



# Measurement and correlation of saturated vapor pressure of 2,4,6,8,10-pentamethylcyclopentasiloxane by means of an inclined ebulliometer

Hong Dong, Chuan Wu, Xiongfa Yang, Huayu Qiu\*

Key Laboratory of Organosilicon Chemistry and Material Technology, Ministry of Education, Hangzhou Normal University, Hangzhou 310012, China

## ARTICLE INFO

### Article history:

Received 10 July 2008

Received in revised form

13 November 2008

Accepted 18 November 2008

Available online 27 November 2008

### Keywords:

2,4,6,8,10-Pentamethylcyclopentasiloxane

Saturated vapor pressure

Antoine equation

Molar evaporation enthalpy

## ABSTRACT

High pure 2,4,6,8,10-pentamethylcyclopentasiloxane was obtained by vacuum distillation method and its saturated vapor pressures at various pressures ranging from 1325 to 91,325 Pa were determined by means of an inclined ebulliometer. The correlations between saturated vapor pressures and temperatures were conducted with relative errors ranging from 0 to 0.87%. The molar evaporation enthalpy ( $\Delta_{\text{vap}}H_m$ ) of 2,4,6,8,10-pentamethylcyclopentasiloxane in the range of 330.80–437.93 K was also estimated by Clausius–Clapeyron equation.

© 2008 Elsevier B.V. All rights reserved.

## 1. Introduction

The saturated vapor pressure is one of the most important thermodynamic parameters for pure chemicals and their solutions. As one of the absolutely necessary fundamental data for phase equilibrium calculations, the relationship between saturated vapor pressure and temperature for many known chemicals with moderated boiling point has been widely investigated. For substances with higher boiling point, experimental saturated vapor pressure data over an extensive range of temperatures are generally hard to obtain. The mole evaporation enthalpy is also one of the important thermodynamic parameters for vapor–liquid equilibrium processes and it can be used for the design and operation of multicomponent systems. 2,4,6,8,10-Pentamethylcyclopentasiloxane (CAS RN: 6166-86-5) is one of the most important chemicals in silicone industry, which can be polymerized with other monomers to produce polymers containing active Si–H bond and functioned as the cross-linking agent for the vulcanization of silicone rubbers or silicone resins. As one of the heat-sensitive chemicals, 2,4,6,8,10-pentamethylcyclopentasiloxane will readily lose some or all hydrogen atoms under higher temperature and

further cross-link each other. Therefore, high pure 2,4,6,8,10-pentamethylcyclopentasiloxane must be purified under reduced pressures at relative lower temperature and the relationship between saturated vapor pressure and temperature should be determined in advance. Unfortunately, fewer such data could be found in literature and the molar evaporation enthalpy of 2,4,6,8,10-pentamethylcyclopentasiloxane was also not reported heretofore [1–4].

In order to acquire fundamental data for engineering applications, the vapor pressure values between 330.80 and 437.69 K for liquid 2,4,6,8,10-pentamethylcyclopentasiloxane were measured by inclined ebulliometer. The relationship between the saturated vapor pressure and temperature was correlated with the Antoine equation and the Antoine constants were regressed by nonlinear least square regression method. The molar evaporation enthalpy and normal boiling point were also calculated.

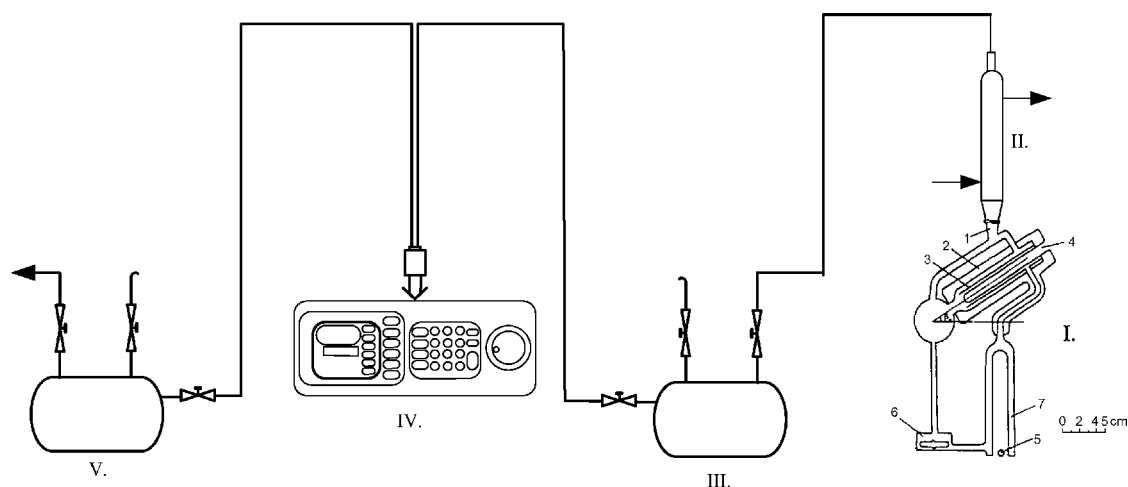
## 2. Experimental

### 2.1. Chemicals

2,4,6,8,10-Pentamethylcyclopentasiloxane was purified by distillation under reduced pressures. Its mass fraction purity, determined by a gas chromatograph equipped with a flame ionization detector (FID), was higher than 99.5%.

\* Corresponding author. Tel.: +86 571 28868362.

E-mail address: [hsdyjg@163.com](mailto:hsdyjg@163.com) (H. Qiu).



**Fig. 1.** Schematic diagram for the measurement of saturated vapor pressure. (I) Inclined ebullimeter with pump-like stirrer [5]; (II) cold tube; (IV) DPI 515 precision pressure controller; (III) and (V) stainless steel buffer tank.

## 2.2. Apparatus

The apparatus used in this work is shown schematically in Fig. 1. It consisted of a set of high-accuracy pressure controller, a set of measurement system, an inclined ebullimeter [5], and a vacuum pump (RZ6 model, Vacuubrand GmbH, Germany). The pressures of the system were controlled by a DPI 515 precision pressure controller. The precision of the pressure controller was higher than 0.02 kPa in the range of 0–200 kPa with a control stability of 0.002 kPa. The measurement stability was 0.001% of reading per annum and the precision for barometric reference was 15 Pa. The calibration standard (Deadweight Tester) accuracy was 0.005% of reading. The temperature was measured by a calibrated mercury thermometer with an uncertainty of  $\pm 0.1$  K.

To check the reliability and accuracy of the apparatus setup, boiling points of ethanol were measured ranging from 11,325 to 101,325 Pa and compared with those calculated from Antoine equation with constants  $A = 10.25500$ ,  $B = 1603.397$  and  $C = -46.0044$ . The Antoine constants listed above were regressed from the experimental data cited in Ref. [6]. The results are listed in Table 1 with maximum relative error no more than 0.37%.

The sample with an approximate volume of 100 mL was charged into the inclined ebullimeter. All measurements were conducted with increase of pressures and in each time, pressure was controlled at desired value. The sample was heated and stirred with a magnetic stirrer to ensure better isothermal conditions and avoid of superheating. When thermal equilibrium was reached, the temperature and pressure of the system were recorded.

**Table 1**  
Comparison of the calculated saturated vapor pressure and the experimental data for ethanol.

$P^s$ (Pa)	$T_{\text{calc.}}$ (K)	$T_{\text{exp.}}$ (K)	RE (%) <sup>a</sup>
11,325	304.58	303.95	0.21
21,325	316.57	315.75	0.26
31,325	324.42	323.50	0.28
41,325	330.36	329.35	0.31
51,325	335.18	334.05	0.34
61,325	339.27	338.05	0.36
71,325	342.83	341.65	0.34
81,325	346.00	344.75	0.36
91,325	348.85	347.55	0.37
101,325	351.46	350.15	0.37

<sup>a</sup> Relative error (RE) ( $|T_{\text{calc.}} - T_{\text{exp.}}|/T_{\text{exp.}} \times 100$ , where  $T_{\text{calc.}}$  is calculated by Antoine constants regressed from experimental data in Ref. [6] and  $T_{\text{exp.}}$  is the experimental value.

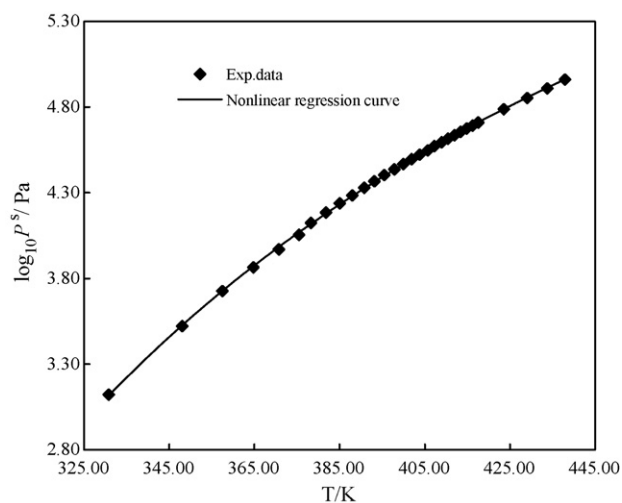
## 3. Results and discussion

### 3.1. Regressed parameters of Antoine equation

Thermodynamic temperature of 2,4,6,8,10-pentamethylcyclopentasiloxane in the range of  $P = 1325$ – $91,325$  Pa were measured by an inclined ebullimeter and the results are listed in Table 3. The experimental data were fitted by Antoine equation.

$$\log_{10}(P^s \text{ (Pa)}) = A - \frac{B}{C + (T \text{ (K)})} \quad (1)$$

The relationship between  $T$  and  $P^s$  in Table 3 was fitted by the nonlinear least square method with EVIEWS 5.0 software (by Gauss-Markov theorem, it attempts to minimize the sum of the squares of the ordinate differences (called residuals) between points generated by the function and corresponding points in the data). Then parameters  $A$ ,  $B$  and  $C$  in Eq. (1) were finally converged after 15 times of iteration and are listed in Table 2. A comparison between the calculated vapor pressure values and experimental values for 2,4,6,8,10-pentamethylcyclopentasiloxane was conducted and the results are listed in Table 3 with maximum relative error no more than 0.87% (Fig. 2). Therefore, the precision and accuracy of the



**Fig. 2.** Nonlinear regression of Antoine equation for 2,4,6,8,10-pentamethylcyclopentasiloxane.

**Table 2**  
The regressed Antoine constants for 2,4,6,8,10-pentamethylcyclopentasiloxane.

A	8.69998
B	1210.811
C	–113.986
R <sup>2</sup>	0.999835

**Table 3**  
Comparison of the calculated saturated vapor pressure and the experimental data and  $\Delta_{\text{vap}}H_m$  for 2,4,6,8,10-pentamethylcyclopentasiloxane.

$P^s$ (Pa)	T (K)		$\Delta_{\text{vap}}H_m$ (J mol <sup>-1</sup> )	RE (%) <sup>a</sup>
	Exp.	Calc.		
1,325	330.80	331.06	49,673.51	0.46
3,325	348.03	347.82	49,955.61	0.28
5,325	357.45	357.43	49,797.01	0.03
7,325	364.75	364.40	49,512.26	0.38
9,325	370.73	369.95	49,169.20	0.80
11,325	375.49	374.60	48,822.96	0.87
13,325	378.23	378.63	48,594.14	0.38
15,325	381.78	382.19	48,264.44	0.38
17,325	385.02	385.39	47,929.79	0.33
19,325	387.96	388.31	47,598.70	0.30
21,325	390.75	390.99	47,259.95	0.21
23,325	393.18	393.48	46,944.36	0.25
25,325	395.46	395.80	46,631.40	0.28
27,325	397.89	397.99	46,279.15	0.08
29,325	399.92	400.04	45,970.93	0.10
31,325	401.90	401.99	45,657.45	0.08
33,325	403.77	403.85	45,348.10	0.06
35,325	405.70	405.61	45,018.19	0.06
37,325	407.22	407.30	44,748.94	0.07
39,325	408.94	408.92	44,434.33	0.01
41,325	410.46	410.48	44,148.32	0.01
43,325	411.98	411.98	43,854.39	0.00
45,325	413.40	413.42	43,572.86	0.02
47,325	414.87	414.82	43,273.89	0.04
49,325	416.19	416.17	42,999.44	0.01
51,325	417.55	417.47	42,707.98	0.06
61,325	423.53	423.47	41,356.06	0.04
71,325	429.06	428.75	39,992.32	0.20
81,325	433.77	433.48	38,739.61	0.18
91,325	437.93	437.79	37,565.69	0.09

<sup>a</sup> Relative error (RE) ( $|T_{\text{calc.}} - T_{\text{exp.}}|/T_{\text{exp.}} \times 100$ ).

above Antoine constants could basically satisfy the requirements for engineering design and application.

### 3.2. Relationship between $\Delta_{\text{vap}}H_m$ and temperature

The influence of pressure on the molar evaporation enthalpy ( $\Delta_{\text{vap}}H_m$ ) usually can be neglected if pressure changes little. While the effect of temperature on  $\Delta_{\text{vap}}H_m$  should not be ignored because  $\Delta_{\text{vap}}H_m$  decreases with the increase of temperatures. Deducing from the differential equation of Clausius–Clapeyron (see Eq. (2)), the function relationship between  $\Delta_{\text{vap}}H_m$  and temperature could be obtained and showed in Eq. (3).

$$\frac{d \ln(P^s \text{ (Pa)})}{dT} = \frac{\Delta_{\text{vap}}H_m}{R(T \text{ (K)})^2} \quad (2)$$

**Table 4**  
Comparison between the calculated value and literature data.

$P^s$ (mmHg)	$P^s$ (Pa)	T (K)		AE (K)	RE (%)
		Literature data	Calc. <sup>a</sup>		
755	100,658	441.75–442.05 [1]	441.48	0.26–0.56	0.06–0.13
43	5,733	358.15 [2]	359.01	0.86	0.24
14	1,867	333.15 [3]	337.01	3.86	1.16
760	101,325	441.15 [4]	441.74	0.59	0.13

<sup>a</sup> Calculated by Antoine equation with constants listed in Table 2. Absolute error (AE) =  $|T_{\text{calc.}} - T_{\text{lit.}}|$ , relative error (RE) ( $|T_{\text{calc.}} - T_{\text{lit.}}|/T_{\text{lit.}} \times 100$ ).

$$\Delta_{\text{vap}}H_m = \left( \frac{d \ln(P^s \text{ (Pa)})}{dT(T \text{ (K)})} \right) R(T \text{ (K)})^2 \quad (3)$$

The integration form of Eq. (2) was regressed by quadratic polynomial equation with correlation coefficient  $R^2 = 0.99981$  when using experimental vapor pressure and temperature data listed in Table 3. Thus Eq. (4) could be obtained.

$$\ln(P^s \text{ (Pa)}) = -26.7098 + 0.1505(T \text{ (K)}) - 1.4487 \times 10^{-4}(T \text{ (K)})^2 \quad (4)$$

When taking Eq. (4) into Eq. (3), the temperature dependency of molar evaporation enthalpy (Eq. (5)) could be further deduced. The value of  $\Delta_{\text{vap}}H_m$  at each experimental temperature was calculated from Eq. (5) and listed in Table 3.

$$\Delta_{\text{vap}}H_m = 1.2508(T \text{ (K)})^2 - 2.4089 \times 10^{-3}(T \text{ (K)})^3 \quad (5)$$

### 3.3. Estimation of $\overline{\Delta_{\text{vap}}H_m}$ for 2,4,6,8,10-pentamethylcyclopentasiloxane

The accurate value of vapor pressure can be used to reliably estimate the value of molar evaporation enthalpy. The mean molar evaporation enthalpy  $\overline{\Delta_{\text{vap}}H_m}$  between 330.80 and 437.69 K and the normal boiling point at  $P^s = 101,325$  Pa for 2,4,6,8,10-pentamethylcyclopentasiloxane could be obtained from Table 3.

$$\overline{\Delta_{\text{vap}}H_m} = 45.53 \text{ kJ mol}^{-1}$$

The calculated value of normal boiling point for liquid 2,4,6,8,10-pentamethylcyclopentasiloxane was 441.74 K, which was derived from the Antoine equation and presented in Table 4.

### 3.4. Reliability analysis of the parameters

To check the reliability of regressed parameters obtained from the Antoine equation, values of boiling point for 2,4,6,8,10-pentamethylcyclopentasiloxane were calculated at  $P = 1867, 5733, 100,658$  and  $101,325$  Pa. The comparison between calculated values and literature data was conducted and the results are listed in Table 4. It could be seen that calculated values agree well with those in literature, except for  $P = 1867$  Pa. Parameters with higher reliability can be further found in the range of  $P = 1325$ – $91,325$  Pa, which could satisfy the estimation requirements for the development and design of chemical engineering process.

## 4. Conclusion

The saturated temperature of 2,4,6,8,10-pentamethylcyclopentasiloxane at various pressures ranging from 1325 to 91,325 Pa was determined by means of an inclined ebulliometer. The Antoine parameters for 2,4,6,8,10-pentamethylcyclopentasiloxane were regressed by nonlinear regression method with EVIEWS 5.0 software and the results were  $A = 8.69998$ ,  $B = 1210.811$  and  $C = -113.986$ . The correlations between the saturated vapor pressure and temperature were conducted with relative error less than 0.87%. The calculated values were in good agreement with literature values, except for

$P = 1867$  Pa. In the range of 14,325–101,325 Pa, the absolute error of boiling point between literature values and calculated values was less than 3.86 K.

The relationship between  $\Delta_{\text{vap}}H_m$  and temperature for 2,4,6,8,10-pentamethylcyclopentasiloxane was also estimated between 330.80 and 437.93 K by Clausius–Clapeyron equation. The obtained  $\overline{\Delta_{\text{vap}}H_m}$  was  $45.53 \text{ kJ mol}^{-1}$  and the calculated normal boiling point was 441.74 K, which was in good agreement with those in literature. The obtained Antoine parameters and molar evaporation enthalpy for 2,4,6,8,10-pentamethylcyclopentasiloxane are foundation for design and operation of rectifying tower.

### Acknowledgements

The authors would like to acknowledge Professor Weidong Yan (Zhejiang University), associate professor Lianzhong Zhang and Dongshun Deng (Zhejiang University of Technology) for their instructions and advices on this experiment.

This work was supported by a grant from the National High Technology Research and Development Program of China (863 Program) (Grant No. 2006AA050203-1) and Zhejiang Provincial Technologies R&D Program of China (Grant No. 2007C21G2150010).

### References

- [1] R.O. Sauer, W.J. Scheiber, S.D. Brewer, Derivatives of the methylchlorosilanes. V. Polysiloxanes from methylchlorosilane, *Journal of the American Chemical Society* 68 (1946) 962–963.
- [2] N.N. Sokolov, K.A. Andrianov, S.M. Akimova, Organocyclosiloxanes. I. Methylchlorocyclo-siloxanes, *Zhurnal Obshchei Khimii* 26 (1956) 933–936.
- [3] T. Tanaka, Heat of combustion of 1,3,5,7,9-pentamethylcyclopentasiloxane, *Technology Reports of the Osaka University* 8 (1958) 437–442.
- [4] T.L. Krasnova, *Zhurnal Obshchei Khimii* 55 (1985) 1528–1533.
- [5] H.R. Li, S.J. Han, Y. Teng, Bubble points measurement for system chloroform–ethanol–benzene by inclined ebulliometer, *Fluid Phase Equilibria* 113 (1995) 185–195.
- [6] F. Fang, Z.Y. Wu, Parameter regression in the mathematical relation of vapor pressure and temperature, *Journal of Hebei University (Natural Science Edition)* 23 (2003) 402–406.