LXXII.—*Pseudo-ternary Systems containing Sulphur. Part II. The System Sulphur–Benzoic Acid.*

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KRUYT (*Z. physikal. Chem.*, 1909, **67**, 330) observed that when mixtures of sulphur and benzoic acid are heated slowly, a cloud (new liquid phase) appears in the sulphur-rich layer in the neighbourhood of 170° and disappears on still further raising the temperature. This behaviour is what would be expected if the solubility curve for liquid sulphur in liquid benzoic acid became retrograde in the neighbourhood of 170° and at higher temperatures resumed its original direction, *i.e.*, if the miscibility curve for liquid sulphur and benzoic acid were of the Type η predicted by Kruyt as one of the possible types for pseudo-ternary systems containing sulphur (compare *ibid.*, **65**, 486). Kruyt, however, rejects this explanation on the grounds that according to his experiments the solubility of benzoic acid in liquid sulphur increases slightly with temperature in the region where the clouding effect occurs. Further, he claims that at about 170° the solubility of benzoic acid increases from

2·2% when the two phases are left in contact for a few minutes to 2·8% when they remain together for 5—10 hours. He concludes that in the neighbourhood of 170° three liquid layers can coexist, *viz.*, a solution of sulphur in benzoic acid, a solution of benzoic acid in a liquid sulphur that is mainly S_λ, and a second solution of benzoic acid in a liquid sulphur that is mainly S_μ.

We have determined equilibria in the system sulphur–benzoic acid by the synthetic method used in our previous investigations on sulphur systems (J., 1926, 1995). Weighed quantities of pure sulphur and benzoic acid (m. p. 121·7°) were sealed in bulb tubes and the necks drawn out to long spindles so that the melted contents could be well mixed by rotating the spindles. Equilibrium temperatures were determined by observing the formation and disappearance, in a regulated thermostat, of the cloud of droplets constituting a second liquid phase. The sulphur-rich phases at lower temperatures contain quantities of benzoic acid of the order of 2%, and, as will be seen from Fig. 1, their composition varies with temperature in a complicated way within a very small range of concentrations. Consequently the mixtures had to be made up with the greatest care. The benzoic acid was introduced into the bulbs first, so that any particles adhering to the walls would be swept in by the large excess of sulphur that was introduced next. The loss in weight that occurred on sealing the bulbs was found to be practically constant at 0·001 g. The contents of the bulbs weighed from 4 to 7 g.

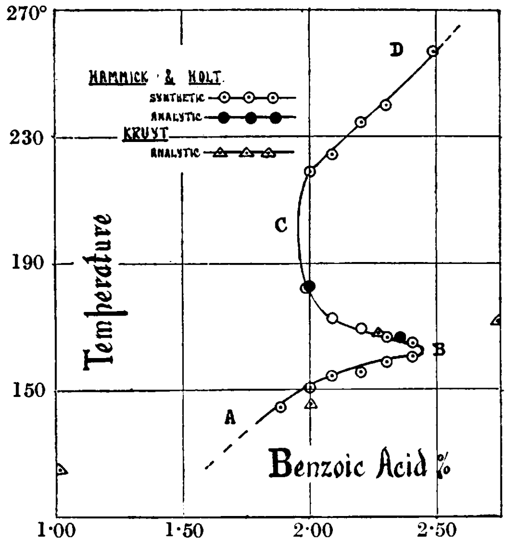
The results obtained are given in Table I; T_1 denotes the temperatures at which heterogeneous liquid mixtures of sulphur and benzoic acid first become homogeneous. On raising the temperature to T_2, the mixture again becomes heterogeneous; at still higher temperatures, it becomes dark and viscous and finally clears again at temperature T_3. The accuracy of temperatures T_1 and T_2 is about ±1°; the final clearing temperatures, T_3, are much more difficult to observe, but are probably correct to ±2°. All the values of T quoted are means of several observations made with rising and falling temperatures.

TABLE I.

Benzoic acid (%) ...	1·89	2·00	2·09	2·20	2·30	2·40	2·49
T_1	145°	151°	154·5°	156°	159·5°	161·5°	—
T_2	—	183	173	170	167·3	165	—
T_3	—	219	225	235	—	242	257·5°

The above results are plotted in Fig. 1, and it will at once be seen that the diagram gives an explanation of the clouding phenomena observed by Kruyt. Most of his mixtures contained considerable percentages of benzoic acid, and hence, at all temperatures below the critical solution temperature, he had two liquid layers present. On heating such a mixture, separation of the benzoic-acid-rich phase in the sulphur layer will take place directly the point of inflexion B in Fig. 1 is passed. Owing to the viscosity of the sulphur-rich layer, the separated droplets will not at once coalesce with the benzoic acid layer, but will finally disappear at higher temperatures at some point along the curve CD. Any mixture of sulphur and benzoic acid on cooling from high temperatures will show a clouding effect directly the conditions represented by the curve CD or its prolongation are reached. Between 165° and 175° reabsorption of part or all of the cloud of droplets will occur. When mixtures in which the amounts of benzoic acid lie between 2·0% and 2·4% are used, the above phenomena are more clearly defined and more readily controlled. For instance, a mixture containing 2·30% of benzoic acid is homogeneous at 250°; on cooling, turbidity occurs at about 240° and persists until 167° is reached. The mixture becomes homogeneous again whilst the temperature drops to 159°. The heterogeneous region is now re-entered and the liquid clouds. In short, the sulphur-rich side of the diagram for the system is of the type predicted by Kruyt (*loc. cit.*) as possible in pseudo-ternary sulphur systems, and it is not necessary, in order to account for the clouding phenomena, to suppose that three liquid layers coexist in equilibrium in the neighbourhood of 170°.

Fig. 1.



There remains, however, the question of the increase in solubility of benzoic acid in liquid sulphur indicated by Kruyt's experiments between 170° and 185° in direct contradiction to our results obtained by the synthetic method. We have therefore made direct analyses of the sulphur layers at 169° and 183°. Mixtures containing roughly equal quantities of sulphur and benzoic acid and weighing 7—8 g. were enclosed in sealed tubes for 4, 8, and 12 hours, respectively, in the vapour of a specimen of phenetole of b. p. 169°. The tubes were rapidly cooled and allowed to stand over-night. They were then opened and about 1 g. of the solid sulphur layer removed. This was dissolved in carbon disulphide and titrated with $N/100$-sodium hydroxide after the addition of alcohol. The percentages of benzoic acid found in the sulphur layer were 2·25, 2·35, and 2·30. Similarly, a mixture kept in the vapour of boiling aniline (183°) for 8 hours gave a sulphur layer containing 2·04% of benzoic acid. These two solubility values are shown on the diagram as large black points and are seen to agree excellently with the results obtained by the synthetic method. Kruyt's value of 2·2% at 169—170° for a mixture heated for a short time agrees well enough with our result; we are, however, unable to confirm the increase in solubility which he found when the heating was prolonged. Furthermore, we find by both the synthetic and the analytic method that the solubility of benzoic acid in sulphur decreases from 169° to 183° (2·30% to 2·04%), whereas Kruyt finds 5·8% at 185° (*loc. cit.*, p. 333).

The discrepancy is probably due to the fact that Kruyt's mixtures were heated in contact with the air, whereas ours were enclosed in sealed tubes. Liquid sulphur can readily be shown to undergo considerable oxidation in the air at the temperatures employed, and the presence of sulphur oxides in the sulphur layer would obviously account for the high values for solubilities deduced from the alkali titre of such a layer. In order to test this view, we heated a mixture in an unsealed tube at the temperature of boiling phenetole (169°) for 10 hours; on analysis the sulphur layer was found to have an apparent content of 2·62% of benzoic acid and gave a positive test for the presence of sulphuric acid with barium chloride.

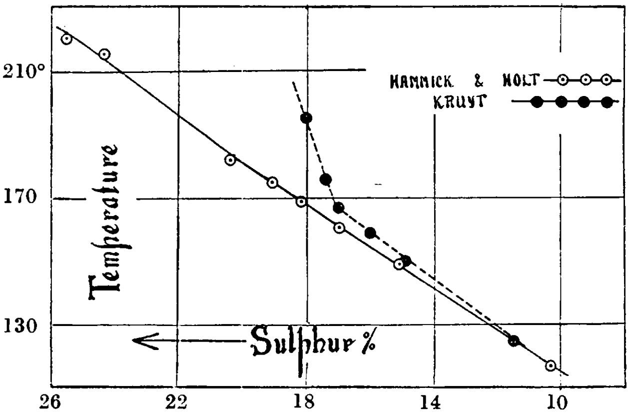
It thus seems to be established that on the sulphur side of the diagram the equilibrium curve is of Kruyt's Type η; our experiments, however, give no indication of a corresponding inflexion on the benzoic acid side. Our equilibrium temperatures and compositions are given in Table II and are plotted, together with Kruyt's data, in Fig. 2. It will be seen that again we do not agree with Kruyt, whose figures indicate a break in the curve at about 170°.

TABLE II.

Sulphur (%)	10·35	15·1	16·9	18·2	19·25	20·4	24·3	25·5
Temp.	117°	149·5°	160·5°	168·5°	175°	182°	215°	220°

These equilibria were determined as described above for the sulphur side of the system. The temperatures at which the clouds of second liquid phase separated on slow cooling were sharp, reproducible to within 1°, and remained unchanged on keeping the bulbs for several days. Owing, however, to the rapidity with which the droplets coagulated into large drops, it was not possible to obtain equilibrium temperatures by noticing temperatures at which the droplets disappeared.

FIG. 2.



The benzoic acid side of the system thus appears to be simple. The absence of the clouding and clearing phenomena found on the other side makes it practically certain that the minute region of retrograde solubility found there has no counterpart on the benzoic acid side.

Summary and Conclusion.

The diagrammatic representation of the equilibria in the system sulphur–benzoic acid is, on the sulphur side, of Kruyt's Type η. On the benzoic acid side, it is of the type ordinarily found for two partly miscible liquids. The facts embodied in the whole phase-diagram give an adequate explanation of the clouding phenomena noticed by Kruyt, without the necessity for his conclusion that in the neighbourhood of 170° three liquid layers can coexist.

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