of nitric acid will be discussed and described below. Uranium(VI) was determined complexometrically after reduction to uranium(IV) with sodium dithionite /4/. Corrections for different thermal expansions of the phases were made according to density data on water /5/ and barren solutions of TBP /6/. The corrections were small (2% or less) and uncertainties caused by neglecting the presence of uranium(VI) and nitric acid did not play any significant role. An automatic titration device, equipped with a combined glass - saturated calomel electrode (Metrohm), was used for alkalimetric titrations.

RESULTS AND DISCUSSION

Determination of Nitric Acid

First we checked the applicability limits of the determination of nitric acid by alkalimetric titration after complexing uranium(VI); this method was used in obtaining the results /2,3/ the plausibility of which was to be verified in this work. In the modification elaborated in this institute /7/, i.e. with a 50/50 wt.% mixture of ammonium oxalate and sodium fluoride as a complexant for uranium(VI), the method proved to be inapplicable for samples of the or-

ganic phase containing $\geqslant 0.4M$ U(VI) and $\leqslant 0.05M$ HNO_3. With decreasing acid concentration the inflex point became less sharp and did not appear at all at very low acid concentrations. We therefore tried to find a method based on the separation of uranium(VI) by precipitation and a subsequent alkalimetric titration of nitric acid in the supernatant. The precipitation of uranium(VI) as a cesium salt of a chlorocomplex /8/ is only effective in isopropanol and would not be suitable for analyzing voluminous samples in other solvents. Attempts to precipitate uranium(VI) as hexacyanoferrate(II or III) were not successful, because irreproducible amounts of hydrogen ions, large enough to interfere in our particular case, were released during the precipitation. We succeeded in precipitating uranium(VI) as uranyl iodate. The precipitate had very weak ion exchange properties and the amount of hydrogen ions released in the course of the precipitation was not only very small, but also reproducible. So a calibration of the method under standard conditions was possible.

The following standard procedure was used: In analyzing the organic phase, a 5 ml sample was pipetted into a centrifugal tube containing 20 ml 0.35M potassium iodate, 5 ml water and 5 ml 2-ethylhexanol (the alcohol supported transfer of nitric acid and uranium(VI) from the organic sample into the aqueous iodate solution). To keep the conditions constant in analyzing the aqueous phase, an aqueous sample (up to 5.00 ml) was pipetted into a centrifugal tube containing 20 ml 0.35M potassium iodate, 5 ml of a barren TBP solution and 5 ml 2-ethylhexanol; if the aqueous sample was smaller than 5 ml, the volume of the aqueous solution in the tube was adjusted with water to 25.0 ml. The content of the tube was then shaken for 10 min. The two initially present liquid phases and the solid uranyl iodate formed during the shaking were separated by centrifuging and a suitable aliquot of the aqueous supernatant was taken for the

alkalimetric titration. Before the titration, the aliquot
was diluted with water to about 60 ml and a sodium fluoride
plus ammonium oxalate mixture (~50 mg) was added for mas-
king eventual residues of uranium(VI) not precipitated as
iodate.

Standard solutions of uranyl nitrate and nitric acid we-
re used for the calibration of the method. To avoid a pos-
sible influence of free nitric acid present in uranyl nit-
rate hexahydrate taken for the preparation of the solutions,
all calibration and distribution experiments were made with
the same stock solution of uranium(VI). To calculate the
concentration of nitric acid in the aliquot taken for the
titration, the equation $C_H' = -0.00169 + 1.20C_{H,f} - 0.0161C_U'$
was applied. The parameters of the equation were found by a
least square treatment of the results of the calibration ex-
periments, C_H' is the actual concentration of nitric acid in
the aliquot after dilution to 25 ml, $C_{H,f}$ is the acid con-
centration found in the titration and C_U' is the concentra-
tion of uranium(VI) in the aliquot after dilution to 25 ml.
The calibration was made in the ranges $C_H' = 0.002$ to $0.009M$
and $C_U' = 0.06$ to $0.14M$. The reproducibility of the method
was ~2%.

Concentrations of nitric acid higher than 1M in the aque-
ous phase were determined, parallelly to the above method
or exclusively, by the usual alkalimetric titration without
separating uranium(VI) and with masking it by the fluoride-
oxalate mixture /7/.

The Distribution of Nitric Acid and Uranium(VI)

We measured the distribution of nitric acid and uranium-
(VI) at their equilibrium concentrations in the aqueous
phase ranging from 0.18 to 4.1M HNO_3 and from 0.3 to 1.13M
U(VI). The temperature was 25, 40 and 60°C. The results are
numerically listed in /1/ under the source numbers 57201 to

57261. Our distribution ratios of nitric acid at 25°C are compared in Fig. 1 with those of Vereshchagin and Renard /2,3/ at 26°C. Our results were obtained under avoiding an influence of uranium(VI) on the determination of nitric acid and the distribution ratios are essentially lower than those given in /2,3/, where uranium(VI) was probably partially cotitrated with nitric acid during the alkalimetric titration. So it is clearly shown that uranyl nitrate does not salt-out nitric acid from the aqueous phase. Much more the uranium(VI) bonds a large fraction of TBP present in the organic phase, the concentration of free TBP is very low and nitric acid is expectedly weakly extracted. The implausibility of the distribution ratios of nitric acid reported in /2,3/ is further illustrated by their decrease with increasing concentration of nitric acid and decreasing concentration of uranium(VI) at low acidities of the aqueous phase (Fig. 1).

Only a part of our data can be graphically presented as a dependence of the distribution ratio on the concentration of nitric acid at a constant concentration of uranium(VI) and vice versa, because keeping one of the two variables strictly constant in a series of measurements would be time consuming. Therefore, we smoothed our data with a mathematical model and show here calculated dependences of the distribution ratio. Since the fraction of TBP not bound to uranium(VI) is very small and can only be calculated as a difference of two similar values, namely the analytical TBP concentration and the double organic concentration of uranium(VI), the use of the equilibrium quotient of the extraction reaction for a mathematical description of the data would not be relevant. Instead we used a model the principle of which is elucidated in /9/. Since data measured in limited concentration regions are to be described, the equations derived in /9/ reduce to the simple form

$$D_H = c_H^a / b c_{U6}^c \quad \text{and} \quad D_{U6} = u N^v / (1 + x N^y c_{U6}^z),$$

where D_H and D_{U6} are the distribution ratios of nitric acid and uranium(VI) respectively, C_H and C_{U6} are equilibrium concentrations of nitric acid and uranium(VI) respectively in the aqueous phase and N is the equilibrium analytical concentration of nitrate ions in the aqueous phase defined as $N = C_H + 2C_{U6}$. The parameters of the equations were found by a least square treatment of the experimental data and are

	$25^\circ C$	$40^\circ C$	$60^\circ C$
a	0	0.0907	0.1535
b	73.0	55.1	40.4
c	0.655	0.782	0.641
u	4.03	2.23	1.69
v	1.866	1.95	2.27
x	8.16	4.30	3.48
y	1.865	1.98	2.32
z	0.908	0.945	0.924

Examples of smoothed dependences $\log D_H = f(\log C_H)$ and $\log D_{U6} = f(\log C_H)$ at $C_{U6} = 1.0M$ are given in Fig. 2. It is seen that the distribution ratio of uranium(VI) is practically independent of the concentration of nitric acid at this high uranium(VI) concentration, because the organic phase is loaded with uranium(VI) almost to its full capacity. For this reason also the distribution ratio of nitric acid remains practically unchanged when the acid concentration is increased at $25^\circ C$ from 0.2 to 4M. The distribution ratio of uranium(VI) slightly decreases with increasing temperature. Since even a slight decrease of the distribution ratio of uranium(VI) causes a large relative enhancement of the free TBP concentration, the distribution ratio of nitric acid visibly increases with the temperature and becomes dependent on the acid concentration at $40^\circ C$ and $60^\circ C$.

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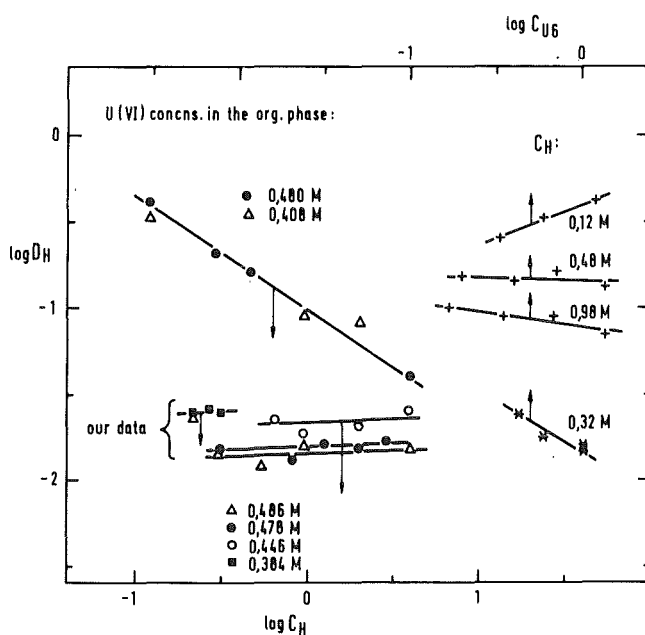/9/ Z. Kolarik and G. Petrich, Ber. Bunsenges. Phys. Chem. 83,1110(1979).

Fig. 1

Log D_H = f(log C_H) dependencies (left part) and log D_H = f(log C_{U6}) dependencies (right part) at different aqueous equilibrium concentrations of HNO_3 at 25°C. Data above log D_H = -1.5 were taken from [2,3] and are valid for 26°C. For symbols see p. 6.
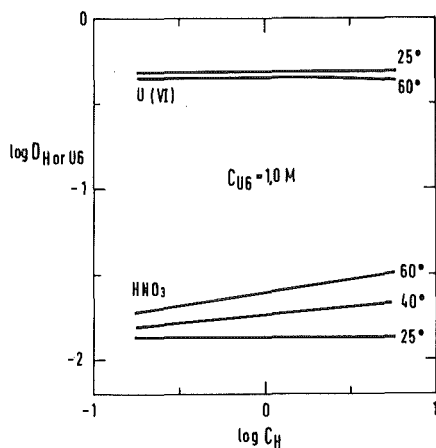

Fig. 2

Smoothed dependencies of log D_H = f(log C_H) and log D_{U6} = f(log C_H) at different temperatures. For symbols see p. 6.