STUDY OF METASTABLE EQUILIBRIA BETWEEN LIQUID PHASES. VI.

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In previous communications [1-4] we presented the results of studying the metastable equilibria existing between two liquid phases in ternary systems and examined the resultant consequences. It was experimentally shown that in the metastable liquid state in ternary systems there are present the same basic forms of two-phase equilibria as exist in them in the stable liquid state. It can be postulated that in the metastable state in ternary systems it should be possible to realize equilibrium of three liquid phases, since this situation prevails in them in the stable state. A stable three-phase liquid equilibrium in ternary systems was discovered in 1887 [5]. Further study of this phenomenon led at the start to a development of the isothermal schemes for its formation [6-8], and then to an elucidation of the polythermal scheme for its origin and changes [9]. As a result, it becomes necessary experimentally to elucidate the very possibility of realizing a metastable three-phase liquid equilibrium in ternary systems, and in case of a satisfactory solution to this problem, to determine the degree of applicability of the indicated polythermal scheme to its origin. To obtain an experimental solution to these questions we selected the ternary system salicylic acid-water-benzine.

EXPERIMENTAL

We took the following reagents for our work: c.p. salicyclic acid with m.p. 155°, twice-distilled water, and the benzine fraction boiling in the range 90-120°. Equilibrium between two and between three liquid phases was studied by the visualpolythermal method of V. F Alekseev [10]. The starting substances were heated in sealted glass ampuls in an oil thermostat. The crystallization of the mixtures was studied in these ampuls; in this connection needlelike crystals of salicylic acid formed at the boundary of two liquid layers.

The ternary system salicyclic acid-water-benzine contains the following binary systems.

The System Salicylic Acid-Water was studied by V. F. Alekseev [11] by the method of fusion and stratification. Metastable equilibrium between two liquid phases was revealed in it. The upper critical point on the equilibrium curve lies at 89.1° and corresponds to 32% salicylic acid. Above the stratification curve the crystallization curve possesses a nearly horizontal portion at about 105°, stretching from 20 to 60% salicylic acid.

System Water-Benzine The mutual solubility of water and benzine was studied by a number of authors [12]. At temperatures up to 100° it is on the average several hundredths of a percent, and from 100 to 200° it is on the average several tenths of a percent. The small value of the mutual solubility and its increase with rise in temperature show that a stable equilibrium between two liquid phases with a very highly situated upper critical point is present in the system. The advantages and disadvantages of operating with benzine, instead of with individual hydrocarbons, has already been discussed earlier [13].

The System Salicylic Acid-Benzine was investigated by the fusion method in the present study. The obtained numerical data are collected in Table 1 and plotted in Fig. 1. As Fig. 1. shows, the crystallization curve of salicylic acid occupies nearly the whole concentration interval of the system. The curve is very gentle over nearly its whole extent, and its slope shows a very sharp increase when the benzine content exceeds 70%. The presence of a gentle portion on the crystallization curve gives rise to the theory that a lowly situated metastable equilibrium between two liquid phases exists in this system. However, even with very great supercooling (by 60°) this equilibrium could not be revealed experimentally. As will be shown below, the existence of a region of metastable stratification with an upper critical solution temperature can be demonstrated indirectly.

TABLE 1

Equilibrium in the System Salicylic Acid-Benzine

Amount of benzine (wt. %)	Crystallization temperature
0.00	155.0°
15.03	148.5
30.00	145.0
53.11	139.5
68.14	135.0
81.05	127.0
91.50	113.0
95.00	102.5

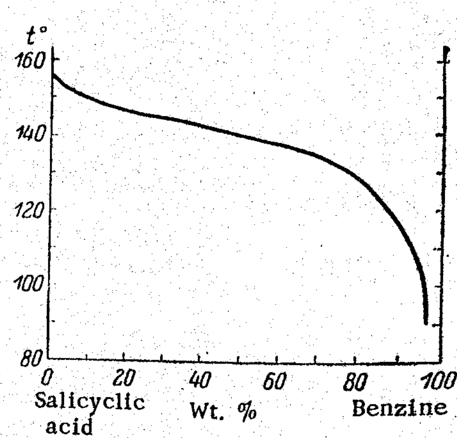

Fig. 1. Equilibrium in the system salicylic acid-benzine.

The Ternary System Salicyclic Acid-Water-Benzine was studied by means of the polythermal sections drawn through its temperature-concentration prism. A total of six such sections was studied, proceeding from the salicylic acid edge to the boundary of the binary system water-benzine, with a benzine content of 5, 20, 40, 60, 80 and 95%. The numerical material obtained for the sections is presented in Table 2. In the nature of an example one of the polytherms is depicted in Fig. 2. In view of the small mutual solubility of the solid and liquid phases close to the boundary of the binary system water-benzine, the solubility in this portion of the ternary system was not studied. For this reason a graphical representation of the monotectic reaction of three phases is not given on the isotherms of the ternary system (Fig. 3) or in its polythermal prism (Fig. 4.).

As Fig. 2 shows, in the polythermal section the crystallization curve (Cr) intersects the equilibrium plane of two liquid phases and in that way divides it into two portions— an upper portion with stable stratification and a lower portion with metastable stratification. Beneath the crystallization curve, in the plane of metastable stratification, a curve with a maximum is present, bounding the equilibrium plane of three liquid phases. The crystallization curve has a gentle, nearly horizontal portion above the plane of the three-phase liquid state. On both sides, in the concentration limits outside of this plane, the curve drops sharply with decrease in temperature. The described form of the salicyclic acid crystallization curve in the polythermal section is similar to the one found in the binary system salicyclic acid-water. In both cases the form of the crystallization curve is conditioned by the presence beneath it of metastable equilibrium between the liquid phases. As a result, here the interesting fact is established that a three-phase metastable liquid equilibrium exerts an influence similar to that of a two-phase equilibrium on the crystallization course.

In the studied ternary system the equilibrium of two liquid phases depends very slightly on the temperature, for which reason in Fig. 2 the curve of the two-phase liquid state is nearly vertical. Thus, a temperature rise of 50° increases the mutual solubility of the two liquid phases a total of only 2%. The curve, bounding the plane of the three-phase liquid state, rises sharply with elevation of the temperature, and shows a gentle maximum in its middle portion (Fig. 2). Thus, in mixtures corresponding to the middle portion of the curve a temperature increase of 1° raises the solubility by 10%; in mixtures containing either less than 10 or more than 35% salicylic acid, a temperature increase of 15° raises the solubility a total of only 3%.

The fact that in all of the polythermal sections the plane of equilibrium of three liquid phases is situated beneath the crystallization curve shows that in the ternary system the whole volume of the three-phase liquid state is found beneath the crystallization surface of salicylic acid. As a result, in the studied ternary system the three-phase liquid equilibrium is metastable at all concentrations and temperatures. In going from section to section, in measure with increasing the percent of benzine in them, the planes of the ternary liquid state gradually shrink. Consequently, the volume of the equilibria of three liquid phases is located in the prism of the ternary system between the benzine edge and the boundary of the binary system salicylic acid-water as Table 2 shows, in all of the polythermal sections the maximum on the curve bounding the plane of the three-phase liquid state, is found at a temperature of about 103.5°. Consequently, in the studied ternary system 103.5° corresponds to the

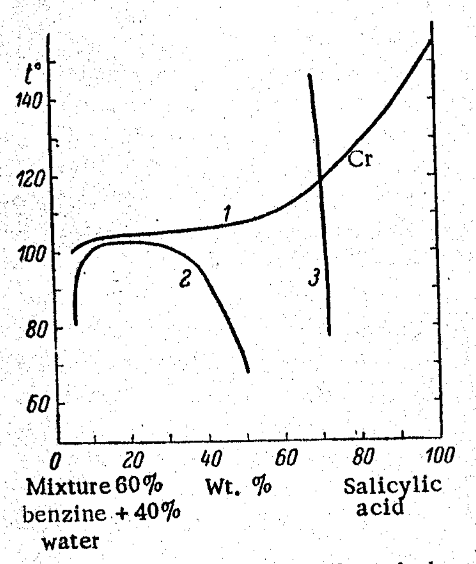

Fig. 2. Polythermal section through the prism of the ternary system water-benzine-salicylic acid. 1) Region of two-phase equilibrium; 2) region of three-phase metastable equilibrium; 3) region of two-phase metastable equilibrium.

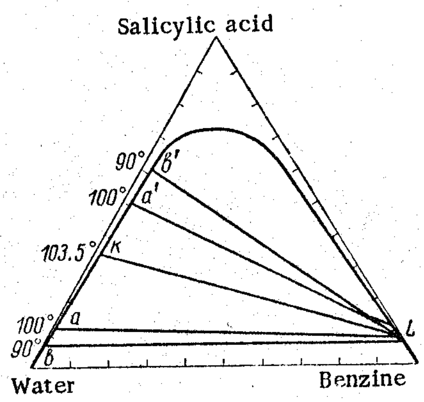

Fig. 3. Isotherms of the ternary system water-benzine-salicylic acid.

temperature of the critical conode of the equilibrium volume of three liquid phases.

From the experimentally obtained polytherms we constructed the isothermal sections of the prism for the ternary system water-benzine-salicylic acid at 90 and 100°. The projection of the lines of the sections on the composition triangle is depicted in Fig. 3, where the projection of the critical conode KL is also plotted. The curve of the two-phase liquid equilibrium at 100° is not shown in Fig. 3, since it nearly coincides with the similar curve at 90°. Due to the fact that in the ternary system salicylic acid-water-benzine the critical conode is found at 103.5°, then above this temperature the stratification of the binary system water-benzine homogenizes into the salicyclic acid ternary system. This is explained by the structure of the salicylic acid molecule, containing both a hydrocarbon radical and functional groups – carboxyl and hydroxyl – the latter both capable of hydration. The maximum amount of salicyclic acid in the heterogeneous mixtures of the ternary system at 90° is 72%. In Fig. 3. the triangle aa'L represents the equilibrium triangle of the three liquid phases at 100°, the compositions of which correspond to the vertexes of the triangle. The triangle bb'L is a similar triangle at 90°. The fields lying adjacent to the sides of these triangles are fields of two-phase liquid equilibrium, in which connection due to the fact that the stratification region lying adjacent to the side aa' (or bb') is extremely narrow, it could not be bounded experimentally and in Fig. 3. coincides with the indicated side. Point K corresponds to the mixture 2% benzine, 64% water and 34% salicylic acid, and L corresponds to 91% benzine, 1% water and 8% acid.

The described polythermal and isothermal sections permit making a plot of the temperature-concentration prism of the ternary system water-benzine-salicylic acid. Due to the extremely small mutual solubility of the phases in some portions of the equilibrium diagram the prism is depicted in simplified qualitative form in Fig. 4, where the components of the ternary system are designated by their initial designation letters. In the figure the plane $9K_110$ is the stratification plane of the binary system salicylic acid-water, and the plane $7K_28$ is the stratification plane of the binary system benzine-water. The volume KLNOP is the equilibrium volume of the three liquid phases. It is bounded by the two surfaces - KLNP and KLNO, along which the limiting conodes of the two-phase liquid state shift with change in the temperature. Close to the benzine edge these surfaces meet at an angle on the curve LN, and at the top they merge into the critical conode KL. Close to the boundary of the binary system salicylic acid-water the indicated volume is bounded by the plane OKP, along which the limiting equilibrium conodes of two liquid phases shift with change in the temperature. With elevation of the latter these conodes become shorter and at 103.5° they migrate into the initial critical point K of the three-phase liquid equilibrium. Above this temperature the volume of the two-phase liquid state $3bK_24$ of the ternary system gradually shrinks and migrates into the upper critical point K_2 of the binary system water-benzine. As was described, the equilibrium of the three liquid phases of the system is completely unstable. In accord with this the volume of the three-phase liquid state KLNOP is situated entirely under the salicylic acid crystallization surface ABC.

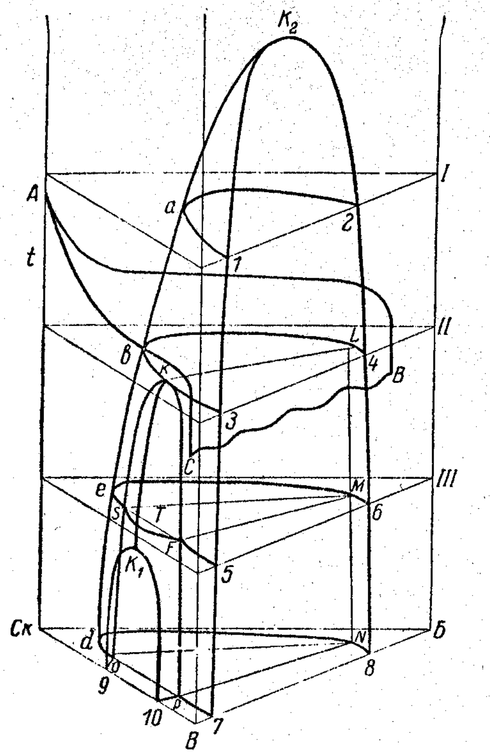

Fig. 4. Simplified qualitative form of the temperature-concentration prism of the ternary system water-benzine-salicylic acid. (The three-phase monotectic reaction is not shown).

A metastable equilibrium of three liquid phases, realized in the ternary system water-benzine-salicylic acid, originates and changes in the following manner. There is one stratification region 1a2 (Fig. 4, Section I) in the ternary system at elevated temperatures. Under these conditions the stratification of the binary system water-benzine homogenizes into the ternary system containing salicylic acid. When the temperature is reduced to 103.5° (Fig. 4, Section II) the initial critical point K of the three-phase liquid equilibrium arises on the binodal curve. The coexisting solution L corresponds to it. As a result, the critical conode KL of the three-phase liquid state appears on the stratification region 3b4. Beginning with this temperature the critical conode develops into the equilibrium diagram of the three liquid phases and the volume of the three-phase liquid state is formed in the prism. Triangle MSF divides the region of the two-phase liquid equilibrium into three portions. This condition is depicted in Fig. 4 in Section III, found at one of the temperatures between 103.5° (temperature of the critical conode) and 89.1° (upper critical solution temperature in the binary system water-salicylic acid). Each of these portions lies adjacent to one of the sides of the three-phase triangle. At the same time its sides are the limiting conodes of the formed two-phase liquid equilibrium regions. The region 5FM6 is situated between the solubility break 5, 6 of the binary system water-benzine and the limiting conode FM. With reduction in the temperature the region STF expands from its limiting conode SF to the boundary of the binary system salicylic acid-water and at 89.1°, i.e., at the temperature of the crit. pt. for the system, it reaches its limits in the critical point K_1. Further reduction of the temperature leads to the formation of region 9OP10, situated between the solubility break 9, 10 of the binary system salicylic acid-water and the limiting conode OP.

As a result, if above 89.1° the predominating system in the ternary system water-benzine-salicylic acid is the binary system salicylic acid-water, then below this temperature the predominating system becomes the binary system salicylic acid-benzine. This is supported by the fact that the binary predominating system of the given ternary system appears as such only in certain temperature limits and does not appear unalterable in the whole temperature range of the ternary system. Consequently, 89.1° is the temperature of change in predominance for the ternary system water-benzine-salicylic acid. It is quite evident that in ternary systems with equilibrium of three liquid phases the temperature of change in predominance will always coincide with the critical solution temperature of the binary component system that occupies an intermediate position between the other two in this respect.

With reduction of the temperature the region SMe stretches from the limiting conode SM toward the boundary of the binary system salicylic acid-benzine, here close to stratification. With further reduction in the temperature the indicated region reaches the boundary of the binary system salicylic acid-benzine, and in this system from this moment a solubility break will appear and expand. Consequently, the binary system salicylic acid-benzine should be considered as being a system with stratification and, with a very lowly situated upper critical solution temperature. The latter is found considerably below 89.1°.

The described picture of the origin of metastable equilibrium between three liquid phases is completely analogous to the situation that prevails for a stable three-phase liquid equilibrium. This means that the origin and change in the stable and metastable equilibria of three liquid phases in ternary systems proceed by the same

TABLE 2

Polytherms of the System Salicylic Acid-Water-Benzine

Section No.	Amount of salicylic acid (wt. %)	Temperature of		
		Crystallization	Two-phase stratification	Three-phase stratification
Section *I*	49.00	—	90.0	—
	50.00	—	109.0	—
Section *II*	6.00	—	—	89.0
	7.00	—	—	96.0
	10.00	102.0	—	98.0
	20.00	101.0	—	102.0
	30.00	104.5	—	103.0
	40.00	105.0	—	101.0
	45.00	—	—	99.0
	55.00	—	—	90.0
	60.00	106.0	—	81.0
	69.00	—	120.0	—
	70.00	110.0	105.0	—
	71.00	—	78.0	—
	80.00	119.0	—	—
	90.00	134.0	—	—
	100.00	155.0	—	—
Section *III*	7.00	—	—	92.0
	10.00	103.0	—	100.0
	20.00	104.0	—	103.0
	30.00	105.0	—	104.0
	40.00	106.0	—	100.0
	50.00	107.0	—	90.0
	60.00	108.0	—	—
	70.00	112.0	125.0	—
	72.00	—	102.0	—
	73.00	—	80.0	—
	80.00	121.0	—	—
	90.00	147.0	—	—
	100.00	155.0	—	—
Section *IV*	6.00	—	—	85.0
	9.00	103.0	—	100.0
	18.00	104.0	—	102.5
	23.00	104.5	—	103.0
	33.00	105.0	—	100.0
	37.00	105.0	—	98.0
	41.00	106.0	—	89.0
	50.00	108.0	—	70.0
	60.00	110.0	—	—
	69.00	—	136.0	—
	70.00	118.0	113.0	—
	71.00	—	91.0	—
	80.00	128.0	—	—
	90.00	140.0	—	—
	100.00	155.0	—	—
Section V	6.00	—	—	80.0
	7.30	—	—	100.0
	9.00	107.0	—	103.0
	16.00	108.0	—	104.0
	22.00	—	—	100.0
	23.00	109.0	—	96.0
	28.00	109.5	—	87.0
	40.00	112.0	—	—
	50.00	113.0	—	—
	60.00	115.0	—	—
	69.00	—	141.0	—
	70.00	123.0	124.0	—
	71.00	—	98.0	—
	80.00	134.0	—	—
	90.00	146.0	—	—
	100.00	155.0	—	—
Section *VI*	48.00	—	80.0	—
	49.00	—	102.0	—
	50.00	—	125.0	—

polythermal scheme. In the studied ternary system, together with the stable two-phase equilibrium of the binary system water-benzine, the metastable equilibrium between the two liquid phases of the other two binary systems formed by salicylic acid participated in the formation of the volume of the metastable three-phase liquid state.

SUMMARY

1. The binary system salicylic acid-benzine was studied by the fusion method. The gentle slope of the salicylic acid crystallization curve and other tokens indicate the presence in the system of metastable equilibrium between two liquid phases with an upper critical solution temperature situated considerably below 89.1°.

2. A study was made of the equilibrium of the solid and liquid phases in the ternary system water-benzine-salicylic acid. A volume of metastable equilibrium between the three liquid phases was shown to be present at temperatures below 103.5° (temperature of the critical conode). The compositions of the coexisting solutions of the critical equilibrium conode of the three liquid phases were determined. In the prism of the ternary system the indicated volume is situated between the boundary of the binary system water-salicylic acid and the benzine edge. The shape and temperature-concentration limits of the volume of the three-phase equilibrium were found.

3. It was shown that the polythermal scheme for the origin and change of metastable equilibrium between three liquid phases in ternary systems is the same as for the case of stable equilibrium.

4. An understanding of the temperature of change in predominance was elucidated. In the studied ternary system it is equal to 89.1°.

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