[CONTRIBUTION FROM THE NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS AIRCRAFT ENGINE RESEARCH LABORATORY]

# The System Cyclopentane–Neohexane–Aniline

BY K. T. SERIJAN, R. A. SPURR AND L. C. GIBBONS

The possibility of the purification of commercial cyclopentane by extraction with aniline led to the investigation of the ternary system cyclopentane–neohexane–aniline. Analysis of the commercial hydrocarbon mixture based on physical constants showed neohexane to be the only contaminant. This was in agreement with the assumption made by Tooke who investigated similar material.[1] The proximity of the boiling points of these two hydrocarbons eliminated the feasibility of purification by fractional distillation.[2] The use of aniline as a solvent for similar hydrocarbon mixures has been previously described.[3,4]

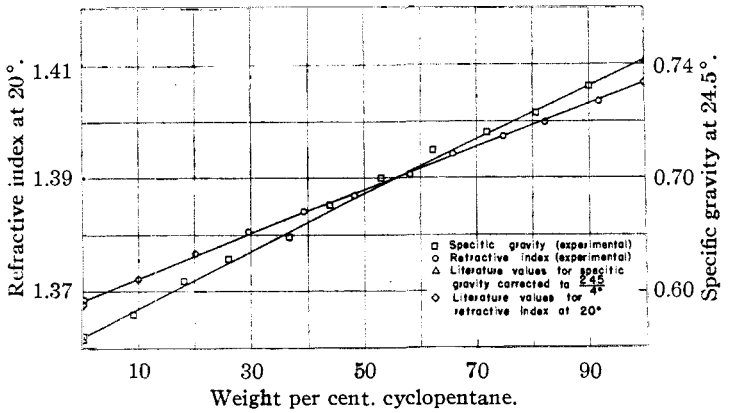


Fig. 1.—Variation of specific gravity and refractive index with weight per cent. cyclopentane in mixtures with neohexane at 24.5°.

## Experimental

### Materials

**Commercial Cyclopentane.**—Purchased from Phillips Petroleum Company. Fractionation of the material on a 50-theoretical plate column gave very little separation of the impurity. The material used in the determination of the phase diagrams was distilled through a 12-inch Vigreux column. The physical constants were identical with those of the original material: $n^{20}D$ 1.4029, $d^{20}_4$ 0.7364; • literature values for pure cyclopentane, $n^{20}D$ 1.4064, $d^{20}_4$ 0.7454.[2]

**Neohexane.**—Obtained from the same source and triply distilled before use; $n^{20}D$ 1.3691 and $d^{20}_4$ 0.6501, indicating a reasonable degree of purity; literature constants, $n^{20}D$ 1.3688 and $d^{20}_4$ 0.6492.[2]

**Aniline.**—J. T. Baker C. P. material was used which, after distillation, had the values $n^{20}D$ 1.5858 and $d^{20}_4$ 1.0228.

### Method

Commercial cyclopentane and neohexane were mixed in various proportions. The refractive index and specific gravity values of the mixtures are shown in Fig. 1. The latter values for

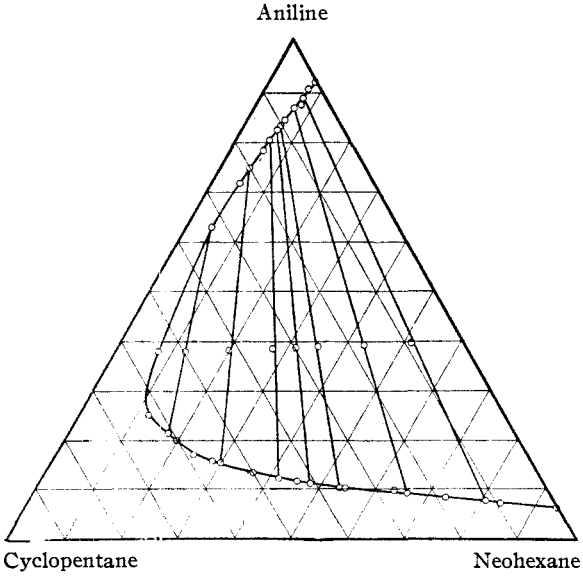


Fig. 2.—Solubility and composition of conjugate liquids (weight percentage) for the system cyclopentane–neohexane–aniline at 25°.

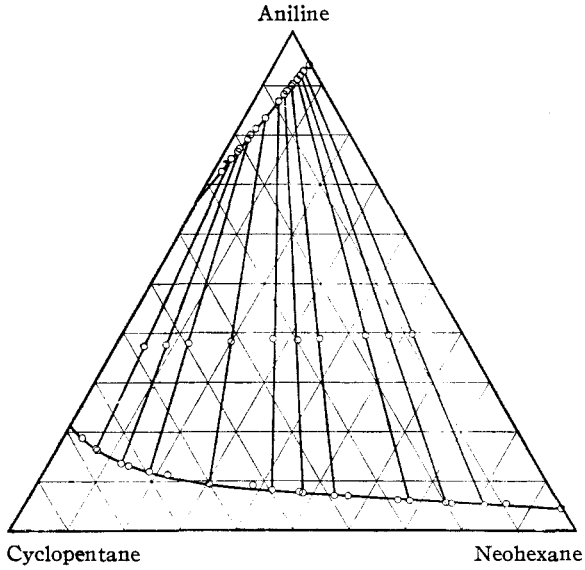


Fig. 3.—Solubility and composition of conjugate liquids (weight percentage) for the system cyclopentane–neohexane–aniline at 15°.

(1) Tooke, *Ind. Eng. Chem.*, **35**, 992 (1943).

(2) Doss, "Physical Constants of the Principal Hydrocarbons," 4th ed., The Texas Company, New York, N. Y., 1943, pp. 1, 110.

(3) Varteressian and Fenske, *Ind. Eng. Chem.*, **29**, 270 (1937).

(4) Darment and Winkler, *J. Phys. Chem.*, **47**, 442 (1943).

the pure hydrocarbons were corrected to 24.5°.[5,6] Calculations were then made using these data in order to determine the composition of the commercial hydrocarbon.

Mixtures of known weight ratios of cyclopentane and neohexane were made up and placed in large test-tubes in a thermostated water-bath with a temperature control of ±0.05°. Aniline was then added with stirring from a water-jacketed buret at the same temperature. The amount of aniline used in each titration to the point of turbidity fixed the lower portion of the two-phase boundary of the phase diagram (Figs. 2 and 3). Similarly, known weights of aniline were placed in the test-tubes and mixtures of known weight ratios of cyclopentane and neohexane were added to obtain turbidity. The amount of hydrocarbon used fixed the upper portion of the two-phase boundary. Refractive indices were taken of the resulting mixtures at 25° in the case of the 25° diagram and at 20° in the case of the 15° diagram. When plotted against appropriate composition parameters, these indices serve to identify the composition of the top and bottom layers in the mixtures made up to determine the tie lines.

The data, as expressed by the tie lines, were obtained by selecting three-component mixtures whose compositions are shown by the points in the two-phase region. The mixtures were held at constant temperature for seventy-two hours with occasional agitation.

The data for the solubility curves and the compositions of conjugate liquids are shown in Tables I and II.

TABLE I

SOLUBILITY DATA AND THE COMPOSITION OF CONJUGATE LIQUIDS AT 25°

| Hydrocarbon layer (weight per cent.) Cyclopentane | Neohexane | Refractive index, $n^{25}D$ | Solvent layer (weight per cent.) Cyclopentane | Neohexane | Refractive index, $n^{25}D$ |
|---|---|---|---|---|---|
| Solubility Data | | | | | |
| 0.0 | 93.8 | 1.3765 | 0.0 | 8.1 | 1.5646 |
| 9.5 | 83.5 | 1.3812 | 1.9 | 7.5 | 1.5625 |
| 18.5 | 73.3 | 1.3861 | 4.8 | 7.5 | 1.5562 |
| 27.0 | 63.2 | 1.3903 | 6.5 | 6.8 | 1.5528 |
| 35.3 | 54.4 | 1.3954 | 8.9 | 6.5 | 1.5498 |
| 43.0 | 45.4 | 1.4006 | 16.3 | 5.5 | 1.5355 |
| 50.1 | 36.8 | 1.4068 | 23.7 | 4.7 | 1.5272 |
| 55.9 | 28.2 | 1.4124 | 32.4 | 4.6 | 1.5187 |
| 58.6 | 24.2 | 1.4162 | | | |
| 60.0 | 19.9 | 1.4212 | | | |
| 60.6 | 15.8 | 1.4268 | | | |
| 62.3 | 12.3 | 1.4332 | | | |
| 54.5 | 7.7 | 1.4550 | | | |
| Composition of Conjugate Liquids (extremities of tie lines) | | | | | |
| 0.0 | 93.8 | 1.3765 | 0.0 | 8.1 | 1.5646 |
| 11.9 | 80.5 | 1.3824 | 3.7 | 7.1 | 1.5581 |
| 25.1 | 65.9 | 1.3892 | 6.4 | 6.7 | 1.5531 |
| 36.3 | 53.4 | 1.3960 | 10.3 | 6.1 | 1.5460 |
| 40.9 | 48.0 | 1.3988 | 11.7 | 5.9 | 1.5437 |
| 45.7 | 42.0 | 1.4027 | 13.9 | 5.6 | 1.5413 |
| 54.6 | 30.0 | 1.4113 | 20.0 | 4.9 | 1.5321 |
| 60.8 | 17.7 | 1.4238 | 32.5 | 4.5 | 1.5188 |

## Results and Discussion

The refractive index and specific gravity values of the mixtures shown in Fig. 1 were found to be linear with respect to composition. The extrapolated value for cyclopentane agreed with the literature value for the pure hydrocarbon. The assumption that the impurity was largely neohexane was thereby substantiated. The calculated composition of the commercial hydrocarbon using these data gave identical results using either the refractive index or the specific gravity value, namely, 91.8% cyclopentane and 8.2% neohexane by weight. These values were used in the calculation of composition of all known mixtures in the determination of the phase diagrams.

The refractive indices of the two phases corresponding to the ends of the tie lines were found to be in agreement within experimental error with those determined for the turbid boundary mixtures of known composition. The $\beta$ values[3] for this system representing the ratio of cyclopentane to neohexane in the extract layer to the same components in the raffinate layer were 2.37 ± 0.14 at 25° and 1.68 ± 0.15 at 15°.

(5) Egloff, "Physical Constants of Hydrocarbons," Vol. I, Reinhold Publishing Corporation, New York, N. Y., 1939, p. 38.

(6) Egloff, *ibid.*, Vol. II, 1940, p. 54.

TABLE II

SOLUBILITY DATA AND THE COMPOSITION OF CONJUGATE LIQUIDS AT 15°

| Hydrocarbon layer (weight per cent.) Cyclopentane | Neohexane | Refractive index, $n^{20}D$ | Solvent layer (weight per cent.) Cyclopentane | Neohexane | Refractive index, $n^{20}D$ |
|---|---|---|---|---|---|
| Solubility Data | | | | | |
| 0.0 | 95.9 | 1.3770 | 0.0 | 6.1 | 1.5705 |
| 9.7 | 85.1 | 1.3815 | 0.7 | 6.0 | 1.5697 |
| 19.1 | 75.4 | 1.3857 | 1.5 | 5.9 | 1.5685 |
| 28.1 | 65.8 | 1.3898 | 2.4 | 5.7 | 1.5664 |
| 36.7 | 56.5 | 1.3939 | 3.6 | 5.5 | 1.5642 |
| 45.0 | 47.4 | 1.3982 | 4.9 | 5.1 | 1.5632 |
| 52.3 | 38.4 | 1.4030 | 6.7 | 4.9 | 1.5588 |
| 60.0 | 30.3 | 1.4071 | 9.0 | 4.5 | 1.5554 |
| 66.5 | 22.0 | 1.4128 | 11.0 | 3.7 | 1.5522 |
| 72.4 | 14.3 | 1.4179 | 15.8 | 3.1 | 1.5435 |
| 76.7 | 6.9 | 1.4251 | 18.5 | 2.6 | 1.5382 |
| 77.9 | 3.2 | 1.4302 | 21.7 | 2.0 | 1.5320 |
| | | | 26.4 | 1.1 | 1.5246 |
| Composition of Conjugate Liquids (extremities of tie lines) | | | | | |
| 0.0 | 95.9 | 1.3770 | 0.0 | 6.1 | 1.5705 |
| 13.5 | 81.5 | 1.3830 | 1.7 | 5.6 | 1.5678 |
| 19.9 | 74.7 | 1.3859 | 2.7 | 5.5 | 1.5660 |
| 26.2 | 67.9 | 1.3888 | 3.7 | 5.3 | 1.5641 |
| 39.0 | 54.0 | 1.3951 | 5.4 | 4.9 | 1.5611 |
| 44.1 | 48.2 | 1.3978 | 7.3 | 4.5 | 1.5575 |
| 49.3 | 42.5 | 1.4015 | 8.9 | 4.3 | 1.5555 |
| 60.0 | 30.3 | 1.4080 | 13.0 | 3.7 | 1.5470 |
| 69.4 | 18.5 | 1.4150 | 17.5 | 2.8 | 1.5400 |
| 73.4 | 12.8 | 1.4195 | 20.9 | 2.1 | 1.5340 |
| 76.5 | 7.1 | 1.4245 | 23.4 | 1.4 | 1.5298 |

## Summary

The ternary system cyclopentane–neohexane–aniline has been investigated experimentally at 25 and 15°. Data for the solubility curves and the composition of conjugate liquids and the phase diagrams are given.

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