



Chemical Engineering Thermodynamics

Vapor Pressure, Vaporization Enthalpy, Standard Enthalpy of Formation and Standard Entropy of *n*-Butyl Carbamate



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ARTICLE INFO

Article history:

Received 25 March 2013

Received in revised form 25 May 2013

Accepted 8 July 2013

Available online 20 August 2014

Keywords:

n-Butyl carbamate

Vapor pressure

Standard enthalpy of formation

Standard entropy

ABSTRACT

The vapor pressures of *n*-butyl carbamate were measured in the temperature range from 372.37 K to 479.27 K and fitted with Antoine equation. The compressibility factor of the vapor was calculated with the Virial equation and the second virial coefficient was determined by the Vetere model. Then the standard enthalpy of vaporization for *n*-butyl carbamate was estimated. The heat capacity was measured for the solid state (299.39–324.2 K) and liquid state (336.65–453.21 K) by means of adiabatic calorimeter. The standard enthalpy of formation $\Delta_f H^\ominus$ [crystal (cr), 298.15 K] and standard entropy S^\ominus (crystal, 298.15 K) of the substance were calculated on the basis of the gas-phase standard enthalpy of formation $\Delta_f H^\ominus$ (g, 298.15 K) and gas-phase standard entropy S^\ominus (g, 298.15 K), which were estimated by the Benson method. The results are acceptable, validated by a thermochemical cycle.

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1. Introduction

n-Butyl carbamate (BC, CASRN 592-35-8) is a white prismatic or schistic crystal and is also called butyl ester. It can be used as a curing agent for cement [1] and the intermediate for producing 1,6-hexamethylenediurethane [2], which can crackle to obtain isocyanate [3].

Vapor pressure data are critical for process design for evaporation, distillation and two-phase reactions. The vaporization enthalpy of a pure substance $\Delta_{\text{vap}} H^\ominus(T)$, which can be obtained from the vapor pressure data, is also an important thermodynamic parameter. Especially, the standard enthalpy of vaporization $\Delta_{\text{vap}} H^\ominus$ (crystal, 298.15 K) is used for conversion of the enthalpy of formation between liquid state and ideal gas state [4]. The heat capacity and the enthalpy of formation of BC, $\Delta_f H^\ominus(T)$, are important quantities for the design of technological process with BC as a reactant or a product.

However, scarce experimental information on the thermodynamic properties of BC such as vapor pressure and standard enthalpy of formation has been reported. In order to provide better design for chemical reactors and separation equipment, the thermodynamic properties such as heat capacity, vapor pressure, and $\Delta_{\text{vap}} H^\ominus$ (crystal, 298.15 K) of BC are reported in this article.

Many techniques for determining vapor pressure are available [5,6]. In this study, a modified Othmer still [7] is applied to measure the vapor pressure of BC. The vapor pressure and temperature are correlated by the Antoine equation. $\Delta_{\text{vap}} H^\ominus$ (crystal, 298.15 K) of BC is

estimated based on the Othmer method. The values of standard enthalpy of formation $\Delta_f H^\ominus$ (crystal, 298.15 K) and standard entropy S^\ominus (crystal, 298.15 K) of BC are calculated according to $\Delta_f H^\ominus$ (g, 298.15 K) and S^\ominus (g, 298.15 K) obtained by the Benson method. A thermodynamic cycle is designed to validate the reliability of the values of $\Delta_f H^\ominus$ (crystal, 298.15 K) and S^\ominus (crystal, 298.15 K).

2. Experimental

2.1. Materials

BC prepared in the laboratory [8] was recrystallized prior to use and its mass fraction purity determined by GC was higher than 99.0%. *n*-Butanol and urea purchased from Shanghai Chemistry Reagent Co. (China) are of analytical reagent grade.

2.2. Apparatus and procedures

2.2.1. Vapor pressure

The vapor pressure of BC was measured by a modified Othmer still. The apparatus and procedures are similar to those in literature [9,10]. Briefly, the apparatus included a vacuum pump, a temperature measurement system, and a pressure control and measurement system. Nitrogen was introduced into the system at the beginning to remove the air. The temperature was measured using thermocouples with an uncertainty of ± 0.05 K, and the still pressure was controlled at the desired value and measured by a U-tube mercury manometer with an uncertainty of ± 0.03 kPa. The U-tube mercury manometer and thermometers were calibrated before experiments. All the measurements were conducted in a sequence of increasing pressure and the pressure was

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Table 1
Experimental vapor pressure data of *n*-butyl carbamate and calculated deviations

<i>T</i> /K	p^{exp} /kPa	$100\Delta p/p^{\text{cal}}$	<i>T</i> /K	p^{exp} /kPa	$100\Delta p/p^{\text{cal}}$	<i>T</i> /K	p^{exp} /kPa	$100\Delta p/p^{\text{cal}}$
372.37	1.30	0.38	413.31	10.32	−0.01	445.94	38.15	0.90
375.18	1.51	1.22	415.06	11.38	−2.07	447.03	39.85	0.54
377.43	1.71	1.79	419.13	13.06	1.77	449.12	42.52	1.64
380.12	2.07	−2.76	423.24	15.66	0.99	450.69	46.29	−1.21
382.32	2.31	−1.77	426.30	18.17	−1.20	453.81	50.99	0.19
384.25	2.54	−0.77	429.01	19.77	1.42	457.68	57.59	1.52
386.19	2.76	1.22	431.19	22.24	−1.60	459.61	63.45	−1.54
388.12	3.11	−0.91	434.04	24.13	1.53	463.48	71.76	−0.77
391.98	3.74	0.50	435.65	25.63	1.78	467.34	81.32	−0.50
395.85	4.64	−1.73	436.83	27.77	−1.67	469.27	85.04	1.33
401.64	6.01	0.51	437.96	29.15	−2.17	472.14	94.53	0.01
405.01	7.04	0.51	440.84	31.57	0.81	474.10	102.31	−1.66
407.51	7.89	0.72	442.59	34.54	−1.59	477.31	111.38	−0.07
409.15	8.56	0.02	444.65	37.15	−1.21	479.27	117.57	0.60

[Ⓛ] $100\Delta p/p = 100(p^{\text{cal}} - p^{\text{exp}})/p^{\text{exp}}$, where p^{cal} is the calculated value and p^{exp} is the experimental value.

controlled at the desired value [11]. The sample (about 100 ml) was heated with an electric heater and stirred well with a magnetic stirrer to provide isothermal condition and to prevent superheating. When the readings on the U-tube mercury manometer maintained constant for 10 min, the system reached thermal equilibrium, and the temperature and pressure were recorded. The experiment was repeated 3 to 4 times at each pressure and the average value was taken.

A vapor pressure measurement of water was made from 299.27 K to 374.43 K to check the accuracy of the apparatus. The results show that the apparatus is reliable.

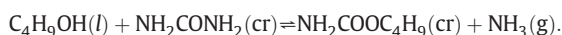
2.2.2. Heat capacity

A precision automatic adiabatic calorimeter was used to measure the heat capacity of BC. The principles of operation and structure of the instrument were detailed in literature [12]. Briefly, the adiabatic system consists of a sample cell, inner and outer adiabatic shields, a high vacuum can, a high precision temperature controller, and two sets of six-junction chromel–copel thermocouple piles. The heat capacity of α -aluminum oxide was measured to validate the reliability of the system. The deviation between the experimental data and those of NIST [13] was within $\pm 0.4\%$ over the temperature range from 298 K to 440 K.

The experiment was carried out by heating the sample and measuring the temperature alternately. The temperature increments were 1–5 K. Considering the effect of impurities in the substances, the estimated uncertainty of the C_p measurement was less than $\pm 0.8\%$.

2.2.3. Equilibrium constant measurement for BC synthesis

The reaction equation for BC synthesis is



The apparatus and procedures are similar to that described in literature [14]. Urea and *n*-butanol were charged into an autoclave reactor (300 cm³). The mixture was heated to the desired temperature after the system was evacuated. During the process, the sample was constantly stirred at the temperature for enough time for the reaction to reach equilibrium. A thermocouple was applied to measure the temperature with uncertainty of ± 0.05 K. The system was airtight and generated ammonia was in the reactor. The pressure of the system was measured using a pressure transducer (PM10) connected to a 1/2 digital multimeter (YXS-4), with ± 0.002 kPa. When the temperature and pressure of the system remained unchanged for 20 min, the system achieved equilibrium, and samples were withdrawn from the liquid and vapor phases. The liquid phase was analyzed by HPLC (Waters 1515, USA) and GC (2000II, Shanghai, China). The vapor phase was analyzed using an online GC equipped with a thermal conductivity detector and an AT.AMINE capillary column.

3. Results and Discussion

3.1. Vapor pressure of BC

The experimental vapor pressure data for BC from 372.37 K to 479.2 K are listed in Table 1.

The experimental data are fitted by the Antoine equation

$$\ln p = A - B/(T + C) \quad (1)$$

where p is the saturated vapor pressure at temperature T , and A , B and C are adjustable parameters. The parameters obtained by fitting the experimental vapor pressures are presented in Table 2.

Fig. 1 illustrates the deviation distribution of the correlations, where the deviation is defined as

$$\Delta p/p = (p^{\text{cal}} - p^{\text{exp}})/p^{\text{exp}} \quad (2)$$

where p^{exp} is the experimental value and p^{cal} is the calculated value from Eq. (1).

3.2. The enthalpy of vaporization at boiling point $\Delta_{\text{vap}}H^0(T_b)$

The Clausius–Clapeyron equation is a general equation relating vapor pressure and enthalpy of vaporization of a pure substance in equilibrium with the gas phase. It can be deduced as [15]

$$\frac{d \ln p}{d(1/T)} = \frac{-\Delta_{\text{vap}}H^0(T)}{R\Delta Z} \quad (3)$$

where $\Delta_{\text{vap}}H^0(T)$ is the enthalpy of vaporization at temperature T , $\Delta Z = Z_G - Z_L$ is the difference between the compressibility factors of vapor and liquid, and R is the gas constant.

Table 2
The Antoine constants of *n*-butyl carbamate and ethyl butyrate

Component	Antoine constants			Temperature/K
	<i>A</i>	<i>B</i>	<i>C</i>	
<i>n</i> -Butyl carbamate $\ln p = A - B/(T + C)$	17.09376	4917.79395	−80.12233	372.37–479.27
Ethyl butyrate $\lg p = A - B/(T + C)$ [19]	4.33187	1509.443	−45.284	254.7–394

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