Soviet-era science, translated into English

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1962

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Abstract

Full Text

CHEMISTRY

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INVESTIGATION OF THE SYSTEM URANYL NITRATE–WATER–NITRIC ACID–TRIBUTYL PHOSPHATE IN THE REGION OF STRATIFICATION

The study of this system was undertaken in order to clarify the general regularities of extraction equilibria from the standpoint of physicochemical analysis. The data available in the literature concern mainly the dependence of distribution coefficients on the concentration of the aqueous phase in the region of rather low acidities. From the literature data it was possible to use only the results of Colani (^{1}), concerning the aqueous part of the system, namely the composition of saturated aqueous solutions of uranyl nitrate and the corresponding solid hydrates.

The study was carried out at a temperature of $22 \pm 1^\circ$ in the region of stratification. Equilibrium was attained by shaking the phases in graduated separatory funnels. Redistilled tributyl phosphate was used. The analysis of the aqueous and organic phases was performed by potentiometric titration with alkali (NaOH). Table 1* gives the experimental data from which the diagram of the system was constructed (Fig. 1). A tetrahedron was adopted for the representation; in the aqueous part of the system the isolines of the distribution coefficients are also plotted. The vertices of the tetrahedron correspond to the pure components $UO_2(NO_3)_2$, HNO_3, TBP, H_2O; each face corresponds to four ternary systems, and the volume inside the pyramid to the quaternary system. The base of the diagram corresponds to equilibrium aqueous solutions. Since the solubility of tributyl phosphate in water, and especially in salt solutions, is extremely small, this entire region practically coincides with the base of the tetrahedron. The upper surface corresponds to equilibrium organic solutions. The thin lines connecting these surfaces are tie-lines. The entire volume enclosed between the conjugate surfaces corresponds to the region of stratification. Thus, a homogeneous region corresponds to a small part of the volume lying beyond the field of equilibrium organic phases. Let us follow the motion of the figurative point m during extraction, located in the plane of the base of the tetrahedron (in the aqueous part). As is seen from Fig. 1, the system at this point is heterogeneous: the aqueous solution corresponds to composition m', and the solid phase to composition S. Upon addition of tributyl phosphate to

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Fig. 1. Quaternary system $UO_2(NO_3)_2$—HNO_3—TBP—H_2O in the region of separation. Temperature 22 ± 1°.

Figure 1: Fig. 1. Quaternary system $UO_2(NO_3)_2$—HNO_3—TBP—H_2O in the region of separation. Temperature 22 ± 1°.

the system m, the overall composition will change along the line mM, while the composition of the aqueous part of the system will change along the line mm', i.e., the system will be three-phase until all the solid uranyl nitrate hexahydrate has dissolved. Upon reaching composition M, the system will become two-phase and will consist, respectively, of an aqueous layer of composition m' and an organic layer m''. Upon further addition of TBP, the change in the aqueous phase will correspond to the line $m'n_3$, while the composition of the organic phase will practically not change (it is saturated with uranyl nitrate).

The surface of conjugate organic solutions is bounded on two sides by the lines $m''A'$ and $m''O$. The line $m''O$ corresponds to the onset of stratification of the ternary system TBP–$UO_2(NO_3)_2$–H_2O and lies in the plane of this face. The line $m''A'$ represents the totality of compositions of organic solutions conjugate with the branches of saturated aqueous solutions of hexa-, tri-, and dihydrates of uranyl nitrate. In this case, just as in the system $UO_2(NO_3)_2$—NH_4NO_3—H_2O—$(C_2H_5)_2O$ (^{2}), only one form of uranyl nitrate corresponds to the ether branch of the saturated solutions. The solutions corresponding to this line contain no water; therefore it lies in the HNO_3—TBP—$UO_2(NO_3)_2$ plane. The continuation of the line $m''A'$ falls at the point of 100% HNO_3.

Fig. 1. Quaternary system $UO_2(NO_3)_2$—HNO_3—TBP—H_2O in the region of separation.
Temperature 22 ± 1°.

Consequently, the ratio TBP : $UO_2(NO_3)_2$ is constant and equal to 2 : 1. In the aqueous part of the system, seven extraction rays (^{3}) are plotted: R, m', T, N, F, B, A. The rays R, m', T, and N are straight lines converging at the pole, which is the angle of the tetrahedron corresponding to 100% $UO_2(NO_3)_2$. This indicates that in this concentration region only one uranyl nitrate (anhydrous) is extracted from the aqueous solution. Confirmation of this is also provided by the convergence of the nodes at the point m''. With a further increase in the acidity of the aqueous solutions, along with uranium nitrate, TBP ···

nitric acid also begins to be extracted. This immediately affects the behavior of the extraction rays: they no longer have a pole and deviate from the straight line toward H_2O, and the more so, the higher the acid concentration; i.e., in this region the extraction of nitric acid and uranyl nitrate are commensurate, and the ray shown proves to be the resultant one, as can easily be shown by the

* Because of limited space, not all data are given in Table 1.

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rule of vector addition.

Table 1

Compositions of the aqueous and organic phases of the system $UO_2(NO_3)_2$–TBP–HNO_3–H_2O

Rays	Aqueous phase, wt. %	Aqueous phase, wt. %	Aqueous phase, wt. %	Organic phase, wt. %	Organic phase, wt. %	Organic phase, wt. %	Distribution coefficient	Distribution coefficient
Rays	HNO_3	H_2O	$UO_2(NO_3)_2$	HNO_3	$UO_2(NO_3)_2$	TBP + H_2O	HNO_3	$UO_2(NO_3)_2$
R	8,90	46,90	44,20	0,86	43,50	55,64	0,097	0,99
R	9,72	51,48	38,80	0,86	42,20	56,94	0,089	1,08
R	11,00	59,13	29,87	0,93	40,70	58,37	0,085	1,36
R	12,54	67,96	19,50	0,73	41,20	57,94	0,061	2,11
R	15,00	81,79	3,20	0,83	39,00	60,17	0,055	12,20
Y	0,82	51,12	48,00	0,47	42,60	56,97	0,57	0,89
Y	0,86	58,39	40,75	0,44	40,10	59,46	0,52	0,98
Y	0,95	79,55	19,50	0,43	40,10	59,47	0,45	2,06
Y	1,17	88,58	10,25	0,54	34,50	64,96	0,46	3,37
m'	16,41	47,09	36,50	1,70	43,62	54,68	0,10	1,19
m'	17,66	49,84	32,50	1,85	43,25	54,90	0,10	1,33
m'	19,11	54,11	26,78	1,66	42,50	55,84	0,087	1,59
m'	21,04	60,56	18,40	1,93	41,13	56,94	0,092	2,25
m'	24,73	70,77	4,50	1,91	40,18	57,91	0,077	8,93
T	26,30	43,40	30,30	1,81	44,10	54,09	0,07	1,46
T	31,50	49,05	19,45	2,03	44,90	53,07	0,06	2,31
T	36,21	59,59	4,20	2,76	42,20	55,04	0,08	10,00
T	33,98	65,58	0,44	14,70	10,71	74,59	0,43	24,31
B	53,40	17,40	29,20	17,40	37,90	44,70	0,33	1,30
B	58,20	21,60	20,20	17,10	35,00	47,90	0,29	1,78
B	63,06	19,89	17,05	19,89	34,40	45,71	0,32	2,00
B	66,78	21,20	12,02	20,40	29,55	50,05	0,31	2,46
A	65,55	11,00	23,45	27,80	34,00	38,20	0,42	1,45
A	70,64	15,55	13,82	26,89	30,60	42,51	0,38	2,22
A	75,62	20,15	4,23	28,17	24,58	47,25	0,37	5,81
A	75,98	22,65	1,37	18,60	29,10	52,30	0,38	13,60

Each ray in the aqueous phase corresponds to its conjugate ray in the organic phase. Figure 1 shows 5 such rays. The convergence of these rays ($A'A'_4$; $B'B'_4$; ZL; $F'F'$, L; $W'L$) at two points D and L corresponds to the composition of the solvates formed in the organic phase. Thus, as a result of studying the system $UO_2(NO_3)_2$–TBP–HNO_3–H_2O in the region of stratification, it is possible to indicate which solvates are formed and within what concentration limits. For example, the region $A'DB'$ corresponds to mixtures TBP $\cdot$ $2HNO_3$ + $UO_2(NO_3)_2 \cdot 2TBP$; the region $DB'L$ corresponds to TBP $\cdot$ $2HNO_3$ + TBP $\cdot$ HNO_3 + $UO_2(NO_3)_2 \cdot 2TBP$, etc. The rays R, m^1, T, within the concentration range from 1% to $UO_2(NO_3)_2$ and above, practically have no conjugate rays in the organic phase, since the organic phase consists of the pure complex $UO_2(NO_3)_2 \cdot 2TBP$. In this region the salting-out action of uranyl nitrate in the organic phase is so great that it practically contains no nitric acid.

An interesting feature of this system is the character of the conjugation of the stratification surfaces: the predominant part of the aqueous conjugation surface corresponds to an insignificant part of the field of organic solutions, and vice versa. Such a structure of the diagram is characteristic of systems with a markedly pronounced chemical interaction of the components. In the case of formation in the system of low-strength solvates, where the main role is played by van der Waals–

forces, the conjugation between the aqueous and organic surfaces will be more diffuse, without the concentration of tie lines at definite points on the surfaces. In systems in which strong complexing agents are used as the extractant, the surface of the conjugate organic phases will degenerate into a point. In this sense the system $UO_2(NO_3)_2$—HNO_3—TBP—H_2O occupies an intermediate position.

As already mentioned, in the aqueous part of the system described there are isolines of distribution coefficients. In the behavior of these isolines a definite regularity is apparent: the lines lying near the branches of saturated solutions of $UO_2(NO_3)_2$ hydrates repeat the course of the solubility isotherms. As the concentration of uranyl nitrate decreases, the course of the isolines becomes smoother, and then the inflection points disappear altogether. Such a course of the isolines is undoubtedly connected with the structural features of aqueous uranyl nitrate solutions and, in particular, with the generally known proposition concerning the similarity of the structure of concentrated solutions to the structure of the corresponding crystalline hydrates.

In this system, as in those published earlier ([2,3]), there are four extraction regions: a region of low extraction (near the coordinate axes), a region of maximum extraction (less than 1% $UO_2(NO_3)_2$ and 30-40% HNO_3), a region of normal extraction (the overwhelming part of the surface of the diagram), and a threshold region (near the coordinate axes). The character of these regions is somewhat different, which is explained by the strong salting-out action of nitric acid, as well as by its own extraction.

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Received
14 IV 1962

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