

INVESTIGATION OF PHASE EQUILIBRIA IN THE SYSTEM ANTHRANILIC ACID - WATER - ETHANOL

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Translated from *Zhurnal Obshchei Khimii*, Vol. 30, No. 4, pp. 1078-1081, April, 1960

Original article submitted December 29, 1959

The simplest form of metastable equilibria between liquid phases was found in the ternary system salicylic acid - water - ethanol [1]. In the diagram of state of the system the volume, corresponding to metastable equilibria, begins at the plane of the binary system (salicylic acid - water) and ends within the prism of the ternary system; it has no special geometric elements. Anthranilic acid is similar to salicylic acid in its molecular structure and its behavior in binary systems with water (see below). On the strength of this it might be supposed that their ternary systems with aqueous-alcoholic solvents would present similar pictures of phase equilibria. To elucidate the given question, the ternary system anthranilic acid - water - ethanol was investigated with regard to stratification and melting point in the present work.

EXPERIMENTAL

Of the binary systems which are components of the given ternary one, the system water - ethanol was described in detail earlier [1]. It belongs to the class of systems with simultaneous decomposition of associated components and chemical interaction. The system anthranilic acid - water was investigated with regard to melting point and stratification [2]. In it (as in the system with salicylic acid) a curve of metastable liquid-phase equilibrium, with an upper critical point at 78° and an anthranilic acid content of 38%, was found. The system anthranilic acid - ethanol was studied with regard to melting point in the present work.

TABLE 1
Equilibrium in the System
Anthranilic Acid - Ethanol

Anthranilic acid (wt. %)	Crystallization temperature
40.11	60.5°
49.87	73.0
59.91	85.0
70.00	97.5
80.11	111.0
90.00	124.5
100.00	145.0

The following reagents were used: anthranilic acid, m. p. 145°, redistilled water, and distilled 96% ethanol, b. p. 78°; the latter was not dehydrated, since aqueous-alcoholic mixtures were prepared from it, the water contained in it being taken into account.

Investigations with regard to stratification were carried out by V. F. Alekseev's visual-polythermal method [3] in sealed glass ampules in a glycerol thermostat, crystallization being delayed. The latter was studied in the same ampules.

In the System Ethanol - Anthranilic Acid, crystallization of the latter was studied in the interval from its melting point to 60° by the Shreder method [4], and also by the method of internal priming [5]. Numerical data obtained are given in Table 1; the crystallization curve is shown in Fig. 1 (Curve 0). The latter drops sharply downward; this indicates that the solubility of salicylic acid in ethanol depends only slightly on temperature.

The Ternary System Anthranilic Acid - Water - Ethanol was studied with regard to stratification and melting point (by the indicated methods) through the investigation of polythermal sections through its prism,

passing from the anthranilic acid edge to the face of the binary system water – ethanol. Numerical data obtained are given in Table 2; the polytherms are shown in Fig. 1, in which melting-point (Cr) and stratification (St) curves of the system anthranilic acid – water are given. Stratification was found only in the case of the first two sections. The stratification polytherms are qualitatively similar to the stratification curve of the system anthranilic acid – water. On moving from the latter to the second section they bound all smaller regions of liquid-phase equilibria and have decreased upper consolute temperatures. The crystallization curves of the ternary mixtures drop sharply downward, but in sections with stratification over the crystallization curves, the latter have gently sloping portions.

TABLE 2

Polytherms of the Ternary System Anthranilic Acid – Ethanol – Water

Anthranilic acid (wt. %)	Temperature		Anthranilic acid (wt. %)	Temperature	
	of stratifi- cation	of crystalli- zation		of stratifi- cation	of crystalli- zation
Section 1: 10% ethanol, 90% water			Section 3: 40% ethanol, 60% water		
10.21	—	85.0°	30.10	—	80.5°
20.04	65.0°	87.5	40.00	—	83.0
29.80	71.5	89.0	49.89	—	85.5
40.11	76.0	91.5	60.12	—	91.5
49.90	77.0	94.5	70.08	—	98.5
60.00	75.0	98.5	80.00	—	110.5
70.07	70.5	103.0	90.00	—	124.5
80.14	—	111.0			
89.90	—	121.5			
Section 2: 20% ethanol, 80% water			Section 4: 60% ethanol, 40% water		
9.63	—	79.0°	49.85	—	63.0°
20.10	—	84.0	60.07	—	78.0
30.00	—	85.5	70.13	—	92.5
40.13	67.0°	86.0	80.00	—	106.5
50.00	75.0	88.5	90.00	—	123.5
60.00	68.0	93.0			
70.11	—	100.0			
79.00	—	108.0			
89.92	—	120.5			
			Section 5: 80% ethanol, 20% water		
			50.0	—	66.0°
			60.06	—	80.0
			70.00	—	93.5
			80.00	—	108.0
			89.05	—	124.0

Figure 1 shows that the stratification curves of all sections (as in the binary system anthranilic acid – water) lie under the crystallization curves of the acid. Hence, the entire stratification surface of the ternary system lies under the crystallization surface of anthranilic acid. Thus the entire stratification volume of the ternary system is a volume of metastable liquid-phase equilibrium.

Five solubility isotherms of the ternary system anthranilic acid – water – ethanol were constructed from the polytherms obtained: stratification isotherms at 70, 75, and 77° and crystallization isotherms at 80 and 85° (Fig. 2). The stratification isotherms clearly show that the volume of the two-phase liquid state adjoins the side of the binary system and lies along it. Therefore, the upper point of this volume is the critical point C of the indicated binary system at 78°. From Fig. 2, it is evident that the stratification volume is very narrow, and extends only up to a content of 13-15% ethanol in the mixtures, in the prism of the ternary system. Thus, ethanol is a very powerful homogenizer of stratification in the binary system anthranilic acid – water.

The crystallization isotherms for solid anthranilic acid in water – ethanol mixtures have solubility maxima. It is of interest that these maxima occur in the binary system water – ethanol at a molar ratio of about 1:1 between the components, as in the ternary system with salicylic acid. Therefore, the binary system water – ethanol is a solvent system [6] with respect to anthranilic acid.

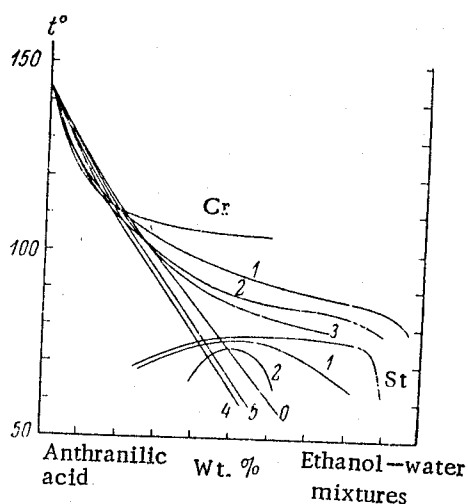


Fig. 1. Polytherms of the ternary system anthranilic acid - water - ethanol. α) Crystallization curve of the system anthranilic acid - ethanol; Cr and St are crystallization and stratification curves, respectively, of the system anthranilic acid - water. Ethanol content in ethanol - water mixtures (in %): 1) 10; 2) 20; 3) 40; 4) 60; 5) 80.

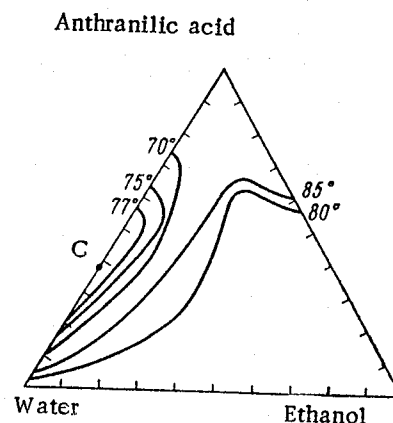


Fig. 2. Solubility isotherms of the ternary system anthranilic acid - water - ethanol. C is the critical point of the system anthranilic acid - water.

SUMMARY

1. The ternary system anthranilic acid - water - ethanol was studied with regard to stratification and melting point. It was found to be a ternary system with one narrow volume of metastable equilibrium between liquid phases, adjoining the plane of the binary system anthranilic acid - water.
2. It was shown that the binary system water - ethanol is a solvent system for anthranilic acid.

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* Original Russian pagination. See C. B. translation.