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The Solvent Extraction of Fe (III) and U (VI) with Mixtures of Tri-*n*-octylamine and Thenoyltrifluoroacetone in Benzene and Nitrobenzene

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Mixtures of tri-*n*-octylamine (TOA) chloride and thenoyltrifluoroacetone (HTTA) in benzene extract Fe(III) from 0.5 M HCl better than any single extractant. The effect is attributed to the change in dielectric constant of the solvent with composition. In nitrobenzene there is no increase in the extraction of Fe(III) by the mixture.

An enhanced extraction of U(VI) from 2 M HNO₃ takes place with mixtures of TOA-nitrate and HTTA both in benzene and nitrobenzene. If nitrobenzene is the diluent, experimental data indicate that the increase in the extraction is due to the formation of an organic species with a stoichiometric ratio UO₂:HTTA:TOA of 1:1:1.

The extraction of metal species in mixed solvents has been extensively investigated in past years. However, for solvent systems containing long-chain amines and thenoyltrifluoroacetone (HTTA) few data are available.^{1,2} Only in one case, *i. e.* for thorium, synergic extraction was reported.²

The present paper provides information on the extraction of Fe(III) from chloride and UO₂²⁺ from nitrate solutions with mixtures of tri-*n*-octylamine (TOA) salt and HTTA in benzene or nitrobenzene diluent. Under certain conditions both metal species exhibit an enhancement of extraction in the solvent mixture, although the effect is due to different extraction mechanisms.

EXPERIMENTAL

The extractants TOA (*Eastman Kodak* product) and HTTA (*British Drug House* product) were vacuum distilled. The primary and secondary amine content of TOA determined by the method of Wagner *et al.*³ was negligible. Benzene and nitrobenzene were washed and distilled in the usual way.⁴

The radioisotope ⁵⁹Fe was used as a tracer for iron (III). After equilibration, aqueous and organic aliquots containing Fe(III) were measured in a well-type gamma scintillation counter. Uranium in the aqueous phase was determined spectrophotometrically by the arsenazo-III method of Savvin,⁵ and in the organic phase by a modification of the same method.⁶

The extraction experiments were performed in the following way: organic and aqueous solutions were pre-equilibrated, adjusted, and the metal species (a few drops of a stock solution) introduced into the aqueous solution. Usually 5 ml. of the aqueous solution were equilibrated with an equal volume of the organic solution in a stoppered glass tube on a mechanical shaker at a temperature of 23–25° C. The equilibration time of uranium samples was 2 hours, but the Fe(III) samples were equilibrated for 16 hours since the equilibrium with HTTA is attained rather slowly. To prevent reduction of the ferric iron, the aqueous phase contained about 10⁻⁴ M potassium

dichromate. After phase separation, aliquots of both phases were taken for analysis and the extraction coefficient (conc. org./conc. aq.) was calculated by taking the average value of at least two independently equilibrated samples.

Under the prevailing experimental conditions, TOA was always in the form of the salt, TOAH^+Cl^- or $\text{TOAH}^+\text{NO}_3^-$. Extraction experiments were made in series in such a way that in each series the aqueous composition was kept constant, while in the organic phase the fraction

$$X = \frac{[\text{HTTA}]}{[\text{HTTA}] + [\text{TOAH}^+\text{X}^-]} = \frac{[\text{HTTA}]}{c}$$

($\text{X}^- = \text{Cl}^-, \text{NO}_3^-$) varied from zero to one. However, the sum of the concentrations $c = [\text{HTTA}] + [\text{TOAH}^+\text{X}^-]$ in the organic phase was always constant for a given extraction series. Under these conditions the extraction coefficient q_x depends only on the fraction x (if the species is present in tracer amounts).⁷ At $x = 0$ and $x = 1$, the corresponding extraction coefficients q_0 and q_1 refer to the single extractants (TOAH^+X^- and HTTA) of concentration c in the diluent. The fraction of TOAH^+X^- is, of course, $1 - x$.

RESULTS AND DISCUSSION

The extraction of Fe (III) from 0.5 M HCl and of UO_2^{2+} from 2 M HNO_3 is shown in Fig. 1, in which four typical extraction curves for certain selected aqueous and organic compositions are presented.

First, let us examine the extraction with the single extractants. This can be seen at $x = 0$ and $x = 1$ in Fig. 1. For example, HTTA in benzene extracts Fe^{3+} appreciably ($q_1 = 0.67$ at $x = 1$, curve 1), but not in nitrobenzene ($q_1 = 0.009$ at $x = 1$, curve 2). The reason for such a decrease in the extraction is probably due to strong interaction between HTTA and the polar nitrobenzene molecules. If the loosely bound protons of HTTA are involved in the interaction, the net effect could indeed be a decrease in the extraction.

The effect of diluents on the other extractant, *i. e.* on the amine salt, is in the opposite direction: the extraction increases if nitrobenzene is the diluent instead of benzene. The increase is particularly pronounced for Fe (III) (compare q_0 at $x = 0$ for curves 1 and 2). This effect can be explained in terms of a favorable solvation of the amine ion-pairs in polar diluents. The polar nitrobenzene is a »monomerizing« diluent in contrast to non-polar diluents in which amine salts polymerize.

Extraction with mixed extractants (the region $0 < x < 1$) differs widely with respect to the metal species, mineral acids and diluents. For example, curve 1 clearly shows that in benzene the mixed extractants extract Fe (III) considerably better than either of them alone. Let us assume that the extraction of Fe^{3+} from HCl depends on the first power of the TOAH^+Cl^- concentration^{3,9} (if the amine salt is the sole extractant), and on the third power of HTTA¹⁰ (again if it is the sole extractant). Then, if the mixture behaves additively, the extraction coefficient q_x should equal

$$q_x = q_0(1 - x) + q_1x^3 \quad (1)$$

The »additive« extraction curve defined by eq. (1) is reproduced in Fig. 1 by the dotted line. As seen, the actual curve 1 closely follows the »additive« extraction curve from $x = 0$ up to $x = 0.4$. The maximum departure from additivity is near $x = 0.9$, *i. e.* at a solvent composition where HTTA is the predominant extractant, but also where the highly polar TOAH^+Cl^- ion-pairs cause a great increase in the dielectric constant of the solvent, compared with

$x = 1$ (where HTTA is the sole extractant). In this case the increase in extraction is probably due to the change of the activities of species and to the change of the dielectric constant of the solvent.¹¹ Probably, the amount of extracted water depends strongly on the solvent composition. However, when, under similar conditions, Fe (III) is extracted in nitrobenzene, the extractants are swamped in a polar diluent ($\epsilon = 35$), and the dielectric properties of the

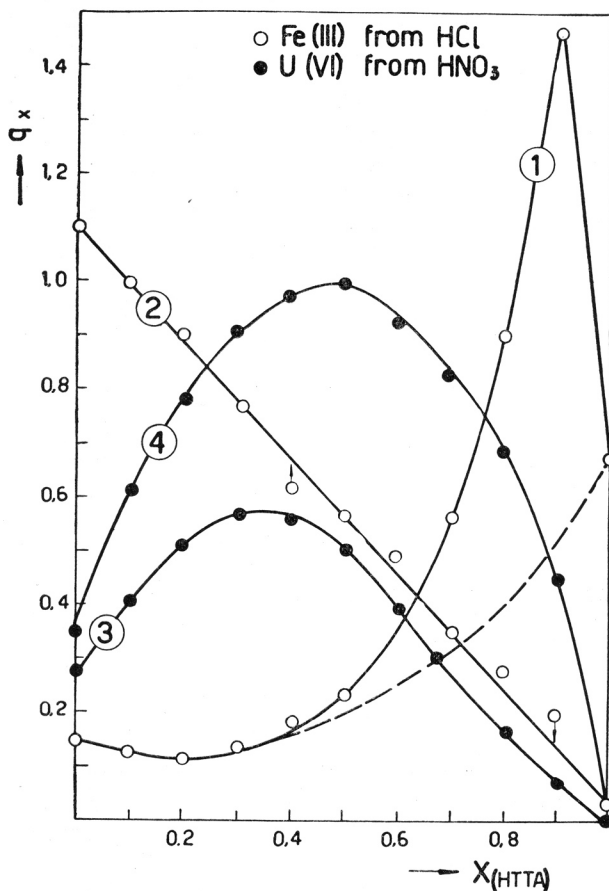


Fig. 1. — Extraction coefficient q_x vs. HTTA fraction x .

Curve 1. Equilibrium aq. HCl 0.5 M, total Fe^{3+} 1.10^{-4} M, total extractants $c = 0.04$ M, diluent benzene.

Curve 2. As curve 1, but $c = 0.02$ M, diluent nitrobenzene.

Curve 3. Equilibrium aq. HNO₃ 2 M, total UO_2^{2+} 1.10^{-3} M, total extractants $c = 0.2$ M, diluent benzene.

Curve 4. As curve 3, but diluent nitrobenzene.

solvent do not depend much on the composition. In nitrobenzene, q_i is very low for reasons given earlier, so that eq. (1) is reduced to

$$q_x = q_0(1 - x) \quad (2)$$

An inspection of curve 2, Fig. 1., shows that the extraction in nitrobenzene closely follows the simple linear relation expressed by eq. (2).

The extraction of UO_2^{2+} from 2 M HNO_3 (curves 3 and 4, Fig. 1) indicate a different extraction mechanism. When benzene is the diluent (curve 3) a rigorous analysis of the extraction curve is hardly possible because the various association reactions between the extractants (e.g., $\text{TOAH}^+\text{NO}_3^- + \text{TOAH}^+\text{NO}_3^-$; $\text{TOAH}^+\text{NO}_3^- + \text{HTTA}$, etc.) cannot be neglected in the non-polar diluent. However, in nitrobenzene these association reactions are probably less important because strong solvation of the amine salt takes place. If this assumption is correct, the extraction curve of UO_2^{2+} in nitrobenzene (curve 4, Fig. 1) can be explained in terms of the uranium species extracted. It is known that pure $\text{TOAH}^+\text{NO}_3^-$ in nitrobenzene extracts the species $[\text{UO}_2(\text{NO}_3)_3\text{-TOAH}^+]^{12}$ in a very wide range of TOA (10^{-2} —0.3 M) and HNO_3 (0.2—6 M) concentrations. Taking this into account, the shape of the extraction curve and the position of its maximum can be analysed as reported in an earlier paper.⁷ The analysis implies that besides the normal uranyl nitrate-amine ion-pair, another uranium species with a stoichiometric ratio HTTA : TOA of 1 : 1 is also extracted. As the extraction of the former species should depend on the first power of the amine concentration, and the extraction of the latter species on the first power of both amine and HTTA concentrations, the extraction coefficient (for low total uranium concentration) can be expressed⁷ as

$$q_x = q_0(1 - x) + q_m(1 - x)x \quad (3)$$

where q_m is a constant parameter at constant aqueous composition and constant c . Indeed, eq. (3) fits excellently the experimental curve 4 in Fig. 1. It is easily shown that the function

$$Q_x = q_x - q_0(1 - x)$$

derived from eq. (3), (measuring the difference in extraction between the mixture and single extractants), is symmetrical and has a maximum at $x = 0.5$.

$$Q_x = q_m(1 - x)x \quad (4)$$

$$x = 0.5 \text{ when } dQ_x/dx = 0$$

We repeated the extraction curve of UO_2^{2+} in nitrobenzene at various aqueous HNO_3 concentrations and various total extractant concentrations. In all cases the extraction curves closely followed eq. (3) and (4). The parameter q_m was fairly constant over the whole range $0 < x < 1$, but for different extraction curves it depends, as expected, on c and the HNO_3 concentration. Hence, our experimental data strongly support the view that in nitrobenzene, besides the $[\text{UO}_2(\text{NO}_3)_3\text{-TOAH}^+]$ species, another species with a stoichiometric ratio $\text{UO}_2 : \text{HTTA} : \text{TOA}$ of 1 : 1 : 1 is also extracted. A tentative formula for the latter species could be $[\text{UO}_2(\text{NO}_3)_2(\text{TTA})\text{S}_2]^{+}(\text{TOAH})^+$, where the TTA^- anion is taken to be bidentate ligand and $\text{S} = \text{H}_2\text{O}$, HNO_3 or $\text{C}_6\text{H}_5\text{O}_2$.

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IZVOD

Ekstrakcija Fe (III) i U (VI) sa smjesama tri-*n*-oktilamina i tenoiltrifluoroacetona u benzenu i nitrobenzenu

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Smeša tri-*n*-oktilaminhlorida (TOA-hlorid) i tenoil-trifluoroacetona (HTTA) u benzenu bolje ekstrahuje Fe (III) iz 0,5 M HCl nego bilo koji od ekstragenasa posebno. Efekt se objašnjava promenom dielektrične konstante organskog rastvarača sa sastavom. Ako je nitrobenzen razblaživač mesto benzena, efekt se ne javlja.

U (VI) se sinergistički ekstrahuje iz 2 M NH_3 smešom ekstragenasa TOA-nitrat i HTTA u benzenu ili nitrobenzenu. Kad je nitrobenzen razblaživač, eksperimentalni rezultati ukazuju da efekat povećane ekstrakcije treba pripisati stvaranju jedne specije, rastvorne u organskoj fazi, a čiji je stehiometrijski sastav $\text{UO}_2 : \text{HTTA} : \text{TOA}$ u odnosu 1 : 1 : 1.

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