THE APPLICATION OF THE METHOD OF TWO SOLVENTS TO THE STUDY OF INTERACTION IN LIQUID SYSTEMS

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The method of two solvents [1], from the point of view of its practical application, involves the study of of a binary system from the separation of phases in two solvents, one polar and the other non-polar. This makes possible a penetrating study of the details of chemical interaction in the binary system. On the other hand, the method of two solvents makes it possible to study the interaction between the components of a binary system from the separation of phases even when this is not reflected at all, or is inaccurately reflected , on the surface of separation of phases in a ternary system. The working out of just such an example of the application of the method of two solvents is the aim of the present work.

There are cases in the literature where the formation of a chemical compound in a binary predominating system has been reflected inaccurately by the geometrical elements of the surface of separation of phases of the ternary systems [2]. In such cases the geometrical elements mentioned do not fall on a rational compound composition, but on another, often irrational, composition. Up to the present time, however, no way has been suggested for avoiding such an anomalous reflection. The theoretical basis of the method of two solvents [1] shows that it may be used as a means of avoiding an inaccurate reflection. To confirm this possibility, in the present work the interaction in the binary system benzoic acid–antipyrine was studied from the separation into phases in two solvents: the polar solvent – water – and the non-polar solvent – benzine.

EXPERIMENTAL

The objects of study were the two ternary systems: benzoic acid–antipyrine–water and benzoic acid–antipyrine–benzine. Both systems were studied from the separation into phases by the visual polythermal method of Alekseev [3] in sealed glass ampoules in an oil-filled thermostat. In each ternary system a study was made of the polythermal sections through their temperature-concentration prisms, going from the water (or benzine) edge to the face of the binary predominating system benzoic acid–antipyrine.

The following materials were taken for the work: pharmacopoeia purity antipyrine with m.p. 113°, chemically pure benzoic acid with m.p. 121°, the benzine fraction boiling between 120 and 140°, and twice-distilled water. The advantages and disadvantages of working with benzine instead of individual hydrocarbons have been pointed out earlier [1]. Antipyrine is a powerful monoacidic base, but contains two tertiary amino groups.

The binary systems making up the ternary are characterized by the following data. The benzoic acid–antipyrine system has been studied from the melting points [4]. This showed one chemical compound, melting congruently at a temperature of 66°, containing 39.3% benzoic acid and 60.7% antipyrine (molar ratio 1: 1). Antipyrine is completely miscible with water. The benzoic acid–water system has been studied from the melting points and the separation of phases [5]. This showed a stable separation of phases with an upper critical point (temperature 116.2°, 34% benzoic acid). The antipyrine–benzine system has been studied from the separation of phases [1]. This shows a stable separation of phases with an upper critical point situated at high temperatures. Benzoic acid is completely soluble in benzine.

In the ternary system benzoic acid–antipyrine–water, seven polythermal sections have been studied. The numerical data obtained are given in Table 1 and the solubility polytherms are shown in Figure 1. Figure 1 shows that all the polytherms have the same form with maxima of mutual solubility of the liquid phases. The

latter rise from section 1 to section 5 and fall from section 5 to section 7. The polytherms of section 5 is thus the highest. In all the sections the maxima of the polytherms are displaced towards the water edge. The solubility of water in mixtures of antipyrine and benzoic acid is approximately 3 times greater than the solubility of these mixtures in water. In mixtures coming close to the ends of the polytherms, the mutual solubility of the liquid phases is only very slightly dependent on temperature, so that the curves of separation of the components rise steeply. In mixtures lying in the central regions of the curves, these two factors are strongly dependent, so that the central parts of the polythermals are sloping.

TABLE 1

Polytherms of the System Benzoic Acid–Antipyrine–Water

Section 1 20% BA, 80% An*		Section 2 33% BA, 67% An		Section 3 39.3% BA, 60.7% An		Section 4 48% BA, 52% An	
water (% by weight)	temperature of separation of phases	water (% by weight)	temperature of separation of phases	water (% by weight)	temperature of separation of phases	water (% by weight)	temperature of separation of phases
40.00	55.0°	21.50	75.0°	17.00	85.0°	10.00	48.0°
51.02	92.0	26.70	105.0	20.00	96.0	15.30	88.0
55.00	96.0	30.00	114.0	25.14	115.0	20.00	107.0
60.00	103.0	40.00	127.0	30.20	127.0	30.80	136.0
70.00	108.0	50.00	133.0	40.00	135.0	40.00	141.5
80.04	111.0	60.11	135.0	50.10	139.0	50.20	145.0
90.00	96.0	70.00	134.5	60.00	140.0	60.00	146.0
95.00	64.0	80.00	130.0	70.00	141.0	70.00	147.0
		90.00	112.0	80.00	138.0	80.00	141.0
				90.00	119.0	90.00	124.0
				93.12	105.0	95.00	96.0
Section 5 60% BA, 40% An		Section 6 70% BA, 30% An		Section 7 80% BA, 20% An			
13.00	80.0°	15.00	83.0°	14.00	74.0°		
15.20	95.0	20.00	110.0	20.00	99.0		
20.00	113.0	30.09	133.0	30.00	125.0		
30.00	137.0	40.00	142.0	40.00	135.0		
40.00	146.0	50.00	146.0	50.20	138.0		
50.00	148.0	60.00	147.0	60.00	140.0		
60.13	149.0	70.00	145.0	70.00	141.0		
70.00	148.0	80.00	141.0	80.00	139.0		
85.00	139.0	90.00	128.0	90.06	127.0		
90.00	127.5	95.30	102.0	95.00	101.0		
95.00	102.0			96.00	91.0		
96.00	88.0						

* In both Tables, BA – benzoic acid, An – antipyrine.

Four solubility isotherms of the given ternary system at temperatures 80, 100, 135 and 145° were constructed from the polytherms obtained. As Figure 3 shows, the isotherms at 80 and 100° start from breaks in the solubility of the binary system benzoic acid–water and pass inside the prism of the ternary system. The isotherms at 135 and 145° have the form of closed curves. In the ternary system being studied, therefore, the separation of phases in the binary system benzoic acid–water is homogenized by the antipyrine; at the same time an upper ternary critical point is formed. The latter lies at 150° and corresponds to a composition of 23% benzoic acid, 17% antipyrine and 60% water.

Each isotherm shows minima for the mutual solubility of water and mixtures of benzoic acid and antipyrine. The minima of all the isotherms lie in the binary system benzoic acid–antipyrine at the composition of a complex in which the ratio between the molecules of the components mentioned is 2 : 1. The turning points of the isotherms, therefore, do not lie at the composition of a compound which is established from the melting point curves of the predominating system. A similar phenomenon is observed even on the isotherm at 80°, which is situated a total of 14° above the melting point of the compound detected from the fusibility. On the strength

of this the above deviation cannot be ascribed to thermal dissociation of the compound, as takes place in systems with irrational turning points. It can only be explained by the influence of the strongly polar solvent – water – on the reacting system. To confirm this suggestion, the interaction of the binary system benzoic acid–antipyrine was studied in the non-polar solvent – benzine.

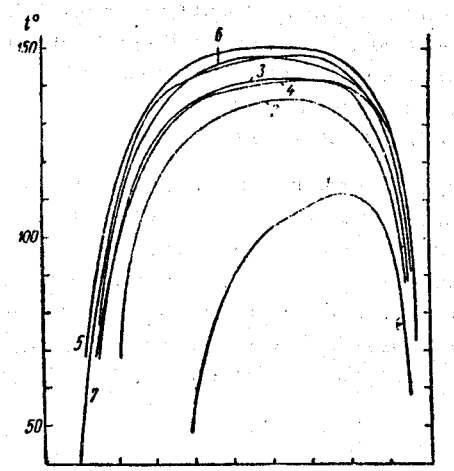

Fig. 1. Solubility polytherms of the ternary system benzoic acid–antipyrine–water.

In the ternary system benzoic acid–antipyrine–benzine, seven polythermal sections were studied. The numerical data obtained are given in Table 2 and the polythermals of separation of phases are shown in Figure 2. In the majority of the polythermals the maxima of the mutual solubility of the liquid phases are situated at high temperatures and could not therefore be determined. The polythermal maxima were found only in sections 6 and 7, in which they are displaced towards the benzine edge. In all the sections (except 7) the mutual solubility of the liquids is only very slightly dependent on temperature, so that all the solubility curves rise steeply.

Three isotherms of separation of phases at temperatures 100, 130 and 150°, shown in Figure 4, were constructed from the polythermals obtained. In this case the separation of phases in the binary system antipyrine–benzine is homogenized by the benzoic acid. As a result of this all the isotherms start from breaks in the solubility of the binary system antipyrine–benzine and are closed inside the prism of the ternary system. Each isotherm shows minima for the mutual solubility of benzine and mixtures of benzoic acid and antipyrine. The minima of all the isotherms lie in the binary predominating system benzoic acid–antipyrine on the composition of the compound established from the fusibility diagram (i.e., of composition 1 : 1), and this also fixes its presence in the liquid phase of the ternary system. The presence of the above-mentioned minima on the isotherms of separation of phases and the concentric decrease of the latter with increase in temperature indicate that in the ternary system being studied there exists an upper ternary critical point. This, however, could not be detected since it is situated at high temperatures.

Comparison of the isotherms of separation of phases in the 2 ternary systems described shows that solvents of different polarity show a specific and qualitatively different influence on the interaction in the reacting system benzoic acid–antipyrine. In the ternary system benzoic acid–antipyrine–benzine, in the non-polar solvent, benzine, the most highly developed processes are those of association of molecules and dissociation of the associated molecules. These processes take place in the predominating system and also in the reaction of this with the third component. As a result of this the antipyrine benzoate, fixed by the fusibility diagram, is present in the liquid phase of the given ternary system and is stabilized in it by association processes. The minima of the separation of phases lie at the composition of the compound, which is thus established. The formation of minima on the isotherms of separation of phases is explained by the more extensive dissociation of the components of the predominating system than of its compound. Studies by a number of authors [6, 7] have shown that benzoic acid exists in hydrocarbon solutions in the form of double molecules. The dissociation of the associated molecules of benzoic acid leads to its unlimited mutual solubility in benzine. The dissociation processes in the system antipyrine–benzine lead to homogenization of the separation of phases.

The ternary system benzoic acid–antipyrine–water contains the polar solvent – water. The components of the reacting system, benzoic acid and antipyrine, are capable of being extensively hydrated; thus, antipyrine has the tertiary amine groups, while benzoic acid has the carboxyl group and is highly polar (dipole amount equal to $1 \cdot 10^{18}$ [8]). As a result of this, hydration processes are the most highly developed in the ternary system. These processes determine the character of the interaction between the predominating system and the third component, i.e., the character of the influence of the polar aqueous medium on the interaction in the reacting binary system. On the one hand, the extensive hydration of antipyrine, which leads to its unlimited solubility in

water makes the stabilization of the compound with composition 1: 1 in the liquid phase impossible. On the other hand, the separation of phases in the binary system benzoic acid–water weakens the interaction between its components. As a result of these factors and the high polarity of the benzoic acid, the interaction between the acid and the compound with composition 1: 1 is strengthened and a complex with composition 2: 1 formed (2 molecules of benzoic acid to 1 molecule of antipyrine). The interaction between benzoic acid and antipyrine is a process of salt formation in which the functional groups react with one another. The complex obtained is responsible for the appearance of the solubility minima on the isotherms of the separation of phases since the components of the reacting system are more extensively hydrated than its complex. With increase in temperature in the binary system benzoic acid–water, the separation of phases is homogenized and the hydration of the benzoic acid is increased. This process, together with the continued extensive hydration of the antipyrine, leads to dissociation of the complex and to the disappearance of the upper ternary critical point for which it is responsible; in this way complete homogenization takes place in the given ternary system.

Thus in the ternary system benzoic acid–antipyrine–water, the compound formed in the predominating system is reflected inaccurately on the isothermals of separation into phases as a result of the influence of the polar solvent on the interaction. This results from the formation of the second complex under the influence of water. Replacement of the latter by the non-polar solvent, benzine, cuts out the hydration processes and the secondary interaction of the compound, stabilizes it in the liquid phase, and it is accurately reflected on the solubility isotherms of the ternary system. At the same time it is confirmed that the method of two solvents can indeed be used to avoid the anomalous reflection of the chemical interaction on the diagrams of separation of phases.

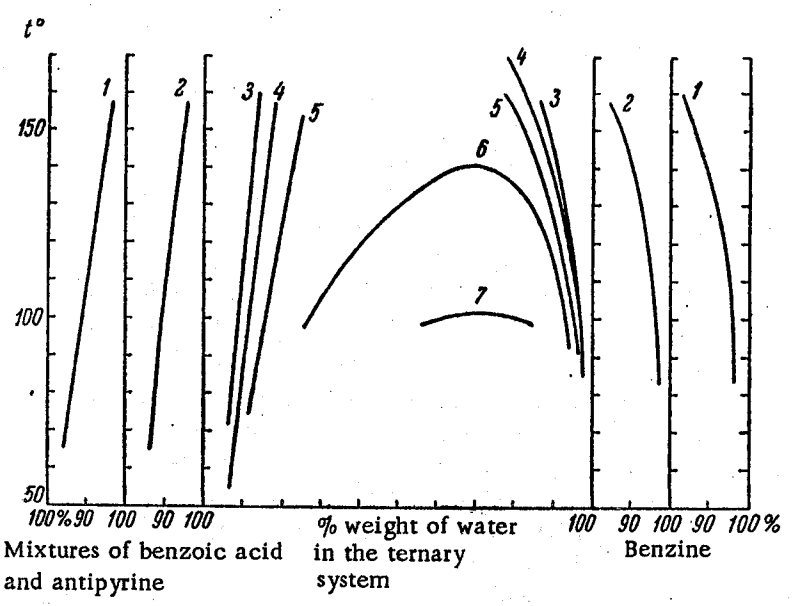

Fig. 1. Solubility polytherms of the ternary system benzoic acid–antipyrine–

In working out the method of two solvents [1], it has been shown that when the solvents are changed, transformation of the ternary systems from one type to another takes place. A ternary system with an upper ternary critical point was converted into a system with a synclinal singular edge. The present work confirms the possibility of the transformations indicated among ternary systems with an upper ternary critical point, which both the systems described contain. In this case a system with chemical interaction inaccurately reflected is converted into a system in which it is accurately reflected.

TABLE 2

Polytherms of the System Benzoic Acid–Antipyrine–Benzine

Section 1 20% BA, 80% An		Section 2 30% BA, 70% An		Section 3 39.3%BA, 60.7% An		Section 4 50% BA, 50% An	
benzine (% by weight)	temperature of separation of phases	benzine (% by weight)	temperature of separation of phases	benzine (% by weight)	temperature of separation of phases	benzine (% by weight)	temperature of separation of phases
5.07	71.0°	7.00	75.0°	7.00	84.0°	7.20	63.0°
7.00	85.5	8.06	88.0	8.00	95.0	10.00	91.0
10.40	113.0	13.00	137.0	10.10	119.0	12.06	110.0
15.00	148.0	15.00	156.0	13.00	153.0	14.00	125.0
16.00	155.0	85.00	155.0	86.00	157.0	17.00	151.0
85.00	152.5	90.20	140.0	90.00	140.0	80.00	165.0
90.00	136.0	95.00	112.0	95.00	110.0	90.00	137.0
95.00	110.0	97.00	90.0	97.00	90.0	95.00	113.0
96.00	89.0					97.00	95.0
Section 5 60% BA, 40% An		Section 6 70% BA, 30% An		Section 7 80% BA, 20% An			
12.20	81.0°	26.00	99.0°	60.00	101.0°		
15.00	99.0	30.10	106.0	70.00	102.0		
20.00	127.5	40.20	120.0	80.00	101.0		
24.00	150.0	50.90	130.0				
80.40	154.0	60.00	138.0				
90.00	125.0	70.00	141.0				
95.00	98.0	80.00	135.0				
		90.00	114.0				
		93.00	95.0				

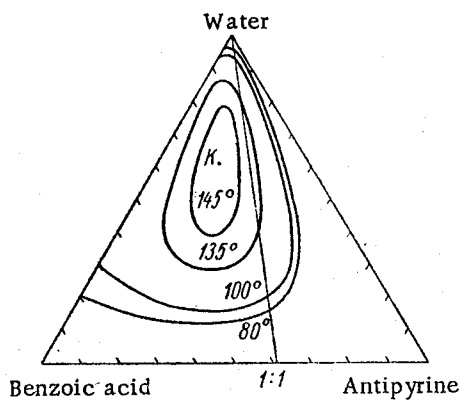

Fig. 3. Solubility isotherms of the ternary system benzoic acid–antipyrine–water.

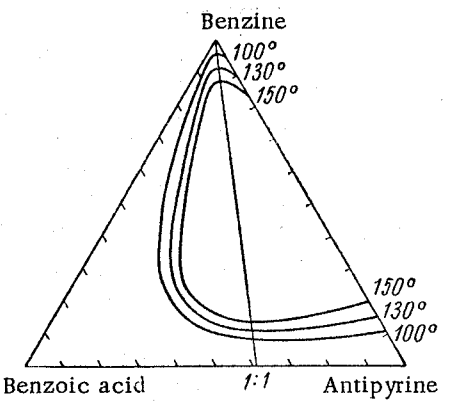

Fig. 4. Solubility isotherms of the ternary system benzoic acid–antipyrine–benzine.

SUMMARY

1. A study has been made of the equilibrium between the liquid phases in the ternary system benzoic acid–antipyrine–water. This shows a surface of separation of phases adjoining the face of the binary system benzoic acid–water, with an upper ternary critical point. It has been found that the interaction in the binary predominating system benzoic acid–antipyrine is inaccurately reflected on the surface of separation of phases of the ternary system as a result of the powerful influence of the polar solvent – water – on the system.

2. A study has been made of the equilibrium between the liquid phases in the ternary system benzoic acid–antipyrine– benzine. In this ternary system the isotherms of separation of phases show solubility minima situated at the composition of the compound of the predominating system; the compound is accurately reflected on the surface of separation of phases.

3. It has been shown that the method of two solvents is a reliable method for avoiding inaccurate reflection of chemical interaction in the predominating system on the surface of separation of phases in a ternary system.

4. It has been confirmed that in using the method of two solvents transformation of ternary systems from one type to another takes place. A transformation of ternary systems with an upper ternary critical point has been achieved; a system with chemical interaction inaccurately reflected has been converted into a system with the interaction accurately reflected.

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