TERNARY SYSTEMS WITH CLOSED LAYERING ISOTHERMS

I.L.Krupatkin

Closed layering isotherms have been found repeatedly in three-component systems with an upper ternary critical point [1]. The causes of their formation were disclosed in R.V.Mertslin's fundamental paper on this problem [1]. This paper derived a schema covering the formation of closed layering isotherms in a ternary system even when no upper ternary critical point is present, as represented in Fig. 1. Theprerequisites for this schema are as follows: the presence of layering with an upper critical solution temperature in one binary mapping system and of layering with a lower critical temperature in another, with the upper critical point being below the lower critical point; and the production of a chemical compound in the third binary system. When these conditions are satisfied, the isotherms located between the critical points will be closed ones.

The present paper deals with the problem of providing experimental confirmation of this schema. The water - phenol - phosphoric acid ternary system was used.[1] To learn whether the selected ternary system satisfied the schema prerequisites, let us consider the physicochemical nature of its binary constituent systems. These systems are as follows: phenol - water, phosphoric acid - water, and phosphoric acid - phenol.

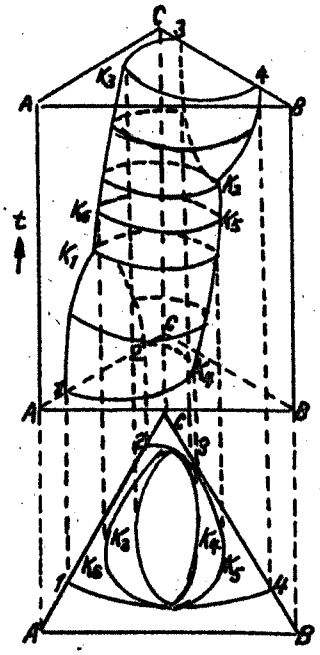

Fig. 1

1. The phenol - water system. In this system there is a stable layering region with an upper critical solution point at 68° [2]. Several authors have also investigated the conductance [3] and viscosity [4] of this system.

2. The phosphoric acid - water system. Investigations of the fusibility of this system [5] have demonstrated the presence within it of a chemical compound of phosphoric acid and water, viz: $H_3PO_4 \cdot 0.5\ H_2O$, with a melting point of 29°. The components of the system are miscible in all proportions in the liquid state.

3. The phosphoric acid - phenol system. We have investigated the equilibrium between the liquid phases in this system. As our researches, described below, have shown, this system exhibits a layering region with a lower critical solution temperature of 100°.

This discussion of the boundary binary systems indicates that two of them contain a layering region, one exhibiting an upper and the other a lower critical solution point, the lower critical solution point being 32° above the upper one. A chemical compound is formed in the third binary system, i.e., it is the

1) V.F.Ust-Kachkintsev did some research in this field [J. Gen. Chem. 7, 25 (1937)], but with a different objective in view.

predominant binary system in the given ternary system. Hence, the selected ternary system of water - phenol - phosphoric acid fully satisfies the prescribed conditions of the foregoing schema.

EXPERIMENTAL SECTION AND EVALUATION OF RESULTS

The following substances were employed in our research:

1. Phosphoric acid was available in the laboratory as an 85% solution. It was concentrated by the Erdmann method and then crystallized. The acid thus produced contained 99.98% H_3PO_4. The percentage of phosphoric acid was determined by titration.

2. The phenol was distilled, the fraction boiling at 182° being collected; its melting point was 42°.

3. Double-distilled water was used.

Several points were plotted in the phenol - water and phosphoric acid - water systems by way of checking our reagents. The results were in good agreement with the figures given in the literature. The research was carried out by Alekseev's method [2], in sealed ampoules immersed in an oil thermostat.

We began with an investigation of the phosphoric acid - phenol system. Then we investigated the phosphoric acid - phenol - water ternary system by passing polythermal sections through its prism, two kinds of sections being studied: some passing from the phenol vertex to the face of the water - phosphoric acid binary system at 5, 10, 20, 30, 50, 70, 85, and 95% of the latter; and others passing from the water vertex to the face of the phosphoric acid - phenol binary system at 21, 35, 50 and 65% of the latter.

TABLE 1

Equilibrium in the Phosphoric Acid - Phenol System

No	t°	Per cent phosphoric acid by weight		Remarks
		Layer A	Layer B	
1	100.5	32.00		Critical point
2	101.0	29.12	35.08	Critical turbidity 93°
3	101.5	-	37.56	
4	103.5	23.67	-	Critical turbidity 95°
5	104.0	-	42.07	
6	106.5	19.95	-	Critical turbidity 97°
7	108.5	-	50.46	
8	114.0	-	60.45	
9	115.0	15.39	-	Critical turbidity 103°
10	118.0	-	70.85	
11	121.5	-	80.36	Tarring set in at a higher temperature
12	129.0	10.14	-	Critical turbidity 119°

The numerical findings on the phosphoric acid - phenol binary system are listed in Table 1. The curve giving the equilibrium between the liquid phases, plotted from the experimental data, is reproduced in Fig. 2. The area outlined by the dashed line is the region in which a critical turbidity exists. As the figure shows, the phosphoric acid - phenol system is one of those possessing a lower critical solution point. As a matter of fact, the curve of equilibrium between the liquid phases exhibits a lower critical point (an Alekseev point [7]) at 32% of phosphoric acid and 68% of phenol and at 100

It is thrown off toward the phenol corner. The solubility of phenol in phosphoric acid and of phosphoric acid in phenol diminishes as the temperature is raised, the solubility of phenol in phosphoric acid being much higher than that of phosphoric acid in phenol between 100 and 130°. The two solubilities nearly level out as 130° is approached, coming within 10% of each other. The effect of temperature upon the solubility of phosphoric acid in phenol increases as the temperature drops. That is why the solubility curve of phosphoric acid in phenol drops steeply at high temperatures and is much flatter at lower temperatures. The effect of temperature upon the solubility of phenol in phosphoric acid is qualitatively the same, though the quantitative picture is wholly different. In this case the flat section of the curve is very long, extending over more than 40%, so that the solubility of phenol in phosphoric acid is very high in the 100-120° range, the lower critical solution point being thrown off toward the phenol corner. A change occurs in the components in the vicinity of the phosphoric acid corner, the liquid turning black, thus making it impossible to plot the curve in this region of the diagram. As we see from the graph, the region of critical turbidity is rather large, extending from the critical point leftward to the phenol corner.

The numerical data secured in our investigations of the polythermal sections through the phosphoric acid - phenol - water ternary system are listed in Tables 2 - 9. It should be noted that the section at 95% phosphoric acid has been traced only near the vertex, where the polytherm is a vertical line dropping to 3% phenol. The polytherms of these sections are reproduced in Fig. 3, in which the liquid phase equilibrium curve for the phenol - water binary system is plotted for the sake of comparison.

TABLE 2

Section at 5% Phosphoric Acid

No.	t°	% Phenol by weight	
		Water layer	Phenol layer
1	41.0	7.57	-
2	49.0	-	86.80
3	57.5	9.96	-
4	75.0	-	84.91
5	79.0	19.79	-
6	84.0	27.11	-
7	87.0	39.17	-
8	90.0	56.06	-
9	92.0	-	81.35
10	92.5	70.66	-
11	94.5	75.05	-
12	95.0	-	78.76

TABLE 3

Section at 10% Phosphoric Acid

No.	t°	% Phenol by weight	
		Water layer	Phenol layer
1	23.0	-	94.71
2	49.0	7.15	-
3	64.0	-	91.21
4	76.0	11.20	-
5	88.0	15.56	-
6	97.0	24.80	-
7	102.0	34.96	-
8	108.0	45.32	-
9	110.0	-	85.97
10	114.5	54.48	-
11	125.0	63.92	-
12	129.0	74.05	-
13	130.0	-	81.35

The sections extending from the water vertex to the side of the phenol - phosphoric acid binary system were investigated only in the vicinity of that side. They are reproduced in Fig. 4. The experimental polytherms were used in plotting the derived isothermal sections: at 60°, i.e., at a temperature below the critical one in the phenol - water binary system; at 85°, i.e., at a temperature between the upper and lower critical points in the boundary binary systems; and at 120°, i.e., at a temperature above the critical in the phenol - phosphoric acid binary system. The resultant isotherms are plotted in Fig. 5.

TABLE 4

Section at 20% Phosphoric Acid

No.	t°	% Phenol by weight	
		Water layer	Phenol layer
1	44.0	5.60	-
2	50.0	-	94.50
3	74.0	6.73	-
4	80.0	-	93.53
5	94.0	9.53	-
6	107.5	13.31	-
7	109.0	-	90.78
8	117.5	-	89.46
9	123.0	20.23	-

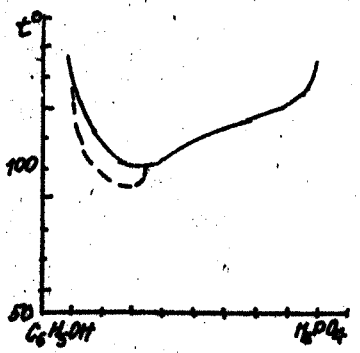

Fig. 2.

TABLE 5

Section at 30% Phosphoric Acid

No.	t°	% Phenol by weight	
		Water layer	Phenol layer
1	39.0	3.26	-
2	60.0	-	95.18
3	69.0	4.51	-
4	78.0	5.11	-
5	81.0	-	94.46
6	102.0	7.34	93.15
7	116.0	-	91.54
8	122.0	9.92	-

TABLE 6

Section at 50% Phosphoric Acid

No.	t°	% Phenol by weight	
		Water layer	Phenol layer
1	49.0	2.33	-
2	52.0	-	96.02
3	80.0	-	95.59
4	92.0	3.28	-
5	98.0	-	94.72
6	110.0	4.04	-
7	117.0	-	93.52
8	126.0	5.53	-

TABLE 7

Section at 70% Phosphoric Acid

No.	t°	% Phenol by weight	
		Water layer	Phenol layer
1	56.0	-	96.04
2	71.0	2.03	-
3	74.0	-	95.77
4	90.0	-	95.51
5	99.0	2.48	-
6	114.0	3.11	-
7	123.0	3.60	-
8	128.0	-	94.87

TABLE 8

Section at 85% Phosphoric Acid

No.	t°	% Phenol by weight	
		Water layer	Phenol layer
1	55.0	-	95.98
2	72.0	1.96	95.46
3	93.0	2.35	-
4	110.0	-	94.59
5	115.0	2.74	-
6	120.0	3.04	-
7	130.0	-	94.03

The numerical data indicate that the solubility of water in mixtures of phosphoric acid and phenol is negligible, of the order of 1%, the solubility dropping still lower as the temperature is raised and becoming practically independent of the composition of the mixture. The solubility of phosphoric acid - phenol mixture in water, on the other hand, is fairly high, increasing with rising temperature. The solubility of a phosphoric acid - water mixture in phenol is only slightly affected by temperature, but varies sharply with the concentration of phosphoric acid in the solutions. In strong solutions of phosphoric acid the solubility is low, of the order of 5%, rising sharply,

TABLE 9

Sections Passing from the Water Vertex to the Side of the Phenol - Phosphoric Acid Binary System

Section	t°	% water by weight
Section at 21.35% phenol	121.0	0.00
	90.0	0.72
	67.0	1.24
Section at 50.00% phenol	108.5	0.00
	85.0	0.50
	68.0	0.85
Section at 65.00% phenol	101.0	0.00
	80.0	0.40
	62.0	0.74

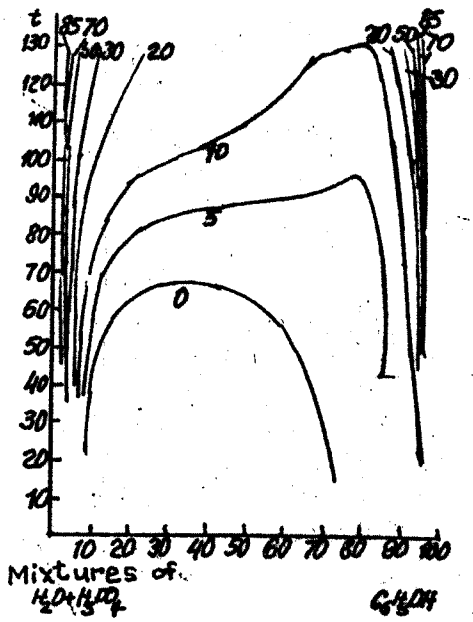

Fig. 3.

however, as the acid concentration drops, finally reaching complete miscibility. The solubility of phenol in phosphoric acid solutions likewise depends upon the concentration of the latter. In strong phosphoric acid solutions, say up to 40%, the phenol's solubility remains constant at about 5%, and is only slightly affected by the temperature. As the concentration of phosphoric acid falls below 40%, the phenol's solubility rises substantially. This increase in solubility likewise rises with rising temperature, reaching miscibility in all proportions. The decrease in the solubility of the phenol as the phosphoric acid concentration rises fully agrees with the theory of the origin of closed layering isotherms in ternary systems, since it is precisely at high concentrations of phosphoric acid in aqueous solutions that it forms a hydrate with the water.

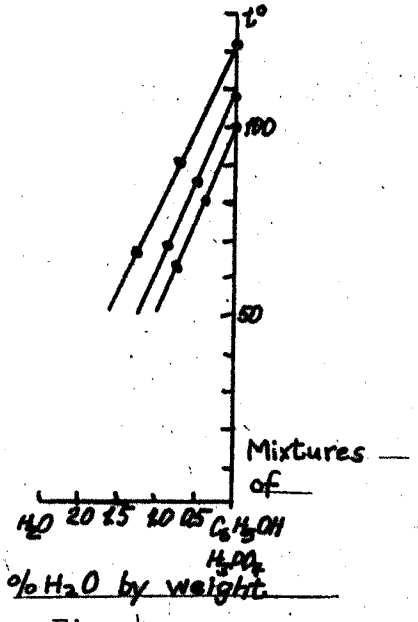

Fig. 4.

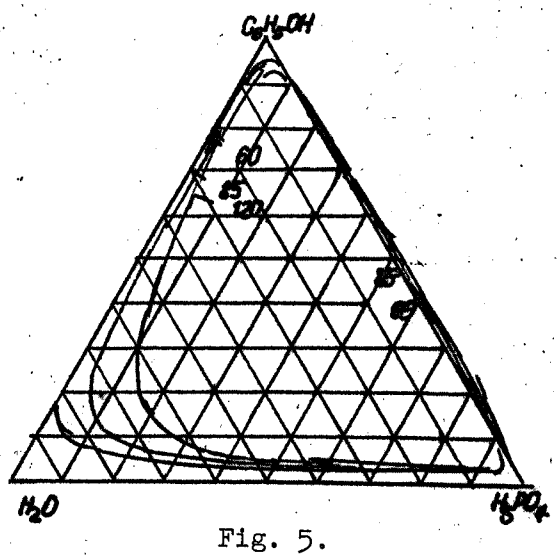

Fig. 5.

The 60° isotherm constitutes a layering region that starts at the break in solubility at this temperature in phenol - water binary system and extends over a large part of the concentration triangle. It is an example of an isotherm located below 68°, i.e., below the critical point in the water - phenol binary system, since all such isotherms will look like this. The 120° isotherm constitutes a layering region extending over much of the concentration triangle, from the solubility discontinuity at this temperature in the phosphoric acid - phenol binary system. All the isotherms that are located above the lower critical temperature in the phosphoric acid - phenol binary system, i.e., above 100°, will exhibit the same qualitative traits. The 85° isotherm is an example of an isotherm lying between the upper and lower critical temperatures in the boundary binary systems. It is a closed curve covering most of the concentration triangle. All isotherms above 68° and below 100° will also be closed curves of this sort.

Despite the fact that the upper and lower critical points are so close together (the temperature difference between them being slightly more than 30°), the polytherms rise steeply upward. This may explain the poor homogenizing action of the third components in binary layering, namely, of phosphoric acid toward layering in the phenol - water system at low temperatures, and of water toward layering in the phosphoric acid - phenol system at high temperatures.

Thus, the results of our research on the phenol - water - phosphoric acid ternary system indicate that closed layering isotherms exist in this system at temperatures that lie between the upper and lower critical points in the water - phenol and phenol - phosphoric acid systems, respectively, with a chemical compound existent in the phosphoric acid - water system. This is full experimental confirmation of the schema cited above for the origin of layering isotherms in ternary systems, provided the upper critical temperature is one of the boundary binary systems is lower than the lower critical temperature in another system and that the third system exhibits a chemical compound.

SUMMARY

1. The liquid phase equilibrium in the phenol - phosphoric acid system has been investigated. A stable layering region, with a lower critical solution temperature, has been found.

This lower critical point occurs at 68% phenol and 32% phosphoric acid and at a temperature of 100°.

2. The liquid phase equilibrium in the phosphoric acid - water - phenol system has been investigated. Closed layering isotherms have been found to exist in this ternary system in the 68 - 100° temperature range.

3. It has been shown that this ternary system provides complete experimental confirmation of the schema cited for the origin of closed layering isotherms, based upon the following prerequisites:

a) The presence of upper and lower critical points in two of the binary systems.

b) The location of the upper critical point in one system below the lower critical point in the other system.

c) The formation of a chemical compound in the third binary system.

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Received April 18. 1950

Chair of Chemistry,

Cherkassy State Pedagogical Institute.