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Abstract

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Corresponding Member of the Academy of Sciences of the USSR A. V. NIKOLAEV, V. G. TORGOV,
V. A. MIKHAILOV, I. L. KOTLYAREVSKII

EXTRACTION OF URANYL NITRATE BY DERIVATIVES OF PYRIDINE-*N*-OXIDE

In a previous work (^{1}), on the basis of a study of the interaction of pyridine-*N*-oxide $C_5H_5N \rightarrow O$ and its derivatives with uranyl salts, we proposed the possibility of using these compounds as extractants for uranium. Somewhat earlier, Heller (^{2,3}) had also pointed to this possibility; however, the pyridine- and quinoline-*N*-oxide compounds with uranyl nitrate that he synthesized proved to be insoluble in organic solvents. In recent years a large number of complex compounds ($^{4-10}$) formed by pyridine-*N*-oxide and some of its derivatives with Pt, Fe(II), Fe(III), Co, Mn, Zn, and other metals have been described; however, organic *N*-oxides have not yet been used as extractants. The present paper gives data on the extraction of uranyl nitrate by several derivatives of pyridine-*N*-oxide.

The extraction properties of pyridine-*N*-oxides must be determined, first of all, by the strength of the $N \rightarrow O \cdots UO_2^{2+}$ bond in the solvates formed during extraction and by the solubility of the solvates in organic solvents. A study of the thermal stability of uranyl nitrate compounds with various derivatives of pyridine-*N*-oxide showed that the $N \rightarrow O \cdots UO_2^{2+}$ bond is so strong that even the introduction into the pyridine-*N*-oxide molecule of strong electrophilic substituents ($-Cl$, $-C_6H_5$, $-NO_2$) does not lead to its noticeable weakening. The formation of a strong $N \rightarrow O \cdots UO_2^{2+}$ bond is also confirmed by the strong ($\simeq 50$ cm^{-1}) shift to the long-wavelength region of the band of stretching vibrations of the $N \rightarrow O$ bond in the region of 1200 cm^{-1} upon going from pyridine-*N*-oxides (irrespective of the nature of the substituents introduced) to their compounds with uranyl nitrate of the general formula $UO_2(NO_3)_2 \cdot 2PyOx$.

Thus, the task of creating extractants for uranyl nitrate on the basis of the functional group $N \rightarrow O$ is reduced to finding compounds that form solvates sufficiently soluble in organic solvents. It was shown that the greatest solubility in organic solvents is possessed by compounds formed by unsymmetrical

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

α-alkylpyridine-N-oxides (cf. (11)). Thus, in the series β-picoline-N-oxide, γ-picoline-N-oxide, α-picoline-N-oxide, the solubility in chloroform of compounds of the composition $UO_2(NO_3)_2 \cdot 2PyOx$ increases 80-fold. Lengthening of the alkyl chain in the α-position to $C_5 - C_9$ leads to a further increase in the solubility of the solvates in organic solvents. Branching of the hydrocarbon chain also promotes an increase in solubility in organic solvents. α-n-amylpyridine-N-oxide and similar compounds of higher molecular weight already prove suitable for the efficient extraction of uranyl nitrate; however, the solubility of the products of their addition to uranyl nitrate in saturated hydrocarbons still remains insufficient.

Some of the distribution isotherms of uranyl nitrate obtained by us between water and solutions of α-alkylpyridine-N-oxides in various organic solvents are shown in Fig. 1. For comparison, there were also obtained

distribution isotherms of uranyl nitrate between water and solutions of tributyl phosphate (TBP). As can be seen from Fig. 1, the distribution isotherms for α-alkylpyridine-N-oxides and TBP are for the most part similar. The limiting attainable concentration of uranyl nitrate in the organic phase, as in the case of TBP, corresponds to the formation of the disolvate $UO_2(NO_3)_2 \cdot 2PyOx$. The formation of the disolvate is also confirmed by the quadratic dependence of the distribution coefficient of uranyl nitrate on the extractant concentration at constant composition of the aqueous phase and by direct synthesis.

We have also shown that bidentate derivatives of pyridine N-oxide
$(O \leftarrow N-C_5H_5-(\beta)-(CH_2)_4-(\beta)-C_5H_5N \rightarrow O,\ O \leftarrow N-C_5H_5-(\beta)-(C \equiv C)_2-(\beta)-C_5H_5N \rightarrow O)$,
like analogous compounds with a phosphoryl group (12), combine with uranyl nitrate in a molar ratio of $1:1$. The solvates formed by bidentate derivatives of pyridine-N-oxide are practically insoluble in water and in organic solvents.

Fig. 1. Distribution isotherms of uranyl nitrate between water and 0.1 M solutions:
1 —α-n-nonylpyridine-N-oxide in C_6H_6,
2 —α-n-amylpyridine-N-oxide in $CHCl_3$,
3 —2-(α-pyridine-N-oxide)-nonane in CCl_4,
4 —TBP in $CHCl_3$.

Fig. 2. Effect of the pH of the aqueous phase on extraction of $UO_2(NO_3)_2$ at $C_{UO_2(NO_3)_2} = 0.0435\,M$.
1 —0.1 M α-n-amylpyridine N-oxide in $CHCl_3$,
2 —0.1 M TBP in C_6H_6.

Thus, the mechanism of extraction of uranyl nitrate by α-alkylpyridine-N-oxides and by neutral organophosphorus compounds is analogous and is described by the equation

$$\mathrm{UO}_{2\,\mathrm{aq}}^{2+} + 2\mathrm{NO}_{3\,\mathrm{aq}}^{-} + 2S_{\mathrm{org}} \rightleftarrows \mathrm{UO}_2(\mathrm{NO}_3)_2 \cdot 2\mathrm{S}_{\mathrm{org}}.$$

The equilibrium constants of this process for several extractants, calculated from the equation

$$K = \frac{C_{\mathrm{UO}_2(\mathrm{NO}_3)_2\cdot 2\mathrm{S}_{\mathrm{org}}}}{4\,(m\gamma_\pm)^3\left(C_{S_{\mathrm{org}}} - 2C_{\mathrm{UO}_2(\mathrm{NO}_3)_2\cdot 2\mathrm{S}_{\mathrm{org}}}\right)^2},$$

are given in Table 1*.

* In calculating the equilibrium constants for solutions of α-n-amylpyridine-N-oxide in C_6H_6 and CCl_4, the distribution coefficients of the extractant itself, equal to 5.8 and 2.5, respectively, were taken into account.

As is evident from the data presented, α-alkylpyridine N-oxides, when benzene and chloroform are used as diluents, exceed TBP in extraction ability by a factor of 100–200.

An interesting feature of α-alkylpyridine N-oxides, not observed in the extraction of uranyl nitrate by neutral organophosphorus compounds, is the enhanced extraction of uranyl nitrate from its dilute aqueous solutions, which is manifested in the nonlinearity of the isotherms in this concentration range of uranyl nitrate (see Fig. 1). Deviations of the isotherms from

Table 1

Equilibrium constants

Extractant	Diluent: benzene	Diluent: CCl_4	Diluent: $CHCl_3$
α-n-amylpyridine N-oxide	$(1.1 \pm 0.1) \cdot 10^4$	$(3.50 \pm 0.15) \cdot 10^2$	145 ± 4
α-n-nonylpyridine N-oxide	$(1.4 \pm 0.1) \cdot 10^4$	$(6.6 \pm 0.1) \cdot 10^2$	122 ± 5
2-(α-pyridine N-oxido)-nonane	$(1.2 \pm 0.1) \cdot 10^4$	$(5.1 \pm 0.4) \cdot 10^2$	129 ± 3
9-(α-pyridine-N-oxido)-heptadecane	$(7.7 \pm 0.3) \cdot 10^3$	$(4.3 \pm 0.2) \cdot 10^2$	76 ± 6
TBP	126 ± 1	48 ± 0.3	0.63 ± 0.02

a straight-line course cannot be explained either by the presence of unoxidized alkylpyridines in the extractants or by dissociation of the solvate in the organic phase. The extraction of uranyl nitrate by solutions of α-alkylpyridine N-oxides, in contrast to extraction by TBP, improves up to a certain limit with increasing pH of the aqueous phase (Fig. 2), which indicates extraction into the organic phase of products of uranyl nitrate hydrolysis. More detailed consideration of the question made it possible to establish that at low concentrations of uranyl nitrate, beginning with $C \approx 0.02\,M$, and at elevated pH, nitrouranic acid is extracted into the organic phase in the form of the solvate $UO_2(OH)NO_3 \cdot 2PyOx$.

In conclusion, we note that the study of the extraction of uranyl nitrate by various extractants from solutions with elevated pH can provide valuable information on hydrolytic equilibria in uranyl nitrate solutions.

Institute of Inorganic Chemistry
Siberian Branch of the Academy of Sciences of the USSR

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