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Thermodynamic properties of pyrrole, 1-methylpyrrole, 2,4-dimethylpyrrole, and 2,5-dimethylpyrrole: Experimental and computational results

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ABSTRACT

New measurements of critical temperature, saturated liquid heat capacity from temperature T ≈ 315 K to T ≈ 550 K, and saturated liquid density from T = 323 K to T ≈ 475 K are reported for pyrrole (Chemical Abstracts registry number [109-97-7]), 1-methylpyrrole [96-54-8], 2,4-dimethylpyrrole [625-82-1], and 2,5-dimethylpyrrole [625-84-3]. New measurements of vapor pressure are reported for 2,4-dimethylpyrrole {338 < (T/K) < 477} and 2,5-dimethylpyrrole {341 < (T/K) < 479}, as well as the enthalpy of combustion determined with oxygen-bomb calorimetry for 2,4-dimethylpyrrole. These new measurements are combined with literature values to calculate thermodynamic properties in the ideal-gas state for extended ranges of temperature for all compounds: pyrrole {298 < (T/K) < 550}, 1-methylpyrrole {298 < (T/K) < 530}, 2,4-dimethylpyrrole {298 < (T/K) < 600}, and 2,5-dimethylpyrrole {298 < (T/K) < 560}. Molar thermodynamic functions (enthalpies, entropies, and Gibbs energies) for the liquid and ideal-gas states were derived from the experimental studies at selected temperatures. Statistical calculations were performed with optimized geometries, scaled vibrational frequencies, and methyl rotational potentials performed using B3LYP hybrid density functional theory with the def2-TZVPPD basis set. Methyl torsional barriers were evaluated at the DLPNO-CCSD(T)/def2-QZVP level of theory using the B3LYP/def2-TZVPPD geometries. Computed ideal-gas properties are shown to be in excellent accord with ideal-gas entropies derived from thermophysical property measurements, as well as with reported experimental heat capacities for the ideal-gas state. All experimental results are compared with property values available in the literature.

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1. Introduction

This work is a continuation of our investigations [1–9] into quantification of uncertainties for thermodynamic properties derived with computational methods. Entropies for the ideal-gas state can be calculated with structural information and computational methods, as well as through appropriate combination of experimentally determined thermodynamic properties. These two methods are independent, and comparison of the results allows for mutual validation, as well as highlighting of limitations. The importance and applications of ideal-gas properties in thermodynamic analyses has been discussed previously [6].

The experimental work described here was completed within the Bartlesville Thermodynamics Laboratory (National Institute of Petroleum and Energy Research; Bartlesville, Oklahoma, U.S.A.) during the 1980s and 1990s. Combination of these high quality results with modern computational methods allows for stringent testing of thermodynamic consistency of the measured properties, as well as insights into uncertainties and limitations of the computed results.

This article describes thermodynamic property measurements and analysis for pyrrole (Chemical Abstracts registry number [109-97-7]), 1-methylpyrrole [96-54-8], 2,4-dimethylpyrrole [625-82-1], and 2,5-dimethylpyrrole [625-84-3]. The analysis involves combination of new experimental results with previously published property values [10–15], also measured in the Bartlesville Thermodynamics Laboratory. A summary of the experimental property measurements both newly reported here and taken from the literature is provided in Table 1. Entropies for the ideal-gas state were derived from the thermophysical property measurements, and these are compared with those calculated independently with the methods of computational chemistry. This work is our first report involving computations for the pyrrolic ring.

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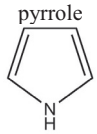
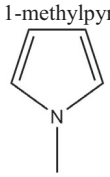
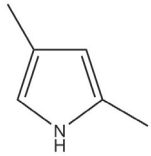
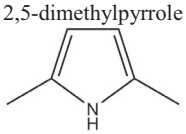
Table 1
Summary of experimental results used or reported in the present research, including sample sources and purities.

Property	Method	T-Range[a]/K	Source[b]
pyrrole 			
heat capacity [c]	adiabatic calorimetry	11 to 360	Scott et al. [10]
heat capacity	d.s.c.[d]	310 to 550	This research
vapor pressure	comparative ebulliometry	339 to 439	Scott et al. [10]
density	vibrating-tube densimetry	323 to 468	This research
enthalpy of combustion	bomb calorimetry	298.15	Scott et al. [10]
critical temperature	d.s.c.[d]		This research
			Cheng et al. [15][e]
mole fraction sample purity [10] = 0.99994 [f]			
1-methylpyrrole 			
heat capacity [c]	adiabatic calorimetry	11 to 370	Messerly et al. [12]
heat capacity	d.s.c.[d]	310 to 530	This research
vapor pressure	comparative ebulliometry	322 to 423	Osborn and Douslin [11]
density	vibrating-tube densimetry	323 to 448	This research
enthalpy of combustion	bomb calorimetry	298.15	Good [14]
critical temperature	d.s.c.[d]		This research
mole fraction sample purity [12] = 0.99998 [f]			
2,4-dimethylpyrrole 			
heat capacity [c]	adiabatic calorimetry	12 to 441	Chirico et al. [13]
heat capacity	d.s.c.[d]	315 to 595	This research
vapor pressure	comparative ebulliometry	338 to 477	This research
density	vibrating-tube densimetry	323 to 448	This research
enthalpy of combustion	bomb calorimetry	298.15	This research
critical temperature	d.s.c.[d]		This research
mole fraction sample purity [13] = 0.9998 [f]			
2,5-dimethylpyrrole 			
heat capacity [c]	adiabatic calorimetry	12 to 400	Messerly et al. [12]
heat capacity	d.s.c.[d]	315 to 555	This research
vapor pressure	comparative ebulliometry	341 to 479	This research
density	vibrating-tube densimetry	323 to 508	This research
enthalpy of combustion	bomb calorimetry	298.15	Good [14]
critical temperature	d.s.c.[d]		This research
mole fraction sample purity [12] = 0.9989 [f]			

[a] The temperature range of the measurements.
[b] The source of the experimental results.
[c] Results included determination of the crystal-liquid-gas triple point temperature and enthalpy of fusion.
[d] Differential scanning calorimetry.
[e] The critical temperature for pyrrole determined in this research and that of Cheng et al. [15] are in accord. The value measured by Cheng et al. [15] was used in further calculations because of its significantly lower uncertainty, as described later in the text. This is the only measurement result used in the present research that was not determined in the Bartlesville Thermodynamics Laboratory.
[f] The samples of pyrrole, 1-methylpyrrole, and 2,5-dimethylpyrrole were prepared as part of an A.P.I. (American Petroleum Institute) project done in cooperation with the U.S. Bureau of Mines in the 1950 s (API-USBM 52-2). The sample of 2,4-dimethylpyrrole was synthesized by Prof. E. J. "Pete" Eisenbraun of Oklahoma State University. Samples were fractionally distilled prior to measurements for each property. The mole fraction purities were determined by fractional melting as part of the studies with adiabatic calorimetry.

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