Chemistry

Corresponding Member of the Academy of Sciences of the USSR A. V. Nikolaev, Yu. A. Dyadin,

1965

SovietRxiv

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

Abstract

Full Text

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Corresponding Member of the Academy of Sciences of the USSR A. V. Nikolaev,
Yu. A. Dyadin,
I. I. Yakovlev

SOLUBILITY POLYTHERM IN THE TERNARY SYSTEM

HNO_3—H_2O—$(C_4H_9O)PO(C_4H_9)_2$

Phase equilibria in extraction systems are the least studied area. Meanwhile, knowledge of them is necessary, since, as a rule, only by studying the fusion diagram can one give a direct answer as to the presence or absence of chemical interaction between the components, if these compounds or solvates cannot be isolated by ordinary preparative methods.

The aim of the present work was to study the mutual solubility of water and the butyl ester of dibutylphosphinic acid (BEDBP) in the presence of nitric acid at different temperatures. This ternary system is part of the quaternary system $(C_4H_9O)PO(C_4H_9)_2$—H_2O—HNO_3—$UO_2(NO_3)_2$, which we previously studied in the region of stratification in the presence of carbon tetrachloride (1). The mutual solubility of water and BEDBP, as well as of other extractants of this class, has been studied by us and is shown in Fig. 1. As follows from these data, both branches of the conjugate solutions have a solubility minimum and show a tendency toward the formation of a closed stratification curve. Tributylphosphine oxide has a lower critical solution temperature, while for the other extractants it is not realized because of the intersection of the stratification curve with the crystallization line.

Fig. 1. Mutual solubility in extractant–water systems as a function of temperature:
I –H_2O–TBP, *II* –H_2O–DBBP*, *III* –H_2O–BEDBP, *IV* –H_2O–TBPO.

Fig. 2. Mutual solubility in the nitric acid–water–BEDBP system. 1 –10° isotherm, 2 –25° isotherm, 3 –40° isotherm.

* BEDBP –butyl ester of dibutylphosphinic acid.

Phase-separation diagrams of binary systems organophosphorus extractant—water have a number of features that shed light on the nature of their interaction with water.

Table 1

Polytherm of mutual solubility in the system HNO_3–H_2O–BEDBP

BEDBP, wt.%	Phase-separation temperature, °C	BEDBP, wt.%	Phase-separation temperature, °C	BEDBP, wt.%	Phase-separation temperature, °C
$HNO_3 : H_2O = 1.46 : 98.54$	$HNO_3 : H_2O = 1.46 : 98.54$	$HNO_3 : H_2O = 68.10 : 38.90$	$HNO_3 : H_2O = 68.10 : 38.90$	$HNO_3 : H_2O = 88.66 : 11.34$	$HNO_3 : H_2O = 88.66 : 11.34$
0.193	50.0	0.221	12.0	37.75	8.6
0.411	24.2	0.287	19.5	41.24	14.7
0.591	14.9	0.342	23.7	45.33	21.8
$HNO_3 : H_2O = 8.43 : 91.57$	$HNO_3 : H_2O = 8.43 : 91.57$	0.415	28.0	49.97	29.5
0.126	48.4	0.505	34.2	56.06	40.1
0.152	39.5	0.639	40.3	62.95	48.9
0.230	22.8	1.011	51.5	72.61	61.7
0.280	13.2	2.237	73.5	75.95	one phase in the interval 0 −100°
0.328	6.2	$HNO_3 : H_2O = 76.83 : 23.17$	$HNO_3 : H_2O = 76.83 : 23.17$	$HNO_3 : H_2O = 90.25 : 9.75$	$HNO_3 : H_2O = 90.25 : 9.75$
$HNO_3 : H_2O = 21.19 : 78.81$	$HNO_3 : H_2O = 21.19 : 78.81$	0.817	1.2	43.76	6.1
0.0733	51.3	1.518	14.8	47.50	10.8
0.0766	41.2	2.286	23.1	48.46	11.4
0.0783	37.7	3.760	32.9	55.71	24.2
0.0844	29.0	6.624	44.4	56.04	26.2
0.0957	21.0	10.26	53.9	64.05	30.4

BEDBP, wt.%	Phase-separation temperature, °C	BEDBP, wt.%	Phase-separation temperature, °C	BEDBP, wt.%	Phase-separation temperature, °C
0.123	8.1	$HNO_3 : H_2O = 80.06 : 19.94$	$HNO_3 : H_2O = 80.06 : 19.94$	67.72	31.0
0.161	does not mix at 0°	2.731	6.4	71.80	26.5
$HNO_3 : H_2O = 45.29 : 54.71$	$HNO_3 : H_2O = 45.29 : 54.71$	4.933	15.9	73.00	20.5
0.0402	10.7	8.234	24.1	74.8	1.0
0.0408	15.6	11.88	30.9	$HNO_3 : H_2O = 91.72 : 8.28$	$HNO_3 : H_2O = 91.72 : 8.28$
0.0453	25.3	15.26	38.9	59.69	4.4
0.0514	28.9	18.06	46.1	62.61	8.9
0.0583	40.6	26.09	66.9	67.96	11.3
0.0742	53.0	$HNO_3 : H_2O = 84.70 : 15.30$	$HNO_3 : H_2O = 84.70 : 15.30$	70.74	9.6
$HNO_3 : H_2O = 57.00 : 43.00$	$HNO_3 : H_2O = 57.00 : 43.00$	17.28	10.8	72.13	on cooling to 0° does not phase-separate
0.0592	12.2	21.13	19.5	$HNO_3 : H_2O = 36.95 : 63.05$	$HNO_3 : H_2O = 36.95 : 63.05$
0.0707	18.9	23.94	26.4	80.05	16.0
0.0842	25.6	28.28	35.1	80.56	24.2
0.104	32.9	33.88	48.7	80.86	30.2
0.159	46.2	$HNO_3 : H_2O = 86.22 : 13.78$	$HNO_3 : H_2O = 86.22 : 13.78$	81.19	38.8
0.197	52.0	22.70	6.9	81.42	42.8
		29.86	21.8	81.72	50.2
		35.29	31.6	81.79	53.7
		40.66	44.0		

Fig. 3

Figure 2: Fig. 3

BEDBP, wt.%	Phase-separation temperature, °C	BEDBP, wt.%	Phase-separation temperature, °C	BEDBP, wt.%	Phase-separation temperature, °C
		53.11	70.5		

Examination of phase diagrams known from the literature with a lower critical solution temperature leads to the conclusion that compounds are formed in these systems. Thus, for example, diethylamine gives two compounds with water. In all likelihood, triethylamine also forms hydrates with water (although they have not yet been isolated), since the analogous compound—trimethylamine—forms hydrates but does not give phase separation. For nicotine analogues having a closed phase-separation curve with water, either hydrates have likewise been isolated, or their high hygroscopicity is noted.

The compounds listed are fairly strong bases, which undoubtedly argues in favor of their chemical interaction with water. Thus, following this analogy, one may expect the isolation of hydrates of tributylphosphine oxide and, possibly, of the next members of this series of extractants—the monobutyl ester of dibutylphosphinic acid and the dibutyl ester of butylphosphonic acid, for which, as noted above, the lower critical temperature is not realized because crystallization occurs. For tributyl phosphate, judging from the course of the curves of solubility, this temperature is the lowest and can be realized only in the case of deep supercooling (delay of crystallization). Tributyl phosphate is the least hydrophilic of the indicated extractants. The possibility of formation of a compound between components having a tendency to form a lower critical solution temperature, but not realized because of the intersection of the separation curve with the crystallization line, is also indicated by the melting diagram of the pyrimidone—water system, studied by S. I. Kaplan and F. E. Rabinovich (^{2}). Although the authors (^{2}) give only the crystallization and stratification curves of this system, without indicating the phase fields of the diagram, judging from the course of the crystallization line of pyrimidone, one may conclude that an incongruently melting pyrimidone hydrate of composition 1:1 is formed, since the melting curve at a concentration of $\sim$ 90% pyrimidone undergoes a rather sharp break. A final answer on the presence and composition of possible hydrates of the aforementioned organophosphorus extractants can be provided by studying their melting diagrams.

The reagents used and the working procedure have been described previously (^{3}).

Fig. 4

Figure 3: Fig. 4

Fig. 3

Fig. 4

Fig. 3. Solubility of BEDBF in aqueous solutions of nitric acid at various temperatures. 1 —isotherm at 10°, 2 —isotherm at 25°, 3 —isotherm at 40°, 4 —isotherm at 50°.

Fig. 4. Density of organic solutions along the solubility line in the system nitric acid—water—BEDBF. *a* —density at 40°, *b* —density at 25°.

Table 1 gives the experimental data on the basis of which three isotherms of separation (Fig. 2) were constructed for 10, 25, and 40°. From the course of these isotherms, as well as from the appearance of the solubility polytherm of the binary system BEDBF—H_2O, one can represent the separation volume as a whole. The tendency toward formation of a closed separation curve in the binary system extractant—water leaves its imprint on the appearance of the separation volume (in composition—temperature coordinates). If nitric acid, with increasing temperature, continuously decreases the separation volume, i.e., acts in a homogenizing manner, then the heterogeneous region in the binary system extractant—water at first expands along the composition axis with increasing temperature, reaches a maximum, decreases, and then probably disappears.

disappears altogether (the upper critical solution temperature). On the scale of Fig. 2, the left branch of the binodal (the solubility of BEDBP in aqueous solutions of nitric acid) practically merges with the water—nitric acid axis.

Figure 3 shows this branch on another scale, where the sharp dependence of the solubility of BEDBP on acidity and temperature is clearly visible. As can be seen from this figure, with increasing temperature the solubility minimum of BEDBP shifts toward lower acidity, and with a further increase in temperature this minimum probably coincides with the BEDBP—H_2O axis. The minimum of water solubility in nitric-acid solutions of BEDBP also tends to shift toward lower acidity. As a result of the superposition of all the factors—the homogenizing action of nitric acid over a certain temperature interval and the dual effect of temperature on the magnitude of the miscibility gap in the binary system BEDBP—water—the miscibility region has a distinctive form. It contains a region where the solubility depends rather sharply on temperature and, conversely, there are sections where this temperature dependence is practically absent (for example, in the vicinity of the intersection of the isotherms).

For the 40° isotherm in Fig. 2, tie lines are shown connecting the equilibrium phases. The slope of the tie lines is practically independent of temperature. Comparison of the positions of the tie lines for 25 and 40° gives coincident results. Figure 4 shows a plot of the dependence of the specific gravity of the organic phases on the acid content in them for 25 and 40°. At an acidity of ~23% HNO_3, the curve has an inflection, which corresponds to the minimum of water solubility in organic solutions.

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

Received
31.VIII.1964

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