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SOLUBILITIES OF URANYL AND IRON (III) DIBUTYL AND MONOBUTYL PHOSPHATES IN TBP SOLVENT EXTRACTION SOLUTIONS

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ABSTRACT

The solubilities of uranyl dibutyl phosphate, uranyl monobutyl phosphate, ferric dibutyl phosphate, and ferric monobutyl phosphate were measured in aqueous nitric acid solutions ranging from 0 to 3 M and in 30% TBP in Amsco 125-82 solution containing 0-0.7 M HNO_3. For the respective compounds in the aqueous phases, as the acidity increased from 0 to 3 M, the solubilities increased from 0.004 to 0.7 g U/liter, 0.05 to 50 g U/liter, <1 to 30 mg Fe(III)/liter, and 0.003 to 3 g Fe(III)/liter; corresponding solubilities in the organic phases increased with acidity from 14 to 165 g U/liter, 11 to 110 g U/liter, <0.5 to 4 mg Fe(III)/liter, and <0.002 to 1.5 g Fe(III)/liter. All these compounds foamed or formed very flocculent solids in the aqueous phases and tended to settle slowly in the organic phases and rise to the surface in the aqueous phases, suggesting that they would be interface seekers in two-phase aqueous-organic systems.

CONTENTS

1.0 INTRODUCTION

The work described was performed to determine some of the properties of uranyl and ferric dibutyl and monobutyl phosphates in solvent extraction solutions and to help elucidate further the roles of dibutyl and monobutyl phosphoric acids (HDBP and H_2MBP), both of which are degradation products of tributyl phosphate (TBP). Both these acids, plus orthophosphoric acid, are formed by acid dealkylation (1) or radiolysis of TBP (2). Many studies have shown that dibutyl phosphoric acid has various deleterious effects on TBP processing systems, such as increased uranium (3-5) and zirconium (3, 6) retention in the organic phase and the formation of insoluble compounds with some cations (5, 7). Much less is known of the effects of monobutyl phosphoric acid on TBP processing systems, although it is known (8) that the radiolytic yield of H_2MBP is of the order of 10-50% as great as that of HDBP in TBP-Amsco-HNO_3 solutions.

This report presents measurements of the solubilities of uranyl and ferric dibutyl and monobutyl phosphates in separate aqueous and 30% TBP—Amsco solutions of nitric acid, whose concentration range spanned that used in the Purex process. All solutions were analyzed by spectrochemical techniques; in addition, organic solutions of ferric dibutyl phosphate were analyzed by radioactivation techniques.

Most of the experimental work presented in this report was performed by C. T. Thompson. Spectrochemical, activation, and chemical analyses were performed by members of the groups of C. Feldman, G. W. Leddicotte, W. R. Laing, and G. W. Wilson of the ORNL Analytical Chemistry Division.

2.0 EXPERIMENTAL RESULTS

2.1 Solubility Data

Excess quantities of each of the four solid compounds, i.e., uranyl dibutyl and monobutyl phosphates and ferric dibutyl and monobutyl phosphates, were contacted with each of four nitric acid aqueous solutions, with water, with each of four 30% TBP—Amsco—HNO_3 solutions, and with 30% TBP—Amsco—H_2O solution. These solutions were prepared by contacting 30% TBP—Amsco solutions with water or with nitric acid solutions and separating the two phases for use as separate solvents. Nitric acid concentrations in these equilibrated aqueous solutions varied from 0 to 3 M, while corresponding values for the organic phases were 0-0.7 M (Fig. 1 and Tables 1-4).

Solutions and excess solids were agitated for 2-6 weeks, samples of the solution being analyzed, after filtration, after 1-2 weeks of agitation and at the end of agitation. This procedure was followed to ensure the attainment of saturation of the solution with each compound since previous studies with zirconium dibutyl phosphate (6) had shown equilibrium was attained very slowly.

Uranyl Dibutyl Phosphate. Uranyl dibutyl phosphate solubilities in the aqueous phases ranged from 0.004 to ~0.7 g of uranium per liter as the acidity increased from 0 to 3.2 M; corresponding solubilities in the organic phases were 14 to 165 g/liter. There are no significant differences in analytical values of uranium in samples taken after 7 and 14 days of agitation (Table 1).

Ratios of solubilities of uranyl dibutyl phosphate in the organic and aqueous phases are very large, decreasing from about 3600 at 0 M aqueous acidity to about 250 at 3.2 M aqueous nitric acid concentration. Thus, in a two-phase system——aqueous and TBP-Amsco——this compound would greatly favor the organic phase, a fact that has been noted by other investigators.

Uranyl Monobutyl Phosphate. Solubilities of uranyl monobutyl phosphate in the aqueous solutions ranged from 0.05 to ~50 g of uranium per liter as the nitric acid concentration increased from 0 to 3.2 M; corresponding solubilities in the TBP-Amsco solutions were ~11 to ~110 g/liter (Table 2). Duplicate samples of this compound

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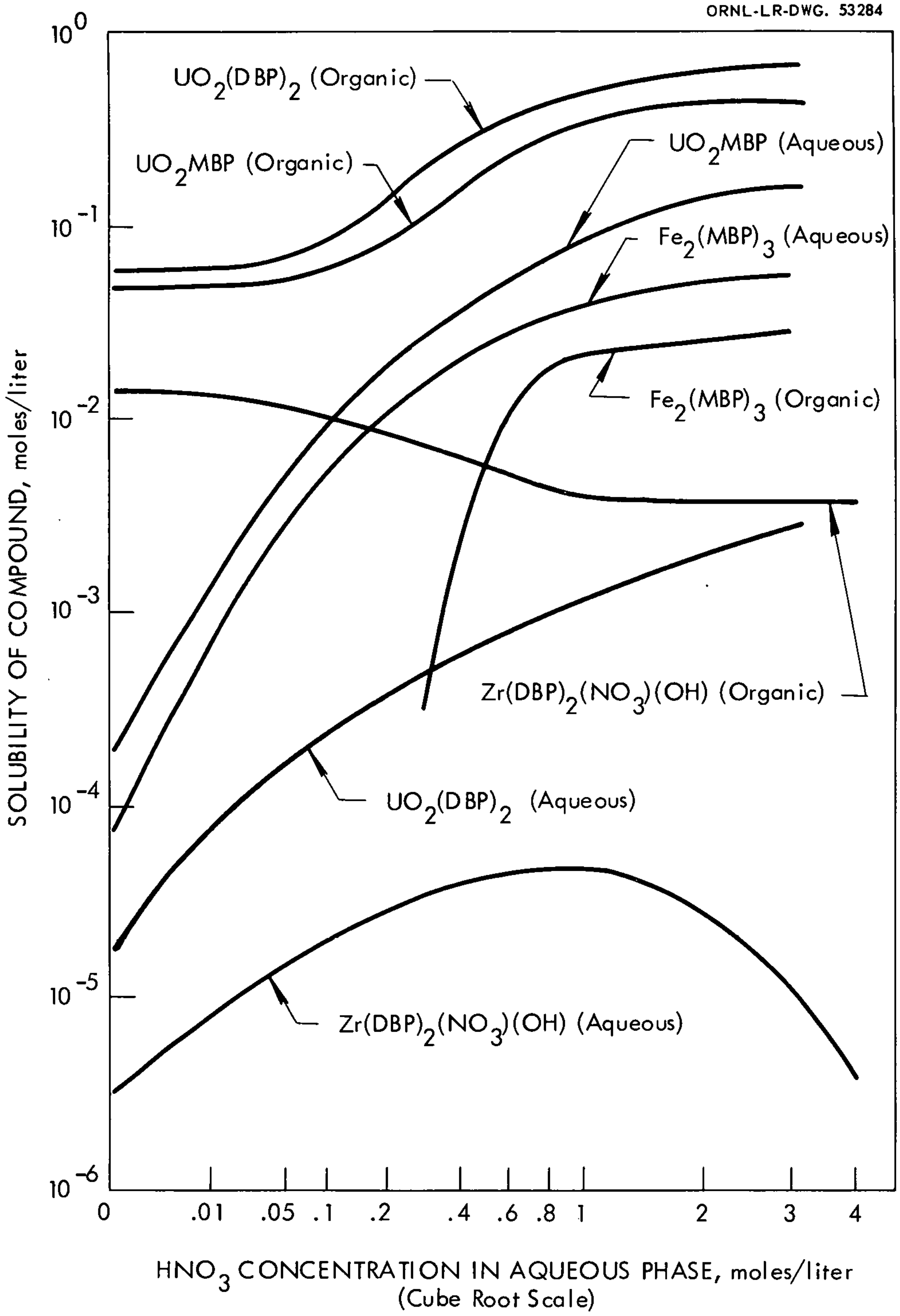

Fig. 1. Solubilities of some dibutyl and monobutyl phosphates in aqueous and organic phases. Basis: aqueous HNO_3 in equilibrium with 30% TBP in Amsco; phases studied separately.

Table 1. Solubility of Uranyl Dibutyl Phosphate in H_2O-HNO_3 and 30% TBP—Amsco—HNO_3 Solutions at 24 ± 2°C

Aqueous Phase				Equilibrium, 30% TBP—Amsco Phase				
Initial HNO_3, M	Agitation Time, days	Final Composition Uranium, g/liter	Final Composition H^+, M	Initial HNO_3, M	Agitation Time, days	Final Composition Uranium, g/liter	Final Composition H^+, M	Ratio of Solubilities, $(S_u)_a^o$
0.000	7	0.004	0.001	0.000	7	13.8	0.000	3400
0.000	14	0.004	<0.005	0.000	14	15.1	0.005 A.D.	3800
0.098	7	0.052	0.10	0.006	7	19.7	0.009	380
0.098	14	0.060	0.10	0.006	14	20.3	0.005	340
0.295	7	0.098	0.29	0.04	7	47.8	0.038	490
0.295	14	0.137	0.31	0.04	14	46.9	0.04	340
1.09	7	0.257	1.06	0.25	7	116.	0.20	450
1.09	14	0.282	1.13	0.25	14	117.	0.22	415
3.19	7	0.816	3.21	0.71	7	168.	0.51	210
3.19	14	0.580	3.20	0.71	14	163.	0.51	280

Table 2. Solubility of Uranyl Monobutyl Phosphate in H_2O-HNO_3 and 30% TBP—Amsco—HNO_3 Solutions at 24 ± 2°C

Aqueous Phase				Equilibrium, 30% TBP—Amsco Phase				
Initial HNO_3, M	Agitation Time, days	Final Composition		Initial HNO_3, M	Agitation Time, days	Final Composition		Ratio of Solubilities, $(S_u)^o_a$
		Uranium, g/liter	H^+, M			Uranium, g/liter	H^+, M	
0.000	7	0.033	0.009	0.000	7	11.1	0.025 A.D.	340
0.000	14	0.043	0.01	0.000	14	15.2	0.006	350
0.000	28	0.053	0.009	0.000	28	7.9	0.023 A.D.	150
0.098	7	1.58	0.113	0.006	7	13.9	0.04 A.D.	8.8
0.098	14	1.90	0.09	0.006	14	17.0	0.003	9.0
0.10	28	3.06	0.11	0.006	28	11.2	0.028 A.D.	3.7
0.295	7	5.20	0.32	0.04	7	29.7	0.02 A.D.	5.7
0.295	14	5.78	0.27	0.04	14	33.6	0.08 A.D.	5.8
0.29	28	7.07	0.31	0.04	28	15.3	0.017 A.D.	2.2
1.09	7	21.0	0.96	0.25	7	58.3	0.15	2.8
1.09	14	21.2	0.95	0.25	14	82.8	0.01	3.9
1.00	28	26.8	1.16	0.21	28	98.5	0.15	3.7
3.19	7	28.5	2.90	0.71	7	66.4	0.44	2.3
3.19	14	39.4	2.86	0.71	14	139	0.01	3.5
2.96	28	50.7	3.21	0.64	28	117	0.15	2.3

Table 3. Solubility of Ferric Dibutyl Phosphate in H_2O-HNO_3 and 30% TBP—Amsco—HNO_3 Solutions at 24 ± 2°C

Aqueous Phase			Equilibrium, 30% TBP—Amsco Phase		
Initial HNO_3, M	Agitation Time, days	Final Fe, mg/liter	Initial HNO_3, M	Agitation Time, days	Final Fe, mg/liter
0.000	14	<0.6	0.000	14	<0.4
0.000	38	<1	0.000	38	<10
0.000	14	<1[a]	0.000	14	<0.5[a]
0.000	40	<1[a]	0.000	40	2[a]
0.10	14	2	0.006	14	<0.4
0.10	38	2	0.006	38	<10
0.10	14	2[a]	0.006	14	---
0.10	40	7[a]	0.006	40	85[a]
0.29	14	4.4	0.04	14	<0.4
0.29	38	6	0.04	38	<10
0.29	14	4.5[a]	0.04	14	<0.5[a]
0.29	40	7[a]	0.04	40	14[a]
1.00	14	12	0.21	14	<0.6
1.00	38	10	0.21	38	<10
1.00	14	13[a]	0.21	14	<0.5[a]
1.00	40	12[a]	0.21	40	<1[a]
2.96	14	27	0.64	14	<0.6
2.96	38	17	0.64	38	<10
2.96	14	29[a]	0.64	14	4[a]
2.96	40	29[a]	0.64	40	1[a]

[a] By activation analysis. All other analyses for iron were by emission spectroscopy.

Table 4. Solubility of Ferric Monobutyl Phosphate in H_2O-HNO_3 and 30% TBP—Amsco—HNO_3 Solutions at 24 ± 2°C

Aqueous Phase				Equilibrium, 30% TBP—Amsco Phase			
Initial HNO_3, M	Agitation Time, days	Fe,[a] g/liter	H^+, M	Initial HNO_3, M	Agitation Time, days	Fe,[a] g/liter	H^+, M
0.000	14	0.001	---	0.000	14	<0.01	---
0.000	38	0.01	---	0.000	38	<0.008	---
0.000	14	0.002	---	0.000	14	<0.002	---
0.000	39	0.002	0.010	0.000	39	<0.01	0.0033
0.10	14	0.089	---	0.006	14	0.01	---
0.10	38	0.44	---	0.006	38	0.01	---
0.10	14	0.368	---	0.006	14	<0.002	---
0.10	39	0.208	0.109	0.006	39	<0.01	0.0073
0.29	14	0.405	---	0.04	14	0.031	---
0.29	38	1.15	---	0.04	38	0.02	---
0.29	14	1.67	0.32	0.04	14	0.003	0.05
0.29	39	0.242	0.308	0.04	39	<0.02	0.037
1.00	14	0.640	---	0.21	14	1.23	---
1.00	38	2.26	---	0.21	38	1.23	---
1.00	14	3.68	1.03	0.21	14	0.94	0.24
1.00	39	1.45	1.03	0.21	39	1.38	0.214
1.00	41	1.24	---	0.21	---	---	---
2.96	14	1.26	---	0.64	14	1.95	---
2.96	38	4.60	---	0.64	38	1.78	---
2.96	14	4.56	---	0.64	14	0.95	0.66
2.96	39	2.24	3.01	0.64	39	1.30	0.65

[a] All analyses for iron by emission spectroscopy.

were agitated with each of the five aqueous and five organic solutions, one unit being sampled after 7 and 14 days and the other after 28 days. It is apparent that solubilities are not so well defined for this compound as they are for uranyl dibutyl phosphate (Table 1). Although there does not appear to be a kinetic effect, provided agitation is for at least 7 days, there is considerable scatter in the solubility data.

Uranyl monobutyl phosphate, in common with but to a lesser extent than the dibutyl phosphate, is more soluble in the organic than in the aqueous phase. In acid-free 30% TBP—Amsco, the ratio of organic to aqueous solubilities is >100; however, this ratio drops rapidly and is only 2.5-3 when the aqueous phase acidity is 3.2 M. Nevertheless, the fact that this compound is more soluble in the organic phase than in the aqueous means that it, too, will increase the extent to which uranium is retained in the organic phase during any stripping of uranium by an aqueous solution.

Ferric Dibutyl Phosphate. Solubilities of ferric dibutyl phosphate in all test solutions were very low; in water and in four of the organic solutions they were below the limit of detectability of emission spectroscopy and activation techniques, i.e., $<1 \times 10^{-3}$ g of iron per liter of H_2O and $\sim 5 \times 10^{-4}$ g per liter of TBP-Amsco phase. At the highest aqueous acidity, ~3 M, the solubility was only ~0.03 g of iron per liter, while in the corresponding TBP-Amsco solution it was only 0.004 g per liter (Table 3).

Ferric Monobutyl Phosphate. Solubilities of ferric monobutyl phosphate in the aqueous phases increased from ~0.003 to ~3 g of iron per liter as the acidity increased from 0 to ~3 M HNO_3. Corresponding TBP-Amsco phase solubilities ranged from $<2 \times 10^{-3}$ to ~1.5 g/liter (Table 4). This compound was also agitated in duplicate samples in each aqueous and organic solution. Analytical data on iron in the latter are as reproducible as could be expected; however, in each aqueous solution the maximum value of dissolved iron is about 5 times the minimum value. This difference does not correlate with agitation time.

2.2 Qualitative Behavior of Solids in Contact with Solutions

Each of the test solids-solution combinations behaved in a manner that would suggest operational difficulties in a countercurrent solvent extraction system. Thus, uranyl dibutyl and uranyl monobutyl phosphates, particularly the latter, foamed extensively in the aqueous phases. Ferric dibutyl phosphate existed as a flocculent solid in the aqueous phases and this collected primarily at the surface, rather than settling, when agitation was stopped. In the organic phases this solid settled to the bottom when agitation was stopped. Ferric monobutyl phosphate became a very flocculent solid in water and formed foams on top of all aqueous solutions. In the organic phases it settled slowly as a voluminous solid.

3.0 EXPERIMENTAL PROCEDURES

Each of the four test solids, i.e., uranyl dibutyl and monobutyl phosphates and ferric dibutyl and monobutyl phosphates, was precipitated by addition of a solution of the sodium salt of the acid to a solution of the nitrate salt of the cation. Each was washed by agitation-decantation methods at least three times with large volumes of water, filtered, and then dried, under vacuum (the uranyl salts) until constant weight was achieved, or in air (the ferric salts). Chemical analyses were as follows:

$UO_2(DBP)_2$:	Found	34.13% U	8.72% P	27.8% C	0.02% Na
	Theoretical	34.58% U	9.00% P	27.91% C	0.00% Na
UO_2MBP:	Found	51.3% U	7.41% P	12.9% C	0.24% Na
	Theoretical	56.39% U	7.34% P	11.38% C	0.00% Na
$Fe(DBP)_3$:	Found	7.86% Fe	14.65% P	0.1% Na	0.04% H_2O
	Theoretical	8.17% Fe	13.60% P	0.0% Na	0.00% H_2O
$Fe_2(MBP)_3$:	Found	15.25% Fe	13.2% P	0.01% Na	8.0% H_2O
	Theoretical	19.56% Fe	16.27% P	0.00% Na	0.0% H_2O

The uranyl nitrate solutions were prepared from water-recrystallized uranyl nitrate hexahydrate and the ferric nitrate solutions from c. p. ferric nitrate nonahydrate. Sodium dibutyl phosphate solutions were prepared by mixing stoichiometric solutions of c. p. sodium hydroxide with dibutyl phosphoric acid prepared in this laboratory (6) or obtained from Victor Chemical Company. Both samples of this acid were free of monobutyl phosphoric acid, within analytical error, and had equivalent weights of about 230, corresponding to solutions of approximately 50 mole % in water. Densities at 27.4°C were 0.985 g/ml.

Monobutyl phosphoric acid was obtained as a commercial mixture of ortho-, monobutyl-, and dibutyl phosphoric acids. The dibutyl phosphoric acid was removed by extraction with CCl_4 (6, 9). The remaining aqueous solution, containing ~4.9 meq H_2MBP and ~4.0 meq H_3PO_4 per milliliter, was saturated with sodium nitrate, which causes the formation of a two-phase system, one enriched in H_2MBP and the other enriched in H_3PO_4. A separation factor, α, of H_2MBP from H_3PO_4 of ~15 was achieved with this solution. The H_2MBP-rich upper phase was separated, diluted with 0.4 vol of water, and resaturated with sodium nitrate to obtain further elimination of H_3PO_4. After a third cycle of separation, dilution, and resaturation, an aqueous product was obtained with the following typical composition: HDBP, below limit of detection; H_2MBP, 9-11 meq/ml; H_3PO_4, 0.3-0.9 meq/ml; $NaNO_3$, ~0.5 meq/ml. When permitted to evaporate at ~23°C on exposure to air, needle-like crystals of H_2MBP slowly precipitated from the mother liquor. These crystals did, however, contain about 0.2 equivalent of sodium per equivalent of H_2MBP.

Test solutions were prepared by contacting portions of 1.126 M TBP in Amsco 125-82 with three successive portions of distilled water or aqueous nitric acid solutions. After the third contact, the phases were separated, filtered, and then separately used in the solubility studies.

4.0 DISCUSSION

Solubility data presented in this report are in agreement with many observations concerning the effects of TBP degradation products, particularly dibutyl phosphoric acid, on uranium retention in the organic phase. In saturated 30% TBP—Amsco—HNO_3 and H_2O-HNO_3 phases, the distribution coefficient, DC_a^o, for uranyl dibutyl phosphate is >200 at aqueous nitric acid concentrations up to 3 M (Table 1, Fig. 1). Even uranyl monobutyl phosphate, which has not received much attention, favors the organic phase, although with a much lower distribution coefficient, i.e., 4-2.5 when the aqueous nitric acid concentration is in the range 1-3 M. In very dilute nitric acid, such as is used in stripping uranium from the organic phase, this distribution coefficient can increase to 10-100.

In the presence of dissolved iron, even at concentrations as low as 10^{-4} M Fe or ~100 ppm (Fig. 1), it is doubtful that uranium would be significantly retained in a TBP—Amsco—HNO_3 solution by complexing with dibutyl phosphoric acid. Instead, this acid would be largely precipitated as an interface-seeking solid, ferric dibutyl phosphate. For example, in 1 M HNO_3 aqueous phase the solubility is only 2×10^{-4} M, and in the corresponding 30% TBP-Amsco phase, $<10^{-5}$ M. The small quantities of iron necessary to cause this precipitation could readily be introduced as impurities in chemicals or by corrosion of iron or steel process equipment.

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