

Vapor pressure data of nicotine, anabasine and cotinine using differential scanning calorimetry



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ABSTRACT

The aim of the present study was to determine the vapor pressures of three tobacco alkaloids using the high pressure differential scanning calorimeter based technique, in accordance with a standard test method ASTM E 1782. The measurements were conducted in the pressure range from 15 to 1000 kPa. Temperature ranges for (L)-nicotine were from 447.7 to 617.8 K, for (±)-anabasine from 478 to 644.3 K and for (–)-cotinine from 537.7 to 669.7 K. Hermetic-type sealable pans with a pierced lid (pinhole diameter 50 μm) and a heating rate of 5 K/min were used. The experimental vapor pressure data were fitted to the Antoine equation. Enthalpies of vaporization and the normal boiling temperatures of the compounds were estimated from the measured data. Comparisons are made with published literature data. In addition, a review of the vapor pressure studies of nicotine and anabasine is given.

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1. Introduction

Tobacco use by smoking (either by water pipe, cigarette, or pipe smoking) is a thermochemical conversion of tobacco with the major processes being pyrolysis and combustion. The tobacco smoke produced is a complex mixture estimated to contain more than 7000 chemical compounds from many different classes [1]. From the chemical engineering point of view, the thermochemical conversion of tobacco is a complex interplay between different type of processes such as chemical, heat-transfer and mass- transfer processes. Therefore, chemical engineering modelling and analysis need wide-variation physicochemical and transport properties. One important physicochemical property is the vapor pressure of both tobacco semi-volatile constituents (occurring naturally in tobacco or added to tobacco as flavors) and tobacco thermal decomposition products, condensable at room temperature [2]. This vapor pressure information is important for describing tobacco devolatilization in thermochemical conversion processes (smoke generation) and smoking devices constructions. In the past two decades there have been several vapor pressure studies in this regard, both on tobacco tar [3,4] and on low volatile compounds generated from tobacco devolatilization [5,6]. Vapor pressure information can also be used to determine the fate and transport of materials released during tobacco smoking in the environment (as second- and third-hand

smoke in an indoor environment) or in the human respiratory system, and additionally in developing safety measures to avoid human exposure. Thus, a large number of tobacco smoke constituents could potentially be of practical interest as target compounds for specific applications, from design to environmental and safety purposes. These constituents can have very different volatilities (very different vapor pressures at specified temperatures) and different thermal stabilities. In addition, being biomass thermochemical conversion products, the majority of these are oxygen and nitrogen hetero-atomic compounds with complex structures (heterocyclic for example) and likely have capability of forming hydrogen bonds.

Therefore, an application of different experimental methods for the determination of vapor pressure curves is of interest in tobacco research and related fields. One of the simplest techniques for experimentally determining vapor pressure curves of volatile organic compounds is the differential scanning calorimetry (DSC) based technique. In this technique, the vapor pressure curve is established by determining, via separate experiments, several boiling points at different pressures, from vacuum to elevated pressures. Each boiling temperature is determined from the onset of a heat effect when the sample is evaporated through a pinhole from a hermetically sealed container at a specified pressure under what is called an “isothermal boiling condition” [7]. The advantage of the technique is that only a very small amount of sample (in total 250 mg or less) can be used to obtain a vapor pressure curve with at least 5 replicated points.

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The experimental conditions for DSC based vapor pressure measurements were standardized in 1996 as The Standard Test Method for Determining Vapor Pressure by Thermal Analyses (ASTM E 1782) [8]. The ASTM task group [8] suggested a heating rate of 5 K/min, sample size of 1–5 mg for solids and 1–5 μl for liquids and a pinhole size smaller than 125 μm . Generally, at these conditions the lower pressure limit is 5 kPa. The upper pressure limit is 2000 kPa, but it depends on the apparatus used and the thermal stability of the materials [8].

The present study focuses on the experimental determination of the vapor pressures of three tobacco alkaloids: (L)-nicotine, (\pm)-anabasine and (–)-cotinine, using differential scanning calorimetry (standard test method ASTM E 1782). There is no reported experimental data for nicotine above the atmospheric boiling point. There is a lack of consistent vapor pressure data for anabasine and only some boiling ranges (at low vapor pressures) were found for cotinine.

2. Experimental

2.1. Chemicals

The tobacco alkaloids examined in this research were L-nicotine, (\pm)-anabasine and (–)-cotinine. The structures of these tobacco alkaloids are presented in Fig. 1.

L-nicotine (CAS No. 54-11-5; systematic IUPAC name: 3-(methylpyrrolidin-2-yl)-pyridine; $\text{C}_{10}\text{H}_{14}\text{N}_2$) with a purity of 99%+, was obtained from Acros Organics. The refractive index of L-nicotine was n_D^{20} 1.5255–1.5285, the optical rotation was $[\alpha]_D^{20}$ -140° to -152° (given by the supplier). The melting point is presumed to be lower than -79°C [9].

(\pm)-Anabasine (CAS No. 13,078-04-1; systematic IUPAC name: 3-(2-piperidyl) pyridine; $\text{C}_{10}\text{H}_{14}\text{N}_2$), with a purity of 97.1%, was purchased from Maybridge (part of Thermo Fisher Scientific, Inc.). The sample had a refractive index of n_D^{20} 1.544 (given by the supplier). The literature melting point is 9°C [10].

(–)-Cotinine (CAS No. 486-56-6; systematic IUPAC name: (5S)-1-methyl-5-(3-pyridyl) pyrrolidin-2-one; $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}$) with purity of 98% (99.9% with GC) was supplied by abcr GmbH and Co., KG. The optical rotation of $[\alpha]_D^{20}$ -19.6° and n_D^{20} 1.5560 were given by the supplier. The literature melting point is approximately 41°C [11].

According to literature the nicotine is thermally stable in an inert atmosphere up to 600°C [12,13]. No thermal stability information was found for the other two tobacco alkaloids; however, the DSC measurements performed did not indicate thermal instabilities in the measured temperature regions.

The reference chemicals used to test the DSC method were toluene and hexadecane. Toluene (CAS No. 108-88-3, anhydrous, purity of 99.8%) was obtained from Sigma-Aldrich and hexadecane (CAS No. 544-76-3, with purity of 98%) was produced by Fisher Chemicals.

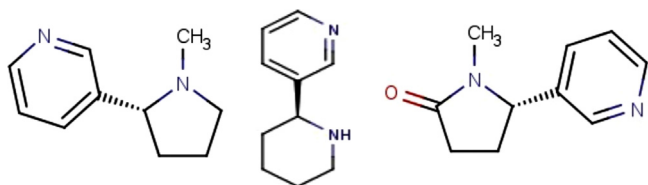


Fig. 1. Structures of L-nicotine, (\pm)-anabasine and (–)-cotinine (from left to right).

2.2. Apparatus

The high pressure differential scanning calorimeter used was a Netzsch DSC 204HP Phoenix with accompanying DSC cell and pressure-flow control system. To improve the pressure control stability and pressure measurement accuracy in the pressure region from 100 to 1000 kPa an additional pressure controller (Brooks Instrument Model 5866) and pressure sensor (Omegadune Inc., model PX409-150AUSB) were added to the system. The pressure sensor was manufacturer calibrated with a full scale error of 0.008%.

For vapor pressure experiments in a vacuum an extra vacuum control and measurement system was designed. The system consisted of a membrane vacuum-pump (vacuum-brand PC 3001 Vario) with a variable motor-speed controller CVC 3000, a vacuum sensor MKS Baratron (type 626B) and a ballast tank (2 l in volume). The operating range of the vacuum sensor was 0.0133–130 kPa. The sensor was calibrated by the manufacturer and the accuracy was specified to be 0.25% of the reading.

The distance between the sensors (both pressure and vacuum) and DSC cell was approximately 47 cm and the pressure drop less than 0.003 kPa at atmospheric conditions.

2.3. Experimental procedure

The experimental procedure used was selected in accordance with the “Standard Test Method for Determining Vapor Pressure by Thermal Analyses (ASTM E 1782)”. Vapor pressure measurements were performed in the pressure range between 5 kPa and 1000 kPa. The heating rate applied was 5 K/min. Hermetic type sealable pans (40 μl) with laser-drilled pinholes of 50 μm in the lid were used. The liquid samples were injected with a micro-syringe into an aluminum crucible. Then the crucible was mechanically sealed with a lid. Samples were weighed on a micro-analytical balance (Mettler M3/TG). For each sample point, the DSC experiments were repeated with somewhat different sample amounts at least two times or three times if the measured boiling point difference was more than 0.3 K.

Nitrogen was used as a purge gas (purity 99.999%) with a flow rate of 40 ml/min. The DSC cell (i.e., the sample and reference pans) was stabilized in the nitrogen flow at room temperature at the given pressure for about 20–30 min before measurements were started. Inert gas purging for about 20–30 min at atmospheric pressure was also used before the vacuum measurements to avoid oxidation of the samples.

Temperature calibration was carried out with indium, tin, bismuth and zinc standards at 15, 50, 100 (atmospheric pressure),

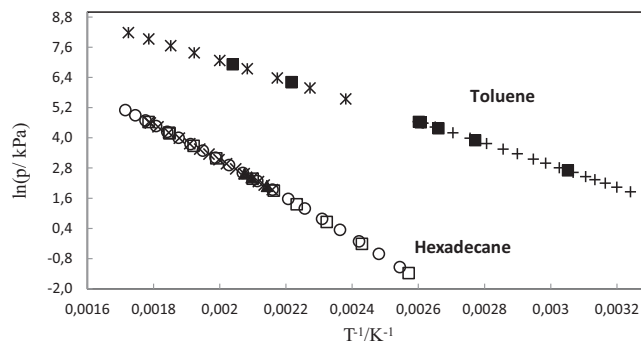


Fig. 2. Comparison of the experimental vapor pressure data with the literature values. Hexadecane: (\blacklozenge) present study; (\times) Camin et al. [14]; (\square) Mills and Fenton [15]; (\circ) Morgan and Kobayashi [16]; (\blacktriangle) Abdi and Meisen [17]. Toluene: (\blacksquare) present study; ($+$) Willingham et al. [18]; ($*$) Ambrose et al. [19].

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