

RECENT REDETERMINATIONS OF THE PHASE DIAGRAM OF THE SYSTEM: TRIETHYLAMINE + WATER

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Liquid mixtures which exhibit a lower critical solution temperature are of two types. The first type contains liquid pairs in which there is a great difference in molecular size between the two components¹. The second, and by far the larger, group contains those in which interaction between the components occurs by means of a hydrogen bond. Triethylamine + water falls into the second group.

The system triethylamine + water has been very widely studied, the earliest work having been done in 1884. Since then a number of determinations of the phase diagram has been made, but later work has only been distinguished by the large number of different results that has been obtained. In *Figure 1* several earlier diagrams are illustrated.

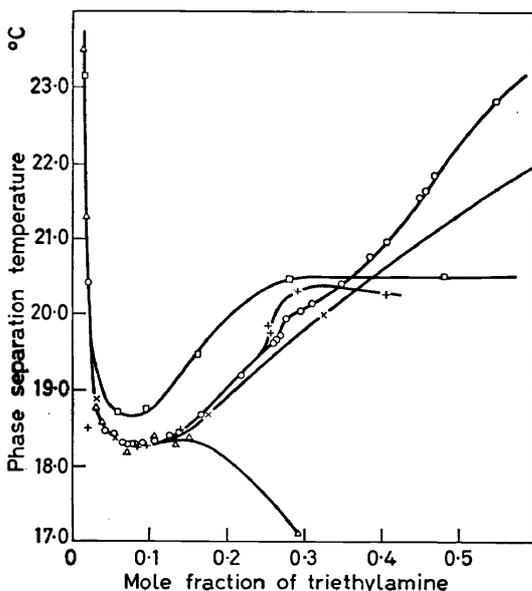


Figure 1. Previous results for the system: triethylamine + water: Δ Guthrie²; \square Rothmund³; \times Roberts and Mayer⁴; $+$ Copp⁵; \circ Counsell⁶

It is well known that the exact shape of a phase diagram is a sensitive criterion of the purity of the materials used. It therefore seems likely that the variety of results can be traced to lack of attention to the purity of the samples.

In recent years a number of redeterminations of the phase diagram has been made and, while the general shape has become clear, it seems of interest to redetermine it so as to eliminate any final points of doubt.

It has been noticed by previous workers that, even after rigorous purification of the components and sealing of the samples under vacuum in glass ampoules, the phase separation temperature decreases with time. In *Figure 2* are shown the results with a set of initially pure samples sealed *in vacuo* in "Pyrex" glass by J. F. C. and re-examined eighteen months later by R. J. M. The lowering of the phase separation temperature was probably caused by solution of the glass of the sample tube, leading to the introduction of a small quantity of silicate ion which in turn affected the phase diagram.

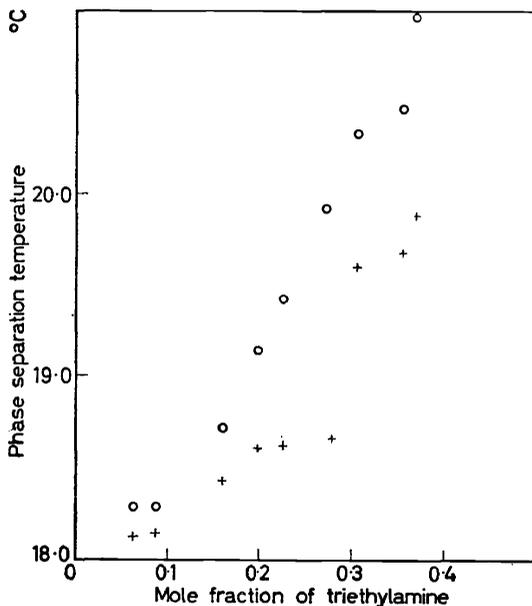


Figure 2. ○ initial results (J. F. C.); + results with same samples 18 months later (R. J. M.)

The most recent determination of the phase diagram has been made using composite tubes of "Pyrex" and silica glass. However, the phase separation temperature still exhibited a small time dependence. This, it was felt, could be traced to contact of the vapour phase and the "Pyrex" glass of the upper half of the sample tube. In view of these facts, our latest samples have been prepared in all-silica tubes.

EXPERIMENTAL

Materials

The triethylamine was high purity material obtained from B.D.H. and contained small quantities of lower amines. The material was refluxed with *p*-toluenesulphonyl chloride and potassium hydroxide to remove primary and secondary amines. The colourless amine was then fractionated from metallic sodium under a reflux ratio of approximately 15 : 1.

PHASE DIAGRAM OF TRIETHYLAMINE AND WATER

Following Copp⁵, the fractions accepted from the final distillate were those for which the corrected condensation temperature at the still head was $t^{\circ}\text{C}$, where t is given by $(t - 89.50) = 0.042 (P - 760)$, P the atmospheric pressure in turn being corrected to standard conditions. The temperature at the still head could be controlled to $\pm 0.01^{\circ}\text{C}$.

The water used in all experiments was conductivity water with a specific conductance of $4 \times 10^{-7} \Omega \text{ cm}$.

The samples were prepared by distilling weighed quantities of the liquids into the silica sample tube under high vacuum. Before the final distillation into the sample tube, the liquids were degassed by frequent melting and freezing under vacuum. The sample tube was cleaned with chromic acid, nitric acid and distilled water, then baked out at 400°C for twelve hours.

The phase separation temperature of a sample was found by placing the silica tube, attached to the bulb of a large mercury-in-glass calorimeter thermometer, inside an unsilvered Dewar vessel, which in turn stood in a large thermostat. Both the Dewar and thermostat were fitted with efficient stirrers. By a judicious selection of the temperature in the thermostat, it was possible to raise the temperature in the Dewar at the rate of 0.1°C an hour. The observation of the phase separation temperature presented no particular problems. The phase separation temperature was taken as that at which the first heterogeneity appeared in the sample.

In order to minimize any effects due to contact between the sample and the silica vessel, the phase separation temperature was determined as shortly after the sample's preparation as possible. In retrospect this precaution seems to have been unnecessary as the phase diagram determined 18 months later with the same samples showed a maximum fall of 0.08°C in the phase separation temperature at the highest amine concentration.

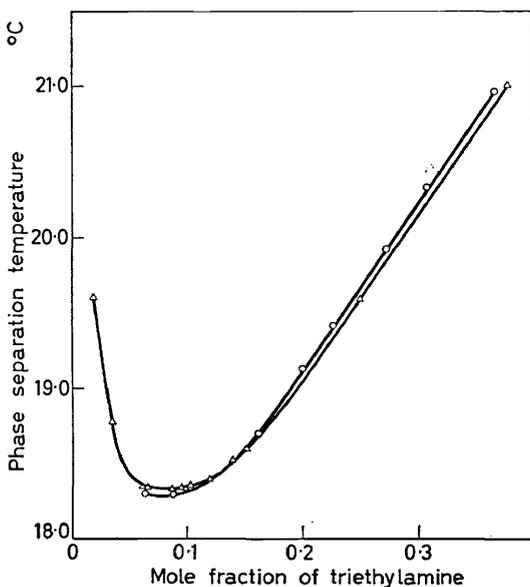


Figure 3. Δ Kohler and Rice⁷; \circ present work

RESULTS

In *Figure 3* the results of the present work are compared with those of Kohler and Rice⁷. The agreement with the work of Kohler and Rice is very satisfactory.

References

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- ⁷ F. Kohler and O. K. Rice. *J. Chem. Phys.*, **26**, 1614 (1957)