[JOINT CONTRIBUTION FROM MELLON INSTITUTE AND THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF PITTSBURGH]

# Some Physical Properties of 2-Picoline

BY HENRY FREISER[1] AND WILLIAM L. GLOWACKI[2]

Most of the work reported here was done as a part of an extensive program sponsored by the Koppers Company for the determination of physical constants of coal tar bases, A number of factors pointed to the need for this program. Interest in 2-picoline and other tar bases has mounted in recent years. Much of the physical constant data necessary for their full exploitation are either lacking or old. With large amounts of materials available it seemed desirable to purify 2-picoline carefully and redetermine its physical properties.

**Purification of 2-Picoline.**—Over two liters of commercial 2-picoline (Koppers Company 2° alpha picoline) was subjected to a careful fractional distillation at atmospheric pressure by means of a 40-in rectifying column of one-inch inner diameter, packed with 3/32 in. Fenske stainless steel helices. The temperature of the distilling picoline was measured with a single-junction copper–constantan thermocouple and a portable potentiometer. The product was collected at a rate of 30 ml./hr. Thirty-seven fractions of 50 ml. each, boiling within 0.1°, were collected. The distillate was protected from atmospheric moisture and carbon dioxide by a stream of dry nitrogen and was later stored in a dry box. The cuts were examined preparatory to further purification by the determination of the freezing points of selected fractions.[3] The freezing points of cuts 7–36 (*ca.* 1500 ml.) were substantially constant at −66.63° and of a purity estimated from the melting point slope of 99.76 mole %.

Distillation cuts 6–39 were further purified by crystallization and centrifugation. The recrystallized 2-picoline was dehydrated by distillation in the one-inch laboratory column, most of the material distilling over a 0.05° range. The purity of this material, which was used in the determination of the physical properties, was estimated from its melting point curve slope to be 99.85 mole %. It is of interest to note that the dehydration distillation data of the recrystallized picoline indicated that the total moisture picked up during the entire series of manipulations involved in the recrystallization was somewhat less than 0.5 weight % (the mother liquor fraction may have more than this amount). The literature reports about the extreme hygroscopicity of 2-picoline and perhaps those about the other tar bases may be somewhat in error.

## Experimental

### Determination of Properties

**Freezing Point.**—The apparatus and procedure was essentially a modification of that in use at the National Bureau of Standards.[4] The single-junction copper–constantan thermocouple was calibrated at the sublimation point of carbon dioxide. The potentiometer used was sensitive to 0.1 microvolt (0.003°) and reproducible from day to day to 1 microvolt (0.03°). Two modifications of crystalline 2-picoline were observed, needle-like prisms and white opaque platelets, the former being more stable at the freezing point. Due to excessive supercooling, melting curves instead of freezing curves were used to determine the freezing point for zero impurity. The freezing point of pure 2-picoline (saturated with nitrogen) was found to be −66.55 ± 0.08° at 730–740 mm. pressure, and the purity of the sample was estimated, from the slope of its melting curve, to be 99.85 mole %, assuming its cryoscopic constant to have the same value as that of 3-picoline.[5] This assumption is approximately confirmed by an experiment in which approximately 0.71 mole % water was found to depress the freezing point of 2-picoline by 0.31°. Previously reported values of the freezing point are −69.9°[6] and −64°.[7]

**Density and Expansion Coefficient.**—Two 20-ml. flask-type pycnometers having graduated 1-mm. capillary necks were used. The capillaries were calibrated by measuring lengths of weighed mercury threads by means of a traveling microscope. The volumes of the pycnometers were determined at 20, 40, 60 and 80° in a water-bath maintained to ±0.005°. The bath temperatures were measured by thermometers which had been compared with those certified by the Bureau of Standards and used at the points tested, with a probable accuracy of ±0.03°. When no further change occurred in the level of the liquid in the pycnometer, the level was read with the aid of a telescope, and suitable calculations made to relate the volume to a certain mark. Fillings with 2-picoline were made in the dry box using a filling tube constructed of stainless steel and nickel tubing. The picoline was protected from the atmosphere by a device which kept dry nitrogen flowing over it at all times, including that of level adjusting. The densities were determined in duplicate at 20, 40, 60, and 80° on the same sample of picoline, and pycnometers being refilled for the series at 30, 50, and 70°. Weighings were made using as tares identical pycnometers which received the same external treatment as the ones in which the measurements were made. The weights employed were certified by the Bureau of Standards. All weights were corrected to values *in vacuo*. The respective density values obtained at 10° intervals from 20 to 80° are $0.94432_0$, $0.93491_3$, $0.92556_5$, $0.91607_2$, $0.90665_8$, $0.89706_6$ and $0.88722_2$ g./ml. with an average deviation of duplicate measurements of 0.000027 g./ml. The following equation, obtained by the application of least squares to the data, $d_t$ (g./ml.) $= 0.962809 - 9.0569 \times 10^{-4}t - 1.369 \times 10^{-6}t^2 + 2.45 \times 10^{-8}t^3 - 1.7 \times 10^{-10}t^4$, reproduces the experimental results with an average departure of 0.000017 g./ml. The density of 2-picoline at 25° calculated from the above equation is 0.93963 g./ml. The values previously reported in the literature are 0.9395,[8] 0.9400,[9] 0.9401,[10] 0.9494,[11] and 0.94099.[12]

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(3) A. J. Streiff, E. T. Murphy, V. A. Sedlak, C. B. Willingham and F. D. Rossini, *J. Research N. B. S.*, **37**, 331 (1946).

(4) A. R. Glasgow, Jr., A. J. Streiff and F. D. Rossini, *ibid.*, **35**, 355 (1945).

(5) W. L. Glowacki, unpublished work.

(6) J. Timmermans, *Bull. soc. chim. Belg.*, **30**, 62 (1921).

(7) F. M. Jaeger, *Z. anorg. allgem. Chem.*, **101**, 1 (1917).

(8) M. A. G. Rau and B. N. Narayanaswamy, *Z. physik. Chem.*, **26B**, 23 (1934).

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(11) J. G. Heap, W. J. Jones and J. B. Speakman, THIS JOURNAL, **43**, 1936 (1921).

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The expansion coefficients of 2-picoline at various temperatures were calculated simply by dividing the instantaneous rate of change of density with temperature by the density at that temperature employing the density equation and its temperature derivative. The values thus obtained varied from 0.000992 at 20° to 0.001127 at 80° and are consistently from 2–7% lower than those calculated from the only other reported data.[13] This earlier work was done before any distinction between the isomeric picolines was recognized and probably was carried out on impure material.

**Viscosity.**—A Cannon–Fenske viscometer (size 50), having an efflux time for water at 20° of 265.22 seconds, was used for the determination of viscosities from 0–80° in 10° intervals. Efflux times were measured in triplicate with an electrical timer having an average reproducibility of 0.05 second. The viscometer, placed in a bath held constant to 0.01° was calibrated at each temperature with distilled water. Efflux times obtained from two separate fillings checked to within better than 0.1 second. The identical procedure was employed with 2-picoline with additional precautions taken to prevent contamination with atmospheric moisture. The viscometer was charged in the dry box and while in the bath was protected by means of devices which kept dry nitrogen in contact with the picoline. Results from two fillings checked to ±0.04 second.

Since the viscosity determinations were made at temperatures other than that at which the viscometer was charged, a correction for the change in the average driving head due to thermal changes in volume was applied to the observed efflux time. For water, this correction was always less than 0.3 second, while with the picoline, whose expansion coefficient is greater than that of water, the maximum correction amounted to 0.8 second.

Another correction applied to the efflux time was that needed to compensate for the change in driving head with surface tension of the liquid under test. This correction enters because of the difference of capillary action in the upper and lower reservoirs which are of different diameter. For the convenient calculation of this correction, water at 40° was used as a standard. The correction for the other water runs was always less than 0.4 second, but for the picoline, whose surface tension is about half that of water, the correction varied from 0.7 to 1.3 seconds. A graphical interpolation of Jaeger's data[7] for the surface tension of 2-picoline was employed for these calculations.

The corrected efflux times of the water determinations, in conjunction with the viscosity and density data for water in the "International Critical Tables," were used for the calculations of the viscometer constant. In an analogous manner, the observed efflux times for 2-picoline were corrected and employed along with the density data herein obtained to calculate the viscosities presented in Table I.

TABLE I

VISCOSITY OF 2-PICOLINE

| Temp., °C. | Viscosity, cp. | Temp., °C. | Viscosity, cp. |
|---|---|---|---|
| 0 | 1.0970 | 50 | 0.5621 |
| 10 | 0.9351 | 60 | .5054 |
| 20 | 0.8102 | 70 | .4585 |
| 30 | 0.7096 | 80 | .4165 |
| 40 | 0.6296 | | |

The results presented here have a probable accuracy of somewhat better than 1%. The value of the viscosity at 25° interpolated from a graphical representation of the data of Table I is 0.757 cp., as compared to the value of 0.7918 cp. reported in 1907.[12] The difference of 4.7% is probably due in large part to the use of insufficiently pure picoline by these early workers.

The relation between the viscosity and the temperature may also be expressed by the following equation obtained graphically from the data

$$\log_{10}\eta \text{ (centipoise)} = 504.4/T - 1.811$$

where $T$ is the absolute temperature and which reproduced the data to an average of 5 p. p. m. with an extreme of 14 p. p. m. The activation energy of viscous flow, $E_{\text{vis.}}$, may be found from the above equation to be 2308 cal./mole.

**Boiling Point.**—A simple Swietoslawski ebulliometer, suitably modified to protect its contents from atmospheric moisture, was dried and charged with 2-picoline in the dry box. The condensation temperature was measured with a single-junction copper–constantan thermocouple that was calibrated with an accuracy of 0.02° at the melting point of a Bureau of Standards sample of benzoic acid. Barometric pressure readings were made simultaneously with boiling temperature measurements. The observed boiling temperatures were corrected to 760 mm. by means of the $dT/dp$ value of 0.046° C./mm. calculated from the vapor pressure data of Riley and Bailey.[14]

The boiling point so obtained, 129.44°, remained constant even after several portions of the liquid were distilled away. The probable accuracy of the value is somewhat better than 0.1°. Previously reported values are 129.21,[15] 129.27–129.32,[9] 128.9,[14] and 129.1°.[8]

**Refractive Index.**—The refractive indices of 2-picoline at 20 and 30° in a Bausch & Lomb Precision Refractometer at three wave lengths, 5893 Å. (Na$_D$ line), 5461 Å., and 4358 Å. (Hg green and blue lines). Circulating water from a constant temperature bath maintained the prisms to ±0.02° during the measurement. The refractometer was calibrated by means of highly pure benzene and chlorobenzene. These results, along with the molar refractions, are presented in Table II.

TABLE II

REFRACTIVE INDEX AND MOLAR REFRACTION OF 2-PICOLINE

| Wave length, Å. | Temp., °C. | $n$ | $R_M$ |
|---|---|---|---|
| 5893 | 20 | 1.50105 | 29.056 |
| | 30 | 1.49592 | 29.093 |
| 5461 | 20 | 1.50493 | 29.246 |
| | 30 | 1.49982 | 29.286 |
| 4358 | 20 | 1.52170 | 30.062 |
| | 30 | 1.51667 | 30.118 |

Other values of the $n^{20}$D are 1.50122[14] (corrected from the value reported at 18° by means of the temperature dependence of $n$D found in this work) and 1.501.[16]

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[13] T. E. Thorpe, *J. Chem. Soc.*, **37**, 222 (1880).

[14] F. T. Riley and K. C. Bailey, *Proc. Roy. Irish Acad.*, **38B**, 450 (1929).

[15] E. J. Constam and J. White, *Am. Chem. J.*, **29**, 2 (1903).

[16] "International Critical Tables," Vol. I.

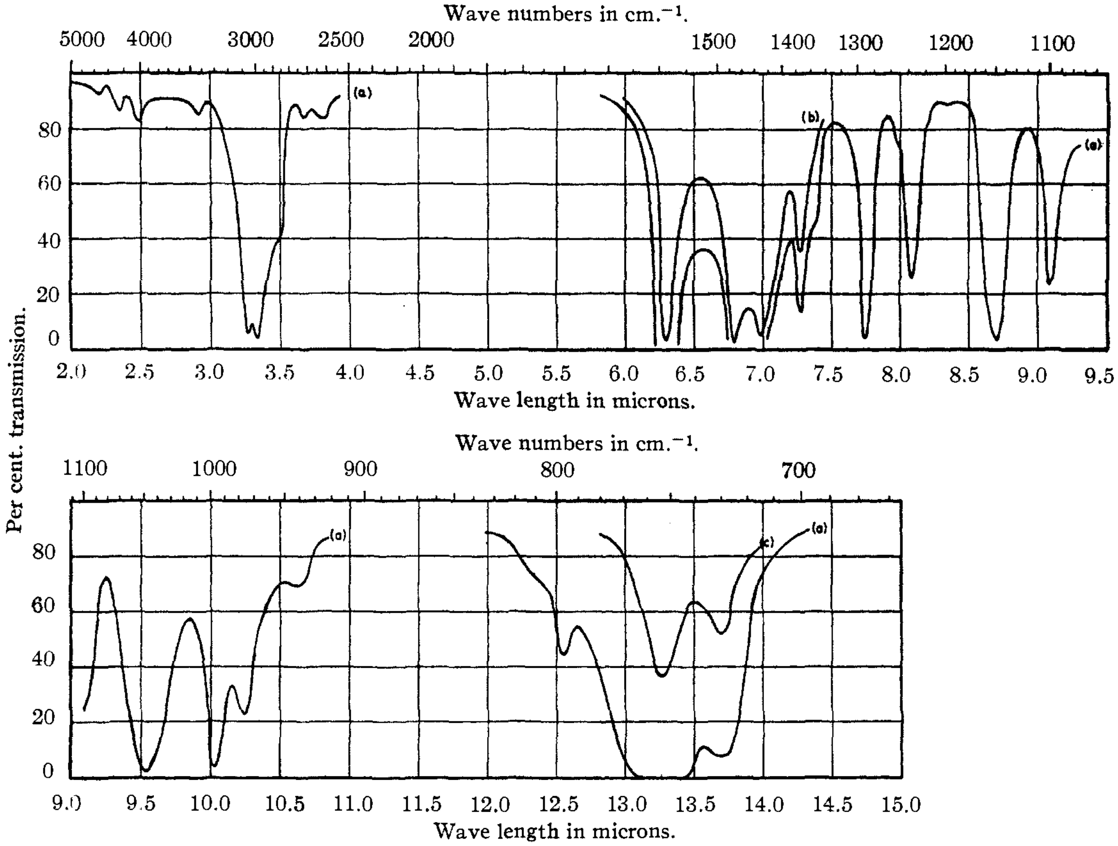

Fig. 1.—Infrared spectra of 2-picoline: α-picoline (2-methylpyridine), 99.8%, liquid at 27°; cell length, (a) 0.08 mm., (b) 0.04 mm., (c) 0.02 mm.

The $n_\infty^{30}$ and corresponding $MR_\infty$ were calculated for use in the dipole moment work by means of a simple Sellmeier expression, $n - 1 = a\lambda^2/\lambda^2 - b$, using the refractive indices of two of the three reported above. In order to estimate the validity of this expression, the value of $n_\infty^{30}$ was calculated by using two pairs of $n\lambda$. In this manner $n_\infty^{30}$ was found to have an average value of 1.4729 ± 0.00016 with a corresponding $MR_\infty$ = 27.94 ml.

**Dipole Moment.**—The dipole moment of 2-picoline in benzene solution at 30.00 ± 0.03° was measured by means of a heterodyne beat method. The apparatus used for the dielectric constant measurements will be described in a future publication. The densities of the solutions were measured in pycnometers of 100 ml. capacity similar to the ones described in the section on density.

The dielectric constants $\epsilon$ and $d$ of the solutions containing mole fraction $f_2$ of the polar solute and the polarization of polar solute $P_2$ are given in Table III.

TABLE III

DIELECTRIC CONSTANTS, DENSITIES AND POLARIZATION

| $f_2$ | $\epsilon$ | $d$ | $P_2$ |
|---|---|---|---|
| 0.042803 | 2.4860 | 0.871443 | 103.5 |
| .053407 | 2.5421 | .872239 | 102.8 |
| .074254 | 2.6588 | .873802 | 102.5 |

A value of 104.7 ± 0.4 ml. was obtained for $P_\infty$ by extrapolating the $P_2$–$f_2$ curve to infinite dilu-

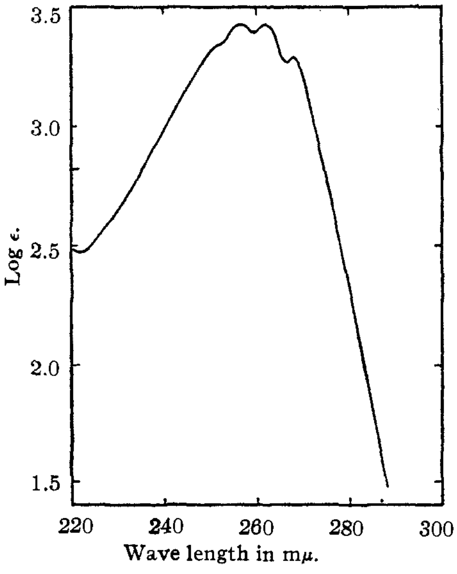

Fig. 2.—Ultraviolet spectra of 2-picoline: purity, 99.8 mole %; solvent, cyclohexane.

tion. The electronic polarization $P_E$ was obtained from the molar refraction at infinite wave length, 27.9 ml. Assuming $P_A$ to be 10% of $P_E$, the dipole moment of 2-picoline is calculated to be 1.92 *D* with a probable accuracy of ±0.01°. This value is not in good agreement with that of 1.72 *D* (the only previously reported work) obtained by Rau and Narayanaswany[7] because these workers employing the temperature solution method obtained a falsely high value, 23.2 ml. for $P_A$.[17] The value obtained by Rau and Narayanaswany for the total polarization at infinite dilution $P^{30}_{2\infty}$ is 111.36 ml., in fair agreement with the value obtained here.

**Absorption Spectra.**—In Figs. 1 and 2 are presented the infrared and ultraviolet absorption curves, respectively, for 2-picoline. The main infrared absorption maxima are presented in Table IV. The main ultraviolet absorption maxima are located at 252, 256.5, 262, and 268 millimicrons. The data were kindly determined by the Koppers Spectrographical Research Laboratory under the direction of Dr. J. J. McGovern.

TABLE IV

MAIN INFRARED ABSORPTION MAXIMA OF 2-PICOLINE

| λ in μ | $I^a$ | λ in μ | $I^a$ |
|---|---|---|---|
| 1.70 | w | 7.74 | m |
| 2.20 | w | 8.09 | m |
| 2.34 | w | 8.70 | m |
| 2.47 | w | 9.09 | m |
| 2.93 | w | 9.53 | m-i |
| 3.33 | m | 10.03 | m-i |
| 3.66 | w | 10.24 | m |
| 3.82 | w | 10.65 | w |
| 6.29 | m-i | 11.29 | w |
| 6.80 | m-i | 12.55 | w |
| 6.99 | m | 13.28 | i |
| 7.28 | w | 13.69 | m |

[a] Approximate intensity: w = weak, m = moderate, i = intense.

## Summary

1. 2-Picoline has been purified by fractional distillation and recrystallization to an estimated 99.85 mole % purity.

2. The following properties have been determined for the purified material: freezing point, boiling point, density at 10° intervals from 20 to 80°, the expansion coefficients in the same temperature range, the viscosity at 10° intervals from 0 to 80°, refractive indices at 20 and 30° at 5893, 5461 and 4358 Å., the dipole moment, and the infrared and ultraviolet absorption spectra.

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(17) "The temperature solution method gives only the dipole moment qualitatively and seriously misleads investigators regarding the magnitude of the atomic polarization," H. O. Jenkins, *Trans. Faraday Soc.*, **30**, 741 (1934).

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# The Density of Aqueous Hydrogen Peroxide Solutions[1]

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## Introduction

A relatively small amount of exact density data exists for aqueous solutions of hydrogen peroxide, due to the decomposition caused by the catalytic activity of glass surfaces which introduces error in the density determination because of combined gas formation and loss of peroxide. A solution of this major problem was found in the preconstruction treatment of the interior surface of the glass from which the vessels were blown, combined with the employment of certain precautions during their use.

The literature reveals that the determinations of Maass and Hatcher[2] reported at both 0 and 18° are the most accurate data available. Independent verification of the data, however, has not appeared, and independent values in the region of high peroxide concentration are particularly desirable in view of the surface activity of the glass unless very special precautions are taken.

In this investigation a technique has been developed for preparing vessels whose interior surfaces are insensitive toward the decomposition of peroxide, determining with precision the densities of aqueous solutions of hydrogen peroxide at 0°. The mean coefficient of change of density with temperature to 20° has also been measured.

**Treatment to Render Glassware Inactive to Hydrogen Peroxide.**—The following procedure was found to produce inactive container Pyrex glass surfaces.

All glassware was constructed of Pyrex tubing, selected for freedom from visible surface imperfections. Prior to the glassblowing the tubing was cleaned with hot fuming sulfuric acid (150–175°), rinsed with conductivity water, and allowed to drain until dry in a dust-free case. This treatment is important in that it removes foreign matter which might otherwise decompose or "ash" and become embedded in the surface of the glass during the glassblowing operation. The air required in the glassblowing was passed through a filter of fresh medicinal cotton to prevent contamination through air-borne dust or decomposition of organic vapors from the breath.

After the vessels had been constructed, they were filled with hot fuming sulfuric acid and allowed to stand overnight. Following thorough rinsing with conductivity water, the vessels were tested with 90–95% peroxide. If no bubbles of oxygen appeared, the vessels were ready for use.

In the few instances where decomposition was detected,

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(1) The authors express their acknowledgment to the Naval Bureau of Ordnance for the support and release of this work.

(2) O. Maass and W. H. Hatcher, THIS JOURNAL, **42**, 2548 (1920).