STUDY OF THE METASTABLE EQUILIBRIA BETWEEN LIQUID PHASES. V.

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In previous communications [1-4], ternary systems were described in which critical solution temperatures in the metastable state almost reached those for binary systems. Further study of metastable equilibria between liquid phases brought up the question of the possibility of realizing triple critical solution points in the metastable state and if possible, the principles of their formation. A solution of these problems is the object of the present work.

In selecting systems for study, we started from the fact described in previous communications, that ternary systems with metastable layer formation give similar types of equilibrium diagrams between the liquid phases as systems with stable layer formation. As a result of this, a ternary system of the layer formation type was sought on the basis of similarities found in ternary systems with upper triple critical points on the surfaces of the stable layer formation [5], with calculation of the special features of the form of equilibrium under investigation. In this way, a ternary system, in the binary part of which chemical compounds are formed, and in others (one or both), binary systems are realized by the phenomenon of metastable layer formation,and the desired form of diagram of state may be expected. With reference to such a system, the ternary system quinoline–diphenylamine–sulfur, was selected for study.

EXPERIMENTAL

For the work we took chemically pure diphenylamine, m. p. 54°, quinoline, purified by alkali and distilled off from the selected fraction, b. p. 237°; the sulfur had been recrystallized from benzene, m; p. 117° and therefore consisted of a mixture of the monoclinic and rhombic forms [6].

Of the binary systems, made up from the ternary system quinoline–diphenylamine–sulfur, the system sulfur–diphenylamine has already been described [5]. In it, below the crystallization curve for sulfur, there is a curve for equilibrium between the liquid phases, with an upper critical solution temperature of 104°, corresponding with a 32% diphenylamine content. Above the curve with layer formation there is a practically horizontal portion of the crystallization curve for sulfur at 105°. The system sulfur–quinoline has also been reported in the literature [7] and is similar to the previous system: in it the upper critical point corresponds to 102.5° and 26.5% quinoline content; the practically horizontal portion of the crystallization curve for sulfur is realized at 104.5°. The system diphenylamine–quinoline was investigated in the present work.

The system diphenylamine–quinoline was studied for fusibility and viscosity. Mixtures in this system form viscous and poorly crystalline solutions which do not fuse with diphenylamine. This investigation on fusibility was carried out by two parallel methods, the Shreder method [8] and the method of internal fusion. For carrying out the method, the ampoule containing the mixture was drawn out firmly to a tip, instead of being sealed. On shaking up the ampoule, the drop of mixture which had collected in it, froze. Throughout the period of cooling, the ampoule was vigorously shaken in order to distribute the liquid in contrast with the solidified clot, which played the part of a primer. The results obtained by both methods agreed within the limits of experimental error. The figures obtained for the material are given in Table 1 and the fusion curves are illustrated in Fig. 1, a. As seen from the data obtained, two compounds are formed between quinoline and diphenylamine, corresponding with the molecular proportions 1:1 and 5:3. The first of these melts congruently at 41.0° and contains 43.29% quinoline, the second compound melts at 37.0° incongruently and contains 55.99% quinoline; thus this latter melting point corresponds to the transition point E. The eutectic point found, e, corresponds to 32° and 25% quinoline. Mixtures with quinoline contents greater than 80% were not capable of crystallization.

TABLE 1

Equilibrium in the System Diphenylamine—Quinoline

Quinoline (wt. %)	Crystallization Temp., °C
0.00	54°
10.00	46
20.00	38
22.19	35
25.87	34
31.07	39
37.95	41
42.46	41
50.00	39
55.31	37
60.88	36
64.18	34
69.98	29
75.08	24
80.24	15

TABLE 2

Viscosity in the System Diphenylamine—Quinoline at 50°

Quinoline (wt. %)	Viscosity (centipoises)
20.79	5.848
30.96	5.676
40.00	5.521
43.28	5.470
45.00	5.203
46.67	4.902
50.00	4.558
54.00	4.561
56.12	4.558
60.39	4.145
65.00	3.610
70.17	3.199

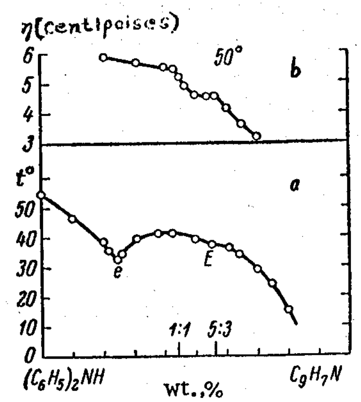

Fig. 1. Fusibility (a) and viscosity (b) in the system diphenylamine—quinoline.

A study of the viscosity was carried out in a capillary viscosimeter by the usual method [9]. The viscosity of the mixture was measured at 50°, i. e., on the one hand as near as possible to the melting points of the compoinds described and on the other hand at a sufficiently high temperature for crystallization of diphenylamine not to hinder the measurement at a high internal concentration. The figures obtained are given in Table 2 and the viscosity isotherms are represented in Fig. 1, b. As Fig. 1, b shows, there are two breaks in the viscosity isotherms, located between the viscosity values of the components; both these points correspond to the composition of compounds formed on fusion and their formation and presence are confirmed in the liquid phase.

The ternary system quinoline—diphenylamine—sulfur was investigated by the polythermal layer formation method of V. F. Alekseev [10] in sealed glass ampoules in an oil thermostat and partly by fusion. For this, sections were studied through the prism of the ternary system going from the sulfur edge to the side of the binary system quinoline—diphenylamine. In all, 8 such sections were studied, with quinoline contents of 20.0, 30.0, 40.0, 43.3, 50.0, 56.0, 60.0 and 80.0%. On studying the fusibility, it was found that with increasing quinoline content from section to section, and with increase in sulfur content in each section, crystallization became all the more difficult. In view of this, practically the complete sulfur crystallization curve was studied only in the first section with 20.0% quinoline; in the remaining sections, part of the sulfur crystallization curve, beginning at 40%, could not be obtained. Nevertheless, on accidental spontaneous crystallization of the compounds which separated, at a concentration interval of the layer formation, among them in each section were located mixtures which crystallized at much higher temperatures than the critical point of mixture in the liquid phase section. Crystallization of quinoline and diphenylamine in the ternary system was not studied. Figures relating to the sections are given in Table 3 and examples of the polytherms are illustrated in Fig. 2, where Fig. 2, a corresponds to the first section with a complete sulfur crystallization curve (Cr) and Fig. 2, b corresponds to the sixth section, a curve situated very high with layer formation.(Ra).

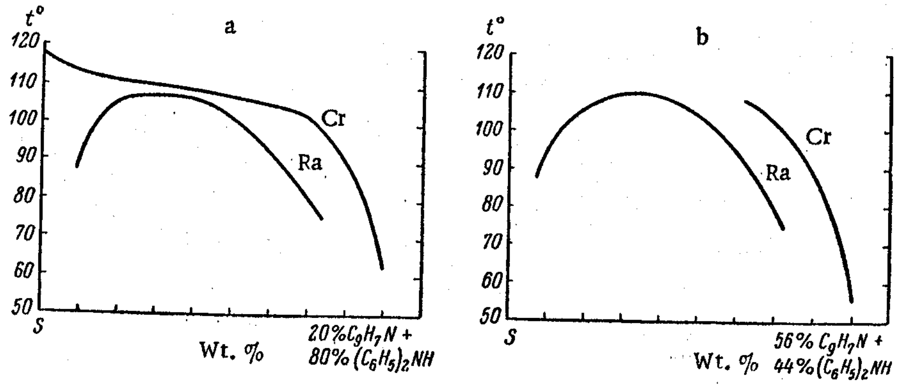

Fig. 2. Examples of polythermal sections of the prism of the system quinoline – diphenylamine – sulfur.

The results of the investigation show that the polytherms of the ternary system do not differ qualitatively from the polytherms of binary systems with layer formation. In a metastable liquid, the state of solubility of sulfur in mixtures of amines depends to an extent several times greater on temperature than the solubility of amines in sulfur; in this case, with increase in temperature the solubility of the liquid phase increases up to complete displacement. As a result of this the polythermal layer formation has maxima displaced to the sulfur side. The solubility of solid sulfur varies slightly with temperature at low temperatures up to 100-110°, the solubility temperature coefficient being markedly increased; therefore the crystallization curve has a very sloping part below the layer formation curve.

If a critical line is passed through the critical solution points of the binary system formed by sulfur and the maximal points of the polytherm of layer formation, then its projection to the edge of the binary system diphenylamine – quinoline will have the form represented in Fig. 3, curve K_1AKK_2. Beginning with the binary system sulfur – diphenylamine, the critical solution temperatures in the sections slowly increase up to the section with a composition of the compound with proportions 1:1 (point A). Beginning with this section, a rise in temperature takes place much more quickly and reaches a maximum figure of 109° in the section with composition of the compound, ratio 5:3 (point K) and then suddenly goes down. Already this variation in temperature shows that both compounds of the prevailing system diphenylamine – quinoline are reflected in the critical line and that on the surface of layer formation of the ternary system there is realized a singular line and an upper critical point.

With the polytherms obtained, the solubility isotherms of the solid and liquid phases of the ternary system quinoline – diphenylamine – sulfur were constructed and are illustrated in Fig. 4. In all, 6 isotherms with layer formation were constructed for 80, 90, 100, 105, 107 and 109°; they are shown in Fig. 4, a, from which it is seen that the surface of layer formation of the ternary system presents its own single surface linked with the surface of the ruptured solubility of the two binary layered systems. On this surface there is a synclinal singular edge corresponding to the binary system diphenylamine – quinoline and a compound with a molecular ratio of 1:1 with its own type of formation; for this, singular points were discovered on the enclosed isotherm of the layer formation.

Beginning at 104°, i. e., at the critical solution temperature, with the binary system sulfur – diphenylamine, the isotherms with layer formation are situated enclosed by the minima of the reciprocal solubilities of the liquid phases of sulfur admixed with amine and with two singular points; at the very highest temperatures, the isotherms decrease and at 109° are displaced to the upper triple critical point K. The latter rises not much above the rest of the surface; together with the minimum solubility it lies in the section corresponding to the binary system diphenylamine – quinoline, with a composition of the compound with a ratio of 5:3 and at the same time its formation is established at the minima shown. The upper triple critical point is situated at the composition 65.0% sulfur, 19.6% quinoline and 15.4% diphenylamine. The formation of this upper critical point is stipulated by the formation in the prevailing system diphenylamine – quinoline, of the chemical compound composition 5:3, with its organic solubility in the third component sulfur, and stable in the liquid phase to 109°. In this way the reasons for the formation of the upper triple critical points are the same for the stable and the metastable states.

TABLE 3

Polytherms of the System Quinoline—Diphenylamine—Sulfur

Wt. % of sulfur	Temperature: crystallization	Temperature: layer formation
Section 1: 20% Quinoline 80% Diphenylamine		
9.99	65	—
20.07	90	—
30.03	102.5	82.0
40.02	104.5	92.0
50.00	106.5	102.0
55.07	107.5	104.5
58.04	108	106.0
60.00	—	107.0
69.99	—	107.0
80.01	—	105.5
90.03	—	92.0
Section 2: 30% Quinoline 70% Diphenylamine		
10.00	66.0	—
20.00	89.0	—
30.07	103.0	76
39.78	110.0	92
50.00	—	102
60.00	—	107
70.05	—	108
80.00	—	105
90.00	—	94
Section 3: 40% Quinoline 60% Diphenylamine		
9.90	65	—
20.23	90	—
29.99	104	74
39.73	112	90
52.24	—	103
60.00	—	107
70.04	—	108
79.97	—	105
89.99	—	89
Section 4: 43.3% Quinoline 56.7% Diphenylamine		
12.00	70	—
20.00	88	—
30.07	103	76
39.76	—	90.5
50.00	—	101.5
60.00	—	107
69.87	—	108
80.00	—	105
84.88	—	100
90.00	—	92
Section 5: 50% Quinoline 50% Diphenylamine		
10.01	63	—
20.27	89	—
30.11	103	79
41.23	—	94
50.00	—	103
60.05	—	109
70.09	—	109
80.00	—	106.5
90.07	—	93
Section 6: 56% Quinoline 44% Diphenylamine		
10.00	60	—
20.00	88	—
30.00	92	79
40.00	—	95
50.00	—	103
60.36	—	109
70.05	—	109
80.00	—	105
90.00	—	95
Section 7: 60% Quinoline 40% Diphenylamine		
10.76	68.5	—
19.66	89	—
25.06	97	—
30.21	101.5	78
39.82	—	92
47.63	—	101
59.59	—	108
70.52	—	108
80.06	—	105
90.13	—	93
Section 8: 80% Quinoline 20% Diphenylamine		
9.97	62	—
20.11	86	—
25.08	92	—
30.07	96	77
39.78	102.5	92
50.13	105	98
59.76	—	103
68.51	—	103
80.03	—	101.5
88.22	—	97

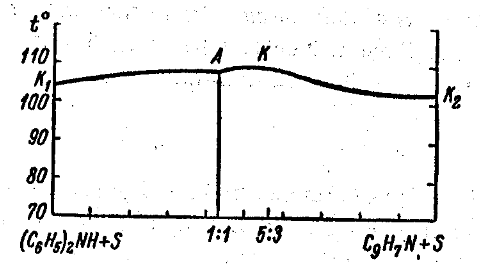

Fig. 3. Projection of critical line.

Nevertheless, the conditions for the formation of ternary systems of this type will differ from those for systems with stable layer formations; and it is necessary here, in order to have in the binary systems obtained (one or two) a metastable liquid phase equilibrium.

In Fig. 4, a, besides the layer formation isotherms, projections are shown of the critical line K_1AKK_2 for the composition triangle. In it a compound with the ratio 1:1 is illustrated in the form of the singular point A, corresponding to 108° and the higher point of a singular edge depicted with a compound of composition 5:3, in the form of an inflection point K, corresponding with the upper triple critical point.

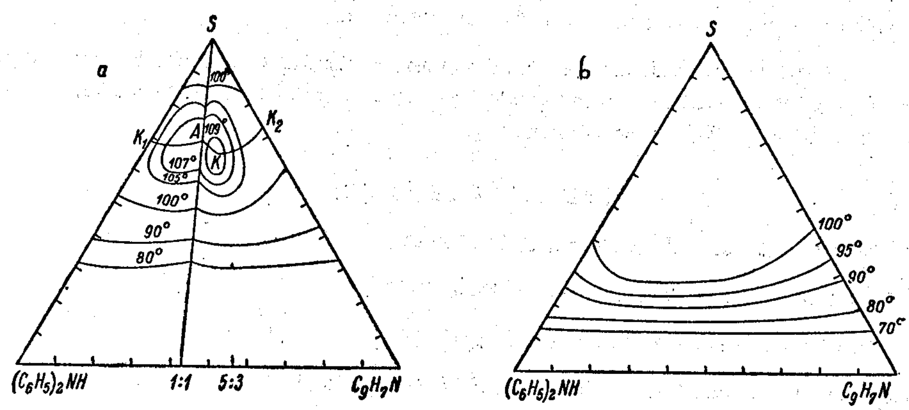

Fig. 4. Isotherms with layer formation (a) and crystallization (b) in the system quinoline–diphenylamine–sulfur.

In Fig. 4, b, the solubility isotherms are illustrated of solid sulfur in the system quinoline–diphenylamine–sulfur at 70, 80, 90, 95 and 100°. Each isotherm presents a minimum curve with a strongly diffused solubility minimum which is clearer with increasing temperature, when, at the same time the branch isotherms approach each other. This fact and the spontaneous crystallization of sulfur in the sections described above, illustrates the fact that the surface of crystallization of sulfur in the prism of the ternary system must have predominance, passing along the section through the sulfur edge between the edges of the two binary layer-formation systems. This result is brought about naturally and is in agreement with the relevant experimental facts. Actually, earlier [1], there was described the close relationship between metastable layer formation and crystallization and their mutual effect on each other. Externally this effect is shown by the fact that the curves and surfaces of layer formation and crystallization have a common course. Thus, if the surface of metastable layer formation has a saddle-shaped point, the surface of crystallization above it displays concavity [3]. A similar effect of the common course is also displayed between the isotherms of stable layer formation and crystallization [11]. In this way it is natural that the presence in the ternary system in the metastable state, of upper critical points, corresponds to the concavity mentioned above, of the crystallization surfaces.

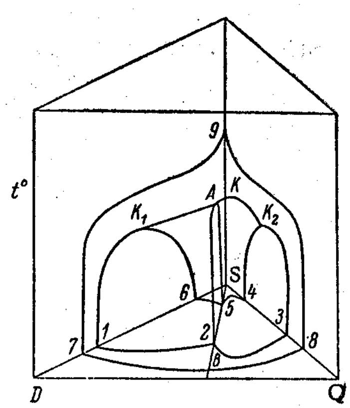

Fig. 5. General view of temperature-concentration prism of system quinoline–diphenylamine–sulfur.

The mutal arrangement of all the geometric elements of the diagram is seen in Fig. 5 where the usual qualitative forms of the temperature-concentration prisms of the system quinoline–diphenylamine–sulfur, are illustrated, components being denoted at the corners by the first letters of their names. Here, the surfaces of metastable equilibrium between the liquid phases 1, 3, 4, 6, K_1, K, K_2 have a singular edge, 2, A, 5 with a surface triple critical point K; 7, 8, 9 are the surfaces of crystallization of sulfur, with a minimum B.

SUMMARY

1. The binary system diphenylamine–quinoline has been studied, with reference to fusibility and visccsity. In it two chemical compounds are formed with molecular proportions of quinoline and diphenylamine 1:1 and 5:3 respectively; the first of these compounds melts congruently and the second, incongruently.

2. The ternary system diphenylamine–quinoline–sulfur has been studied with reference to layer formation, partly with reference to fusibility. In it the surface of the metastable layer formed has asynclinal singular edge and an upper triple critical point. The layer formation surface of the ternary system is linked with a flattening of the ruptured solubility of the two binary systems with layer formation.

3. It is explained that the formation of upper triple critical points on the surfaces of layer formation both for the stable and the metastable states is due to the same reasons.

4. In the ternary system studied, on the closed isotherms with layer formation, singular points were established. It has been found that the formation of chemical compounds in the prevailing binary system is reflected in the critical line of the ternary system.

LITERATURE CITED

[1] I. L. Krupatkin, J. Gen. Chem. Supp. I, 151 (1953).

[2] I. L. Krupatkin, J. Gen. Chem. Supp. II, 1221 (1953).

[3] I. L. Krupatkin, J. Gen. Chem. 23, 1096 (1953) (T. p. 1147).*

[4] I. L. Krupatkin, J. Gen. Chem. 25, 1640 (1955) (T. p. 1599).*

[5] R. V. Mertslin, J. Gen. Chem. 6, 1828 (1936).

[6] Yu. V. Karyakin, Pure Chemical Reactions (State Chem. Press, 1947).

[7] Landolt-Bornstein Tables (1923), 5th edition.

[8] I. F. Shreder, Mineral. J. 1890, 11.

[9] I. L. Krupatkin, J. Gen. Chem. Supp. II, 771 (1953).

[10] V. F. Alekseev, J. Russ. Chem. Soc. 8, 249 (1876).

[11] R. V. Mertslin and V. D. Vasev, J. Gen. Chem. 21, 417 (1951) (T. p. 463).*

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