Measurement and Correlation of the Vapor Pressure of Ethyltrimethoxysilane

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Pure ethyltrimethoxysilane was obtained by the distillation method, and its saturated temperatures at various pressures ranging from (2325 to 101 325) Pa were measured by means of an inclined ebulliometer. The correlation between vapor pressure and temperature was conducted with relative errors ranging from (0.03 to 0.38) %. The molar evaporation enthalpy ($\Delta_{vap}H_m$) of ethyltrimethoxysilane in the temperature range from (306.4 to 397.2) K was estimated from the Clausius−Clapeyron equation.

1. Introduction

Being one of the absolutely necessary fundamental pieces of data for phase equilibrium calculations and one of the most important thermodynamic parameters for pure chemicals and their solutions, the relationship between vapor pressures and temperatures for many known chemicals has been widely investigated. Meanwhile, as one of the important thermodynamic parameters for vapor−liquid equilibrium (VLE) processes, the mole evaporation enthalpy is also investigated because it is useful for the design and operation of multicomponent systems.

As one of the most important chemicals in the silicone industry, ethyltrimethoxysilane (CAS RN: 5314-55-6) is widely used in fields of hydrophobic surface treatment and functioned as important intermediates for the synthesis of silanes and silicone chemicals. Therefore, the purity has a more important influence on the subsequent reactions and properties of the products thus obtained. To prepare highly pure ethyltrimethoxysilane, distillation under reduced pressures at a relative low temperature is absolutely necessary, and the relationship between saturated vapor pressure and temperature should be determined in advance. Although the normal boiling point of pure ethyltrimethoxysilane has been reported by Simpson,[1] Sigma-Aldrich,[2] Dow Corning,[3] and Syracuse Research Corporation of Syracuse,[4] the reported values were different from each other; on the other side, the VLE data of pure ethyltrimethoxysilane in the pressure range of (2325 to 101 325) Pa have not been reported before, which could not satisfy the estimation requirements for the practical development and design of the chemical engineering process.

To improve the data reliability and overcome the data deficiency in organosilicon chemistry and provide the detailed fundamental data for engineering fields, the 37 temperatures at various pressures ranging from (2325 to 101 325) Pa were measured by means of an inclined ebulliometer.

It is well-known that the range of experimental values should be as wide as possible. The saturated temperature of ethyltrimethoxysilane is significantly influenced by its saturated vapor pressure, and it would be easily transformed from the liquid to the vapor phase under 2325 Pa. Considering the operating parameters and the efficient operation region beneficial to the distillation process, the lower limit for pressure data acquisition is set to 2325 Pa. The local atmospheric pressure was 101 325 Pa when the experiment was processing. So, the saturated temperatures at various pressures ranging from (2325 to 101 325) Pa corresponding to temperatures ranging from (306.4 to 397.2) K were measured. The relationship between the saturated vapor pressures and temperatures was correlated with the Antoine equation. The equation was regressed by the nonlinear least-squares regression method, and thus the Antoine constants were obtained. The molar evaporation enthalpy and the normal boiling point were also calculated.

2. Experimental Section

2.1. Chemicals. Ethyltrimethoxysilane was purified by distillation under controlled pressure. The temperature and pressure conditions for the distillation of ethyltrimethoxysilane are 397.2 K and 101 325 Pa, respectively. Its mass fraction purity, determined by a gas chromatograph equipped with a HP-5 column and a flame ionization detector (FID), was higher than 0.995.

2.2. Apparatus. The apparatus used in this work has been described previously.[5] It includes a high-accuracy pressure controller, a measurement system, an inclined ebulliometer, and a vacuum pump (RZ6 model, Germany Vacuubrand GMBH+CO KG). The pressures of the system were controlled by a DPI 515 precision pressure controller. The precision of the pressure controller was greater than 0.02 kPa at pressures up to 200 kPa with a control stability of 0.002 kPa. The temperature was measured by a calibrated mercury thermometer with an uncertainty of ± 0.1 K.

The sample with an approximate volume of 100 cm^3 was charged into the inclined ebulliometer. All measurements were conducted in a sequence of increasing pressures, and the pressure was controlled at the desired value at each experimental point. At each desired pressure, the sample was heated and stirred with a magnetic stirrer to provide isothermal conditions and to prevent superheating. When thermal equilibrium was reached, the temperature and pressure values of the system were recorded. The uncertainty of experimental temperature values measured three times at the same pressure value is less than 0.1 K.

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Table 1. Comparison of the Calculated (Equation 3) Saturated Temperature at Pressure p^s and the Experimental Data and $\Delta_{vap}H_m$ for Ethyltrimethoxysilane

p^s	T/K		$\Delta_{vap}H_m$	RE[a]
Pa	exptl	calcd	$J \cdot mol^{-1}$	%
2325	306.4	305.7	43510.51	0.23
3325	311.5	311.8	43608.95	0.10
4325	316.0	316.4	43641.23	0.13
5325	319.8	320.3	43627.46	0.16
6325	324.2	323.6	43563.34	0.19
8325	328.7	329.1	43442.87	0.12
10325	334.2	333.7	43218.07	0.15
13325	339.0	339.3	42950.16	0.09
16325	343.7	344.0	42621.21	0.09
19325	347.7	348.0	42288.03	0.09
22325	351.4	351.6	41935.29	0.06
25325	354.6	354.8	41595.04	0.06
28325	357.5	357.7	41258.03	0.06
31325	360.2	360.4	40919.39	0.06
34325	362.7	362.9	40584.17	0.06
37325	365.0	365.2	40257.13	0.05
40325	367.6	367.4	39865.68	0.05
43325	369.7	369.4	39532.46	0.08
46325	371.1	371.4	39301.77	0.08
49325	374.1	373.3	38784.17	0.21
52325	375.9	375.0	38458.24	0.24
55325	376.5	376.7	38347.02	0.05
58325	379.9	378.4	37692.13	0.39
61325	381.2	379.9	37430.58	0.34
64325	382.6	381.4	37141.96	0.31
67325	383.2	382.9	37016.04	0.08
70325	384.9	384.3	36652.00	0.16
73325	385.9	385.7	36432.81	0.05
76325	386.7	387.0	36254.76	0.08
79325	387.6	388.3	36051.56	0.18
82325	389.0	389.5	35729.37	0.13
85325	390.0	390.7	35494.66	0.18
88325	391.0	391.9	35256.13	0.23
91325	393.0	393.1	34767.52	0.03
94325	393.1	394.2	34742.68	0.28
97325	393.8	395.3	34567.74	0.38
101325	397.2	396.7	33690.80	0.13

[a] Relative error (RE) = $(|T_{calcd} - T_{exp}|/T_{exp}) \cdot 100$.

3. Results and Discussion

3.1. Regressed Parameters of the Antoine Equation. Thermodynamic temperatures of ethyltrimethoxysilane in the pressure range from (2325 to 101 325) Pa were measured by an inclined ebulliometer, and the results are listed in Table 1. The vapor pressure of ethyltrimethoxysilane is similar to that of vinyltrimethoxysilane(CAS RN: 2768-02-7) as given by DIPPR.[6] The experimental data were fitted by the Antoine equation.

$$\log_{10}(p^s/\mathrm{Pa}) = A - \frac{B}{C + (T/\mathrm{K})} \qquad (1)$$

The relationship between T and p^s in Table 1 was fitted by the nonlinear least-squares method with EVIEWS 5.0 software as shown in Figure 1. Then parameters A, B, and C of eq 1 are listed in Table 2. The comparison between the calculated vapor pressure values and the experimental data for ethyltrimethoxysilane was conducted, and the results were listed in Table 1 with a maximum relative error of no more than 0.38 %. Therefore, the precision and accuracy of the above Antoine constants could basically satisfy the requirements for engineering design and application.

3.2. Relationship between $\Delta_{vap}H_m$ and Temperature. The influence of pressure on the molar evaporation enthalpy ($\Delta_{vap}H_m$) usually can be neglected if pressure changes little, while the effect of temperature on $\Delta_{vap}H_m$ should not be ignored because $\Delta_{vap}H_m$ decreases with the increase in temperature. Deducing from the differential equation of Clausius−Clapeyron (see eq 2), the function relationship between $\Delta_{vap}H_m$ and temperature could be obtained and is shown in eq 3.

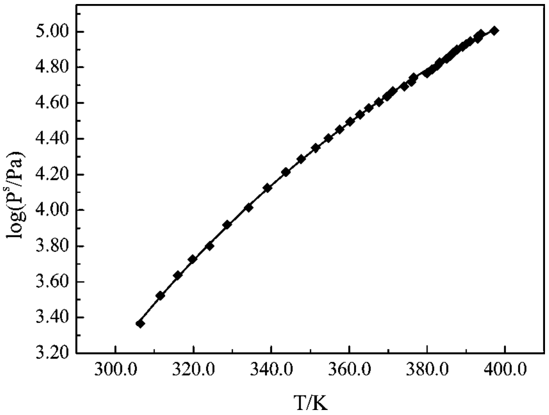

Figure 1. Nonlinear regression of the Antoine equation for ethyltrimethoxysilane. ◆, experimental data; the smoothed line is a nonlinear regression curve.

Table 2. Regressed Antoine Constants for Ethyltrimethoxysilane

A	B	C/K	R^2
8.472245	982.2452	−113.3460	0.999540

$$\frac{\mathrm{d}\ln(p^s/\mathrm{Pa})}{\mathrm{d}T} = \frac{\Delta_{vap}H_m}{R(T/\mathrm{K})^2} \qquad (2)$$

$$\Delta_{vap}H_m = \left(\frac{\mathrm{d}\ln(p^s/\mathrm{Pa})}{\mathrm{d}(T/\mathrm{K})}\right) \cdot R(T/\mathrm{K})^2 \qquad (3)$$

To solve eq 3 and obtain the relationship between $\Delta_{vap}H_m$ and temperature, the relationship between experimental vapor pressure and temperature data listed in Table 1 was regressed by a quadratic polynomial equation with the correlation coefficient $R^2 = 0.99927$. Thus, eq 4 could be obtained.

$$\ln(p^s/\mathrm{Pa}) = -24.792 + 0.15718(T/\mathrm{K}) - 1.6553 \cdot 10^{-4}(T/\mathrm{K})^2 \qquad (4)$$

When taking eq 4 into eq 3, the temperature dependency of molar evaporation enthalpy in eq 5 could be further deduced. The value of $\Delta_{vap}H_m$ at each experimental temperature was calculated from eq 5 and listed in Table 1.

$$\Delta_{vap}H_m = 1.3068(T/\mathrm{K})^2 - 2.7524 \cdot 10^{-3}(T/\mathrm{K})^3 \qquad (5)$$

3.3. Estimation of $\Delta_{vap}\bar{H}_m$ for Ethyltrimethoxysilane. Accurate vapor pressure values can be used to estimate the molar enthalpy of vaporization from eq 6. The linear fitting equation (eq 7) was determined by means of the linear least-squares method with the correlation coefficient $R^2 = 0.99925$.

$$\ln p^s = (-\Delta_{vap}\bar{H}_m/R(T/\mathrm{K})) + C \qquad (6)$$

$$\ln p^s = -4958.38/(T/\mathrm{K}) + 24.073 \qquad (7)$$

Both the averaged molar evaporation enthalpy $\bar{\Delta}_{vap}H_m$ of ethyltrimethoxysilane within the range of experimental temperatures and the normal boiling point at $p^s = 101\,325$ Pa could be further obtained from eq 7.

$$\Delta_{vap}H_m = 41.22\ \mathrm{kJ \cdot mol^{-1}}$$

The calculated value of normal boiling point for liquid ethyltrimethoxysilane was 396.7 K, which was derived from the Antoine equation and presented in Table 3.

Table 3. Comparison between the Calculated Value and Literature Data

p^s	T/K		AE[a]	RE[a]
Pa	lit. data	calcd[b]	K	%
101 325	396.2 to 398.2[1]	396.7	0.5 to 1.5	0.13 to 0.38
101 325	397.8[2]	396.7	1.1	0.28
101 325	396.2 to 397.2[3]	396.7	0.5	0.13
101 325	397.5[4]	396.7	0.8	0.20

[a] Absolute error (AE) = $|T_{\text{calcd}} - T_{\text{lit.}}|$. Relative error (RE) = $(|T_{\text{calcd}} - T_{\text{lit.}}|/T_{\text{lit.}})\cdot 100$. [b] Calculated by Antoine equation with constants listed in Table 2.

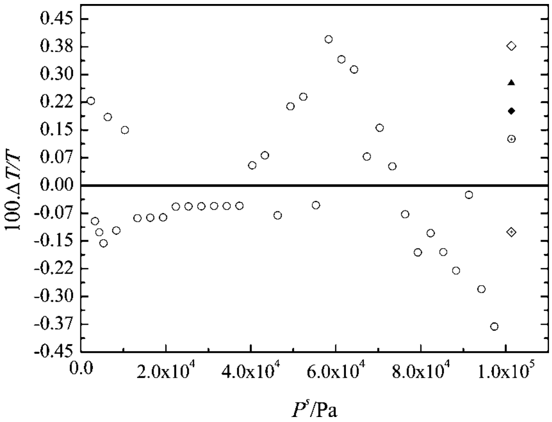

Figure 2. Fractional deviations $\Delta T = T(\text{exptl}) - T(\text{calcd})$ of the experimental saturated temperatures T(exptl) and $\Delta T = T(\text{lit.}) - T(\text{calcd})$ of the literature values T(lit.) of ethyltrimethoxysilane at pressures ranging from (2325 to 101 325) Pa from values T(calcd) obtained with the Antoine equation in this work. ○, this work; ◇, ref 1; ▲, ref 2; +, ref 3; ◆, ref 4.

3.4. Reliability Analysis of the Parameters. To check the reliability of the regressed parameters obtained from the Antoine equation in this range, values of the boiling point for ethyltrimethoxysilane were calculated at $p = 101\,325$ Pa. The comparison between the above calculated values and the literature data were conducted, and the results are listed in Table 3. Fractional deviations of the experimental saturated temperatures and the literature values of ethyltrimethoxysilane at pressures ranging from (2325 to 101 325) Pa from calculated values obtained with the Antoine equation are plotted in Figure 2. It could be seen that calculated values agree well with those in literature. The parameters could satisfy the estimation requirements for the development and design of the chemical engineering process.

4. Conclusion

The saturated temperature of ethyltrimethoxysilane at various pressures ranging from (2325 to 101 325) Pa was determined by means of an inclined ebulliometer. The results were fit to an Antoine equation. The correlations between the saturated vapor pressure and the temperature were conducted with a relative error less than 0.38 %.

The relationship between $\Delta_{\text{vap}}H_{\text{m}}$ and temperature for ethyltrimethoxysilane was also estimated between (306.4 and 397.2) K by the Clausius−Clapeyron equation. The obtained $\Delta_{\text{vap}}\bar{H}_{\text{m}}$ was 41.22 $\text{kJ}\cdot\text{mol}^{-1}$, and the calculated normal boiling temperature was 396.7 K. The obtained Antoine parameters and molar evaporation enthalpy for ethyltrimethoxysilane are useful fundamental data for the design and operation of rectifying tower.

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