Corresponding Member of the Academy of Sciences of the USSR A. V. NIKOLAEV, Yu. A. DYADIN,

I. I. YAKOVLEV

1964

SovietRxiv

Abstract

Full Text

CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR A. V. NIKOLAEV, Yu. A. DYADIN,
I. I. YAKOVLEV

ON THE SOLUBILITY OF WATER AND URANYL NITRATE IN TRIBUTYL PHOSPHATE IN THE RANGE 0–100°C

The data available in the literature on the solubility of uranyl nitrate in tributyl phosphate (TBP) are somewhat contradictory. Thus, Healy and McKay (^{1}) consider that in the temperature range 0–50° the solubility of uranyl nitrate does not depend on temperature and that the ratio of the number of moles of TBP to $UO_2(NO_3)_2$ is equal to 2 ± 0.02. Wendlandt and Bryant (^{2}) showed that this ratio is not an integer, as it is for the nitrates of other elements; the number of moles of TBP per mole of uranyl nitrate was found to be less than two (1.89). Fedor, Ross, and Fogel (cited in (^{1})) obtained a solution of uranyl nitrate with a TBP-to-$UO_2(NO_3)_2$ ratio equal to 1.4 when very dilute TBP in dichloroethane was contacted with uranyl nitrate dihydrate.

Fig. 1 Fig. 2

Fig. 1. Dependence of the solubility of $UO_2(NO_3)_2$ in TBP on temperature
Fig. 2. Water content in the organic phase as a function of temperature

We studied the solubility of uranyl nitrate in tributyl phosphate in the temperature range 0–100°. Equilibrium was established in thermostatted test tubes; the constancy of temperature was maintained with a U-8 thermostat. Temperatures of 0 and 100° were obtained in melting ice and boiling water. The experiments were carried out in such a way that at equilibrium three phases were present: two liquid phases (aqueous and organic) and one solid phase*, i.e., with this experimental arrangement the solubility was studied along the eutectic lines of the ternary system $UO_2(NO_3)_2$–TBP–H_2O. The uranium content in the organic and aqueous phases was determined by the method of Klygin (^{3}) with minor modifications (^{4}). Water in the organic phase was determined by the K. Fischer method. The solubility data are presented in Table 1 and in Figs. 1 and 2.

As is evident from Fig. 1, the solubility of uranyl nitrate in TBP increases with increasing temperature and reaches 53.11% at 100°. If one takes into account that the conten-

* Excluding the hydrate transition points.

the water content in the organic phase at this temperature is 1.59%, and the molar ratio of uranyl nitrate to tributyl phosphate is 1 : 1.26. When uranyl nitrate hexahydrate is dissolved in tributyl phosphate with solid $UO_2(NO_3)_2 \cdot 6H_2O$, two liquid phases are in equilibrium—aqueous and organic.

Table 1

Solubility of uranyl nitrate and water in tributyl phosphate
at temperatures of 0–100°C

	0°	25°	50°	65°	78°	92°	100°
Solubility, wt. %	Solubility, wt. %	Solubility, wt. %	Solubility, wt. %	Solubility, wt. %	Solubility, wt. %	Solubility, wt. %	Solubility, wt. %
$UO_2(NO_3)_2$	42.31	44.26	46.30	48.38	50.14	51.70	53.11
H_2O	0.15	0.25	0.54	0.76	1.14	1.53	1.59

organic. If this system is gradually dehydrated, we enter the region of crystallization of uranyl nitrate hexahydrate from the organic phase. The crystallization branch of $UO_2(NO_3)_2 \cdot 6H_2O$ from organic solutions is very small, and tracing its course at the given experimental accuracy is very difficult. To determine the composition of the solid phase upon further dehydration of the organic solutions, the following experiment was carried out. The organic phase, in equilibrium with water and uranyl nitrate trihydrate, was separated from the latter at 100° and cooled to room temperature. Crystals precipitated; after one day they were squeezed free of mother liquor and analyzed for uranium (86.51% $UO_2(NO_3)_2$) and water (11.57%). The ratio of water to uranyl nitrate, somewhat low in comparison with the trihydrate, is explained by insufficient removal of the mother liquor. This is also indicated by the discrepancy in the balance (98.08%). To remove the remaining mother liquor, we washed the precipitate with a small amount of dry benzene (distilled over metallic sodium). The results of the analysis confirmed our expectations (87.88% $UO_2(NO_3)_2$ and 12.17% H_2O). As is evident from these data, the molar ratio of water to uranyl nitrate is 3; i.e., the next crystallization branch from organic solutions is the branch of uranyl nitrate trihydrate. The schematic arrangement of the phase regions in the ternary system $UO_2(NO_3)_2$—TBP—H_2O is shown in Fig. 3.

Fig. 3. Schematic representation of the system $UO_2(NO_3)_2$—TBP—H_2O:
1 —homogeneous aqueous solutions; 2 —stratification region; 3 —homogeneous organic solutions; 4 —aqueous solution + solid $UO_2(NO_3)_2 \cdot 6H_2O$; 5 —solid $UO_2(NO_3)_2 \cdot 6H_2O$ + two liquid phases; 6 —organic solution + solid $UO_2(NO_3)_2 \cdot 6H_2O$; 7 —organic solution + solid $UO_2(NO_3)_2 \cdot 3H_2O$; 8 —organic solution + solid $UO_2(NO_3)_2 \cdot 6H_2O$ + solid $UO_2(NO_3)_2 \cdot 3H_2O$.

As is known, an increase in temperature decreases the solubility of water in tributyl phosphate (^{5}). The increase in the water content in the organic phase with rising temperature in the presence of uranyl nitrate confirms that hydrates of the latter are extracted. The ratio of excess uranyl nitrate (relative to the solvate $UO_2(NO_3)_2 \cdot 2TBP$) to water in the organic phase fluctuates around 3.

One of the features of this system is the unusual character of the fields of separation and crystallization of the compounds formed in it. This is associated with the low solubility of TBP in water and of water in organic solutions of uranyl nitrate. The sharp concentration dependence of the distribution of uranyl nitrate between the aqueous and organic phases leaves its imprint on the structure of the separation field: a small region of aqueous solutions corresponds to a large field of conjugate organic phases, and vice versa. The conodes of the separation field in this case form two oppositely directed bundles. This is somewhat reminiscent of the phenomenon of solutropy. The nonuniformity of the structure of the separation surface is not accidental and may be caused either by the formation of chemical compounds or by the strong nonideality of the organic phases.

The second feature of the system is the small extent of the crystallization branches of the solid phases formed in this system. The presence of these features accounts for the difficulties in the experimental study of phase equilibria and may serve as a source of fundamental errors in the interpretation of experimental results. Thus, for example, the relative constancy of the composition of the organic phase, close to the stoichiometric one, over a wide range of concentrations of the aqueous phase may be taken for a compound of constant composition, although there may not be sufficient grounds for this.

Institute of Inorganic Chemistry
Siberian Branch of the Academy of Sciences of the USSR

Received
26 VI 1964

REFERENCES

1. T. V. Healy, H. A. C. McKay, Trans. Farad. Soc., **52**, 633 (1956).

2. W. Wendland, J. M. Bryant, J. Phys. Chem., **60**, 1145 (1956).

3. V. K. Markov, A. V. Vinogradov et al., *Uranium. Methods of Its Determination*, Moscow, 1960, p. 175.

4. A. V. Nikolaev, Yu. A. Dyadin et al., Dokl. Akad. Nauk SSSR, **153**, 118 (1963).

5. V. A. Mikhailov, S. K. Kharchenko, A. G. Nazin, Izv. SO AN SSSR, **7**, 50 (1962).

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