SEPARATION OF PHASES IN SYSTEMS WITH TWO CHEMICAL COMPOUNDS

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The study of ternary systems from the separation of phases is widely used for the examination of chemical reaction in their binary predominating systems. Until recently binary reacting systems in which one chemical compound is formed were also studied for the most part by this method. Reacting systems with two chemical compounds have hardly ever been studied from the separation of phases; a few examples of such work are known [1, 2]. This is explained not so much by the complexity of these systems as by the fact that in them it often happens that only one compound is accurately reflected on the surface of separation of phases. The second compound is either not reflected at all or else is reflected inaccurately, i.e., the geometrical elements of the surface of separation of phases do not fall on the composition of the compound but on another, often irrational composition. It may be supposed that the application of the method of two solvents to systems with two chemical compounds will make it possible to obtain a complete, accurately reflected picture of the chemical reaction in these systems [3].

In the present work the binary system quinoline–phenol is studied from the separation of phases in two solvents: the highly polar solvent – water – and the non-polar solvent – sulfur; the dipole moments of the solvents are $1.84 \cdot 10^{18}$ and 0, respectively.

EXPERIMENTAL

The following materials were taken for the work: the quinoline was purified with alkali and distilled, the fraction boiling at 237° being collected; the phenol was distilled, the fraction boiling at 181° being collected, m.p. 42°; the sulfur was recrystallized from benzene, had m.p. 117° and consisted of a mixture of the monoclinic and rhombic forms [4]; the water was distilled twice. The work was carried out by the visual polythermal method of V. F. Alekseev [5]. The mixtures, in sealed glass ampoules, were placed in an oil-filled thermostat. In the study of the binary system phenol–sulfur, the crystallization was studied in the same ampoules. The ternary systems were studied from their sections across the temperature-concentration prisms. The sections were taken from the sulfur (or water) edge to the face of the binary system quinoline–phenol.

The binary systems making up the three-component systems studied have the following properties. The quinoline–phenol (Q–P) system has been studied from the melting points [6]. In this system two chemical compounds were detected; one of them melts congruently at 7.2°, contains 53 % phenol and 47% quinoline (molecular ratio 2 : 1); the other compound melts congruently at 22.4°, contains 32.5% phenol and 67.5% quinoline (molecular ratio 2 : 3). The quinoline–sulfur system has been studied from the melting points [7]. This system possessed a curve for a metastable equilibrium between the liquid phases with an upper critical point situated at a temperature of 102° and 69.77% sulfur. In the present work this system had the form of a homogeneous system since the study of the ternary systems was carried out at temperatures above 102°. The phenol–water system has been studied from the melting points and the separation of phases [8]. This system shows a curve for a stable separation of phases with an upper critical point (66°, 34 % phenol). In this work this system had the form of a homogeneous system for the same reason as given previously. The quinoline–water system has been studied from the separation of phases [9]. It has been established that with increase in the temperature, the solubility of quinoline in water increases, while the solubility of water in quinoline decreases. The phenol–sulfur system is studied in the present work.

The phenol–sulfur system was studied from the melting points and the separation of phases. The numerical data are given in Table 1, and the part of the composition diagram studied is shown in Figure 1. This system was

not studied in the sulfur corner because of the low mutual solubility of the liquid phases. Figure 1 shows that in this system a stable separation of phases takes place with an upper critical point in a high position. Monotectic equilibrium is established at 105°. The point F corresponds to 88% phenol. The solubility of sulfur in phenol is almost independent of temperature, so that as the temperature is raised both the curve of the separation of phases (Sep) and the crystallization curve (Cryst) rise steeply.

TABLE 1

Equilibrium in the System Phenol–Sulfur

Phenol concentration (% by weight)	Temperature of crystallization	Temperature of separation of phases
80.56	105.0°	145.0°
85.05	—	125.5
87.00	—	117.0
90.17	103.0	—
92.50	98.0	—
95.32	75.0	—

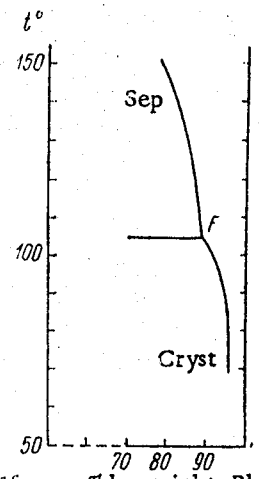

Fig. 1. Equilibrium of solid and liquid phases in the sulfur–phenol system. Sep – separation of phases, Cryst – crystallization.

In the ternary system phenol–quinoline–sulfur, six sections were studied. The numerical data obtained are given in Table 2 and the solubility polythermals themselves are shown in Fig. 2. Increasing polytherm numbering corresponds to increasing quinoline content in the sections. The mutual solubility of the liquid phases in the sulfur corner in sections 1-5 was not studied for the same reason as in the binary system phenol–sulfur. Figure 2 shows that the first three sections differ from the remainder in that their polythermals are situated very close to one another. In all the sections the mutual solubility of the liquid phases shows little dependence on temperature, so that as the temperature is raised all the polythermals rise steeply.

TABLE 2

Polytherms of the System Quinoline–Phenol–Sulfur

Section 1: 25% quinoline, 75% phenol		Section 2: 35% quinoline, 65% phenol		Section 3: 47% quinoline, 53% phenol	
sulfur concentration (% by weight)	temperature of separation of phases	sulfur concentration (% by weight)	temperature of separation of phases	sulfur concentration (% by weight)	temperature of separation of phases
10.00	80.0°	13.00	100.0°	10.00	67.0°
15.08	111.0	18.00	120.0	15.00	97.5
20.00	134.0	23.00	140.0	20.00	126.0
				25.10	144.0
Section 4: 57% quinoline, 43% phenol		**Section 5: 67.5% quinoline, 32.5% phenol**		**Section 6: 80% quinoline, 20% phenol**	
15.00	90.0	15.00	74.0	20.00	86.0
20.00	111.0	20.21	94.0	30.00	110.5
25.14	129.0	30.16	126.0	40.09	134.0
		35.00	139.0	90.00	137.0
				92.00	110.0
				93.00	90.0

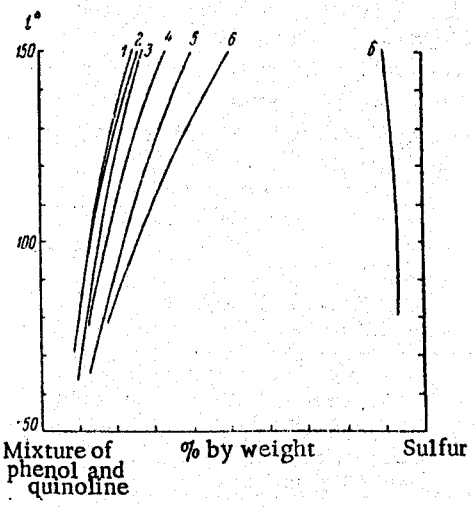

Fig. 2. Solubility polytherms of the ternary system quinoline–phenol–sulfur.

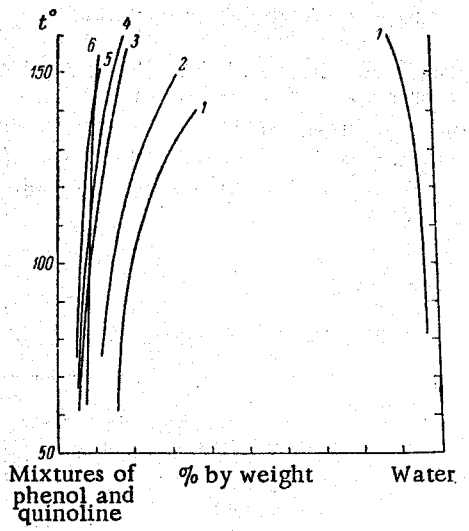

Fig. 3. Solubility polytherms of the ternary system quinoline–phenol–water.

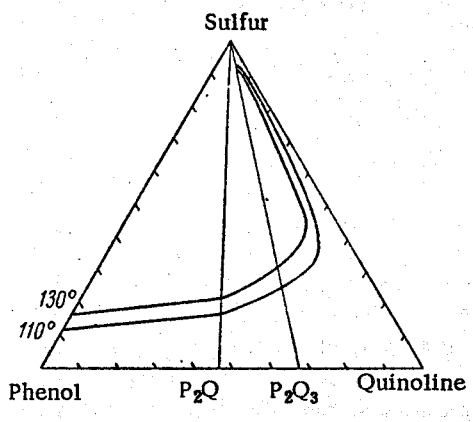

Fig. 4. Solubility isotherms of the ternary system quinoline–phenol–sulfur.

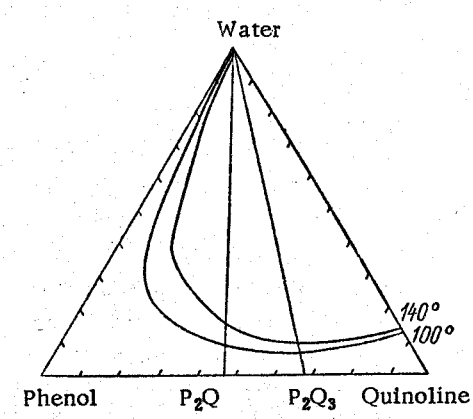

Fig. 5. Solubility isotherms of the ternary system quinoline–phenol–water.

Two isotherms for the separation of phases in the ternary system phenol–quinoline–sulfur at 110 and 130° (Figure 4) were constructed from the polytherms obtained. Figure 4 shows that in the ternary system, at temperatures above the critical for the binary system sulfur–quinoline, the quinoline acts as a homogenizer. The compound P_2Q_3 is not reflected at all on the solubility isotherms of the ternary system. The compound P_2Q is reflected in the form of an anticlinal singular edge slightly raised above the surface of separation of phases. The shape of the polytherms referred to above also confirms the presence of this compound. Similar ternary systems with slightly raised anticlines on the surface of separation of phases have been known earlier [10]. The sulfur–P_2Q section is thus a quasi-binary section. It divides the ternary system studied here into two ternary systems: phenol–P_2Q–sulfur and sulfur–P_2Q–quinoline. In the first of these there is a normal relation between the components of its predominating system, phenol and the compound P_2Q. As a result of this the isotherms of its separation of phases are straight lines. In the second ternary system the separation of phases in the binary system sulfur–P_2Q is

homogenized by the quinoline. The linear isotherms of the first system intersect the curves of the second in singular points in the quasi-binary section, forming an anticline. In the ternary system phenol–quinoline–sulfur there takes place a transition from a metastable equilibrium between the liquid phases of the binary system quinoline–sulfur to the stable equilibrium of the binary system phenol–sulfur via the anticlinal singular edge.

In the ternary system phenol–quinoline–water, six sections were studied. The system was not studied in the water corner for sections 2-6 because of the low mutual solubility of the liquid phases. The numerical data for the sections are given in Table 3. Figure 3 shows that all the polytherms are curves which rise steeply as the temperature is raised. This shows that the mutual solubility of the liquid phases is only slightly dependent on the temperature. The polytherms of the fifth section is the furthest displaced towards the side of the phenol–quinoline mixture.

TABLE 3

Polytherms of the System Phenol–Quinoline–Water

Section 1 25% quinoline, 75% phenol		Section 2 35% quinoline, 65% phenol		Section 3 47% quinoline, 53% phenol	
water concentration (% by weight)	temperature of separation of phases	water concentration (% by weight)	temperature of separation of phases	water concentration (% by weight)	temperature of separation of phases
32.10	136.0°	13.00	90.0°	15.00	146.0°
25.10	121.0	18.00	118.0	10.00	112.0
20.00	106.0	27.00	142.5	7.06	86.0
16.50	84.0			6.00	70.5
90.00	157.0				
95.00	136.0				
97.00	90.5				
Section 4 57% quinoline, 43% phenol		Section 5 67.5% quinoline, 32.5% phenol		Section 6 80% quinoline, 20% phenol	
15.00	154.5	10.00	148.0	10.00	148.0
10.00	125.0	7.50	129.5	8.00	101.5
7.00	99.0	5.00	89.0	7.50	70.0
5.21	81.0				

Two solubility isotherms for the ternary system phenol–quinoline–water at 100 and 140° were constructed from the experimentally determined polytherms. Figure 5 shows the compound P_2Q_3 reflected on the isotherms as solubility minima. From this, an upper ternary critical point should be present in the ternary system. This point was not found experimentally, however, since it is situated at high temperatures. The compound P_2Q is not reflected at all on the isotherms. In this ternary system, at temperatures above the critical for the binary system water–phenol, the latter acts as a homogenizer. As a result of salt formation in the binary system phenol–quinoline, when its components react at their functional groups, there is less hydration of the compound P_2Q_3 than of its component substances. This results in a lowering of the solubility of the compound P_2Q_3 in water by comparison with phenol and quinoline and accounts for the formation of solubility minima on the isotherms of separation of phases of the ternary system.

In the ternary system with sulfur, therefore, the compound P_2Q is formed, but the compound P_2Q_3 is not fixed. In the ternary system with water, on the contrary, the compound P_2Q_3 is fixed, but the compound P_2Q is not established. Comparison of the isotherms of both ternary systems reveals the formation of two chemical compounds in the binary system quinoline–phenol. In the same way it is confirmed experimentally that the method of two solvents is a reliable method for studying reaction in binary systems with two chemical compounds.

In the ternary system phenol–quinoline–sulfur, on the one hand, the separation of phases in the binary system sulfur–phenol weakens the interaction between the phenol and the sulfur. In the same way conditions are established for the stabilization of the compound P_2Q, containing a large percentage of phenol. On the other,

to a strengthening of the interaction between the sulfur and the quinoline. As a result of this, compound P_2Q_3, which contains a high percentage of quinoline, becomes unstable in the liquid phase of the ternary system. In the ternary system phenol–quinoline–water the opposite conditions are established; the separation of phases in the binary system quinoline–water weakens the interaction between its components. This promotes the stability of the compound P_2Q_3 with high quinoline content. In the binary system phenol–water, above the critical temperature 66°, the separation of phases is homogenized. This strengthens the interaction between the water and the phenol, which renders the compound P_2Q unstable.

In this way the experimental study of the ternary liquid systems shows that all three constituent binary systems of a given ternary system take part simultaneously in the total interaction. They are linked together by this interaction and influence one another, having a mutual influence on one or other of the forms of interrelationship in each binary system. In a liquid ternary system, the constituent binary systems are connected by the coupled influence of one upon another; this influence operates in such a way that a strengthening of the interaction in one of them leads to a weakening of the interaction in the other two constituent binary systems.

In the study of the stability of compounds in the liquid phase of a ternary system, it is also necessary to take into consideration the general character of the processes taking place in the given system as a whole. In the ternary system quinoline–phenol–water the processes of hydration are developed to the greatest extent. This is connected with the presence of the powerfully hydrating functional groups in the phenol and the quinoline and by the presence of water in the system. As a result of this the compound P_2Q_3 is stabilized in the liquid phase of the ternary system by the hydration processes. The absence of the latter in the ternary system phenol–quinoline–sulfur in the non-polar solvent (sulfur) makes this compound unstable. In the ternary system phenol–quinoline–sulfur, the most highly developed processes are the processes of association of the molecules of the components and the dissociation of their associated molecules. Thus, for example, it is known that sulfur exists in the form of associated molecules undergoing dissociation in organic solvents, particularly in amines [11]. As a result, the compound P_2Q is stabilized in the liquid phase of this ternary system by the association processes. The absence of the latter in the ternary system phenol–quinoline–water accounts for the instability of this compound in the system.

SUMMARY

1. The binary system phenol–sulfur has been studied from the melting points and the separation of phases. In this system there is a stable equilibrium between the liquid phases with an upper critical point in a high position.

2. The ternary system phenol–quinoline–sulfur has been studied from the separation of phases. It has been found that a compound of the predominating system phenol (P)–quinoline (Q) with the composition P_2Q is reflected in the form of an anticlinal singular edge on the surface of separation of the phases in the system; the compound of composition P_2Q_3 is not reflected. A transition takes place here from the metastable separation of phases to the stable, via the anticline.

3. The ternary system phenol–quinoline–water has been studied from the separation into phases. From this and the preceding system, the interaction in the binary system phenol–quinoline has been studied by the method of two solvents. It has been found that the compound P_2Q_3 is reflected on the isotherms of separation of phases in the system in the form of solubility minima; the compound P_2Q is not reflected. It has been shown that this system belongs to the group of systems with an upper ternary critical point.

4. It has been shown that the method of two solvents is a reliable method for the study of the interaction in binary homogeneous liquid systems with formation of two chemical compounds.

5. It has been shown that in a ternary liquid system the constituent binary systems are linked to one another by a coupled influence. A strengthening of the interaction in one of them leads to a weakening of the interaction in the remaining two binary systems.

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