THE OCCURRENCE OF EQUILIBRIUM OF THREE LIQUID PHASES IN TERNARY SYSTEMS

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Until recently stable equilibrium of three liquid phases has been found in ternary systems formed by binary systems with stable phase separation. It has also been shown [1] that equilibrium of three liquid phases can occur in ternary systems which contain a binary system with metastable phase separation. In the case studied, the three-phase liquid equilibrium was also metastable and occurred according to the same scheme as the stable phase separation. Stable equilibrium of three liquid phases in a ternary system containing one or several binary systems with metastable phase separation has not been studied. The study of this type of equilibrium and the method of its formation is the purpose of the present work.

EXPERIMENTAL

We selected for the study of this question the ternary system anthranilic acid–water–benzine. The binary system anthranilic acid–benzine was studied in this work to relate it to systems with metastable phase separation. The system water–benzine belongs to systems with stable phase separation and a very high upper critical point [1]. The system water–anthranilic acid has been studied for stratification [2]. The curve for the metastable phase separation of the system has an upper critical point at 78°, corresponding to 38% anthranilic acid. Thus, the chosen ternary system contains two binary systems with metastable phase separation and one with stable separation.

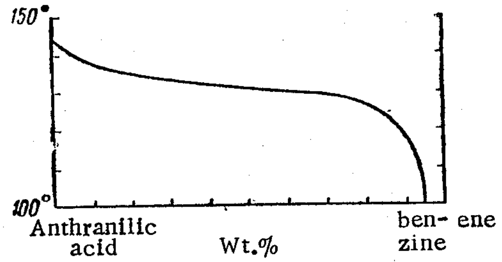

Fig. 1. Equilibrium in the system anthranilic acid–benzine.

TABLE 1

Equilibrium in the System Anthranilic Acid–Benzine

% Anthranilic acid	Temperature of crystallization
5.00	107.0°
20.00	127.0
40.00	130.0
60.00	132.5
80.00	134.5
100.00	145.0

We used the following reagents in the study: C. P. anthranilic acid, m. p. 145°, twice distilled water, and a benzine fraction boiling in the range 90-120°. Equilibrium between two and three liquid phases was studied by the visual-polythermal method of V. F. Alekseev [3] in a sealed glass ampule in an oil thermostat. In the same ampule and thermostat we also studied crystallization in the system anthranilic acid–benzine using an inner heater [4].

The system anthranilic acid–benzine was studied by fusibility (Table 1 and Fig. 1). As Fig. 1 shows, the curve of crystallization of anthranilic acid has a very sloping S-shape and occupies almost all the concentration intervals of the system. Such a form for the crystallization curve should indicate the presence under it of a curve of metastable phase separation. The latter is found at very low temperatures, since experimentally it was not observed with supercooling. Its presence could be shown indirectly, as will be demonstrated below.

The ternary system anthranilic acid–water–benzine was studied by stratification. We studied six polythermal sections through its temperature-concentration prism, going from its anthranilic acid

TABLE 2

Polytherms of the System Anthranilic Acid—Water—Benzine

% Anthranilic acid	Temperature		% Anthranilic acid	Temperature	
	2-phase stratification	3-phase stratification		2-phase stratification	3-phase stratification
Section 1 5% benzine, 95% water			Section 2 20% benzine, 80% water		
49.00	70.0°	—	40.00	—	98.0°
49.50	91.0	—	45.00	—	101.0
50.00	115.0	—	50.00	—	110.0
			55.00	—	116.5
			60.00	—	121.5
			65.00	—	123.5
			70.00	—	121.0
			72.00	—	118.0
			78.00	122.0°	—
			79.00	105.0	—
			79.50	95.0	—
Section 3 40% benzine, 60% water			Section 4 60% benzine, 40% water		
35.00	—	97.0°	35.00	—	95.0°
40.00	—	104.0	40.00	—	106.0
45.00	—	110.0	45.00	—	114.0
50.00	—	116.0	50.00	—	120.0
55.00	—	120.0	55.00	—	123.5
60.00	—	123.0	60.00	—	121.0
65.00	—	124.0	65.00	—	117.0
70.00	—	119.0	70.00	—	112.0
75.00	—	112.0	75.00	—	105.0
80.00	—	105.0	76.00	—	99.0
81.00	—	100.0	84.00	120.0°	—
85.00	119.0°	—	85.00	102.0	—
85.50	108.0	—	85.50	88.0	—
86.00	94.0	—			
Section 5 80% benzine, 20% water			Section 6 98% benzine, 2% water		
35.00	—	100.0°	50.00	93.0°	—
40.00	—	108.0	60.00	109.0	—
45.00	—	115.0	70.00	120.0	—
50.00	—	121.0			
55.00	—	123.5			
60.00	—	115.0			
62.00	—	109.0			
63.00	—	98.0			
80.00	119.0°	—			
82.00	103.0	—			
84.00	90.0	—			

edge to the boundary of the binary system water—benzine (Table 2, Fig. 2). The sections and polytherms were numbered in the order of increasing benzine content in the mixture. In sections 1 and 6 we found equilibrium only between the two liquid phases, in the others, between two and between three liquid phases. As Fig. 2 shows, the polytherm of the two-phase liquid is almost a vertical line. Thus, the reciprocal solubility of the two-liquid phases in the ternary system depends little on temperature. Between these polytherms and the anthranilic acid edge lies a field of unsaturated homogeneous solutions. Between them and the boundary of the system benzine—water lies a field of heterogeneous liquid solutions. The polytherms of the three-phase liquid state are curves with maxima at about the same temperature, 124°. This corresponds to their location on the critical conode of the three-phase liquid equilibrium.

From the experimentally obtained polytherms we constructed the isothermal sections of the prisms of the ternary system anthranilic acid—water—benzine at 100, 110, and 120°. A projection isotherm is shown on the

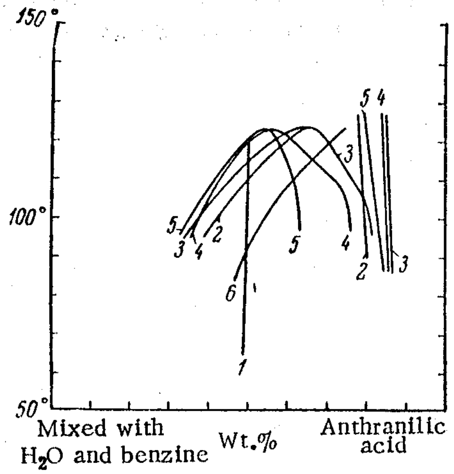

Fig. 2. Polytherms of the ternary system anthranilic acid—water—benzine. Explanation in text.

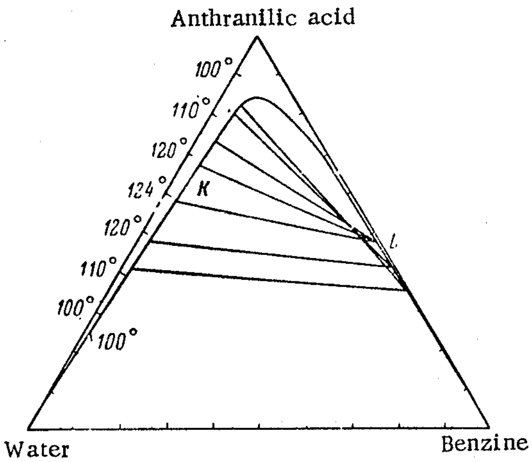

Fig. 3. Isotherms of the ternary system anthranilic acid—water—benzine (KL — critical conode; figures along the sides of the triangle relate to the corresponding conode). Explanation in text.

triangle in Fig. 3, on which is shown the projection of the critical conode KL of the three-phase liquid state. On Fig. 3 the curve of the two-phase liquid state is shown at 100° only; the other two almost agree with it since the liquid phase equilibrium is practically unchanged with temperature. The field of the two-phase liquid state which adjoins the triangle of the three-liquid phases on the side of the binary system anthranilic acid—water is very narrow. Therefore, it was not determined.

In the ternary system anthranilic acid—water—benzine the following processes occur as the temperature is lowered. In the stable state at high temperature, phase separation of the binary system water—benzine is homogenized by anthranilic acid. The content of the latter in the heterogeneous mixture reaches 86%. The system anthranilic acid—water is dominant among the binary systems of the ternary system. At 124° there appears on the binodal curve the critical solution K (composition 67% anthranilic acid, 29.5% water, and 3.5% benzine) and the corresponding solution L (46% anthranilic acid, 1% water, and 53% benzine), and the critical conode KL is formed. When the temperature is lowered the volume of three-phase liquid state develops from the latter. On the isotherm appears the triangular equilibrium of three liquid phases from the side of which to the side of the binary homogeneous system there develops a field of a two-phase liquid equilibrium. In the metastable state at 78° one of the equilibrium fields of two-liquid phases of the ternary system reached the field of binary system anthranilic acid—water. A shift then occurs in the dominant system. The binary system anthranilic acid—benzine becomes dominant. This confirms the idea established earlier that in ternary systems with an equilibrium of three liquid phases the temperature at which the dominating systems change is the critical solution temperature of that binary system which lies between the other two binary systems. As that temperature is lowered further, a third field of a two-phase liquid state of the ternary system reaches the boundary of the binary system anthranilic acid—benzine. In the latter from this moment appears a break in solubility. Because of this the binary system anthranilic acid—benzine must be considered a system with a very low location of upper critical point.

The processes described are analogous to those which occur in the formation of a stable equilibrium of three liquid phases in ternary systems which contain binary systems with stable phase separation. Thus, the polythermal scheme of occurrence and development of stable three phase liquid equilibrium is the same in ternary systems which contain binary systems with stable and metastable phase separation.

SUMMARY

1. We have studied the binary system anthranilic acid—benzine by the fusibility method. We have shown that it belongs to systems with metastable phase separation with a very low position for the upper critical point.

2. We have studied phase separation in the ternary system anthranilic acid—water—benzine. We have found in it a volume of a stable equilibrium of three liquid phases at temperatures below 124° (the critical temperature of the conode). We have found the temperature-concentration boundaries of the area of the three-phase liquid equilibrium and the composition of the corresponding solutions of the critical conode.

3. We have shown that the polythermal scheme of occurrence and development of a stable equilibrium of three liquid phases is the same in ternary systems which contain binary systems with stable and metastable phase separation.

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