INVESTIGATION OF METASTABLE EQUILIBRIA BETWEEN LIQUID PHASES. III.

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In the previous communications an examination was made of the theoretical bases for study of metastable equilibria between liquid phases; two types of these were studied and two new forms of equilibrium diagrams were obtained in this connection. The study of metastable liquid-phase equilibria in three-component systems revealed their close connection with solvent systems [1]. A more detailed elucidationof this connection necessitates a study of a ternary system in which one of the components is in the solid state and dissolves in the other two which are present in the given conditions in the liquid state. It is necessary to actualize the case of solubility of a solid in a liquid mixture of two solvents which do not form stable chemical compounds between themselves. A further requirement is that each of the solvents should form with the dissolved substance a system with metastable stratification. In these conditions we should come close to clarification of the very character of systems with metastable equilibrium between the liquid phases, to clarification of the behavior of compositions of such systems as a function of the temperature. The stated conditions are fulfilled, as preliminary experiments revealed, in the three-component system sulfur-diphenylamine-β-naphthylamine. The study of this sytem is the subject of this paper.

The only binary system involving these components that is mentioned in the literature is sulfur-diphenylamine [2]. Crystallization in this system takes place according to the usual eutectic type. The eutectic point is at 92% diphenylamine and 8% sulfur, and it corresponds to a temperature of 51.5°. Below the sulfur crystallization curve is the curve of the equilibrium between the liquid phases with an upper critical temperature of solution of 104°, corresponding to a composition of 32% diphenylamine and 68% sulfur. Above the stratification curve is a small horizontal portion of the crystallization curve of sulfur. The remaining two systems in the given ternary system —sulfur-β-naphthylamine and diphenylamine-β-naphthylamine —are investigated in this research. The system sulfur-β-naphthylamine is similar to the binary system sulfur-diphenylamine; in it is likewise established a metastable equilibrium between the liquid phases. In the two-component system diphenylamine-β-naphthylamine no compound formation between the components is reflected on the curve of crystallization. In the liquid phase of this sytem, however, the existence of unstable compounds is possible since diphenylamine tended to form similar compounds, e.g., with quinoline.

Hence, in the three-component system sulfur-diphenylamine-β-naphthylamine we have solubility of the sulfur in a mixture of the two liquid amines (diphenylamine and β-naphthylamine) and dissociation of the associated sulfur in them. Both of the amines in the systems with sulfur form a metastable equilibrium between the liquid phases. Unstable complexes are possibly formed between the two amines. Thus, the given ternary system fully satisfies the above-indicated conditions.

EXPERIMENTAL AND EVALUATION OF RESULTS

The following reactants were taken for the investigation: sulfur recrystallized from benzene with m.p. 117°, and apparently consisting of a mixture of the monoclinic and rhombic forms [3]; diphenylamine, chemically pure, with m.p. 54°; β-naphthylamine "pure" with m.p. 112°.

The sulfur and diphenylamine were checked against the system sulfur-diphenylamine as detailed in the literature. The check showed agreement with the literature data. The research was carried out by Alekseev's method [4] in sealed ampoules in an oil thermostat.

System sulfur-β-naphthylamine was studied by fusion and stratifiability. The results are set forth in Table 1 and plotted in Figure 1. The fusion curve of this system has the usual eutectic form; the eutectic point is not low, has a composition of 35% β-naphthylamine and corresponds to a temperature of 100°. The sulfur crystallization curve has, above the curve of metastable stratification, a horizontal portion at 103° extending over the concentration range of 60 and 80% sulfur. Below the sulfur crystallization curve is the curve of metastable stratification with an upper critical solution temperature at 100.5°, displaced toward the sulfur corner, coinciding with the composition 75.05% sulfur and 24.95% β-naphthylamine.

Binary system diphenylamine-β-naphthylamine was studied by the fusion method. The results are set forth

TABLE 1

Equilibrium in the System Sulfur-β-Naphthylamine

No. of expt.	Sulfur (wt. %)	β-Naphthyl-amine (wt. %)	Temperature of crystallization	Temperature of stratification
1	0.00	100.00	112.0	—
2	13.00	87.00	107.0	—
3	20.56	79.44	104.5	—
4	30.00	70.00	102.0	
5	35.00E*	65.00	100.0	—
6	40.35	59.65	101.0	—
7	48.50	51.50	—	96.5
8	49.86	50.14	101.5	—
9	60.00	40.00	102.5	99.0
10	65.00	35.00	—	99.5
11	70.50	29.50	103.0	100.0
12	75.05	24.95	—	100.5
13	80.30	19.70	103.0	100.0
14	100.00	0.00	117.0	—

* = eutectic point

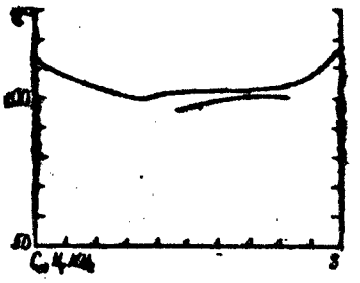

Fig. 1

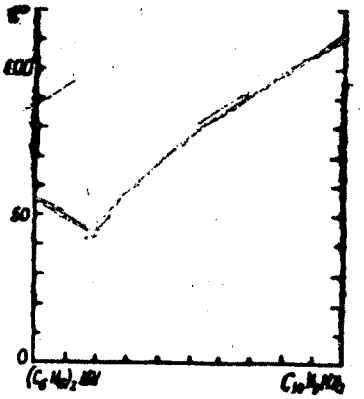

Fig. 2

in Table 2 and plotted in Figure 2. The fusion curve of this system intersects the eutectic point at 42°, the composition then being 83% diphenylamine and 17% β-naphthylamine. Formation of chemical compounds between the components was not observed. Nevertheless, as indicated previously, unstable compounds are possible in this system in the liquid phase.

TABLE 2 Equilibrium in the System Diphenylamine – β-Naphthylamine

No. of expt.	Diphenylamine (wt. %)	β-Naphthylamine (wt. %)	Crystallization temperature
1	0.00	100.00	112.0
2	9.64	90.36	105.0
3	19.14	80.86	100.0
4	29.95	70.05	94.5
5	40.00	60.00	88.0
6	49.92	50.08	81.0
7	59.90	40.10	71.0
8	69.99	30.01	60.5
9	75.00	25.00	54.5
10	80.00	20.00	46.5
11	83.00E*	17.00	42.0
12	85.06	14.94	44.0
13	90.11	9.89	47.0
14	95.00	5.00	50.0
15	100.00	0.00	54.0

*Eutectic point

The ternary system sulfur-diphenylamine-β-naphthylamine was studied by drawing polythermic sections through its prism, extending from the sulfur edge to the boundary of the binary system diphenylamine-β-naphthylamine. Six such sections were studied in all, with contents of 10, 20, 40, 60, 70 and 80% β-naphthylamine. Crystallization and stratification were studied in the polythermic sections. The data for the sections are set forth in Table 3 and plotted in Figure 3, a, b, c, d, e and f. In all the polythermic sections sulfur crystallizes with a very strong undercooling tendency, which is characteristic of systems with metastable equilibrium between the liquid phases, especially above the stratification curve. Due to this, some mixtures cannot be made to crystallize. These mixtures are indicated in the table. Each section consists of the crystallization curve of sulfur in the respective mixture of amines and the curve of metastable equilibrium between the liquid phases with the upper critical solution temperature, displaced to the sulfur corner. The metastability of the stratification in all the sections is an indication of the metastability of the whole equilibrium volume between the phases of the ternary system sulfur-diphenylamine-β-naphthylamine, i.e., of its existence entirely below the surface of crystallization of sulfur.

If the curve of the critical points is drawn through the critical points of the stratification curves of the binary systems and the sections, and if the same is done for the points of the fusion curve located above the critical points, then the projection of both curves on to the plane extending through the critical points of the binary systems will have the shape represented in Fig. 4. On this, the upper curve relates to crystallization and the lower one to metastable

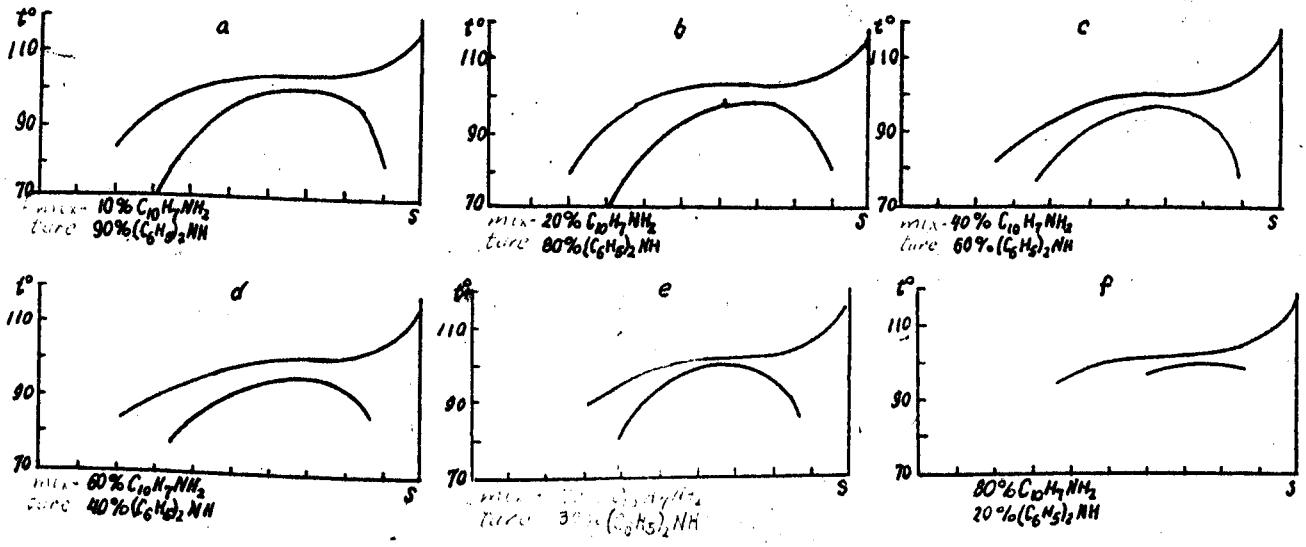

Fig. 3.

TABLE 3

Polytherms of the System Sulfur-Diphenylamine-β-Naphthylamine

No. of expt.	Sulfur (wt. %)	Temperature of crystallization	Temperature of stratification
Section No. 1: 10% β-naphthylamine, 90% diphenylamine			
1	19.88	84.0	—
2	29.82	94.0	70.0
3	39.99	99.5	86.0
4	50.00	103.0	94.5
5	60.11	103.5	99.0
6	70.00	104.0	100.0
7	80.06	105.0	99.0
8	84.91	—	94.0
9	89.89	107.0	80.0
Section No. 2: 20% β-naphthylamine, 80% diphenylamine			
1	20.00	79.0	—
2	29.84	92.0	—
3	31.07	—	81.0
4	39.97	99.0	85.0
5	50.00	101.5	93.0
6	60.60	103.0	—
7	61.99	—	97.0
8	69.39	103.0	99.0
9	80.00	104.0	96.5
10	85.65	105.0	92.0
11	86.99	—	89.0
12	87.99	106.0	87.0
13	90.00	—	81.0
Section No. 4: 60% β-naphthylamine, 40% diphenylamine			
1	19.92	84.0	—
2	30.00	89.0	—
3	34.90	—	79.0
4	40.11	94.0	85.0
5	50.00	98.0	91.0
6	60.07	101.0	95.5
7	69.95	does not crystallize	96.5
8	80.00	102.0	95.0
9	86.68	103.0	88.0
Section No. 5: 70% β-naphthylamine, 30% diphenylamine			
1	30.10	89.0	—
2	40.00	95.0	83.0
3	50.00	99.0	95.0
4	60.05	does not crystallize	99.0
5	69.90	102.0	99.0
6	79.97	103.0	97.0
7	85.03	—	92.0
8	87.00	104.0	88.0

TABLE 3 -- (continued)

No. of expt.	Sulfur (wt. %)	Temperature of crystallization	Temperature of stratification
	Section 3: 40% β-naphthylamine, 60% diphenylamine		
1	25.00	82.5	—
2	30.12	86.0	—
3	39.89	94.0	82.0
4	50.00	98.0	91.0
5	60.00	100.5	95.5
6	69.87	does not crystallize	96.0
7	80.19	101.0	94.0
8	85.65	—	91.0
9	90.00	105.0	79.0
	Section 6: 80% β-naphthylamine, 20% diphenylamine		
1	35.96	94.0	—
2	40.00	96.0	—
3	50.00	100.0	—
4	59.10	101.0	97.0
5	65.12	does not crystallize	98.0
6	75.00	ditto	99.0
7	80.13	103.0	99.0
8	85.65	—	98.0
9	90.00	106.0	—

stratification. This graph alone shows that the equilibrium space between the liquid phases of the ternary system has a saddle-like point. The saddle-like point has a temperature of 96° and occurs on the section of the ternary system containing 46% β-naphthylamine and 54 % diphenylamine in the two-component system — β-naphthylamine-diphenylamine. This composition corresponds to a 1:1 ratio between the molecules of the two amines (strictly it should be 45.83% β-naphthylamine and 54.17% diphenylamine). The projection of the crystallization curve likewise has a minimum which falls on the same section of the ternary system at a temperature of 101°. Both curves exhibit the general course of crystallization and stratification.

Starting from the polytherms of metastable equilibrium between the liquid phases, the stratification isotherms represented in Fig. 5 were plotted. A total of 4 isothermal sections was plotted through the prism of the ternary system at temperatures of 90°, 95°, 97° and 100°. The 97° and 100° isotherms are above the saddle-like point and therefore they possess two separate regions of stratification. The latter start from solubility breaks at the corresponding temperatures in the two-component systems with metastable equilibrium between the liquid phases present inside the prism and they later merge. At 96°, i.e., the temperature of the saddle-like point, they must come into contact with each other. The 90° and 95° isotherms are below the saddle-like point. Hence, in these isothermal sections both regions of stratification, starting from the solubility break in the binary systems, run together inside the prism of the ternary system into one region of stratification of the ternary system. The isotherms of metastable stratification located below the saddle-like point possess maxima of reciprocal solubility of sulfur and mixtures of the amines in the liquid state. These maxima coincide with the polythermal section which, in the binary system, diphenylamine-β-naphthylamine corresponds to the 1:1 molar ratio.

Starting from the crystallization polytherms, plots were constructed of the isotherms of crystallization of sulfur in the ternary system. A total of 5 such isothermal sections was drawn through the prism of the ternary system at temperatures of 85°, 90°, 95°, 100° and 105°. The isotherms are shown in Fig. 6. They all have a similar form with a maximum of solubility of sulfur in the mixture of amines. These maxima fall on the very same polythermal section as the maxima of mutual solubility of the components in the liquid state, namely on the section corresponding in the binary system of the two amines to 1:1 molar ratios.

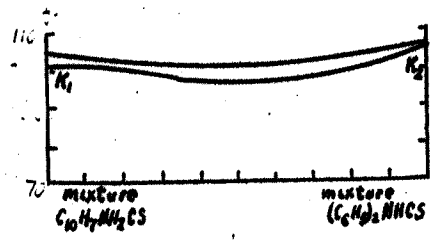

Fig. 4.

The foregoing graphical data permit the representation of the three-component system sulfur-diphenylamine-β-naphthylamine in the form of a prism. This is illustrated in Fig. 7, where B, C, and D respectively denote β-naphthylamine, sulfur and diphenylamine. The diagram clearly shows the space of the two-phase liquid state 1, 2, 3, 4, K_1, K_2, metastable at all temperatures and concentrations, with a saddle. The surface of crystallization of sulfur 5, 6, 7 is observed with its solubility maximum in mixtures of the two amines — diphenylamine and β-naphthylamine.

Consequently, the two-component system β-naphthylamine-diphenylamine is a typical solvent system in relation to sulfur, both

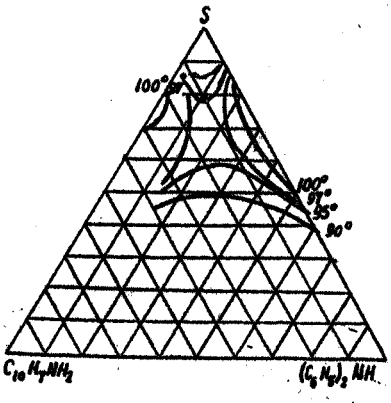

Fig. 5

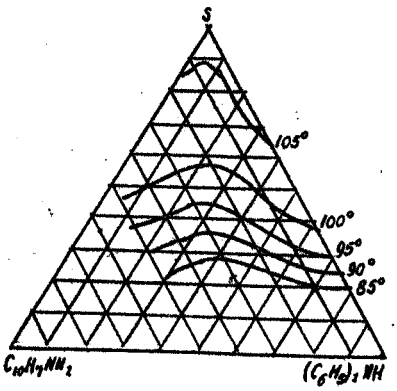

Fig. 6

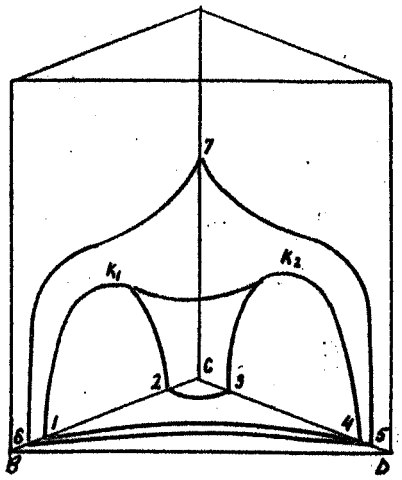

Fig. 7

in its liquid and solid state. Indeed at 95°, for example, the solubility of liquid sulfur in the separate amines is of the order of 45%, whereas in the 1:1 molar mixture of the amines—in which the solubility of sulfur reaches a maximum—the solubility approaches 60%. At the same temperature the solubility of solid sulfur in the amines is only of the order of 30%, but in the 1:1 mixture it reaches 45%. On the basis of the theory of solubility developed by R. V. Mertslin [1], these facts may find an explanation in the following way. First, in the binary system β-naphthylamine-diphenylamine, a chemical compound is formed with 1:1 molar composition. Second, this compound is unstable and easily breaks down at higher temperatures even in such a nonpolar solvent as sulfur. This evidently accounts for the absence of a maximum on the fusion curve of the two-component system diphenylamine-β-naphthylamine. Third, sulfur in the associated state is not passive toward the specified compound and dissociates therein. In this latter connection, we may recall that the dissociation of associated sulfur in amines is a well-known phenomenon.

All the above-stated facts become fully understandable on the assumption of formation of a solvent system. However, an additional factor is necessary for development of solvent systems. This is a type of monotectic crystallization in the three-component system such that crystallization of one and the same component should take place throughout the whole region from one stratifying binary system (in the ternary system in question) to the other. Monotectic crystallization takes place when there is stable stratification in a system, when the curves or surfaces of stratification intersect the curves or surfaces of crystallization and one of the phases of the system disappears with change of temperature. In the case of the three-component system sulfur-diphenylamine-β-naphthylamine, throughout the whole region between the two binary systems with metastable stratification we find crystallization of one and the same component, namely sulfur; here, however, the crystallization is not monotectic since the whole surface of stratification is metastable and does not intersect the surface of crystallization. Nevertheless, as shown by the isotherms of crystallization, the solvent character of the system is also realized at temperatures above the critical temperatures of the metastable equilibrium between the liquid phases. This fact suggests that in a series of cases the two-component systems with metastable stratification may behave like systems with stable equilibrium between the liquid phases. We may, therefore, conclude that in the given systems with metastable stratification at temperatures very much higher than the temperatures of stratification, we obtain a state close to the state of latent stratification. It is clear that compositions in the latently stratified state may often behave like compositions with normal stratification.

The above discussion permits us to explain the process of development of metastable stratification. It must proceed from true homogeneity to latent stratification and from the latter to metastable stratification. The possibility of development of stable stratification by this route is not excluded.

On the basis of the above experimental material we may approach certain problems of prognosis of solvent systems. Clarification of the conditions of formation of solvent systems is particularly important due to its potential practical value in the selection of solvent systems for certain substances for which single solvents cannot be readily found. These problems were analyzed by R. V. Mertslin [1] for ternary systems involving

binary systems with stable equilibrium between the liquid phases. As was shown above, when metastable stratification arises in two binary systems entering into the given ternary system and when there is compliance with the other factors necessary for formation of a solvent system, then such a system is actually developed. From this it follows that if a given binary system contains associated components capable of dissociating in each other or of forming a chemical compound susceptible to mutual dissociation with the dissolved substance, and if its components form binary systems with it with metastable stratification, then we can expect the development of a solvent system.

SUMMARY

1. The binary system sulfur-β-naphthylamine was investigated by the fusibility and stratification methods. The fusion data point to a eutectic form of fusion diagrams. Below the crystallization curve of sulfur is seen a stratification curve; the stratification is metastable at all temperatures and concentrations.

2. The system diphenylamine-β-naphthylamine was investigated by the fusion method. Its equilibrium diagram is of the eutectic type.

3. The equilibrium of the solid and liquid phases in the ternary system sulfur–diphenylamine–β-naphthylamine was investigated. The system contained a field of the two-phase liquid state, metastable at all temperatures and concentrations, with a saddle point, starting from the plane of metastable stratification of its binary systems sulfur-diphenylamine and sulfur-β-naphthylamine.

4. Suggestions are made about the possible mode of development, from the homogeneous solution, of metastable stratification and about its behavior at higher temperatures.

5. Some supplementary conditions for the practical choice of solvent systems are indicated.

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* See Consultants Bureau Translation, p. 463.