# CLXX.—*The System* cyclo*Hexanol and Water.*

By NEVIL VINCENT SIDGWICK and LESLIE ERNEST SUTTON.

WORK on this system had previously been done by de Forcrand, who, after obtaining *cyclo*hexanol in a purer condition than previous workers had done, measured several of its physical properties, including the freezing point and mutual solubility with water at 11° (*Compt. rend.*, 1912, **154**, 1327, 1767); he then investigated the binary system of the alcohol and water over a range of concentrations of *cyclo*hexanol from 89·86 to 100% by weight, and concluded from his results that a compound $C_6H_{12}O,\frac{1}{2}H_2O$ existed (*ibid.*, 1912, **155**, 118).

The present work is an investigation of the greater part of the system, the range of concentration of *cyclo*hexanol being 0—93% by weight, which is sufficient to include the two-liquid-phase region and most of the ice line.

## EXPERIMENTAL.

*Purification of* cyclo*Hexanol.*—The *cyclo*hexanol was obtained from British Drug Houses, Ltd., and purified by fractional distillations at a pressure of about 10 mm. of mercury, the head and tail fractions being rejected. Schreiner and Frivold (*Z. physikal. Chem.*, 1926, **124**, 1) claim to have obtained a product melting at 23·3—23·9° (de Forcrand gives 22·45°) by two fractionations at 2—3 mm., but in the present case no fraction melting higher than 20·6° could be obtained from successive fractionations (the m. p.'s being taken in the first receiver of the distillation apparatus itself). A solution of this *cyclo*hexanol in water gave no trace of a precipitate with bromine water, nor did it immediately destroy the bromine colour, indicating that no appreciable amount of phenol was present and that the most probable remaining impurity was water. Since the cryoscopic constant of *cyclo*hexanol is so large (382·8 according to de Forcrand), the m. p. of our specimen would correspond to a purity of 99·85% by weight, if 23·6° is taken as the true melting point; hence, as water was to be the other component and its concentration was not to be less than 7%, further purification was deemed unnecessary.

Owing to the extremely hygroscopic nature of the alcohol, stock solutions containing about 95% of it were used, as these were not at all hygroscopic.

*Measurement of Points in the Binary System.*—The points on the liquid–liquid curve were obtained by the usual synthetic method, sealed glass bulbs being used at the higher temperatures. When the proportion of *cyclo*hexanol was large, the temperature at which turbidity appeared increased with successive heatings, and, as this was presumably due to decomposition, the first reading was taken in such cases. It was found impossible to obtain points on this curve from 87·9% onwards, for, owing to the steepness of the curve after this point, the turbidity was extremely faint and no accurate determination of the temperature at which it occurred could be made.

The solid separation points over the range 88—93% of *cyclo*hexanol were difficult to obtain. since considerable supercooling was necessary before a solid would separate, and when this eventually occurred the temperature did not rise appreciably. However, by supercooling to produce the solid and then allowing the mixture to warm slowly, and noting at what temperature a trace of the solid could just be retained, approximate values (accurate probably to within 0·5°) were obtained. This difficulty did not arise in tracing the ice line from 0 to 5% of *cyclo*hexanol, for here, when supercooling ceased, there was the usual quick rise to a steady temperature.

The results obtained are given in the following tables and are plotted, together with those of de Forcrand, in Fig. 1.

(1) *The Ice Line.*

| *cyclo*Hexanol, % by wt. | M. p. | *cyclo*Hexanol, % by wt. | M. p. | *cyclo*Hexanol, % by wt. | M. p. |
|---|---|---|---|---|---|
| 1·67 | −0·3°, 0·32 | 88·3 | −1·2° | 90·45 | − 4·9° |
| 3·33 | −0·6 | 88·45 | −1·1 | 91·2 | − 7·6 |
| 5·00 | −0·9 | 89·0 | −2·0 | 92·3 | − 10·2 |
| | | 90·08 | −4·1 | 93·0 | − 15·4 |

(2) *The Liquid–Liquid Curve.*

| *cyclo*-Hexanol, % by wt. | Turbidity temp. | *cyclo*-Hexanol, % by wt. | Turbidity temp. | *cyclo*-Hexanol, % by wt. | Turbidity temp. |
|---|---|---|---|---|---|
| 3·18 | 40·45° & 70·45° | 4·29 | 15·2° | 52·3 | 183·66° |
| 3·19 | 45·8 & 66·3 | 4·41 | 11·2 | 59·4 | 180·1 |
| 3·26 | 40·4 | 4·55 | 12·0 | 68·0 | 169·7 |
| 3·37 | 31.85 & 82·4 | 4·58 | 9·7 | 68·5 | 168·64 |
| 3·41 | 33·6 | 4·78 | 9·4 | 70·1 | 163·03 |
| 3·52 | 27·55 | 5·00 | 7·2 | 74·6 | 150·35 |
| 3·57 | 28·7 | 5·14 | 121·95 | 80·2 | 130·9 |
| 3·75 | 24·6 | 9·22 | 156·9 | 85·3 | 93·63 |
| 3·82 | 20·8 | 15·00 | 174·3 | 85·95 | 72·75 |
| 3·95 | 20·6 | 19·2 | 179·4 | 86·75 | 71·5 |
| 4·09 | 16·3 | 32·4 | 184·72 | 87·9 | 51·55 |
| 4·23 | 14·2 | | | | |

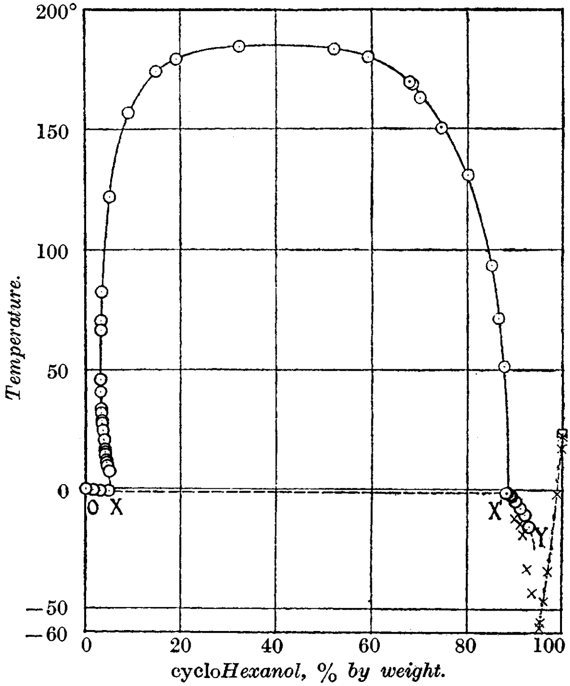
## *Discussion of Results.*

The liquid–liquid system has been examined for water and the following alcohols : *n*-butyl (Orton and Jones, J., 1919, **115**, 1194), *iso*butyl (Alexejew, *Wied. Ann.*, 1886, **28**, 305), *sec.*-butyl (*idem, ibid.* ; Dolgolenko, *Z. physikal. Chem.*, 1908, **62**, 499 ; Timmermanns, Thèse, Bruxelles, 1911), and *iso*amyl (Fontein, *Z. physikal. Chem.*, 1910, **73**, 212). All these resemble *cyclo*hexanol in showing reversed solubility curves on the water side, and all except *sec.*-butyl alcohol in not showing this on the alcohol side.

The existence of the solid hydrate described by de Forcrand (*loc. cit.*) was not confirmed. His solid curve resembles ours but is at a lower temperature, probably because supercooling was not sufficiently avoided. The rapid decrease of steepness of the slope of the curve YX′ as the two-liquid-phase region is approached is a consequence of the flattening out of the vapour pressure–concentration curve prior to becoming a straight line parallel to the concentration axis in this region itself (Sidgwick and Turner, J., 1922, **121**, 2262). There is no sign of a maximum at the concentration corresponding to the composition $C_6H_{12}O,\frac{1}{2}H_2O$ (91·74% *cyclo*hexanol) or of a sharp discontinuity after it; moreover, since a mixture whose total composition lies between X and X′ can be in equilibrium with

FIG. 1.

*The system* cyclo*hexanol and water.*



*Present research* —○—. *Schreiner and Frivold* —□—. *de Forcrand* - · - × - · -

only one solid phase, the solid separating out along either OX or X′Y must be the same substance and, since there is no eutectic in OX, this substance must be ice. Its appearance agreed with that given by de Forcrand, *viz.*, "small opaque crystals." The occurrence of some combination in solution between the alcohol and the water may, however, be assumed to be probable from the existence of the reverse solubility curve.

Our thanks are due to Imperial Chemical Industries, Ltd., for a grant towards the cost of this work.

THE DYSON PERRINS LABORATORY,
OXFORD.

[*Received, April* 29*th*, 1930.]