207. *The System Nitrobenzene–Sulphuric Acid–Water.*

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The ternary system nitrobenzene–sulphuric acid–water, which has been investigated at 0°, 22°, and 34°, presents some unusual features, although partial miscibility occurs only with one pair of the components, nitrobenzene and water, the mutual solubilities of which are very small.

The binary system sulphuric acid–water has been investigated by numerous workers, and the data relevant to the present research have been taken from the "International Critical Tables." The binary system nitrobenzene–sulphuric acid has recently been studied by Masson (J., 1931, 3200), who has confirmed the conclusions of Cherbuliez (*Helv. Chim. Acta*, 1923, **6**, 281) concerning the formation of an equimolecular compound, and has determined the complete f. p. curve of the system.

Experimental.

The Binodal Curve.—Concentrated "pure sulphuric acid" (97%) and oleum were tested for all usual impurities, which were found to be absent. Nitrobenzene, thoroughly dried with calcium chloride and distilled, boiled at 208—209°, froze at 5·60° (corr.), and was of a very pale yellow colour. Further drying was not necessary in this investigation, as the quantity of water present would be very small in comparison with that to be added later. The concentrations of sulphuric acid and oleum were determined by diluting weighed quantities to a known volume with water and titration with standard alkali. The stock of sulphuric acid was stored in stoppered bottles with ground caps, and each batch was standardised immediately before use.

The solubility of nitrobenzene in mixtures of sulphuric acid and water of various compositions was determined by slowly adding nitrobenzene to aqueous acid, or water to mixtures of sulphuric acid and nitrobenzene, according to the composition, until a permanent turbidity was observed. Determinations were carried out in melting ice and at 22° and 34° in a thermostat.

The tie-lines were determined by mixing suitable known weights of the three components in a separating funnel, and allowing the two layers to reach equilibrium in a thermostat at 22°. The acid content of each layer was then determined. It will be seen from the shape of the binodal curve that the determination of the acid content of each layer and a knowledge of the total composition of the mixture suffice to fix the positions of the tie-lines.

Solid Phases.—Three solid phases which can occur in this system at 0° are the compound $C_6H_5{\cdot}NO_2,H_2SO_4$, the hydrate H_2SO_4,H_2O, and anhydrous sulphuric acid. The compositions of solutions in equilibrium with the first two at 0° have been determined. Ternary mixtures of appropriate compositions were made up by weight in a boiling-tube and cooled to 0°. Crystallisation was initiated by dropping in small pieces of solid carbon dioxide, and the mixture was kept in melting ice in a vacuum flask and was stirred at frequent intervals until equilibrium was reached, usually for about 2 days. As much as possible of the solution was sucked off through a small glass-wool filter, and its acid content determined. This, in conjunction with a knowledge of the composition of the original mixture and of the solid phase, was sufficient to establish the composition of the solution without ambiguity. The positions of the intercepts of the solubility curves on the sides of the triangular diagram were taken from the published data (*locc. cit.*). The region in the diagram representing liquids in contact with anhydrous sulphuric acid is very small, and on that account has not been investigated, but its probable form is indicated by a broken line. For the same reason the solubility curve of the compound of nitrobenzene and sulphuric acid has not been followed to its end in the direction of high proportions of nitrobenzene.

Results.

The figures tabulated below (weights %) are represented graphically on a triangular diagram.

Binodal curves.

22°.		
H_2SO_4.	$C_6H_5{\cdot}NO_2$.	H_2O.
64·0	27·3	8·7
79·1	4·0	16·9
79·0	2·0	19·0
63·7	27·7	8·6
61·6	38·4	0·0
72·4	15·5	12·1
74·2	12·8	13·0
76·1	10·2	13·7
77·8	7·7	14·5
78·5	5·7	15·8
79·0	4·5	16·5
79·5	4·3	16·2
77·9	2·5	19·6
58·6	34·1	7·3
62·3	29·4	8·3
30·1	66·8	3·1
13·3	86·7	0·0
76·8	1·9	21·3
49·2	0·0	50·8

0°.		
H_2SO_4.	$C_6H_5{\cdot}NO_2$.	H_2O.
68·4	21·4	10·2
69·8	19·5	9·7
64·3	26·9	8·8
60·5	32·2	6·3
75·5	12·7	11·8
42·5	53·3	4·2
26·6	71·0	2·4
57·2	35·9	6·9
57·6	0·9	41·5
76·4	1·2	22·4
80·0	5·0	15·0

34°.		
74·9	0·5	24·6
79·4	4·6	16·0
72·4	16·1	11·5
64·3	27·2	8·5
54·4	39·7	5·9
77·9	2·0	20·1
78·3	6·4	15·3
74·2	13·5	12·3

Tie lines.

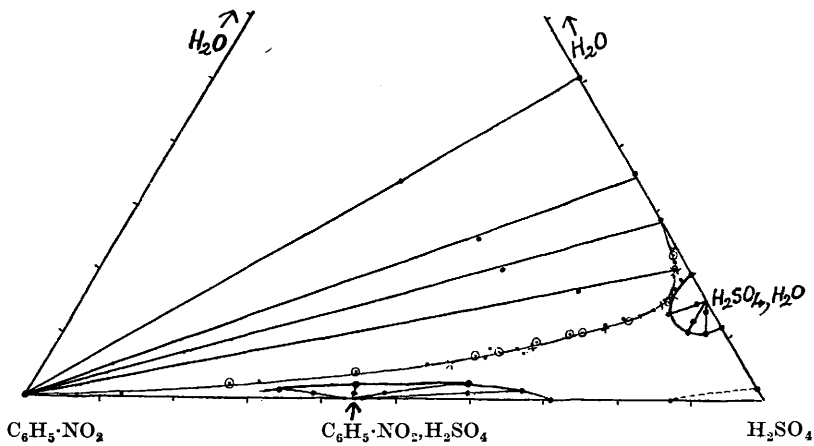
Total composition.			Acid in aqueous layer.	Acid in nitrobenzene layer.
H_2SO_4.	$C_6H_5{\cdot}NO_2$.	H_2O.		
66·3	16·7	17·0	78·1	0·0
33·4	32·4	34·2	49·4, 49·6	0·0
48·5	26·2	25·3	64·2, 64·6	0·0
54·1	25·7	20·2	71·8, 71·8	0·0

Solutions in equilibrium with H_2SO_4,H_2O.

	Total composition.		
Acid, %.	H_2SO_4.	$C_6H_5NO_2$.	H_2O.
79·7	83·1	1·9	15·0
86·2	85·0	0·9	14·1
83·9	84·1	3·2	12·7

Solutions in equilibrium with $C_6H_5{\cdot}NO_2,H_2SO_4$.

66·6	58·5	40·6	0·9
59·7	55·2	43·6	1·2
34·9	38·9	60·5	0·6
44·2	44·6	54·8	0·6



On binodal curve: points at 0°, ⊙; *at* 22°, ●; *at* 34°, ×.

The temperature coefficient of solubility of nitrobenzene in aqueous sulphuric acid is small, as shown by the fact that the same curve can be drawn through the points on the graph, within the limits of experimental error, at all three temperatures. From the flatness of the solubility curve of the solid compound $C_6H_5{\cdot}NO_2,H_2SO_4$ at 0° and from its m. p., 11·6° (Masson, *loc. cit.*), it follows that the slope of the solubility surface must be steep. These two facts are in agreement with Masson's observation that the heat of solution of the compound in water is small.

The unusual position of the tie-lines indicates that the compound is soluble in aqueous sulphuric acid but not in nitrobenzene, which is consistent with its salt-like properties. In no case was any titratable quantity of acid found in the layer rich in nitrobenzene. The composition of this layer must therefore lie on the side of the triangle representing $H_2SO_4 = 0\%$ as well as on the binodal curve. For this reason the tie-lines have all been drawn through that corner of the diagram and as nearly as possible through the other two points.

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