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Abstract

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ON MUTUAL SOLUBILITY IN THE SYSTEM WATER–NITRIC ACID–$(C_4H_9O)PO(C_4H_9)_2$ AT 25°

Butyl ester of dibutylphosphinic acid* is a promising extractant for the extraction of metal salts (uranium, rare-earth elements, etc.) and acids. It has a greater capacity and extraction ability than tributyl phosphate, but is somewhat inferior to it in terms of increased solubility in water. However, if one takes into account that in the presence of salts and acids its solubility in water drops sharply (dilution with inert organic solvents also decreases solubility), then losses of it during extraction will be insignificant even when large phase volumes are used.

The distribution of uranyl nitrate and nitric acid between the aqueous and organic phases in the stratification region in the quaternary system $UO_2(NO_3)_2$—HNO_3—H_2O—$(C_4H_9O)PO(C_4H_9)_2$ was studied by us earlier (^{1}). The present work is devoted to studying the phase diagram of the ternary system water–nitric acid–butyl ester of dibutylphosphinic acid at 25°. In the work, $(C_4H_9O)PO(C_4H_9)_2$ was used, prepared and purified as reported previously (^{1}). Nitric acid of 96.3% was obtained from chemically pure potassium nitrate and sulfuric acid (^{2}). Stratification was determined by the Alekseev method (^{3}) at different temperatures, followed by interpolation to 25° (Table 1). To determine the compositions of conjugate phases, the latter were brought to equilibrium in a U-8 thermostat ($25 \pm 0.1°$), and the nitric acid content was determined both in the aqueous and in the organic phases. In some cases, water in the organic phase was determined by the K. Fischer method (Table 2).

Table 1

Solubility in the system HNO_3—H_2O—BEDBP
(isotherm 25°)

HNO_3, wt. %	BEDBP, wt. %
0	0.445
1.45	0.398
8.41	0.218

HNO_3, wt. %	BEDBP, wt. %
21.17	0.039
45.30	0.046
57.00	0.082
67.81	0.350
74.80	2.53
73.03	8.75
64.81	23.60
58.90	31.62
46.87	47.22
39.85	55.80
23.42	74.01
7.03	80.55
0	80.15

Table 2

Conjugate phases in the system HNO_3—H_2O—BEDBP (isotherm 25°)

Aqueous phase, wt. % HNO_3	Composition of organic phase, wt. % HNO_3	Composition of organic phase, wt. % H_2O	Density of organic phase, d_4^{25}
0	0	19.55	0.9400
1.75	4.19	14.35	0.9563
2.41	5.70	13.40	0.9597
5.10	9.91	–	–
7.63	12.35	7.45	0.9823
10.33	13.82	–	–
13.71	16.21	4.87	0.9962
17.31	18.10	3.94	1.0012
17.52	18.29	–	–
19.80	18.98	3.72	1.0029
32.73	23.30	–	–
38.35	25.62	2.92	1.0266
49.62	30.84	–	–
58.54	36.31	4.08	1.0811
65.76	42.06	–	–
67.35	44.69	–	1.1271
73.42	54.23	–	–

* BEDBP –$(C_4H_9O)PO(C_4H_9)_2$.

Fig. 1

Figure 1: Fig. 1

From the data of Tables 1 and 2 a diagram has been constructed (Fig. 1). As can be seen from the figure, the solubility found by Alekseev’ s method and by direct analysis of the equilibrium phases practically coincides.

An analogous system with tributyl phosphate has been studied in parts by a number of authors, for example ($^{4-8}$), while in work (^{9}) the complete system is presented both from the authors’ own data and from literature data processed by them.

Fig. 1. Mutual solubility in the system HNO_3—H_2O—B **(isotherm** 25°**).**
a –solubility determined by Alekseev’ s method; *b* –solubility determined analytically.

On the solubility curve of the system TBF –HNO_3 –H_2O there is a rather sharp inflection near the singular secant corresponding to the ratio of nitric acid to tributyl phosphate 1 : 1. The existence of a compound of such composition is also indicated by a number of other works, for example (^{10,11}). The formation of undissociated compounds from the components is usually characterized by the presence of singular points on property lines as a function of composition. In the case of the formation of a binary undissociated compound in a ternary system, the crystallization field of this compound is usually accompanied by the presence of a singular fold, which lies on the secant connecting the indifferent component with the composition of this binary compound (^{12}). Upon dissociation of one of the components of this binary compound, the singular folds disappear and the solubility minimum shifts toward the dissociating component. Often the crystallization field of an indifferent component, for example ice, serves in such cases as an indicator of the presence of a slightly dissociating binary compound, where the isotherms have a sharp singular fold corresponding to the composition of the binary compound. In our case, the stratification field may serve as such an indicator. The sharpest fold, corresponding to the extractant-acid compound, is exhibited by the system HNO_3—H_2O—TBF.

As can be seen from Fig. 1, the solubility minimum of water on the isotherm is shifted toward nitric acid from the secant corresponding to the ratio

$$HNO_3 : (C_4H_9O)PO(C_4H_9)_2 = 1 : 1.$$

The absence of a singular fold on the isotherm of the stratification field at this temperature is apparently caused by dissociation of nitric acid, as well as by dissociation of the possible compound $HNO_3 \times B$. Since dissociation has been demonstrated for such a comparatively strong complex as $UO_2(NO_3)_2 \cdot 2TBF$

Fig. 2

Figure 2: Fig. 2

at the melting temperature ([13]), dissociation of the nitric-acid complex with B at temperatures above the melting point is very probable.

Fig. 2. Solubility of B **in aqueous solutions of nitric acid at 25°.**

In work ([14]) we studied the ternary system water —sulfuric acid —B . Comparison of the solubility curves in sulfuric-acid and nitric-acid media shows that they differ sharply from one another. The binodal in the sulfuric-acid medium has no singular elements. This is also evidenced by the structure of the stratification field. All conodes of the sulfuric-acid system have a slope. In the system with nitric acid,

expressed in weight percent, the pole exists only for a limited part of the binodal surface. Then there is water corresponding to a nitric acid distribution coefficient equal to 1 (solutropic water), and afterward inversion occurs, i.e., the pole shifts to the opposite side. Such diversity in the character of the diagrams, seemingly of systems with components close in properties, requires a more detailed study of these systems and, in particular, of the miscibility of the binary acid—extractant systems, as well as the solubility of their ternary systems at different temperatures.

Figure 2 presents a graph of the solubility of butyl dibutylphosphinate in aqueous nitric acid solutions at 25°. As can be seen from the figure, the solubility of BDBP in nitric acid solutions first decreases sharply, reaches a minimum, and then rises sharply. The solubility minimum corresponds to $\sim 42\%$ HNO_3. It is interesting to note that the solubility minimum of tributyl phosphate in aqueous nitric acid solutions also corresponds to this concentration ([4]). When the concentration of HNO_3 in the aqueous phase is increased to $\sim 42\%$, the solubility of BDBP decreases by a factor of 10, which already corresponds to the solubility of tributyl phosphate in pure water.

To make it possible to convert weight concentrations into volume concentrations, we measured the specific gravities of the organic solutions; these are given in Table 2. In the graph of the dependence of the specific gravity of the organic phases on their acid content, there is an inflection at an acidity of 23% HNO_3. This point corresponds to the minimum solubility of water in the organic phase.

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