INVESTIGATION OF THE UNSTABLE EQUILIBRIA BETWEEN LIQUID PHASES. IV.

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Results of investigations have previously been reported [1,2] of those ternary systems with unstable equilibrium between the liquid phases in which stable chemical compounds are not formed between the components. The present work is the next stage in the study of unstable equilibria between the liquid phases, and deals with the introduction into a binary homogeneous (both in the stable and unstable states) system of a third component leading to formation of stable chemical compounds. With this objective a study was made of the ternary system picric acid - salicylic acid - water.

EXPERIMENTAL

The ternary system picric acid - salicylic acid - water contains the following binary systems.

1. System picric acid - water. This was previously studied by the melting and layer-formation methods [3]. In it is observed a region of stable equilibrium between the liquid phases with an upper critical temperature of solution. In this system the upper critical point is not reached; the triple points contain 8.2 and 95.8% picric acid at a temperature of monotectic equilibrium of 104.8°.

2. System salicylic acid - water. This has also been studied by melting and layer formation [4]. It contains a region of unstable equilibrium between the liquid phases with an upper critical temperature of solution. The upper critical point corresponds to a composition containing 32% salicylic acid at a temperature of 89.1°; above it is a nearly horizontal portion of the curve of crystallization at 104°.

3. System picric acid - salicylic acid. This is homogeneous both in the stable and unstable states. As was shown by the investigations described below on layer formation, the components of this system form a picrate containing 6 molecules of salicylic acid to 1 molecule of picric acid, i.e., it contains 21.64% picric acid. This picrate of salicylic acid was stable in the liquid phase in the unstable state.

Consequently the ternary system under investigation contains two binary systems with layer formation (one of them unstable) and a third system with formation of a chemical compound which is stable in the unstable state.

As in the previous studies, the investigations were carried out in sealed ampoules in an oil thermostat by the polythermal method of Alekseev [5]. The following components were taken: picric acid recrystallized from alcohol with m.p. 122.5°; salicylic acid, chem. pure grade with m.p. 155°; twice-distilled water.

In the three-component system, picric acid - salicylic acid – water, a study was made of the polythermal sections through its prism, starting from the water edge on the side of the binary system picric acid - salicylic acid. In all, 8 such sections were investigated with a content of 7, 14, 19, 22, 25, 30, 40 and 50% picric acid. Sections containing more than 50% picric acid were not investigated. In all sections the equilibrium was studied between the liquid phases after preliminary experiments had shown that the equilibrium was metastable in all of them. Nevertheless, for ocular confirmation of this in sections containing 22 and 40% picric acid, the crystallization above the layer formation was studied The numerical data for the polythermal sections are set forth in Table 1, and examples of the polytherms are plotted in Fig. 1.

As Fig. 1 shows, the polytherms of layer formation are unstable and consist of curves with flat maxima. These maxima fall from section to section from both sides with progressive approach of the sections to the composition of the picrate. The polytherms of layer formation located to the left of the composition of the picrate are sharply displaced towards the water corner; the polytherms more to the right of the picrate composition are more and more shifted to the middle of the section with increasing distance from the picrate composition. Above the curves of layer formation the polytherms of crystallization Kp have a nearly horizontal portion, similar to that in the binary system salicylic acid - water.

TABLE 1

Polytherms of the System Picric Acid - Salicylic Acid - Water

No. of section	Water (wt.-%)	Layer formation temp.	No. of section	Water (wt.-%)	Layer formation temp.	No. of section	Water (wt.-%)	Temperature of layer formation	Temperature of crystallization	No. of section	Water (wt.-%)	Temperature of layer formation	Temperature of crystallization
1 7% P.A.* 93% S.A.*	35.00	58.0°	5 25% P.K. 75% S.A.	35.00	61.0°	3 19% P.A. 81% S.A.	40.00	64.0°	–	7 40% P.A. 60% S.A.	30.00	70.0°	–
	40.32	68.5		40.03	68.0		50.00	69.0	–		37.00	79.0	–
	50.00	74.0		50.04	71.0		60.01	69.0	–		40.00	80.0	–
	60.00	76.5		60.31	71.0		70.00	69.0	–		50.00	83.0	–
	70.58	77.0		70.02	70.0		80.43	68.0	–		60.00	83.0	92.0°
	80.04	77.0		80.04	67.0		90.00	65.0	–		70.00	83.0	–
	90.33	74.0		90.00	61.0						80.00	75.0	93.0
	93.00	65.0									85.00	59.5	93.0
2 14% P. A. 86% S.A.	40.30	65.5	6 30% P.K. 70% S.A.	35.00	66.0	4 22% P. A. 78% S.A.	35.00	57.0	–	8 50% P.A. 50% S.A.	25.00	76.0	–
	50.00	70.0		40.61	70.0		40.43	63.0	–		30.00	89.0	–
	60.54	72.0		50.07	73.5		50.03	69.0	104°		40.00	97.0	–
	70.32	72.0		60.05	73.0		60.00	69.0	–		50.00	98.0	–
	80.03	71.0		70.00	71.5		70.07	69.0	99.0		60.00	97.0	–
	90.07	65.5		80.95	67.0		80.03	65.5	–		70.00	96.0	–
				95.00	53.0		90.00	60.0	99.0		80.00	85.0	–
											85.00	62.0	–

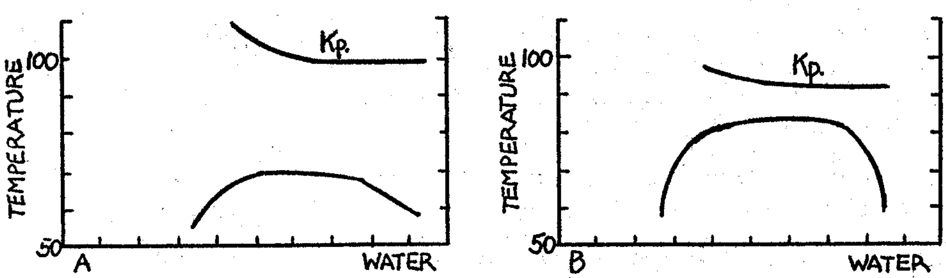

Fig. 1. Solubility polytherms of the system picric acid - salicylic acid - water.
A - mixture of 22% P. A. with 78% S. A.; B - mixture of 40% P. A. with 60% S. A.; Kp - crystallization curve.

Through the critical point K_1 of the system salicylic acid - water and the maximum points of the sections can be drawn the critical line (Table 2, Fig. 2) whose projection on to the side of the system salicylic acid - picric acid is represented by curve K_1 GK, where K is the maximum of the last section with a content of 50% picric acid. The critical curve comprises two branches which intersect with falling temperature at point G lying in the section corresponding to the composition of the picrate and a content of 21.64% picric acid. This section is a quasi-binary section of the prism of the ternary system under examination. In this section point, G corresponds to the critical point of unstable layer formation of the system picrate - water; it lies at 68.5° and has the composition 61% water, 8.4% picric acid and 30.6% salicylic acid.

The projection of the critical line on to the triangle of composition is represented in Fig. 3 by curve K_1GK_2 which has an inflexion point at G in the quasi-binary section. In both projections of the critical line there is observed the interesting feature that the chemical compound of the binary system is reflected on the critical line of the layer formation region of the ternary system.

* P. A. is picric acid, S. A. is salicylic acid.

TABLE 2

Composition of points of the critical line

Temperature	Composition (weight - %)		
	Picric acid	Salicylic acid.	Water
89.1°	0.0	32.0	68.0
77.0	2.1	27.9	70.0
72.0	4.9	30.1	65.0
69.0	7.2	30.8	62.0
68.5	8.4	30.6	61.0
69.0	8.8	31.2	60.0
71.0	11.3	33.7	55.0
73.5	14.1	32.9	53.0
83.0	19.6	29.4	51.0
98.0	25.0	25.0	50.0

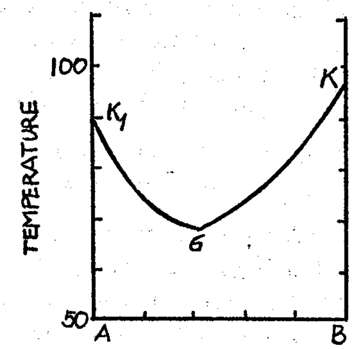

Fig. 2. Projection of the critical line onto the side of the binary system salicylic acid - picric acid. A — mixture of water and S. A., B — mixture of water and 50% mixture of P. A. and S. A. Explanation in text.

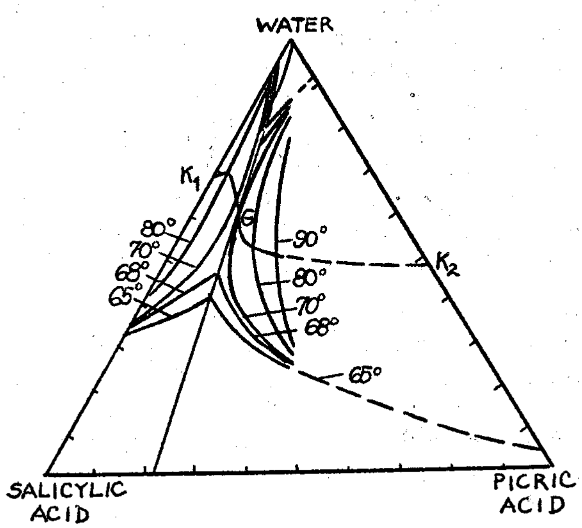

Fig. 3. Solubility isotherms of the ternary system picric acid - salicylic acid - water
Top corner: water. Left: salicylic acid. Right: picric acid

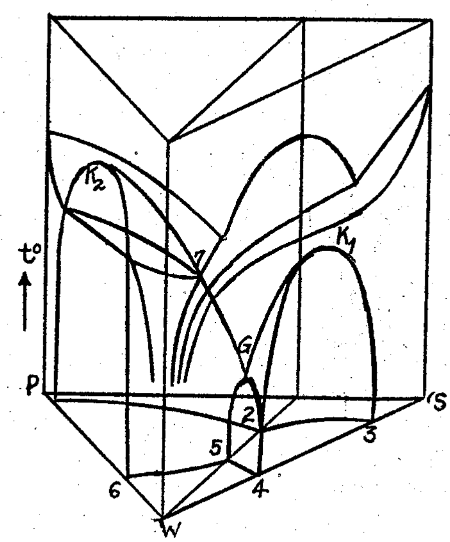

Fig. 4. Temperature-concentration prism of the ternary system picric acid (P) - salicylic acid (S) - water (W).

On the basis of the obtained polythermals of layer formation, plots were prepared of the isothermal sections of the prism of the ternary system, picric acid - salicylic acid - water. In all 5 isotherms were plotted at 65, 68, 70, 80 and 90°, the projection of which onto the triangle of composition is represented in Fig. 3. This diagram shows that at high temperatures (70, 80 and 90°) in the unstable state the isotherms of layer formation deviate from the solubility sections of the corresponding binary systems and are located inside the prism of the ternary system in the form of two separate binodal curves. At 68.5° these curves touch one another in the quasi-binary section of the ternary system, and at lower temperatures they run together to form a singular synclinal edge corresponding to the composition of the picrate. Consequently in this ternary system on the unstable portion of the whole space of equilibrium between the liquid phases, we have a singular synclinal edge corresponding in the binary system picric acid - salicylic acid to the composition in which the ratio of the components of the binary system is 1 : 6. This is evidence that in the binary system, picric acid - salicylic acid, there is formed a chemical compound of the indicated composition which is stable in the liquid phase in the unstable state.

The presence in this ternary system of a singular fold of the synclinal type is accounted for by the specific character of the solubility in the system. The reciprocal solubility of the liquids in the unstable state, starting from that in the binary system salicylic acid - water, gradually increases in the sections with increasing picric acid content and attains a maximum in the quasi-binary section. With further increase of picric acid content in the sections, the solubility in them declines and only amounts to a few percent on reaching the binary system picric acid - water. Consequently, the reciprocal solubility of water and picric acid is considerably greater than that of water and salicylic and picric acids. Actually, at 68° for example, the solubility of water in salicylic acid is 34%, in picric acid 4%, and in their picrate 48%. This character of reciprocal solubility of the components of the system accounts for the synclinal type of singular fold.

Thus investigations of layer formation can establish the existence of chemical compounds in binary homogeneous systems not only in the stable state, as already shown [6,7] but also in the unstable state.

We were unable to apply the melting technique to the study of the binary system,picric acid - salicylic acid; however it is known from numerous investigations [8] that on the melting diagrams curves with a flat maximum (distectics) usually correspond to picrates in binary systems. Consequently binary systems which form picrates (even with amines) must be regarded as irrational systems; this must be particularly true of the system now under consideration in which a picrate of an acid is formed. Nevertheless, notwithstanding even the presence in the mixtures of a polar solvent (water) a singular element was formed in the ternary system at the surface of equilibrium between the liquid phases. Similar cases in physicochemical analysis have been previously encountered in a study of systems by highly sensitive methods, for example by viscosity measurements. Thus in the binary system tin bromide - ethyl acetate [9],2 compounds were detected from the melting diagram: one melting without decomposition with the composition $SnBr_4 \cdot CH_3COOC_2H_5$, and the other melting with decomposition with the composition $SnBr_4 \cdot 2CH_3COOC_2H_5$. The viscosity isotherm at $-5°$ contains a sharp maximum corresponding to a composition almost identical with that of the compound melting with decomposition. Moreover, analogous cases have also been encountered in a study of the stable equilibrium between liquid phases in ternary systems. Thus, in a study of the ternary system,acetic acid - aniline - gasoline,by the layer-formation method [10], a synclinal singular edge was detected in the space of the stable, two-phase liquid state. This edge is present, in the binary irrational system,acetic acid - aniline,even up to the unstable compound $2C_6H_5NH_2 \cdot CH_3COOH$ to which on the melting diagram of this system corresponds a crystallization curve located below the crystallization curve of the stable compound $C_6H_5NH_2 \cdot 2CH_3COOH$. The existence in our system of a similar case in the unstable state indicates, on the one hand, that frequently chemical compounds which appear from the melting diagram to have low stability prove to be adequately stable in the liquid phase at low temperatures. On the other hand these facts confirm the exceptionally high sensitivity of the layer-formation technique of investigation of systems both in the stable and in the unstable state.

In conclusion it should be noted that the study of the ternary system,picric acid - salicylic acid - water,has brought to light a new form of phase diagram of ternary systems containing a stable chemical compound in the unstable state, and in consequence, a singular edge in the space of unstable equilibrium between the liquid phases. The diagram of the system described will have the qualitative character represented in Fig. 4 where the space 1, 2, 3, 4, 5, 6, K_1, K_2 is the equilibrium space between the liquid phases. Part of it, starting from the side of the binary system salicylic acid - water and extending to the polythermic section passing through point 7, corresponds to the unstable liquid-phase equilibria. The section passing through the plane 2, 5, G is quasi-binary.

SUMMARY

1. A study was made of the solid and liquid phases in the three-component system,picric acid - salicylic acid - water. A new form of equilibrium diagram was revealed with a synclinal singular edge in the space of the unstable two-phase liquid state.

2. Layer formation investigations of this ternary system revealed the existence in the binary system,picric acid - salicylic acid,of a chemical compound which is stable in the unstable state and with a picric acid / salicylic acid ratio of 1 : 6.

3. It was shown to be entirely possible to study binary homogeneous systems by the method of investigation of them in ternary systems by observing the layer formation in the unstable state.

4. It was found that formation of a chemical compound in the binary system,picric acid - salicylic acid,is reflected on the critical line of the space of the two-phase liquid equilibrium of the ternary system.

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Received October 2, 1954

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