

654. *The Determination of Thionaphthen in Naphthalene by Infra-red Absorption Spectroscopy.*

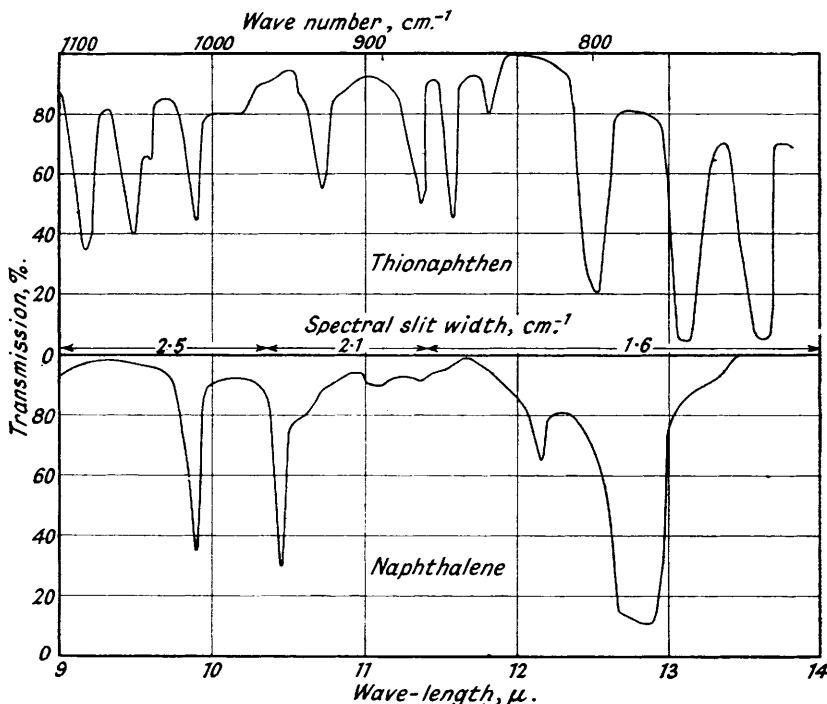
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The infra-red absorption spectra of naphthalene and thionaphthen have been recorded between 9 and 14 μ . The band at 9.48 μ . affords a means of determining thionaphthen in naphthalene. The melting point of pure naphthalene is 80.32°.

THIONAPHTHEN is the main impurity in commercially pure crystal naphthalene. Infra-red absorption spectroscopy affords a convenient method of determining this impurity.

Fig. 1 shows the absorption spectra of 10% solutions of pure naphthalene and thionaphthen in carbon disulphide, obtained on using a cell of nominal thickness 0.14 mm.

FIG. 1.*



The positions of the main naphthalene bands agree with the results of Lambert and Lecomte (*Ann. Physique*, 1932, 18, 366), but the shoulder at 12.15 μ . has been resolved as a band, and the weak band at 10 μ . is found to be at 9.9 μ . and much stronger. There appear to be no previous data for thionaphthen.

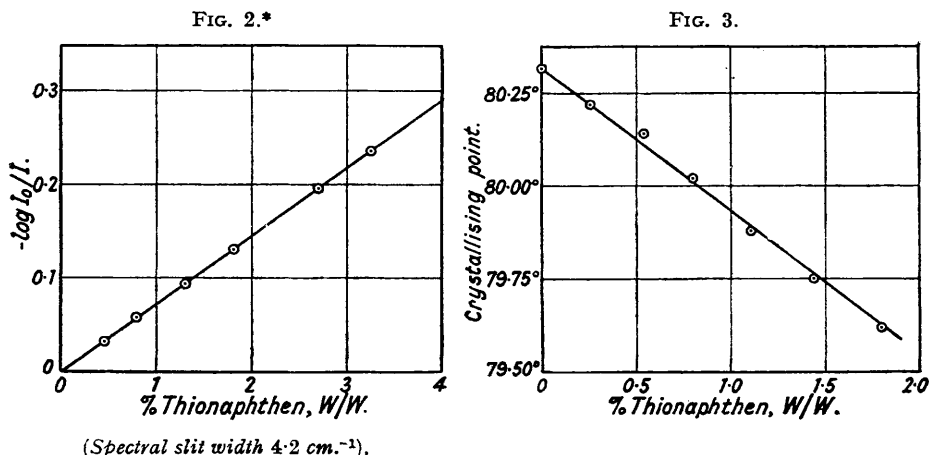
Naphthalene shows almost 100% transmission in the region 9.0 to 9.7 μ ., whereas thionaphthen shows absorption bands at 9.17 and at 9.48 μ .. Further investigation of this region, with molten naphthalene at 100° in a thicker hot cell (nominal thickness 0.56 mm.), showed that naphthalene has a weak band at 9.22 μ . but very little absorption at 9.48 μ ., so this second band was selected for analysis.

Fig. 2 shows the linear Beer's law curve obtained for synthetic mixtures of thionaphthen and naphthalene. I_0 and I are the transmitted energies with pure naphthalene and the synthetic mixture in the cell.

Investigation of a sample of commercial naphthalene showed 1.30% of thionaphthen, agreeing fairly well with the figure of 1.26% calculated from the measured sulphur content of 0.30%. This suggests that the bulk of the sulphur is present as thionaphthen.

* The spectral slit widths in Figs. 1 and 2 are quoted in American units, *i.e.*, they represent half the frequency range passed by the exit slit and should be doubled to conform with British practice.

Fig. 3 shows the relation between the crystallising point and the thionaphthen content of naphthalene for synthetic mixtures. For a thionaphthen content of 1.30%, as found for the



sample of crystal naphthalene, the crystallising point should be 79.84°, whereas the value found was 79.70°. This suggests the presence of smaller amounts of other impurities believed to be mainly methylnaphthalenes.

EXPERIMENTAL.

The spectroscope used was a single-beam instrument, essentially similar to that used by Whiffen and Thompson (*J.*, 1945, 268), except that the light from the exit slit was focused on the thermopile by an ellipsoidal mirror of focal lengths 30.0 and 5.9 cm. The instrument was calibrated with the bands of methylcyclohexane and 1-methylnaphthalene, using the A.P.I. data, and the atmospheric carbon dioxide bands at 14.97 and 13.9 μ .

Amalgamated lead shims were used in the cold cell, with an outer coating round the seal of "Cerrite" lacquer. The hot cell was as described by Richards and Thompson (*Trans. Faraday Soc.*, 1945, 41, 183). All results were corrected for zero drift and for scattered radiation. The data for Fig. 2 were obtained by direct reading of the galvanometer deflection at the preset wave-length.

Commercial crystal naphthalene was heated at 145° for 18 hours with 5% of sodamide, and the residual liquid was fractionated through a 15-inch column, packed with glass helices and jacketed with naphthalene vapour at the boiling point. The sulphur content was reduced to 0.01%. A second treatment reduced the sulphur to less than 0.005%. The product was recrystallised twice from redistilled methanol, and refractionated. The crystallising point was 80.32° (contrast usually accepted value of 80.2°).

"Research-grade" thionaphthen (ex Messrs. Light) was found to have a sulphur content of 23.93% (Carius), compared with the theoretical 23.90%. It had m. p. 31.3°, as had a sample synthesised by the method of Hansch and Blondin (*J. Amer. Chem. Soc.*, 1948, 70, 1561) purified by way of the mercuric acetate derivative and sublimed. It was accordingly used without further purification.

Sulphur in naphthalene was determined by the Grote-Krekeler method. Check tests with pure sulphur and with thionaphthen added to naphthalene gave results 3% low, so that an empirical factor of 1.03 was applied.

Crystallising points were measured with a thermometer graduated in fifths of a degree calibrated by the N.P.L. The emergent-steam correction was determined experimentally.

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* See footnote, p. 3359.