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Abstract

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PHASE EQUILIBRIA IN THE SYSTEMS UO_2SO_4 $-H_2O$ −BEDPhK, H_2SO_4 $-H_2O$ −BEDPhK

Extraction equilibria are a particular case of phase equilibria; therefore, for their systematic study it is necessary to know their state diagrams. Many authors have studied the solubility of uranium(VI) salts in systems of the salt—water—extractant type ($^{1-3}$); the extractable salt was uranyl nitrate. The present work is devoted to the study of equilibria and phase regions of two ternary diagrams, UO_2SO_4 $-H_2O$ −BEDPhK and H_2SO_4 $-H_2O$ −BEDPhK, which constitute a quaternary extraction system. As is known, the extraction ability in the series TBP—DBEPhK—BEDPhK—TBPO* increases, which is explained, from the standpoint of acceptor-donor concepts (^{4,5}), by a decrease in the number of ether oxygens in the extractant molecule. For the work we selected and synthesized BEDPhK (n_D^{20} 1.444, $d = 0.926$, molecular weight 234.3), since it is known that the first two members of the series extract uranium(VI) poorly from sulfate solutions. Table 1 gives comparative data for three extractants of this class. Uranyl sulfate was prepared from uranyl nitrate (chemically pure grade) by evaporating it with concentrated H_2SO_4 until nitrogen oxides were completely removed, and was then recrystallized twice. The contents of uranium and acid were determined by potentiometric titration with NaOH (^{8}). In the analysis of the organic phase, the corresponding weighed sample was dissolved in 20% ethyl alcohol. Water was determined by the Fischer method. Extraction was carried out in graduated test tubes at $25 \pm 0.1°$. Stirring lasted 3-4 hours, which was sufficient to reach equilibrium. The system was then allowed to stand until complete clarification (centrifugation was sometimes used). In the case of formation of a solid phase, it was ground in the test tube and stirred until a homogeneous mass was obtained.

Table 1

Comparative characteristics of the extractants TBP, DAMPhK, BEDPhK

	TBP	DAMPhK	BEDPhK
Solubility in water at 25°C, g/l	0.25	1.99	4.6
Water solubility at 25°C, vol. %	7.0	13.0	18.4
Distribution coefficient of sulfuric acid for the equilibrium aqueous phase (6):4.06 mol/l	0.177	0.333	~0.400
5.54 mol/l	0.268	0.371	0.425

Note. For approximate characterization of DBEPhK, results for DAMPhK (7) are taken. For BEDPhK—our data.

In the work of Vdovenko and co-workers (2,3), diagrams of ternary systems $UO_2(NO_3)_2$ $-H_2O$ —simple ethers are presented. From the diagrams they studied it is clear that the extraction ability of isopropyl ether is the greatest in comparison with the others. In the system with isopropyl ether, a new nonvariant region of equilibrium appears: saturated organic phase—solid etherate—unsaturated (with respect to salt) aqueous phase.

Figure 1 (Table 2) presents the system UO_2SO_4 $-H_2O$ —BEDPhK. As is seen from the diagram, here there is a nonvariant region B, in which equilibrium exists between a solid disolvate, a saturated organic phase, and an aqueous solution unsaturated (with respect to uranyl sulfate). In region B the system separates into three phases. Thus, among all types of diagrams in which interaction occurs by the acceptor—donor type, there is a definite analogy in the order of arrangement of the regions of coexistence of various phases. The contraction or expansion of these regions is associated with the extraction properties of the systems under study. The stronger the interaction of the extractant with the salt, the lower the concentration of water—phase, conjugate with the saturated organic phase. As is seen from the diagram (Fig. 1), the compound $UO_2SO_4 \cdot 2$BEDPK is very poorly soluble in water and therefore has a large crystallization field, as a result of which the delamination region occupies a comparatively small part of the diagram. It should be noted that in some cases, during extraction from unsaturated solutions, the etherate contained more uranium than corresponds to the disolvate, which may indicate

* $(C_4H_9O)_3PO$ $-(C_4H_9O)_2POC_4H_9$ $-C_4H_9OPO(C_4H_9)_2$ $-(C_4H_9)_3PO$.

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

the formation of solid solutions of $UO_2SO_4 \cdot 2BEDPK$ with UO_2SO_4.

Table 2

Solubility isotherm in the system
UO_2SO_4—H_2O—BEDPK

Aqueous phase, %	Organic phase, %	Organic phase, %	Solid phase, %	Solid phase, %	Composition of solid phase
UO_2SO_4	UO_2SO_4	H_2O	UO_2SO_4	H_2O	
0.22	0.85	19.6			
0.40	1.5	19.6			
0.45	1.83	19.2			
0.53	2.0	19.0			
0.86	3.5	18.7			
1.46	7.3	18.0			
1.88	10.2	16.6	42.3	1.7	$UO_2SO_4 \cdot 2BEDPK$
6.5			42.3	–	
11.9			43.5	4.0	$UO_2SO_4 \cdot 2BEDPK$
20.0			42.6	–	$UO_2SO_4 \cdot 2BEDPK$
23.1			43.6	–	
31.8			43.7	–	$UO_2SO_4 \cdot 2BEDPK$
61.0			44.0		$UO_2SO_4 \times 2BEDPK + +UO_2SO_4 \cdot 3H_2O$
61.0	23.6	6.7	44.0		$UO_2SO_4 \cdot 2BEDPK$
			87.0		

The structure of the diagram studied by us is very specific. The "extraction part" proper of this diagram occupies a narrow band in the concentration triangle (region **A**). The largest part of the surface is occupied by the crystallization region of the compound $UO_2SO_4 \cdot 2BEDPK$, which is very poorly soluble in water and is practically not decomposed by water. However, as is seen from the diagram, it is soluble in water incongruently, i.e., with a sufficiently large excess of water it ultimately decomposes into two liquid phases: an aqueous phase—with a uranyl sulfate concentration of 1.88%, and an organic phase—

Fig. 1. Solubility diagram of the system UO_2SO_4—H_2O—$C_4H_9OPO(C_4H_9)_2$ at 25°C.
A —delamination region of the aqueous and organic uranyl sulfate solutions; —nonvariant region: solid disolvate, organic phase, aqueous solution; —region of equilibrium of the solid disolvate with the aqueous phase; —region of equi-

librium of the solid disolvate, trihydrate, and saturated aqueous solution; — region of coexistence of the solid disolvate with the saturated organic phase.

Fig. 2. Solubility diagram of the system H_2SO_4—H_2O—$C_4H_9OPO(C_4H_9)_2$ at 25°C

10.2% UO_2SO_4, 16.6% H_2O, 73.2% BEDPK. In aqueous uranyl sulfate solutions with a concentration greater than 1.88%, this solvate—or, more precisely, compound—is absolutely stable. The nonvariant region of diagram is obtained as a result of intersection of the crystallization volume of the compound $UO_2SO_4 \cdot$ 2BEDPC and the miscibility volume. The areas occupied by these fields depend strongly on temperature. If the temperature is raised above the melting point of the compound $UO_2SO_4 \cdot 2$BEDPC, the miscibility region will increase sharply. We observe this in the system TBP—$UO_2(NO_3)_2$—H_2O, since at ordinary temperature the solvate $UO_2(NO_3)_2 \cdot 2$TBP is liquid and melts at +6°. Such a sharp change in the structure of an isothermal diagram is characteristic of many ternary organic systems in which two organic components are mutually soluble in water only to a limited extent, forming a compound with each other. For example, in this respect the aniline—phenol—water system is illustrative. At a temperature of 25.4° the predominant part of the surface (~90%) is occupied by the miscibility region of aqueous and organic solutions. The crystallization field of the double compound occupies a very narrow strip. When the temperature is lowered by only 8°, the structure of the diagram changes sharply: the crystallization region of the double compound increases, crossing the entire miscibility field and dividing it into two parts. If one takes into account that the addition of a new component may exert an influence analogous to the action of temperature, then in some cases we may expect a sharp change in the structure of the diagram with increasing number of components. Hence the need to study phase diagrams is obvious, as is the impossibility of making any valid judgments about interactions in a system on the basis of accidental sections and fragmentary information on the given system.

Table 3

Solubility isotherm at 25 ± 0.1° in the H_2SO_4–H_2O–BEDPC system

Aqueous phase, wt. %	Aqueous phase, wt. %	Aqueous phase, wt. %	Organic phase, wt. %	Organic phase, wt. %	Organic phase, wt. %
H_2SO_4	BEDPC	H_2O	H_2SO_4	BEDPC	H_2O
0	0.46	99.54	0	80.40	19.60
10.20	0.34	89.46	4.00	77.00	19.00
11.90	0.30	87.80	5.10	76.20	18.70
16.20	0.25	83.55	6.60	75.00	18.40
22.50	0.20	77.30	10.00	72.50	17.50
30.00	0.20	69.80	14.00	69.40	16.60

Aqueous phase, wt. %	Aqueous phase, wt. %	Aqueous phase, wt. %	Organic phase, wt. %	Organic phase, wt. %	Organic phase, wt. %
47.00	0.14	52.86	25.30	59.50	15.20
52.70	0.20	47.10	30.20	54.90	14.90
61.50	0.25	38.25	39.20	45.70	15.10
70.10	0.40	29.50	51.50	34.80	13.70
76.80	0.50	22.70	62.20	25.00	12.00
79.50	2.50	18.00	69.00	19.00	12.00

Works (9–12, 6) have been devoted to the study of the extraction of water and various acids. In these investigations tributyl phosphate was mainly used. The authors of these works believe that sulfuric acid is extracted in the form of various hydrates, beginning with the decahydrate and ending with the anhydrous form. Apparently, preference cannot be given to any one of these forms, and the existence of anhydrous sulfuric acid in the organic phase appears unlikely.

As is evident from the diagram (Fig. 2, Table 3), beginning at approximately 88% sulfuric acid mixes with BEDPC in all proportions. And, apparently, the most probable assumption will be the extraction of a continuous series of aqueous H_2SO_4 solutions. The binodal of the ternary system H_2SO_4–H_2O–BEDPC has the usual form characteristic of organic systems without chemical interaction. The tie-lines connecting conjugate phases have a pole of intersection, which makes it possible to establish the composition of conjugate phases at any point of the miscibility region. As is seen from Fig. 2, the right branch of the binodal is a straight line, which indicates the additive character of the replacement of water by sulfuric acid in the organic phase.

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REFERENCES

1. I. C. Katzin, G. E. Sullivan, *J. Phys. Coll. Chem.*, **55**, 3, 346 (1951).
2. V. M. Vdovenko, I. G. Suglobova, D. N. Suglobov, *Radiochemistry*, **1**, 6, 637 (1959).
3. V. M. Vdovenko, I. G. Suglobova, M. Mezei, *Radiochemistry*, **4**, 4, 388 (1962).
4. A. V. Nikolaev, S. M. Shubina, *ZhNKh*, **6**, 4, 799 (1961).

5. S. Nomura, R. Hara, *Anal. Chem. Acta*, **25**, 3, 212 (1961).
6. K. Naito, T. Suzuki, *J. Phys. Chem.*, **66**, 6, 983 (1962).
7. A. S. Solovkin, *ZhNKh*, **5**, 8, 1857 (1960).
8. V. K. Markov et al., *Uranium and Methods for Its Determination*, Moscow, 1960.
9. E. Hesford, H. A. C. McKay, *J. Inorg. and Nucl. Chem.*, **13**, 1-2, 156 (1960).
10. A. S. Solovkin, N. S. Povitskii et al., *Collection of Articles on Extraction*, 1960.
11. A. S. Solovkin, *ZhNKh*, **5**, 5, 1107 (1960).
12. E. Brauer, E. Hogfoldt, *J. Inorg. and Nucl. Chem.*, **23**, 1-2, 115 (1961).
13. J. Zernike, *Chemical Phase Theory*, Deventer, 1957.

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

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