INVESTIGATION OF IRRATIONAL SYSTEMS BY THE METHOD OF TWO SOLVENTS

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The two-solvent method previously proposed [1] consists of the investigation of a reacting liquid system by phase-separation in two solvents – polar and nonpolar. It has been found that this permits studying the details of the chemical reaction in the system, the effect of a solvent on it, and the nature of the properties of the compounds that are formed. By this means also, conditions are established for the investigation of systems with an abnormal indication of chemical affinity on the phase separation surfaces. In previous work along this line [1] the applicability of this method to binary rational systems was demonstrated. The further development of the two-solvent method raised the question of its application to binary irrational systems. The solution of this problem was the goal of the present work. For this purpose the reaction between phenol and antipyrine was studied in the strongly polar solvent water and in the nonpolar solvent ligroin. Thus, two ternary systems were chosen as the subjects of investigation by the phase separation procedure: phenol-antipyrine-ligroin and phenol-antipyrine-water.

EXPERIMENTAL

The following materials were used for the investigation: pharmacopeia grade antipyrine with m.p. 113°, freshly distilled phenol with m.p. 42°, a ligroin fraction boiling within the limits 120-140°, and twice-distilled water. The work was carried out by the visual-polythermal method of V.F. Alekseev [2]. Sealed glass ampoules containing the mixtures under investigation were placed in an oil thermostat. For the investigation of the three-component systems a study was made of polythermal sections through their temperature-concentration prisms, passing from the water (or ligroin) edge to the face of the predominant binary phenol-antipyrine system.

The binary systems comprising the ternary systems studied had the following characteristics. The phenol-antipyrine system was subjected to a fusion study [3]. In this system one chemical compound was found, which melted at 55.5° and contained 33.33% of phenol (molecular ratio of the components of the system 1:1). This compound was a product of salt formation in the system, since antipyrine is a monoacid base and phenol acts as a monobasic acid. The system phenol-water was investigated by phase-separation and fusion methods [4]. In this system a stable phase-separation curve was found with an upper critical point occurring at 66° and 34% phenol content. In the present work, this system played the part of a homogeneous system, since the study of the ternary systems was carried out above 66°. The antipyrine-ligroin system was studied by phase-separation [1]. In this system a stable phase-separation curve with a very high critical point was found. Antipyrine was infinitely soluble in water. Phenol separated with ligroin at low temperatures, therefore this system here played the role of a homogeneous system. The upper part of the stable phase-separation curve for this system was studied in the present investigation (Table 1). Its upper critical point corresponded to 20° and 42% of ligroin.

TABLE 1

Equilibrium in the System Phenol-Ligroin

Ligroin (wt. %)	Temperature of phase-separation
53.22	18.0°
31.37	19.0
41.74	20.0

In the ternary system phenol-antipyrine-ligroin five sections were studied. The numerical data obtained from the sections are given in Table 2 and the phase-separation polytherms themselves are shown in Figure 1. The latter are curves that rise sharply from their extremities and have flatly sloping maxima in their central parts. In sections 1 and 2 the maxima were not reached because they were located at high temperatures. The form of the phase-separation polytherms indicated that in mixtures at the extremities of the curves the mutual solubility of the liquid phases had little dependence on the temperature; on the contrary in the central portions of the curves the solubility increased rapidly with a rise in the temperature. Thus, for example, in section 4 in the ligroin corner a rise in temperature of 25° increased the mutual solubility of the liquids by 5% in all, but in the central part of this polytherm a total temperature rise of 2° increased the solubility by 35%.

TABLE 2

Equilibrium in the System Phenol-Antipyrine-Ligroin

Section 1: 20% phenol, 80% antipyrine		Section 2: 33% phenol, 67% antipyrine		Section 3: 50% phenol, 50% antipyrine	
Ligroin (wt. %)	Temperature of phase-separation	Ligroin (wt. %)	Temperature of phase-separation	Ligroin (wt. %)	Temperature of phase-separation
6.54	68.0°	9.09	77.0°	11.50	79.0°
10.71	101.0	15.37	113.0	14.70	93.0
21.37	143.0	17.67	119.0	24.81	121.0
80.00	154.0	25.72	141.0	39.76	135.0
90.00	118.0	80.07	149.0	60.00	134.0
95.04	100.0	90.08	116.0	80.00	125.0
		95.00	88.0	90.00	115.0
				95.00	82.0

Section 4: 67% phenol, 33% antipyrine		Section 5: 80% phenol, 20% antipyrine	
Ligroin (wt. %)	Temperature of phase-separation	Ligroin (wt. %)	Temperature of phase-separation
12.43	54.0°	24.81	66.0°
21.67	87.0	40.68	76.0
29.23	97.0	48.34	78.5
50.00	106.0	50.24	78.0
64.87	107.0	55.47	79.0
80.74	107.0	70.02	80.0
90.00	97.0	80.22	75.5
95.00	71.0	84.96	73.0

From the polytherms obtained five phase-separation isotherms were constructed for the ternary system phenol-antipyrine-ligroin, shown in Figure 3. All of the isotherms represent curves running from solubility breaks of the antipyrine-ligroin system into the prism of the ternary system. Consequently, at the temperatures investigated in this ternary system phenol plays the role of a homogenizer. In the isotherms for 70, 100 and 120° there occur irrational maxima of mutual solubility of the liquid phases. At 70° and 100° in the binary phenol-antipyrine system they fit at the composition of the compound recorded in the fusion diagram. In the 120° isotherm the solubility maxima are very diffuse and in the 135 and 150° isotherms they are entirely absent. This indicates on the one hand that the phenol-antipyrine system actually is irrational. On the other hand, it appears that the compound of the phenol-antipyrine system undergoes thermal dissociation in the liquid phase of the ternary system in question and above 120° it is completely dissociated. As shown in Figure 3, at the temperatures studied in the ternary system depicted, the phase-separation surface borders on the side of the binary antipyrine-ligroin system. On lowering the temperature it approaches more and more to the side of the binary phenol-ligroin system and below 20° it must join it.

In the ternary phenol-antipyrine-water system five sections were studied. The data obtained are given in Table 3, and the phase-separation polytherms are shown in Figure 2. All the polytherms have flat maxima and rise sharply upward from their extremities. The polytherms of sections 3 and 4 almost coincide. The maxima of the polytherms increase from sections 1 to 3, remain at the same temperature in 3 and 4, and decrease to section 5. In the water corner all the polytherms approach each other very closely.

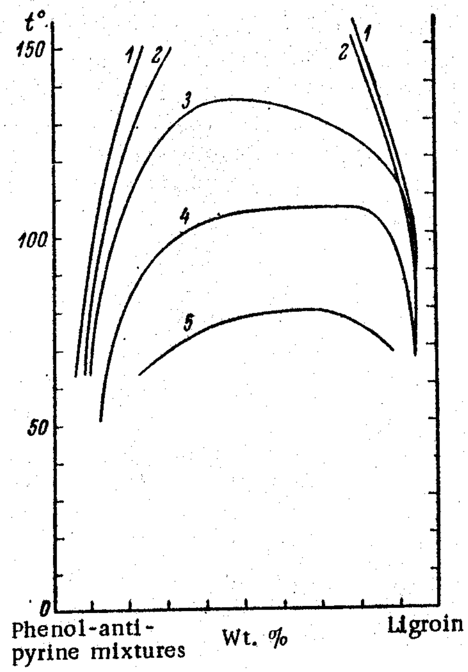

Fig. 1. Polytherms of phase-separation for the ternary system phenol-antipyrine-ligroin. Explanation in the text.

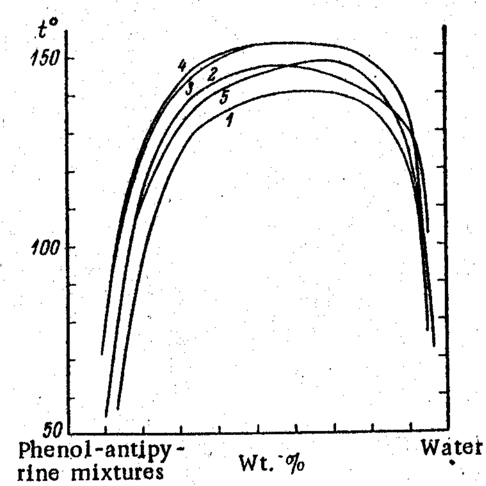

Fig. 2. Polytherms of phase-separation for the ternary system phenol-antipyrine-water. Explanation in the text.

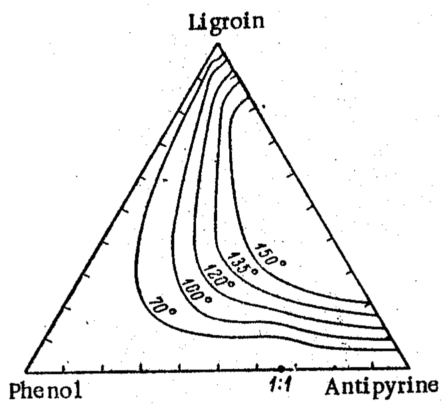

Fig. 3. Isotherms of solubility in the ternary system phenol-antipyrine-ligroin.

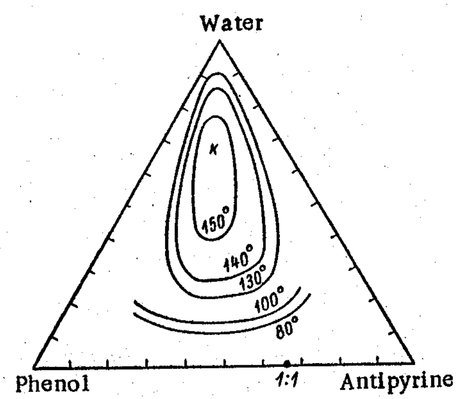

Fig. 4. Isotherms of solubility in the ternary system phenol-antipyrine-water.

From the polytherms obtained five phase-separation isotherms were constructed for the ternary system phenol-antipyrine-water, shown in Figure 4. The isotherms are closed curves, concentrically decreasing with increasing temperature. Thus, in this ternary system there exists an upper, triple, critical point (k); the latter occurs at 153° and a composition of 60% water, 22% phenol and 18% antipyrine. As Figure 4 shows, in the ternary system depicted at the temperatures studied the phase-separation surface is located within its temperature-concentration prism between the water edge and the face of the binary phenol-antipyrine system. At lower temperatures this surface must join the face of the binary separating system phenol-water. All the isotherms have minima of mutual solubility of water and the liquid mixtures of phenol with antipyrine. The upper triple critical point and the minima of the isotherms occur in the binary phenol-antipyrine system not at the composition of the compound, but at an irrational composition – 55.55% phenol and 44.45% antipyrine, in which the molecular ratio of these components is 2.5 : 1.

Comparison of the phase-separation isotherms of the two ternary systems studied shows that the presence in the liquid phase of the compound of the binary system phenol-antipyrine having the 1:1 composition is registered in the ternary system with ligroin by irrational solubility maxima. In the ternary system with water the compound referred to is abnormally reflected because of the formation of a secondary, difficultly soluble complex of irrational composition, which explains the genesis of the upper, triple, critical point. This also demonstrates that the two-solvent method is reliable for elucidating the character of the chemical reaction in binary, irrational, liquid systems. In the case under consideration, by replacing a polar solvent with a nonpolar one an irrational system with an abnormal reflection of the reaction is converted into an irrational system with a normal reflection.

TABLE 3

Equilibrium in the System Phenol-Antipyrine-Water

Section 1: 28% phenol, 72% antipyrine		Section 2: 33% phenol, 67% antipyrine		Section 3: 50% phenol, 50% antipyrine	
water (wt. %)	temperature of phase-separation	water (wt. %)	temperature of phase-separation	water (wt. %)	temperature of phase-separation
15.00	71.0°	12.69	80.0°	10.00	80.0°
20.09	98.0	18.27	109.0	15.00	108.0
25.13	114.5	31.58	139.0	20.20	126.0
35.00	132.0	50.00	147.0	30.00	143.0
45.11	137.0	70.00	145.5	20.14	150.0
59.87	141.0	80.00	140.0	49.86	153.0
70.00	140.0	90.00	132.0	60.00	153.0
80.05	137.0	95.00	103.0	68.05	153.0
90.00	121.0			90.07	138.0
95.00	77.0			93.00	
				96.00	72.0

Section 4: 60% phenol, 40% antipyrine		Section 5: 70% phenol, 30% antipyrine	
water (wt. %)	temperature of phase-separation	water (wt. %)	temperature of phase-separation
9.06	73.0°	10.11	57.0°
15.00	110.0	15.00	91.0
20.00	127.0	20.00	112.0
30.00	144.0	25.00	122.0
40.10	150.5	35.59	138.0
55.14	153.0	50.08	145.0
65.00	153.0	60.00	147.5
74.88	152.0	70.00	149.0
85.00	144.0	80.00	145.0
95.00	90.0	90.00	127.0
		95.04	94.0

The ternary system phenol-antipyrine-water is composed of substances with strongly hydrating functional groups and water. Consequently, in this system hydration processes predominantly appear. The strong reaction of antipyrine with water results in its infinite solubility. The reaction of phenol with water is somewhat decreased because of the presence in the system of a region of phase separation between them at lower temperatures. The strong hydration, which is unequal for the components, leads to the instability of the 1:1 compound in the ternary system and the formation of a complex with a greater phenol content. The hydration processes in the system cannot completely eliminate the reaction of the phenol with the antipyrine. Partial loss of their acid and basic functions upon formation of the complex leads to a decrease in hydration, and consequently to a lesser solubility of the complex in water. This is reflected in the phase-separation isotherms as solubility minima which necessitate

*Figure obscured in Russian text – Publisher.

the emergence of an upper, triple, critical point. Thus, the chemical and phase equilibria in liquid systems are closely related to each other and are mutually dependent; hence all the component binary systems of a given ternary system influence each other. A weakening of the reaction in one of them leads to a strengthening of the reaction in the remaining component binary systems.

In the ternary system phenol-antipyrine-ligroin hydration processes are absent and the 1:1 compound present in the liquid phase of the ternary system is normally reflected in the phase-separation isotherms. Here at reduced temperatures the compound is fixed by association processes. However, upon raising the temperature thermal dissociation sets in more and more, and above 120° the compound is not detected in the phase-separation isotherms. Thus, the nature of the solvant exerts a strong influence on the reacting system, changing the character of the reaction and the stability of the compounds formed.

SUMMARY

1. The ternary system phenol-antipyrine-ligroin has been investigated by the phase-separation method. In the phase-separation isotherms a compound of the predominant system phenol-antipyrine with 1:1 composition is reflected in irrational solubility maxima that disappear above 120°. This indicates thermal decomposition of the chemical compound.

2. The ternary system phenol-antipyrine-water has been investigated by the phase-separation method. It involves the systems with an upper, triple, critical point. The latter occurs in the binary system phenol-antipyrine at an irrational composition.

3. In the investigation of the two ternary systems referred to, the binary irrational system phenol-antipyrine has been studied by the two-solvent method. The applicability of this method to the study of reaction in liquid, binary, irrational systems has been demonstrated. The nature of the effect of solvents of different polarity on the reacting binary system phenol-antipyrine has been clarified.

4. It has been shown that in a liquid ternary system the component binary systems mutually affect each other. A weakening of the reaction in one of them leads to a strengthening of the reaction in the other two binary systems.

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