INVESTIGATION OF CONTINUOUS TRANSITIONS FROM STABLE INTO METASTABLE PHASE SEPARATION

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The conversion of stable phase separation to the metastable state may be of practical interest as a method for obtaining alloys of two substances over the whole range of concentrations of the binary system formed by them. This problem is dealt with in a series of papers [1 - 4] in which the stable phase separation of a binary system is converted into a metastable state by adding a third component to it. It was shown that the continuous conversion that is described occurs in a ternary system through a cross section with a target and a point of contact of the fusion and phase separation curves. A series of basic forms of continuous conversions in the range of stable and metastable phase separation which may occur in ternary systems, as shown in Fig. 1 in the form of polythermal cross sections at mn of the prism of a ternary system A-B-C, may be derived for liquid phase equilibria with upper critical solution temperatures. Here, it is conditionally assumed that the A-B system is homogeneous in the liquid state, the A-C system has metastable phase separation and the B-C system has stable phase separation. The solid line on the cross sections b-e shows the polytherm of phase separation and the dotted line – the fusion polytherm of the A-B system (the fusion polytherm of the cross section mn may have the same form). The first form of the transition (b) is caused by a phase separation surface, without extreme and special points.

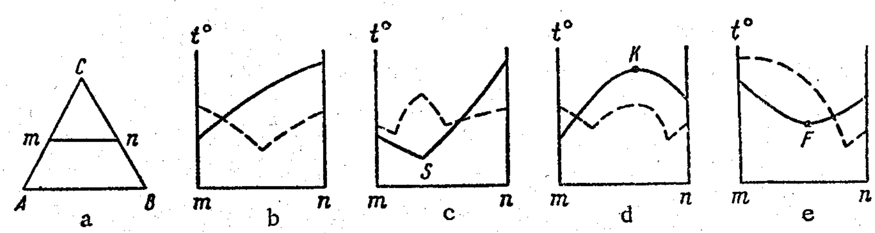

Fig. 1. Forms of continuous transitions from stable to metastable phase separation. Explanation in the text.

The benzoic acid – salicylic acid – water system has this form of transition [1]. A transition of the second form (c) arises from a singular arm (point S lies on this arm). An example of this is the salicylic acid – picric acid – water system [2]. A transition of the third form (d) arises from the triple critical point K of the phase separation surface. This form of transition has not been achieved completely experimentally; a case that is very close to it, when the phase separation surface does not quite reach the boundary of the B-C binary system, occurs in the antipyrine – salicylic acid – water system [3]. The fourth transition form (e) arises from a saddle point F in the phase separation surface.

This transition form has not yet been found experimentally and its detection is the purpose of this work. The transition forms indicated may have various variants due to the changes in the character of geometric elements or changes in the relative position of the fusion and phase separation surfaces. Thus in case (c) the singular arm may be anticlinic, in cases c, d and e the singular arm and critical and saddle points may be either in the region of stable or metastable liquid phase equilibria.

EXPERIMENTAL

Salicylic acid – phenol – water and anthranilic acid – phenol – water ternary systems were used to achieve experimentally continuous reciprocal transitions from stable and metastable phase separation through a saddle point. The binary systems forming them were characterized by the following data. The phenol – water system was investigated by means of its fusion and phase separation [5]. The stable phase separation curve found has an upper critical point at 66°, which corresponds to 34% phenol; the monotectic equilibrium is at 12.2°. The salicylic acid – water system was investigated by means of its fusion and phase separation [6]. The metastable phase separation curve has an upper critical point at 89.1° (32% salicylic acid). The crystallization curve of the acid above the phase separation curve has a horizontal section at 104°. The anthranilic acid – water system was studied by means of its fusion and phase separation [7]. The upper critical point of the metastable phase separation curve at 78° corresponds to a 38% anthranilic acid content in the mixture. The crystallization curve of the anthranilic acid above the phase separation curve has a horizontal section at 105°. There is no data in the literature on systems formed by these acids and phenol. In the present work we attempted to investigate these systems by means of their fusion, though, due to the great viscosity of the mixtures of salicylic acid and phenol only part of the fusion diagram was studied and only separate points of the anthranilic acid – phenol system were obtained. The fusion curve of the first system did not indicate the formation of a compound. In spite of that, the tendency of the ortho derivatives of benzoic acid examined for complex formation suggested the formation of unstable complexes between them and phenol and this was confirmed by the present work. Thus, the presence of two binary systems with stable and metastable phase separation and a third with the formation of a dissociating complex in each of the ternary systems being studied made it possible to achieve transitions of the fourth form (d) in them.

TABLE 1

Equilibrium in the Salicylic Acid – Phenol System

Salicylic acid (weight %)	Crystallization temperature
26.85	76.0°
30.00	95.0
41.60	108.5
60.00	125.0
80.40	141.5
100.00	155.0

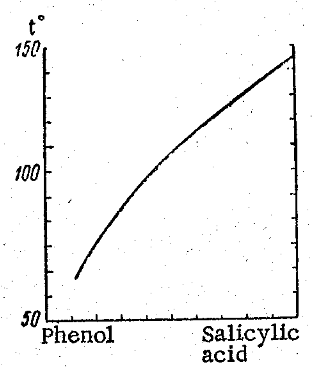

Fig. 2. Crystallization in the salicylic acid – phenol system

In the work we used the following substances: distilled phenol, a fraction boiling at 181° (m.p. 42°), salicylic and anthranilic acids of analytical purity with m.p. 155 and 145°, respectively, and doubly distilled water. The systems were investigated by means of their phase separation by the visual polythermal method of V.F. Alekseev [8] in sealed glass ampules in an oil thermostat. Investigation by means of their fusion was carried out by two methods in parallel – by Shreder's method [9] and by internal seeding [10].

The salicylic acid-phenol system was investigated by means of its fusion (Table 1, Fig. 2). The mixtures located close to phenol did not crystallize and, therefore, there is no data on them. Figure 2 shows that the crystallization curve of salicylic acid did not have either extreme or other special points.

The salicylic acid – phenol – water* ternary system was studied by means of its phase separation (Table 2). Six polythermal cross sections of its temperature–concentration prism, going from the water arm to the boundary of the salicylic acid – phenol binary system were investigated (Table 2, Fig. 3). Figure 3 gives the fusion curve K_p and the phase separation curve P_a of the salicylic acid – water system and the phase separation curve aKb of the phenol – water system and the line of its monotectic equilibrium ab. As in the phase separation curves of binary systems, the reciprocal solubility polytherms of the liquid phases of a ternary system have upper critical solution temperatures. The latter descend from the critical points K and K_1 of phase-separating binary systems when the cross sections move into the prisms of ternary systems. Due to this, a saddle point forms on the phase separation surface of the ternary system between the fifth and sixth cross sections. It is found at 61.5° and a composition of 9% salicylic acid, 26% phenol and 65% water.

*E.F. Leshchinskii participated in the investigation.

TABLE 2

Polytherms of the Salicylic Acid (SA) – Phenol (P) – Water System

Cross section 1: 20% P, 80% SA	
water (weight %)	phase separation temperature
33.00	50.0°
36.00	60.0
41.21	65.0
45.23	69.0
56.65	75.0
61.85	75.5
71.23	76.0
80.03	76.0
90.61	72.0
94.16	60.0
95.07	50.0

Cross section 2: 40% P, 60% SA	
water (weight %)	phase separation temperature
34.00	47.0°
40.00	58.0
45.00	63.0
52.00	67.0
61.70	81.5
70.00	69.0
80.42	69.0
90.73	64.0
94.50	47.0

Cross section 3: 50% P, 50% SA	
water (weight %)	phase separation temperature
34.50	47.5°
39.63	56.5
40.00	64.0
55.60	65.5
65.00	66.0
72.43	66.0
80.67	65.0
88.88	62.0
92.00	55.0
94.00	47.0

Cross section 4: 56.5% P, 43.5 % SA	
36.00	48.0°
40.65	57.0
52.51	63.0
63.50	65.0
67.72	65.0
69.04	65.0
80.86	64.0
91.32	56.0
93.06	51.5
94.00	46.0

Cross section 5: 60% P, 40% SA	
38.00	46.5°
41.55	52.5
48.00	60.0
51.64	62.5
60.42	63.0
67.37	63.0
71.87	63.0
80.14	62.5
91.39	54.0
92.94	48.0

Cross section 6: 80% P, 20% SA	
40.10	49.0°
45.00	55.0
50.96	59.0
60.03	62.0
70.43	62.0
80.02	61.0
85.00	55.0
90.04	48.0

The highest crystallization temperatures in the phase-separating mixtures of the cross sections are at 93, 84, 79, 74, 72 and 37° respectively in the 1, 2, 3, 4, 5 and 6 cross sections. These data show that phase separation is metastable in cross sections 1 – 5 and stable only in cross section 6. Thus, the saddle point of the given system should be located in the region of metastable liquid phase equilibria. In accordance with this, the crystallization surface, starting from the boundary of the salicylic acid – water system, must at first slope upwards but close to the boundary of the phenol – water system it will descend sharply.

Seven phase separation isotherms were plotted for the salicylic acid – phenol – water ternary system, given in Fig. 4, from the experimentally obtained polytherms. The isotherms at 85 - 62°, i.e., at high temperatures, limit phase separation into two separate regions which start at the solubility cross sections of the two binary systems. At 61.5° the phase separation regions abut on saddle point C. At 60 - 50°, i.e., at low temperatures, the isotherms form curves with reciprocal solubility maxima for the liquid phases. The isotherms maxima and the saddle point in the salicylic acid – phenol binary system are at 27% salicylic acid and 73% phenol. This composition corresponds to a complex with a 1:4 molecular ratio of these components. Consequently, the salicylic acid – phenol system is the dominating system in the ternary system being studied. The instability of the complex formed and its strong dissociation in water explain its greater solubility in water than those of its components and causes the formation of maxima on the phase separation isotherms and then the saddle point. An increase in the temperature intensifies these processes and results in a division of the phase separation region of the ternary system into two. In this way, a continuous transition of the stable phase separation of the phenol – water system into the metastable one of salicylic acid – water through a saddle point is achieved in the ternary system described (case e, Fig. 1).

A n t h r a n i l i c   a c i d – p h e n o l – w a t e r   t e r n a r y   s y s t e m. Table 3 gives the results of studying the polythermal cross sections through the temperature-concentration prism, going from the water arm to the boundary of the anthranilic acid – phenol binary system. Figure 5 shows the fusion curve K_p and the phase separation curve P_a of the anthranilic acid – water system and also the phase separation curve aKb and monotectic equilibrium line ab of the phenol – water system. The upper critical solution temperatures decrease from the critical points K and K_1 of the binary systems formed with water, as the cross sections move into the prism of the ternary system. Due to this a saddle point forms on the phase separation surface of the ternary system between the 3rd and 4th cross sections. This point is at 63.5° and corresponds to 10% anthranilic acid, 27% phenol and 63% water.

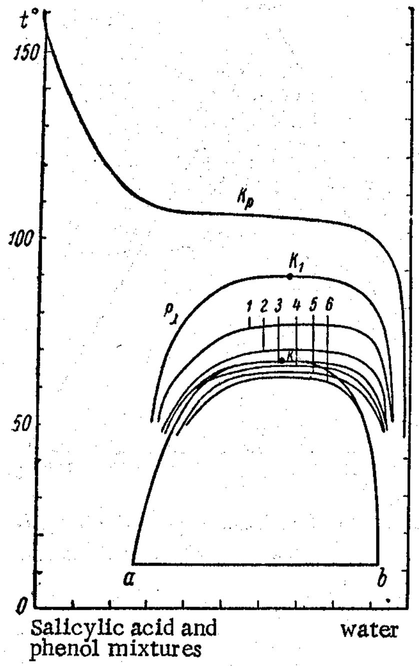

Fig. 3. Polytherms of the salicylic acid – phenol – water system. Explanation in the text.

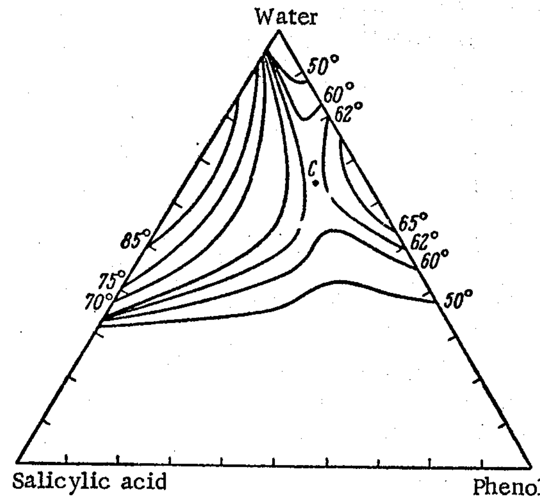

Fig. 4. Phase separation isotherms of the salicylic acid – phenol – water system. Explanation in the text.

Six phase separation isotherms of the anthranilic acid – phenol – water ternary system were plotted from the experimentally obtained polytherms and are shown in Fig. 6. The isotherms located above the saddle point (at temperatures of 73 - 64°) and the corresponding binary system conoids together limit to two the separate phase separation regions which abut on saddle point C at 63.5°. The isotherms located below the saddle point (at temperatures of 62 - 60°) are curves with maxima of reciprocal solubility of the liquid phases. The isotherm maxima and the saddle point in the anthranilic acid – phenol binary system are at 27% anthranilic acid and 73% phenol. This composition corresponds to a complex with a 1:4 molecular ratio. Consequently, the anthranilic acid – phenol system is the dominating system in the given ternary system. The formation of a complex in the dominating system and its decomposition in water explain the formation of the saddle point. Thus, continuous transition of a stable phase separation of the phenol – water system through a saddle point into the metastable one of the anthranilic acid – water system occurs in the anthranilic acid – phenol – water ternary system, i.e., case e, Fig. 1. It is interesting that in the dominating systems of both ternary systems studied a complex is formed with the same molecular ratio of the components. The great similarity of the phase separation diagrams of the ternary systems studied indicates that the properties of the two complexes are also analogous. This is explained by the similarity of the properties of the chemical components forming the complexes.

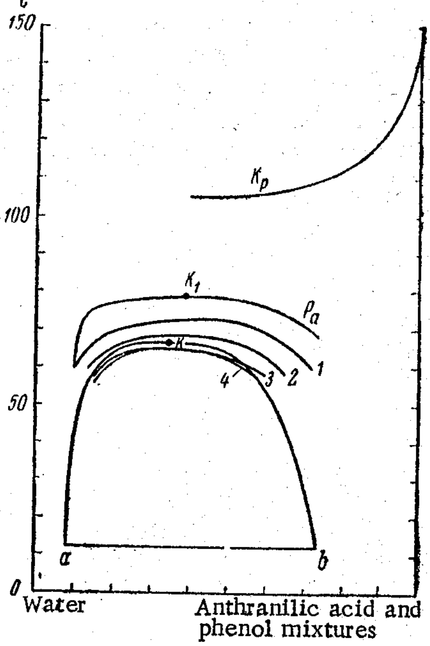

Fig. 5. Polytherms of the anthranilic acid – phenol – water system. Explanation in the text.

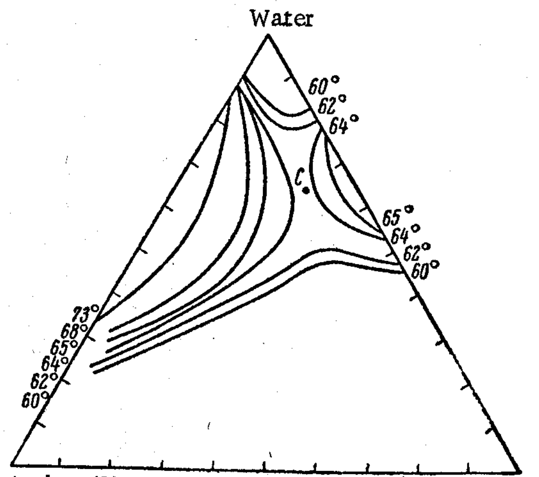

Fig. 6. Phase separation isotherms of the anthranilic acid – phenol – water system. Explanation in the text.

TABLE 3

Polytherms of the Anthranilic Acid (AA) – Phenol (P) – Water System

Cross section 1: 20% P, 80% AA	
water (weight %)	phase separation temperature
30.00	62.0°
40.00	69.0
51.00	72.5
60.00	73.0
70.00	71.0
80.00	69.0
90.00	59.0

Cross section 2: 40% P, 60 % AA	
water (weight %)	phase separation temperature
35.00	58.0°
40.00	63.0
50.00	66.5
60.00	68.5
70.00	67.0
80.00	65.5
85.00	61.0

Cross section 3: 60% P, 40% AA	
40.00	58.0°
48.00	63.0
56.00	64.0
60.00	64.0
70.00	64.0
80.00	62.0
85.00	56.5

Cross section 4: 80% P, 20% AA	
43.00	58.0°
50.00	62.0
60.00	64.5
70.00	64.5
80.00	61.0
85.00	55.0

SUMMARY

1. The forms of continuous reciprocal transitions of metastable and stable phase separation of binary and ternary systems were examined. They were reduced to four basic types.

2. The components of the salicylic acid – phenol binary system, studied by means of its fusion, did not react chemically.

3. The salicylic acid – phenol – water and anthranilic acid – phenol – water ternary systems were studied by means of their phase separation. It was found that in both cases the phase separation volume of the ternary system combines the phase separation planes of the two binary systems formed with water and has a saddle point. The reasons for the formation of such forms of diagram for ternary systems were explained. It was shown that in both ternary systems investigated one of the forms of continuous reciprocal transition of metastable and stable phase separation of binary systems occurred with this transition passing through a saddle point.

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