Thermodynamic properties of indan: Experimental and computational results

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ABSTRACT

Measurements leading to the calculation of thermodynamic properties in the ideal-gas state for indan (Chemical Abstracts registry number [496-11-7], 2,3-dihydro-1*H*-indene) are reported. Experimental methods were adiabatic heat-capacity calorimetry, differential scanning calorimetry, comparative ebulliometry, and vibrating-tube densitometry. Molar thermodynamic functions (enthalpies, entropies, and Gibbs energies) for the condensed and ideal-gas states were derived from the experimental studies at selected temperatures. Statistical calculations were performed based on molecular geometry optimization and vibrational frequencies calculated at the B3LYP/6-31+G(d, p) level of theory. Computed ideal-gas properties derived with the rigid-rotor harmonic-oscillator approximation are shown to be in excellent accord with ideal-gas entropies derived from thermophysical property measurements of this research, as well as with experimental heat capacities for the ideal-gas state reported in the literature. Literature spectroscopic studies and *ab initio* calculations report a range of values for the barrier to ring puckering. Results of the present work are consistent with a large barrier that allows use of the rigid-rotor harmonic-oscillator approximation for ideal-gas entropy and heat-capacity calculations, even with the stringent uncertainty requirements imposed by the calorimetric and physical property measurements reported here. All experimental results are compared with property values reported in the literature.

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1. Introduction

This work is a continuation of our investigations [1–8] into quantification of uncertainties for thermodynamic properties derived with computational methods, with particular focus on entropies for the ideal-gas state. Joint computational and experimental studies for enthalpies of formation in the ideal-gas state are active research areas for several research groups worldwide, including those in Porto, Portugal (*cf.*, [9,10]), Rostock, Germany (*cf.*, [11,12]), and others. 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 their study allows for their mutual validation through analysis of observed differences. The importance and applications of ideal-gas properties in thermodynamic analyses has been discussed previously [6].

This article describes thermodynamic property measurements for indan (Chemical Abstracts registry number [496-11-7]). A summary of the new experimental property measurements reported here is provided in table 1. Entropies for the ideal-gas state are derived from the thermophysical property measurements, and these are compared with those calculated independently with the methods of computational chemistry. Our previous work has focused primarily on molecules that are relatively rigid or involve internal rotations that can be modeled with good confidence. A particular concern in the present work involves proper accounting for possible highly anharmonic out-of-plane vibrations associated with the cyclopentyl ring. Future articles in this series will consider properties of molecules with heteroatoms (nitrogen, oxygen, and sulfur) substituted in the cyclopentyl ring of the indan structure.
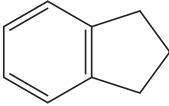
2. Experimental

2.1. Materials

The sample of indan used in this research was synthesized and purified by the research group of Professor E.J. "Pete" Eisenbraun (retired) of Oklahoma State University. Fractionation at reduced pressure of commercial indan did not yield samples of adequate purity. Indan was prepared from 1-indanone (280 g) through the

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Property	Method	Temperature range/K
Heat capacity Phase-transition temperatures[a] Phase-transition enthalpies[a]	Adiabatic calorimetry	5 to 445
Heat capacity	Differential scanning calorimetry	400 to 600
Vapor pressure	Comparative ebulliometry	338 to 495
Density	Vibrating-tube densimetry	323 to 523

[a] The temperature and enthalpy were determined for the crystal(I)-to-liquid and crystal(II)-to-crystal(I) phase transitions.

TABLE 2
Calorimeter and sample characteristics for adiabatic calorimetric studies on indan.[a]

m/g	44.484
$V_i(T = 298.15 \text{ K})$/cm^3	62.47
T_{cal}/K	297.7
p_{cal}/kPa	6.20
$r(T_{max})$	3.2
r_{min}	2.0
$10^2 \cdot (\delta C/C)_{max}$	0.16
x_{pre}	0.00025

[a] m is the sample mass; V_i is the internal volume of the calorimeter vessel; T_{cal} is the temperature of the calorimeter when sealed; p_{cal} is the pressure of the helium and sample when sealed; $r(T_{max})$ is the ratio of the heat capacity of the full calorimeter to that of the empty at the highest temperature $T_{max} \approx 445$ K of these measurements; r_{min} is the minimum value of r observed in this study; $(\delta C/C)_{max}$ is the vaporization correction at the highest temperature measured (i.e., $T_{max} \approx 445$ K); and x_{pre} is the mole-fraction impurity used for pre-melting corrections.

Wolff Kishner reduction using hydrazine hydrate (388 ml), potassium hydroxide (230 g), and diethylene glycol (1.5 l) at $T = 456$ K for 4 h. In this reaction, indan distills from the reaction mixture and collects as the upper layer in a Dean–Stark trap. The upper layer was dissolved in pentane, separated, transferred to a separatory funnel, and washed successively with dilute hydrochloric acid, water, and then dried with MgSO$_4$ and filtered. The filtrate was treated with concentrated sulfuric acid and water, dried with MgSO$_4$, and distilled under an atmosphere of argon at $T = 328$ K and 1.2 kPa. Details of this approach have been described by Eisenbraun and Hall [13]. The mole-fraction purity $x = 0.99975$ was established in a fractional-melting study completed as part of the adiabatic heat-capacity calorimetric results reported here. All transfers of samples were completed under nitrogen or helium or by vacuum distillation. Purification of the water and decane used as reference materials in the reported ebulliometric vapor-pressure measurements has been described [14].

2.2. Physical constants and standards

Property values for indan are reported in terms of molar mass $M = 118.179$ [15] based on the formula C$_9$H$_{10}$ and the gas constant $R = 8.3144598$ J · K^{-1} · mol^{-1} adopted by CODATA [16]. Platinum resistance thermometers were calibrated by comparison with standard thermometers whose constants were determined at the National Bureau of Standards (NBS), now the National Institute of Standards and Technology (NIST). All temperatures were measured in terms of IPTS-68 [17] and were converted to ITS-90 with published temperature increments [18]. The thermometer used in the adiabatic heat-capacity study was calibrated below T/K = 13.81 with the method of McCrackin and Chang [19]. Mass, time, electrical resistance, and potential difference were measured in terms of standards traceable to calibrations at NIST.

2.3. Apparatus and procedures

New property measurements reported here are summarized in table 1. Property values for indan taken from the literature and used in subsequent calculations included the critical temperature and critical pressure measured by Ambrose et al. [20] and the enthalpy of combustion reported by Good [21].

Heat-capacities and enthalpy increments for indan were measured with an adiabatic calorimetric system that has been described [22]. Characteristics of the sample, the platinum sample container, and sealing conditions are given in table 2. Measured energy increments to the filled calorimeter were corrected for

enthalpy changes in the empty calorimeter, for the helium exchange gas, and for vaporization of the sample into the free space of the sealed vessel. The maximum sizes of these corrections are given in table 2.

Densities for the liquid phase at vapor-saturation pressure ρ_{sat} were determined for indan with a vibrating-tube densimeter. The instrument and its operation have been described [23], as have test measurements on benzene for the temperature range $(310 < T/\text{K} < 523)$ [24]. Results for benzene agree within $5 \cdot 10^{-4}$ ρ_{sat} with the critical evaluation in the NIST REFPROP Database [25].

Heat capacities at vapor-saturation pressure $C_{sat,m}$ for the liquid phase over the temperature range $(400 < T/\text{K} < 600)$ were determined with a differential scanning calorimeter (d.s.c.). An intermittent heating method, first described by Mraw and Naas [26], was used with sequential measurements involving the sample, pure sapphire calibrant, and the empty sample pan. Heat capacities of sapphire used in calibration of the d.s.c. were those critically evaluated by Archer [27]. A power-compensated d.s.c. was used (Perkin Elmer DSC II), and the complete experimental method has been described [28,29].

Vapor pressures for indan were measured with comparative ebulliometry and described procedures [30,31]. The compound under study was refluxed with standards of known vapor pressure (decane and water) under a common atmosphere of helium gas. Boiling and condensation temperatures of the sample and standard were determined, and the vapor pressure of indan was derived from the condensation temperatures of the standards. In the pressure range $(25 < p/\text{kPa} < 270)$, water was used as the standard, and the pressures were derived from the international equation of state for pure water [32]. In the pressure range $(2 < p/\text{kPa} < 25)$, decane was the standard, and pressures were calculated with equation (1) of reference [14]. The standard uncertainty u for the temperature measurements in the vapor-pressure studies was 0.002 K. Standard uncertainties in the pressures are described by:

$$u(p) = 0.002\{(dp_{ref}/dT)^2 + (dp_x/dT)^2\}^{1/2}, \tag{1}$$

where p_{ref} is the vapor pressure of the reference substance and p_x is the vapor pressure of the sample under study. The repeatability of the temperature measurements was $5 \cdot 10^{-4}$ K.

3. Experimental results

3.1. Heat capacities and properties of phase transitions measured with adiabatic calorimetry

Measurements of enthalpy increments and derived heat capacities for indan were made with adiabatic calorimetry between the