

Extraction of uranyl nitrate, sulphate and chloride with tri-*n*-octyl amine (TOA) from aqueous solutions

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Extraction of uranyl nitrate, chloride and sulphate with tri-*n*-octyl amine (TOA) in benzene as a function of the TOA concentration has been studied. The concentration based extraction equilibrium constants were calculated from the distribution data of the uranyl salts, fitting the parameters of a chemical model to the experimentally obtained extraction isotherms. The calculated equilibrium constants are 46.5, 89.4 and 4.2×10^4 for uranyl nitrate, chloride and sulphate, respectively. These values are in good agreement with the previously reported extraction equilibrium constants calculated by the inflection point method.

Keywords: uranyl nitrate, uranyl chloride, uranyl sulphate, tri-*n*-octyl amine, extraction equilibria.

INTRODUCTION

High molecular weight alkyl amines as extractants are commonly used for the extraction of uranium salts in the reprocessing process. Tri-*n*-octyl amine (TOA) has a certain advantage compared with tri-*n*-butyl phosphate (TBP), because of the greater radiation susceptibility of TBP. The decomposition products of TOA are soluble in the aqueous phase and they do not disturb the extraction reactions.

TOA is used to determine uranium(VI) in alcoholic solutions of the organic extraction phase by direct current polarography.¹ On the other hand, TOA as extractant is used to recover plutonium and americium from laboratory acidic waste solutions.²

The aim of this work was to calculate the equilibrium constants of the extraction of uranyl nitrate, chloride and sulphate with TOA in benzene solutions, in order to verify the values previously calculated by the inflection point method.

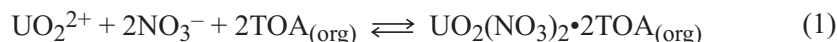
RESULTS AND DISCUSSION

Experimental distribution data, listed in Tables I–III, were used in the previous paper³ to calculate uranyl nitrate, chloride and sulphate extraction constants by the in-

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flection point method.³ In this paper, the equilibrium constants of the extraction equilibria of the same uranyl salts were calculated by fitting the experimental data (Tables I–III) to the distribution isotherms described by the following equations:



$$K = a_{\text{UNT}}/a_{\text{U}}a^2_{\text{N}}a^2_{\text{T}(\text{org})} \quad (2)$$

Here, a refers to the chemical activities of the species involved in the extraction process, while $\text{U} = \text{UO}_2^{2+}$, $\text{N} = \text{NO}_3^-$, and $\text{T} = \text{TOA}$. The standard state of these activities is their infinite dilution in benzene or water. Since the activities of uranyl nitrate and amine in the organic phase are not known, they were approximated with the corresponding stoichiometric concentrations, c . Hence, K is changed to Q , as defined by Eq. (3):

$$Q = c_{\text{UNT}(\text{org})}/a_{\text{U}}a^2_{\text{N}}c^2_{\text{T}(\text{org})} \quad (3)$$

The chemical activities of uranyl nitrate in the aqueous phase are taken from literature.⁴

Combining the mass balance equation:

$$c_{\text{T}(\text{org})}^{\text{tot}} = c_{\text{T}(\text{org})} + 2c_{\text{UNT}(\text{org})} \quad (4)$$

with Eq. (3), the extraction isotherm can be calculated from the following equation:

$$c_{\text{UNT}(\text{org})} = \left[B - \sqrt{B^2 - 16(c_{\text{T}(\text{org})}^{\text{tot}})^2} \right] / 8 \quad (5)$$

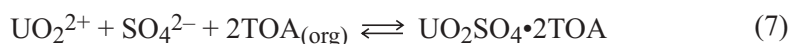
where:

$$B = 4(c_{\text{T}(\text{org})}^{\text{tot}})^2 + (1/4)Qc^3_{\text{UN}}\gamma_{\pm}^3 \quad (6)$$

Here, c_{UN} stands for the equilibrium concentration of uranyl nitrate, and γ_{\pm} for the mean activity coefficient in the aqueous phase.

Identical expressions were used for modeling the uranyl chloride extraction, except that NO_3^- should be replaced by Cl^- in Eq. (1) and N should stand for Cl^- in Eqs. (2–4).

In case of uranyl sulphate, it was assumed that the extraction mechanism follows the following stoichiometric reaction:



Thus, the corresponding concentration based equilibrium constant can be written as:

$$Q = c_{\text{UST}(\text{org})}/a_{\text{U}}a_{\text{S}}c^2_{\text{T}(\text{org})} \quad (8)$$

where $c_{\text{UST}(\text{org})}$ stands for the concentration of the uranyl complex in the amine phase, and a_{S} for the chemical activity of the sulphate anion in the aqueous phase. Combining Eq. (8) with the mass balance Eq. (4) (substituting N with S), one can calculate the concentration of the extracted uranyl sulphate:

$$c_{\text{UST}(\text{org})} = \left[D - \sqrt{D^2 - 16(c_{\text{T}(\text{org})}^{\text{tot}})^2} \right] / 8 \quad (9)$$

where:

$$D = 4(c_{T(\text{org})}^{\text{tot}})^2 + (1/4Qc^2_{USV_{\pm}^2}) \quad (10)$$

The values of the apparent equilibrium constants, defined by Eqs. (3) and (8), have been determined as the best fit values for the experimental data taken from Tables I–III, calculated by Eqs. (5) and (9).

TABLE I. Experimental data on the extraction of uranyl nitrate from 0.1 M nitric acid by TOA in benzene

0.02 M TOA		0.05 M TOA	
$c_{U(\text{aq})}/M$	$c_{U(\text{org})}/M$	$c_{U(\text{aq})}/M$	$c_{U(\text{org})}/M$
0.1013	0.0001	0.1013	0.0002
0.2025	0.0002	0.2025	0.0006
0.3038	0.0003	0.3038	0.0012
0.4051	0.0008	0.4051	0.0034
0.5063	0.0012	0.5063	0.0058
0.6076	0.0019	0.6076	0.0082
0.7089	0.0029	0.7089	0.0114
0.8101	0.0036	0.8101	0.0143
0.9114	0.0049	0.9114	0.0166
1.0127	0.0056	1.0126	0.0179
1.1250	0.0070		
1.2000	0.0087		
1.2750	0.0092		
1.3500	0.0092		
1.5000	0.0092		

The calculated values of the extraction equilibrium constants are presented in Table IV, as well as the previously published values calculated by the inflection point method.³ As it can be seen, the equilibrium constants calculated by the two methods are in good agreement, suggesting that the usage of the simple inflection point method is appropriate for this extraction system.

Figure 1 presents the measured and calculated extraction isotherms of uranyl nitrate by TOA in benzene, as a typical example. It is obvious that the proposed chemical model describes the extraction process quite well and that the calculated equilibrium constants are valid over a broad range of concentrations.

TABLE II. Experimental data on the extraction of uranyl chloride from 0.1 M nitric acid by TOA in benzene

0.02 M TOA		0.05 M TOA	
$c_{U(aq)}/M$	$c_{U(org)}/M$	$c_{U(aq)}/M$	$c_{U(org)}/M$
0.0993	0.0002	0.0986	0.0009
0.1986	0.0004	0.1969	0.0021
0.2976	0.0009	0.2941	0.0045
0.3963	0.0017	0.3901	0.0071
0.4954	0.0021	0.4885	0.0091
0.5936	0.0035	0.5861	0.0109
0.6920	0.0046	0.6830	0.0136
0.7902	0.0054	0.7806	0.0155
0.8894	0.0062	0.9000	0.0164
0.9886	0.0065		
0.075 M TOA		0.10 M TOA	
$c_{U(aq)}/M$	$c_{U(org)}/M$	$c_{U(aq)}/M$	$c_{U(org)}/M$
0.0985	0.0010	0.0986	0.0009
0.1957	0.0034	0.1947	0.0043
0.2908	0.0077	0.2890	0.0096
0.3867	0.0113	0.3831	0.0149
0.4836	0.0139	0.4773	0.0203
0.5785	0.0185	0.5726	0.0245
0.6753	0.0212	0.6680	0.0286
0.7731	0.0230	0.7638	0.0323
0.8715	0.0241	0.8615	0.0340
0.9700	0.0251	0.9599	0.0352

TABLE III. Experimental data on the extraction of uranyl sulphate from 0.1 M nitric acid by TOA in benzene

0.025 M TOA		0.05 M TOA	
$c_{\text{U(aq)}}/\text{M}$	$c_{\text{U(org)}}/\text{M}$	$c_{\text{U(aq)}}/\text{M}$	$c_{\text{U(org)}}/\text{M}$
0.0042	0.0005	0.0084	0.0019
0.0068	0.0008	0.0168	0.0038
0.0092	0.0014	0.0273	0.0065
0.0118	0.0020	0.0370	0.0084
0.0139	0.0024	0.0462	0.0092
0.0171	0.0030	0.0504	0.0101
0.0197	0.0034	0.0647	0.0107
0.0227	0.0040	0.0828	0.0119
0.0262	0.0044	0.0895	0.0128
0.0394	0.0050	0.0975	0.0129
0.075 M TOA		0.10 M TOA	
$c_{\text{U(aq)}}/\text{M}$	$c_{\text{U(org)}}/\text{M}$	$c_{\text{U(aq)}}/\text{M}$	$c_{\text{U(org)}}/\text{M}$
0.0155	0.0049	0.0055	0.0027
0.0378	0.0092	0.0155	0.0065
0.0449	0.0108	0.0218	0.0082
0.0538	0.0125	0.0294	0.0111
0.0655	0.0143	0.0395	0.0126
0.0748	0.0150	0.0483	0.0141
0.0848	0.0164	0.0563	0.0168
0.0949	0.0185	0.0643	0.0189
0.1093	0.0185	0.0727	0.0212
0.1134	0.0185	0.0811	0.0223

TABLE IV. Equilibrium constants of the extraction of uranyl salts with TOA in benzene.

System	Q , inflection point method ³	Q , this work
$\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TOA}$	25	46.5
$\text{UO}_2\text{Cl}_2 \cdot 2\text{TOA}$	251	89.4
$\text{UO}_2\text{SO}_4 \cdot 2\text{TOA}$	5×10^4	4.2×10^4

CONCLUSIONS

In this work, a concentration based chemical model was used to calculate the equilibrium constants for the extraction of uranyl nitrate, chloride and sulphate from aqueous solutions by tri-*n*-octyl amine in benzene. The model satisfactorily describes

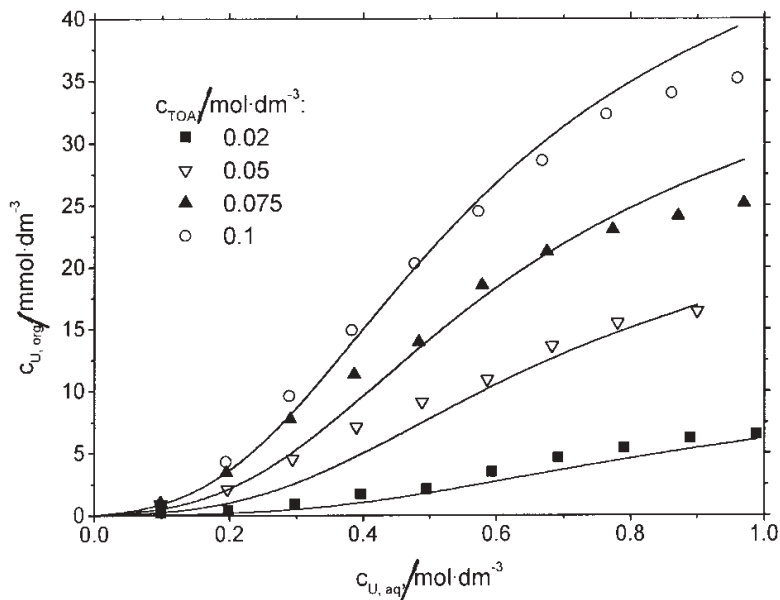


Fig. 1. Experimentally measured (points) and calculated (solid lines) extraction isotherms of the system uranyl chloride in 0.1 M nitric acid – TOA in benzene. The corresponding total concentration of TOA in benzene is indicated in the figure.

the extraction process over a broad range of concentrations. The calculated equilibrium constants are in good agreement with the values previously calculated using the inflection point method.

ИЗВОД

ЕКСТРАКЦИЈА УРАНИЛ НИТРАТА, СУЛФАТА И ХЛОРИДА СА ТРИ-*n*-ОКТИЛАМИНОМ (ТОА) ИЗ ВОДЕНИХ РАСТВОРА

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Испитивана је екстракција уранил нитрата, хлорида и сулфата помоћу три-*n*-октиламина (ТОА) у бензену, у зависности од концентрације ТОА. Израчунате су константе равнотеже екстракције, подешавањем параметара концентрационо зависне једначине, према експериментално одређеним екстракционим изотермама. Вредности константи равнотеже су 46,5, 89,4 и $4,2 \times 10^4$ за уранил нитрат, хлорид и сулфат, респективно. Ове вредности су у доброј сагласности са константама израчунатим методом тачке инфлексije.

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