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Measurement and Correlation of the Vapor Pressure of Methylethoxydichlorosilane

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Pure methylethoxydichlorosilane was obtained by vacuum distillation and its vapor pressure determined at pressures from (11.325 to 101.266) kPa with an inclined ebulliometer. The results were fit with an Antoine equation with parameters $A = 9.74178$, $B = 1715.764$, and $C = -49$ K. The correlation represented the measurements with differences of between (0.01 and 0.08) %. The molar evaporation enthalpy ($\Delta_{vap}H_m$) of methylethoxydichlorosilane at temperatures in the range of (312.9 to 373.6) K was estimated from the Clausius−Clapeyron equation.

1. Introduction

As one of the most important chemicals in silicone industry, methylethoxydichlorosilane (CAS RN: 1825-75-8) is widely used because it can be polymerized with other monomers with hydrolyzable ethoxy groups, which may facilitate the fabrication of some novel silicone polymers. It also reacts with phenylsodium to yield alkoxychloromethylphenylsilane.[1] The reaction temperature is one of the important factors for the heterogeneity of the reactions of alkoxydichloromethylsilanes with phenylsodium reagents in a nonpolar solvent. Moreover, the purity has a more important influence on the reaction. Therefore, methylethoxydichlorosilane must be purified under reduced pressures at relative low temperature, and the vapor pressure is required as a function of temperature. Daniel[2] reported the vapor pressure of methylethoxydichlorosilane at pressures from (0.133 to 101.325) kPa with five measurements at temperatures greater than 293.15 K that could be used in a correlation. For the design of the chemical engineering process, this is insufficient owing to the variation of pressure with temperature.

In this work the vapor pressure has been measured at pressures from (11.325 to 101.266) kPa that correspond to 31 temperatures between (312.9 and 373.6) K with an inclined ebulliometer. The relationship between the vapor pressure and the temperature was correlated with the Antoine equation (Figure 1). The molar evaporation enthalpy and the normal boiling point were also calculated.

2. Experimental Section

2.1. Chemicals. Methylethoxydichlorosilane was purified by distillation at a temperature of 373.15 K and pressure of 101.266 kPa. A gas chromatograph equipped with a HP-5 column and a flame ionization detector were used to determine mass fraction purity, which was greater than 0.995.

2.2. Apparatus. The apparatus used in this work has been described previously.[3] It includes a high-accuracy pressure controller, 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 controlled was < ± 0.02 kPa at pressures in the range of (0 to 200) kPa with a control stability of ± 0.002 kPa. The temperature was measured by a calibrated mercury-in-glass thermometer with an uncertainty of ± 0.1 K.

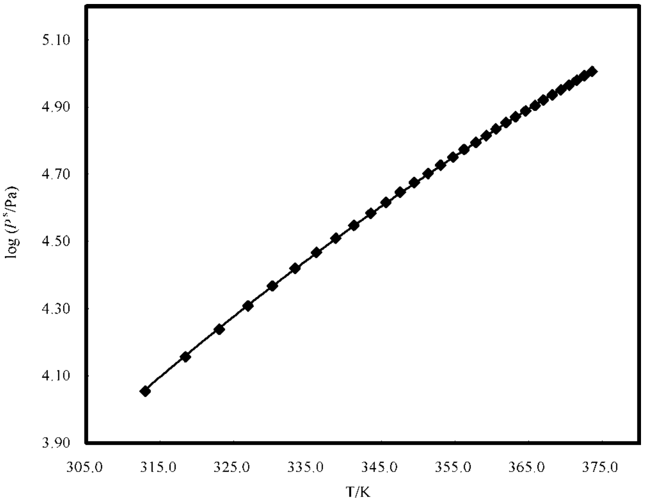

Figure 1. Vapor pressure P as a function of temperature T for methylethoxydichlorosilane. ◆, experimental data; solid line, the Antoine equation eq 1.

The sample with an approximate volume of 100 cm^3 was placed inside 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 were recorded. The uncertainty of experimental temperature values measured three times at the same pressure value is less than ± 0.1 K.

3. Results and Discussion

3.1. Regressed Parameters of Antoine Equation. Thermodynamic temperatures of methylethoxydichlorosilane in the

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Table 1. Vapor Pressure P as Function of Temperature T with Estimated Enthalpy of Evaporation $\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ for Methylethoxydichlorosilane

P^s / Pa	T / K exp.	T / K calc.	$\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ / $\mathrm{J \cdot mol^{-1}}$	RE[a] / %
11325	312.9	312.7	35550.96	0.07
14325	318.4	318.2	35647.81	0.07
17325	323.0	322.8	35683.51	0.06
20325	326.9	326.8	35680.59	0.04
23325	330.2	330.3	35653.51	0.02
26325	333.3	333.5	35608.12	0.05
29325	336.2	336.3	35546.50	0.04
32325	338.8	339.0	35474.33	0.04
35325	341.3	341.4	35393.97	0.03
38325	343.6	343.7	35306.49	0.03
41325	345.7	345.8	35216.43	0.04
44325	347.5	347.8	35126.58	0.07
47325	349.5	349.7	35025.74	0.06
50325	351.4	351.5	34919.14	0.03
53325	353.0	353.2	34816.98	0.04
56325	354.7	354.8	34708.08	0.03
59325	356.2	356.4	34603.20	0.04
62325	357.8	357.9	34488.87	0.01
65325	359.2	359.3	34380.36	0.02
68325	360.6	360.7	34275.13	0.03
71325	361.9	362.0	34161.25	0.02
74325	363.2	363.3	34051.59	0.03
77325	364.6	364.6	33928.59	0.01
80325	365.9	365.8	33810.44	0.03
83325	367.0	366.9	33703.06	0.01
86325	368.2	368.1	33582.25	0.03
89325	369.4	369.2	33462.86	0.05
92325	370.5	370.3	33345.34	0.06
95325	371.5	371.3	33235.67	0.06
98325	372.6	372.3	33117.60	0.07
101266	373.6	373.3	33002.35	0.08

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

Table 2. Parameters of the Antoine Equation 1 for Methylethoxydichlorosilane

A	B	C/K	R^2
9.74178	1715.764	−11.049	0.99991

Table 3. Comparison between the Calculated Boiling Temperature T at a Pressure and the Values Obtained from the Literature

P^s / Pa	T / K literature data[2]	T / K calc.[a]	AE[b] / K	RE[c] / %
7999	305.8	304.9	0.8	0.28
13332	317.3	316.5	0.7	0.23
26664	334.2	333.8	0.3	0.10
53329	353.5	353.2	0.3	0.07
101325	373.8	373.3	0.4	0.11

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

range of P = (11.325 to 101.266) kPa were measured by an inclined ebulliometer, and the results are listed in Table 1. The experimental data were fitted by Antoine equation.

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

The parameters A, B, and C of eq 1 obtained are listed in Table 2. The differences between the calculated and the experimental vapor pressures for methylethoxydichlorosilane are also listed in Table 1, where the maximum relative error is < 0.08 %, that is, sufficient for engineering design.

3.2. Relationship between $\Delta_{vap}H_m$ and Temperature. The Clausius−Clapeyron

$$\frac{\mathrm{d}\ln(P^s/\mathrm{Pa})}{\mathrm{d}T} = \frac{\Delta_{\mathrm{vap}}H_{\mathrm{m}}}{R(T/\mathrm{K})^2} \tag{2}$$

can be rearranged to give

$$\Delta_{\mathrm{vap}}H_{\mathrm{m}} = \left(\frac{\mathrm{d}\ln(P^s/\mathrm{Pa})}{\mathrm{d}(T/\mathrm{K})}\right) \cdot R(T/\mathrm{K})^2 \tag{3}$$

and solved for $\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ with an expression for vapor pressure as a function of temperature, which for the results listed in Table 1 is

$$\ln(P^s/\mathrm{Pa}) = -16.6245 + 0.1222(T/\mathrm{K}) - 1.2549 \cdot 10^{-4}(T/\mathrm{K})^2 \tag{4}$$

The combination of eqs 3 and 4 provides

$$\Delta_{\mathrm{vap}}H_{\mathrm{m}} = 1.0160(T/\mathrm{K})^2 - 2.0866 \cdot 10^{-3}(T/\mathrm{K})^3 \tag{5}$$

that are listed in Table 1.

3.3. Estimation of $\langle\Delta_{vap}H_m\rangle$ for Methylethoxydichlorosilane. Equation 2 can be recast as

$$\ln P^s = (-\overline{\Delta_{\mathrm{vap}}H_{\mathrm{m}}}/R(T/\mathrm{K})) + C \tag{6}$$

to provide the average molar evaporation enthalpy $\langle\Delta_{\mathrm{vap}}H_m\rangle$ = 35.06 $\mathrm{kJ \cdot mol^{-1}}$ and the normal boiling temperature of 373.35 K at P^s = 101.325 kPa. This boiling temperature agrees with that reported in the literature of 373.21 K.[4]

3.4. Reliability Analysis of the Parameters. To check the reliability of regressed parameters obtained from the Antoine equation in this range, values of boiling point for methylethoxydichlorosilane were calculated at P = (8.0, 13.33, 26.66, 53.33, and 101.325) kPa, respectively. The comparison between the calculated and the literature values[2] are listed in Table 3 with relative error of less than 0.3 %.

4. Conclusion

The vapor pressure of methylethoxydichlorosilane at pressures from (11.325 to 101.266) kPa was determined with an inclined ebulliometer. The results were fit by an Antoine equation that represented the data with a relative error less than 0.08 %. The relationship between $\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ and temperature for methylethoxydichlorosilane was also estimated at temperatures between (312.9 and 373.6) K with the Clausius−Clapeyron equation with the result of $\langle\Delta_{\mathrm{vap}}H_{\mathrm{m}}\rangle$ = 35.06 $\mathrm{kJ \cdot mol^{-1}}$, and the calculated boiling temperature was 373.35 K at a pressure of 101.325 kPa.

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