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Abstract

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A QUINARY SYSTEM $UO_2(NO_3)_2$—$(C_4H_9)_2PO(C_4H_9O)$—H_2O—HNO_3—CCl_4 AT A CONSTANT RATIO OF $(C_4H_9)_2PO(C_4H_9O)$ TO CCl_4 IN THE REGION OF STRATIFICATION ==

The present system was studied as a pseudoquaternary one, i.e., a solution in carbon tetrachloride of the monobutyl ester of dibutylphosphinic acid (BEDPA) of constant concentration (27.6 wt.%) was taken as one component. Throughout the investigated region, at this dilution of the extractant, stratification of the system into three liquid phases was not observed. This is one of a series of works devoted to the systematic study of extraction equilibria by the method of physicochemical analysis ($^{1-4}$). The uranyl nitrate used for the work, of "chemically pure" grade, was recrystallized from water. The nitric acid was of "chemically pure" grade. BEDPA was obtained by adding an ethereal solution of *n*-butyl dichlorophosphate at 0° + 2° (cooling with ice water) to n-C_4H_9MgBr in ethereal solution, followed by boiling for one hour. Decomposition was carried out in the usual way (^{5}). The aqueous solution was extracted twice with ether. The yield of the *n*-butyl ester of dibutylphosphinic acid was 80%. The synthesized BEDPA had the following parameters: b.p. 138° at 6 mm Hg; n_D^{20} 1.4440; d^{20} 0.9262. Carbon tetrachloride was purified by distillation before use.

After equilibrium had been reached (in a thermostat at $25 \pm 0.1°$) and the layers had separated, samples were taken for analysis. Uranium was determined by complexometric titration according to the method proposed by Klygin (^{6}).

Table 1

Distribution of uranyl nitrate in the system $UO_2(NO_3)_2$—H_2O—BEDPA—CCl_4 at 25°
(at a constant ratio of BEDPA to CCl_4 equal to 27.6% BEDPA)

No. of run	Equilibrium aqueous phase, wt.%	Equilibrium organic phase, wt.%	Equilibrium organic phase, wt.%	K_p of uranyl nitrate	No. of run	Equilibrium aqueous phase, wt.%	Equilibrium organic phase, wt.%	Equilibrium organic phase, wt.%	K_p of uranyl nitrate
1	55.17	20.20	0.11	0.366	19	0.385	7.15	0.97	18.57
2	49.90	19.66	0.08	0.394	20	0.359	4.89	1.27	13.50
3	41.27	19.40	0.11	0.470	21	0.355	4.24	1.39	11.94

No. of run	Equilibrium aqueous phase, wt.%	Equilibrium organic phase, wt.%	Equilibrium organic phase, wt.%	K_p of uranyl nitrate	No. of run	Equilibrium aqueous phase, wt.%	Equilibrium organic phase, wt.%	Equilibrium organic phase, wt.%	K_p of uranyl nitrate
4	40.07	19.68	0.10	0.491	22	0.353	5.05	1.24	15.59
5	35.62	19.21	0.08	0.539	23	0.264	3.43	1.49	12.99
6	27.98	19.39	0.08	0.693	24	0.264	2.57	–	10.85
7	17.99	18.87	–	1.049	25	0.189	1.90	1.64	10.05
8	16.76	18.72	–	1.117	26	0.135	0.714	–	5.29
9	11.23	18.75	–	1.677	27	0.122	0.590	–	4.83
10	6.91	18.40	0.10	2.66	28	0.109	0.564	–	5.17
11	3.09	17.78	–	5.75	29	0.100	0.501	–	5.01
12	1.95	16.51	–	8.45	30	0.074	0.335	–	4.53
13	1.57	15.88	0.24	10.11	31	0.056	0.283	–	5.06
14	1.54	15.73	–	10.19	32	0.0124	0.204	1.98	16.5
15	1.26	14.35	0.31	11.34	33	0.00177	0.129	–	73.0
16	1.13	14.08	0.35	12.42	34	0.0001	0.042	–	420
17	0.509	8.19	0.90	16.88					
18	0.490	8.36	0.83	17.06					

Instead of the recommended arsenazo (^{6}), the indicator xylenol orange was used; it gave a sharper transition at the equivalence point and made it possible to determine uranium directly in the organic phase without re-extraction, even with a 100-fold excess of BEDPBC. Small concentrations of uranium were determined colorimetrically with arsenazo-1 (^{7}).

Nitric acid was determined by potentiometric titration, and water by the K. Fischer method.

BEDPBC is an intermediate member of the series of so-called neutral extractants from TBP to TBPO and, in its extraction capacity, occupies an intermediate position ($^{8-10}$). Since the quaternary system $UO_2(NO_3)_2$–H_2O–27.6% BEDPBC in CCl_4 is a component part of the quinary system under consideration, preliminary experiments were carried out to study the distribution of uranyl nitrate and water in this quaternary system; the results are presented in Table 1. The region studied covers all compositions from those saturated with respect to uranyl nitrate hexahydrate to pure water. The diagram of this system is characterized by the following regions: a miscibility-gap region, occupying more than 50% of the entire area of the diagram; a region of homogeneous organic solutions ranging from a two-percent aqueous solution to a 20.2% solution of uranyl nitrate in extractant diluted with CCl_4; a region of homogeneous aqueous solutions of uranyl nitrate and organic phases, practically coinciding with the water–uranyl nitrate axis; a region of coexistence of solid uranyl nitrate hexahydrate

Table 2

System $UO_2(NO_3)_2$–HNO_3–H_2O–CCl_4–BEDPBC (27.6%) in the miscibility-gap region

No.	Initial solution, wt. % $UO_2(NO_3)_2$	Initial solution, wt. % HNO_3	Initial solution, wt. % H_2O	Aqueous phase, wt. % $UO_2(NO_3)_2$	Aqueous phase, wt. % HNO_3	Organic phase $UO_2(NO_3)_2$	Organic phase HNO_3	Organic phase H_2O	K_p $UO_2(NO_3)_2$	K_p HNO_3
1	42,09	11,32	46,59	41,18	11,42	20,25	0,03	–	0,478	–
2	–	–	–	37,82	11,88	20,41	–	–	0,543	–
3	–	–	–	35,62	12,11	19,65	0,01	–	0,552	–
4	–	–	–	28,11	13,75	19,53	–	–	0,695	–
5	–	–	–	23,08	14,80	19,56	–	–	0,847	–
6	–	–	–	14,03	16,48	18,62	–	–	1,327	–
7	–	–	–	11,33	17,49	18,97	0,08	–	1,674	–
8	–	–	–	1,61	18,48	17,58	0,19	0,08	10,91	$1,0 \cdot 10^{-3}$
9	–	–	–	0,0234	10,30	14,57	1,36	0,13	622	0,13
10	36,72	16,77	46,51	22,39	20,93	19,48	–	–	0,870	–
11	31,89	24,24	43,87	29,30	24,94	21,04	–	–	0,718	–
12	–	–	–	24,20	26,87	20,10	–	–	0,831	–
13	–	–	–	19,89	28,52	19,80	–	–	0,996	–
14	–	–	–	10,95	31,51	18,95	–	–	1,731	–
15	–	–	–	8,88	32,20	18,61	0,18	0,03	2,096	–
16	–	–	–	4,35	33,94	18,36	–	–	4,220	–
17	–	–	–	0,60	34,74	17,51	0,95	0,05	29,18	$4,2 \cdot 10^{-2}$
18	–	–	–	$4 \cdot 10^{-3}$	20,07	13,04	2,4	0,11	3260	0,12
19	27,19	35,20	37,61	24,73	36,08	20,96	0,02	–	0,848	–
20	–	–	–	19,09	38,73	19,72	0,08	–	1,030	–
21	–	–	–	16,33	39,96	19,56	0,18	–	1,198	–
22	–	–	–	10,10	42,06	18,69	1,94	–	1,850	$2,2 \cdot 10^{-2}$
23	–	–	–	5,08	44,22	18,07	1,84	0,03	3,560	$4,2 \cdot 10^{-2}$
24	–	–	–	1,73	45,65	16,85	1,94	0,07	9,74	$4,2 \cdot 10^{-2}$
25	–	–	–	0,24	44,39	13,96	3,36	0,04	58,66	$7,6 \cdot 10^{-2}$
26	28,81	42,60	28,59	26,82	43,86	19,55	–	–	0,729	–
27	–	–	–	22,87	45,87	18,88	4,34	–	0,826	–
28	–	–	–	18,00	48,23	18,94	–	–	1,052	–

Fig. 1

Figure 1: Fig. 1

No.	Initial solution, wt. % $UO_2(NO_3)_2$	Initial solution, wt. % HNO_3	Initial solution, wt. % H_2O	Aqueous phase, wt. % $UO_2(NO_3)_2$	Aqueous phase, wt. % HNO_3	Organic phase $UO_2(NO_3)_2$	Organic phase HNO_3	Organic phase H_2O	K_p $UO_2(NO_3)_2$	K_p HNO_3
29	–	–	–	14,98	49,91	18,12	5,82	–	1,210	0,12
30	–	–	–	5,25	54,32	16,53	4,76	–	3,148	0,09
31	–	–	–	2,01	54,59	15,35	4,31	–	7,64	0,08
32	–	–	–	1,23	54,90	14,29	–	–	11,62	–
33	29,55	52,19	18,26	27,51	53,14	18,67	10,05	–	0,679	0,19
34	–	–	–	22,68	55,32	17,84	9,08	–	0,787	0,16
35	–	–	–	16,53	59,11	16,86	8,58	–	1,020	0,15
36	–	–	–	3,39	65,27	13,82	8,17	–	4,076	0,13
37	–	–	–	0,99	63,23	11,64	8,29	–	11,76	0,13

with aqueous and organic solutions saturated with uranyl nitrate. Since the organic phase saturated with respect to uranyl nitrate hexahydrate contains practically no water, apparently all intermediate hydrates of $UO_2(NO_3)_2$, from the hexahydrate up to and including the anhydrous form, will correspond to compositions of the organic phases lying practically near one point (compare ([3])).

The quinary system $UO_2(NO_3)_2$–HNO_3–H_2O–27.6% BEDPC in CCl_4 was studied by the method of extraction rays, followed by construction of isolines of the distribution coefficients of uranyl nitrate over the entire field of unsaturated aqueous solutions. The data are presented in Table 2, from which the diagram shown in Fig. 1 was constructed.

Fig. 1

In all, 7 rays were constructed in this system, denoted by Roman numerals *I* –*VII*. As is evident from the figure, rays *I*–*IV* are straight lines converging at the point of 100% $UO_2(NO_3)_2$. In this region of compositions of the aqueous solutions, only uranyl nitrate passes into the organic solvent; this is also confirmed by direct analysis of the organic phase.* With a further increase in acidity the rays become curved, and the more so, the larger the percentage of acid that passes into the organic phase.

Curvature of the rays is observed near the ordinate axis, where the content of $UO_2(NO_3)_2$ in the organic phase sharply decreases and, consequently, salting-out of nitric acid from the organic phase ceases; accordingly, the extraction of nitric acid sharply increases. The considerably greater strength of the solvates of uranyl nitrate with BEDPC compared with that of nitric acid also determines the character of the isolines of the distribution coefficients of $UO_2(NO_3)_2$. In rectangular coordinates they run practically parallel to the ordinate axis, which indicates the absence of a salting-out action of nitric acid in this concentration region. The extraction isotherm of $UO_2(NO_3)_2$ in this system ($C_{\text{org}} = fC_{\text{aq}}$), both in the presence and in the absence of acid, has an interesting feature: starting from the point of formation of the composition of the stoichiometric complex $UO_2(NO_3)_2 \cdot 2$ BEDPC, the concentration

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* I.e., water and nitric acid are practically absent in it.

The amount of $UO_2(NO_3)_2$ in the organic phase increases with increasing concentration of uranyl nitrate in the aqueous phase. First, this indicates that the saturation method cannot always be used to determine the composition of the extracted complex; and, second, that what is extracted is a mixture of solvates with a higher uranium content, or the solvate $UO_2(NO_3)_2 \cdot 2$ BEDPhK with anhydrous $UO_2(NO_3)_2$ dissolved in it.

A partial study of the ternary system $UO_2(NO_3)_2$—BEDPhK—H_2O shows that in the present case the second conclusion is correct, since we found the presence of limited solid solutions between $UO_2(NO_3)_2 \cdot 2$ BEDPhK and $UO_2(NO_3)_2$. The solvate of composition $UO_2(NO_3)_2 \cdot 2$ BEDPhK, isolated by us in the solid state, consists of yellow crystals with well-defined faces, melting at 53.8 ± 0.3° and decomposing at 234°.

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Note: Figure translations are in progress. See original paper for figures.

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