[CONTRIBUTION FROM THE COLOR LABORATORY, BUREAU OF CHEMISTRY, UNITED STATES DEPARTMENT OF AGRICULTURE, No. 124]

STUDIES IN VAPOR PRESSURE. IV. THE NAPHTHOLS

BY ORVILLE E. MAY, J. F. T. BERLINER AND D. F. J. LYNCH

RECEIVED OCTOBER 22, 1926 PUBLISHED APRIL 7, 1927

Introduction

Among the more important dye intermediates for which data on vapor pressures are very meager, are the α- and β-naphthols. A search through the literature reveals a few vapor pressures calculated from the boiling points reported over fifty years ago and apparently never confirmed by subsequent investigations. This condition is surprising in view of the fact that the naphthols entered into commerce in the United States to the extent of approximately 2000 tons in 1924, according to the dye census of the Department of Commerce.

The investigation reported here was undertaken to supply this deficiency. It comprises a determination of the vapor pressures of the naphthols between their melting and boiling points at atmospheric (760 mm.) pressure, the derivation of their latent heats of vaporization and the calculation of their entropies of vaporization. The method used was identical with that described by the authors[1] in a previous paper of this series.

Materials

The naphthols used in this investigation were the purest procurable and were further purified as outlined in the following procedures.

The α-naphthol was recrystallized twice from pure benzene and was then suspended in water and distilled with steam. The recovered product was again steam distilled, filtered, dried and recrystallized twice from boiling water; m. p., 95.8–96.0°. The purified product was then recrystallized twice from pure benzene; m. p., 95.8–96.0°.

The β-naphthol was recrystallized twice from toluene. About 50 g. of the recrystallized product was then washed with 100 cc. of a mixture of equal parts of toluene and petroleum ether and finally with 50 cc. of petroleum ether. About 40 g. of the purified naphthol was recovered, and with this material the above operations were repeated. The β-naphthol obtained was then suspended in water and distilled with steam, filtered, dried and recrystallized thrice from boiling water; m. p., 122.0–122.2°. Three recrystallizations from toluene did not alter this melting point. The purified naphthols were kept in bottles covered with heavy paper, until ready for use, as they tend to decompose to a slight extent when exposed to light.

Results

A series of determinations of the vapor pressures was made from a few degrees above the melting point to a few degrees above the boiling point of each of the naphthols. The pressures were brought to equilibrium and read at approximately 10° intervals on each determination. Five runs

[1] Berliner and May, THIS JOURNAL, 47, 2350 (1925).

were made on each of the compounds and the temperatures were so regulated that when the work on each substance was finished, a complete series of vapor-pressure readings at about 2° intervals was obtained. Different samples were used in three of the runs on each compound and the agreement between the several determinations was quite satisfactory. The results of the observations were plotted on coördinate paper one meter square. No difficulty was experienced in drawing a smooth curve through the experimental points which accurately represented the data (Fig. 1).[2]

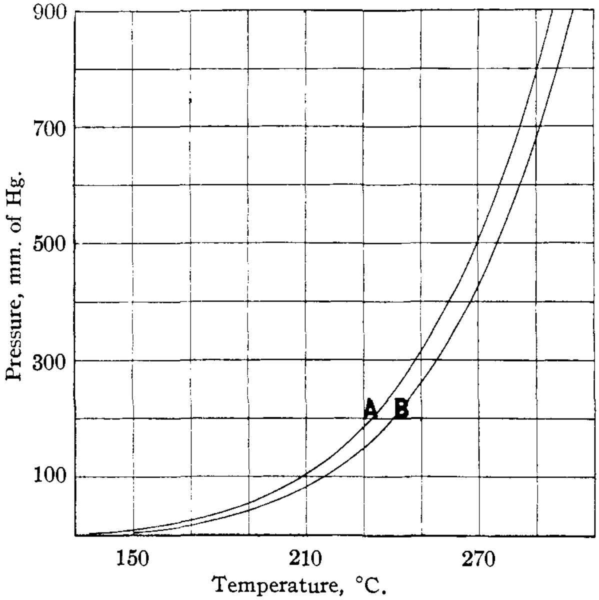

Fig. 1.—Vapor pressure-temperature curves of α- and β-naphthol.

The naphthols decompose to a slight extent at the temperatures of their boiling points at atmospheric pressure, with the formation of tarry compounds. The beta modification undergoes the greater decomposition. The amount of decomposition seemed to depend on the length of time the compounds were held at the temperatures mentioned. By rapid and careful manipulation, vapor pressures could be measured at temperatures several degrees above the boiling points at atmospheric pressure, for when the temperature was raised rapidly enough and the pressure brought to equilibrium quickly, the decomposition did not affect the results to a measurable degree. This was demonstrated by rapidly cooling the samples of each of the naphthols from the temperatures a few degrees above their

---

[2] Copies of tables giving actual vapor-pressure determinations at temperature intervals of 5° for the naphthols may be obtained by application to the Research Information Service of the National Research Council, Washington, D. C.

boiling points to temperatures a few degrees above their melting points, and then repeating the vapor-pressure determination. While lowering the temperature the pressure was also lowered at such a rate as to prevent the ingress of any air or gas into the bulb of the isoteniscope. The results of these experiments agreed with those obtained when fresh samples were used, indicating that with proper control the decomposition was too small appreciably to affect the true values for the vapor pressures of these compounds.

There are few boiling points of the naphthols recorded in the literature. Schaeffer[3] reports a boiling point of 278–280° for α-naphthol and one of 285–290° for β-naphthol, but unfortunately he does not describe the conditions under which these measurements were made and does not state whether the temperatures are corrected. Ebert and Merz[4] report a boiling point of 285–286° for β-naphthol. Beilstein gives 278–280° and 285–286° as the boiling points of α- and β-naphthol, respectively, and cites Schaeffer, and Ebert and Merz as authorities. All of the handbooks of chemistry and most of the organic chemistry textbooks, including the more important works on dye intermediates, give values identical with those found in Beilstein. The only exceptions are a value of 282° for α-naphthol and one of 288° for β-naphthol, but the literature did not reveal the original articles responsible for these two values.

The boiling points found in this investigation were 288.01° for α-naphthol and 294.85° for β-naphthol. The wide difference between our values and those previously reported occasioned much surprise and a survey was undertaken to ascertain any possible source of error in our work. A thorough examination of the apparatus showed that it was functioning properly. The thermocouple used throughout this investigation was carefully recalibrated. The constants obtained agreed perfectly with those resulting from previous calibrations. The methods of purification were sufficiently exhaustive to preclude the introduction of an error of such magnitude from that source. The values found for the boiling points as a result of our vapor-pressure determinations were accordingly assumed to be correct and a search was begun for some factor in the older measurements which would satisfactorily explain the discrepancy between the two sets of values. The temperature measurements of the earlier investigators suggested the most probable source of error, especially when it is recalled that the omission of an emergent stem correction for the usual long-stemmed thermometer in the region of 300° amounts to approximately 10°, which is almost exactly the discrepancy observed. To test this conclusion, some of the α-naphthol was introduced into a 50cc. distillation flask which was fitted with a long-stemmed, calibrated thermometer

---

[3] Schaeffer, *Ann.*, **152**, 281 (1869).

[4] Ebert and Merz, *Ber.*, **9**, 611 (1876).

graduated to 360°. On distillation the naphthol was found to boil at 278° at a pressure of 760 mm. of mercury after the correction from the calibration had been applied, but with no emergent stem correction. Further to confirm our values, each of the naphthols was distilled, the temperature being measured by an Anschutz thermometer which had been accurately calibrated at the United States Bureau of Standards. The thermometer was adjusted so that the thread of mercury was totally immersed in the vapors of the boiling liquid, thus entirely eliminating any stem correction. After the calibration correction had been applied, the boiling points of the naphthols were found to agree within 0.1° with the values found by the vapor-pressure method.

Undoubtedly many of the values given in the literature for the boiling points of the higher-boiling organic compounds are uncorrected and are incorporated in handbooks and textbooks as correct values, when they may be in error by as much as 10°. It cannot be too strongly urged that when a boiling point is reported in an original paper it should be the corrected value or else all the conditions under which the observations were made should be described. If this suggestion were followed, the confusion which now exists in the field of boiling-point measurements would soon disappear.

There are few vapor-pressure values for the naphthols on record. The closest approach to a complete vapor-pressure curve for these compounds is given by Rechenberg,[5] who calculated the vapor pressures of the naphthols, employing a modification of the Dühring relation. As he used the boiling points of the naphthols recorded in the literature as a basis for his calculations, however, his values differ widely from those recorded in this paper.

The equations for the vapor pressures and latent heats of vaporization of the naphthols have been derived from the observed pressures and temperatures by means of the Clapeyron-Clausius equation and are given, together with the calculated boiling points, in Table I.

TABLE I

EQUATIONS FOR VAPOR PRESSURES AND LATENT HEATS OF VAPORIZATION

	Heat of vaporization	Vapor-pressure equation	B. p., °C., at 760 mm.
α-Naphthol	$L = 21557.0 - 14.874T$	$\text{Log } P = 31.85686 - \frac{4711.1}{T} - 7.48624 \log T$	288.01
β-Naphthol	$L = 18923.8 - 8.80292T$	$\text{Log } P = 22.36521 - \frac{4135.6}{T} - 4.43048 \log T$	294.85

It should be pointed out that the foregoing equations were derived primarily to fit the observed data and cannot be used to calculate the entire vapor-pressure curve. The reason for this is obvious when we con-

---

[5] Rechenberg, "Einfache und Fraktionierte Distillation," Schimmel and Co., Leipzig, 1923.

sider that the latent heat of vaporization follows a straight line only over a relatively short range of temperature, and as the temperature is increased the curve expressing L becomes steeper, until at the critical temperature it would be nearly perpendicular to the temperature axis. For this reason these equations cannot be used for calculating critical temperatures and pressures and would be unreliable either much above or below the range of temperatures and pressures given in Fig. 1.

The entropies of vaporization have been calculated in order to determine whether the naphthols form normal or polar liquids. They are found by dividing the latent heat of vaporization at the absolute temperature T, at which the concentration of the vapors is 0.00507 mole per liter, by the product RT. The entropy of vaporization, according to Hildebrand,[6] should be about 13.7 cal. per degree for normal liquids.

TABLE II

ENTROPIES OF VAPORIZATION OF THE NAPHTHOLS ($L/RT = S$)

	Temp. obs., °C.	S
α-Naphthol	477.55	15.2
β-Naphthol	484.60	15.2

Table II shows that the entropies of vaporization of the naphthols do not approach the values of 13.7. Therefore, the naphthols apparently do not form normal liquids.

Summary

The vapor pressures of α-naphthol and β-naphthol have been determined from temperatures a few degrees above their melting points to temperatures a few degrees above their boiling points. Their boiling points at atmospheric pressure were found to be 288.01° and 294.85°, respectively.

The latent-heat equations have been derived, and the calculated and observed results correspond closely.

The entropies of vaporization of the naphthols at a concentration of 0.00507 mole per liter have been calculated. They indicate that the naphthols do not form normal liquids.

WASHINGTON, D. C.

---

[6] Hildebrand, THIS JOURNAL, **37**, 970 (1915).