PHYSICAL CHEMISTRY

1960

SovietRxiv

Abstract

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PHYSICAL CHEMISTRY

M. I. Shakhparonov, S. L. Lelchuk, and K. M. Korchemskaya

THERMODYNAMIC PROPERTIES OF SOLUTIONS OF CHLOROSILANE DERIVATIVES

(Presented by Academician V. I. Spitsyn, April 4, 1960)

Chlorosilane derivatives, as is known, are among the principal intermediates in the laboratory and industrial synthesis of organosilicon polymers. A systematic study of the thermodynamic properties of solutions of these substances is of substantial practical and theoretical importance. In the present communication we give the main results of investigations of the pressure P and density γ of saturated vapors of the following systems: $CH_3SiHCl_2{-}SiCl_4$; $SiHCl_3{-}C_6H_6$; $CH_3SiCl_3{-}SiCl_4$, $(CH_3)_3SiCl{-}CH_3SiHCl_2$, $(CH_3)_3SiCl{-}CH_3SiCl_3$, as well as solutions of CH_3SiHCl_2 and CH_3SiCl_3 in an azeotropic mixture containing 45.93 mole % $(CH_3)_3SiCl$ and 54.07 mole % $SiCl_4$.

The method for measuring P and γ is described in (^{1}). After chemical purification and rectification, the individual liquid components had the following densities d_4^{20} and boiling points at 760 mm Hg: $SiHCl_3$: d_4^{20} 1.3451 and b.p. 31.9°; C_6H_6: d_4^{20} 0.8787 and b.p. 80.1°; CH_3SiHCl_2: d_4^{20} 1.1049 and b.p. 41.1°; $(CH_3)_3SiCl$: d_4^{20} 0.858 and b.p. 57.6°; $SiCl_4$: d_4^{20} 1.483 and b.p. 56.8°; CH_3SiCl_3: d_4^{20} 1.2770 and b.p. 65.9°.

Table 1

Constants of the Antoine equation

System	X_1	A	B	C
$CH_3SiHCl_2(1)$ – $(CH_3)_3SiCl(2)$	1.000	19.6410	18222.2	1046.2
$CH_3SiHCl_2(1)$ – $(CH_3)_3SiCl(2)$	0.900	4.1838	116.03	46.72
$CH_3SiHCl_2(1)$ – $(CH_3)_3SiCl(2)$	0.500	8.9130	2390.0	347.7

System	X_1	A	B	C
$CH_3SiHCl_2(1)-(CH_3)_3SiCl(2)$	0.216	8.4039	2153.5	336.1
$CH_3SiHCl_2(1)-(CH_3)_3SiCl(2)$	0.100	6.7000	1036.2	215.0
$CH_3SiHCl_2(1)-(CH_3)_3SiCl(2)$	0.000	6.2424	829.4	188.6
$SiHCl_3(1)-C_6H_6(2)$	1.000	4.5403	188.85	81.79
$SiHCl_3(1)-C_6H_6(2)$	0.900	5.9874	669.1	180.6
$SiHCl_3(1)-C_6H_6(2)$	0.640	7.0797	1280.32	262.9
$SiHCl_3(1)-C_6H_6(2)$	0.4995	5.8792	684.14	180.53
$SiHCl_3(1)-C_6H_6(2)$	0.300	7.6490	1757.6	311.7
$SiHCl_3(1)-C_6H_6(2)$	0.230	5.4023	523.72	146.55
$CH_3SiHCl_2(1)-SiCl_4(2)$	0.895	6.4484	887.76	206.45
$CH_3SiHCl_2(1)-SiCl_4(2)$	0.690	8.3908	2103.5	337.3
$CH_3SiHCl_2(1)-SiCl_4(2)$	0.495	9.7062	3204.5	422.8
$CH_3SiHCl_2(1)-SiCl_4(2)$	0.200	8.6719	2369.5	356.9
$CH_3SiHCl_2(1)-SiCl_4(2)$	0.060	7.5487	1572.95	281.63
$CH_3SiHCl_2(1)-SiCl_4(2)$	0.000	7.4042	1442.8	261.7
$CH_3SiCl_3(1)-(CH_3)_3SiCl(2)$	1.000	8.6655	2380.6	345.16
$CH_3SiCl_3(1)-(CH_3)_3SiCl(2)$	0.850	8.5799	2324.9	343.17
$CH_3SiCl_3(1)-(CH_3)_3SiCl(2)$	0.532	9.7555	3371.9	428.20

System	X_1	A	B	C
CH_3SiCl_3(1) – $(CH_3)_3SiCl$(2)	0.150	8.12392	2057.4	324.50
CH_3SiCl_3(1) –$SiCl_4$(2)	0.900	7.8405	1774.6	293.2
CH_3SiCl_3(1) –$SiCl_4$(2)	0.600	9.2407	2877.7	391.27
CH_3SiCl_3(1) –$SiCl_4$(2)	0.300	13.0808	7291.1	656.1
CH_3SiCl_3(1) –$SiCl_4$(2)	0.100	7.0783	1274.9	245.4
Azeotrope (1)– CH_3SiHCl_2(2)	1.000	8.4765	2210.91	340.23
Azeotrope (1)– CH_3SiHCl_2(2)	0.950	6.3505	847.59	197.91
Azeotrope (1)– CH_3SiHCl_2(2)	0.500	22.3568	26090.1	1292.9
Azeotrope (1)– CH_3SiHCl_2(2)	0.050	6.2535	793.8	193.48
Azeotrope (1)– CH_3SiCl_3(2)	0.900	8.5736	2449.2	361.6
Azeotrope (1)– CH_3SiCl_3(2)	0.500	9.8962	3458.1	432.9
Azeotrope (1)– CH_3SiCl_3(2)	0.208	7.8291	1790.65	298.06

Table 1 contains the values of the constants of the Antoine equations

$$\lg P = A - B(C + T),$$

calculated from experimental data on the pressure P of the individual components and their solutions.

Fig. 1

Fig. 2

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Fig. 3

Using the equation $\overline{M} = \gamma RT/P$, the average molecular weight of the saturated vapors was calculated, and then their composition was determined from the formula $\overline{M} = \sum_i M_i x'_i$. In parallel, the partial pressures P_i of the component vapors were calculated. The values of P_i and x'_i were independently checked by the conditions of thermodynamic consistency, which made it possible to find these quantities with an accuracy of 1-2%.

Fig. 1 shows the dependence of the total and partial vapor pressures of the $SiHCl_3$—C_6H_6 system on the composition of the solutions at 30°.

Fig. 2 presents the isotherm P and P_i of the CH_3SiHCl_2—$SiCl_4$ system at 40° and of the CH_3SiCl_3—$SiCl_4$ system at 50°.

It follows from Figs. 1 and 2 that the indicated solutions are characterized by small positive deviations from ideality.

Solutions $(CH_3)_3SiCl$—CH_3SiCl_3, CH_3SiHCl_2—$(CH_3)_3SiCl$, azeotrope–CH_3SiCl_3, and azeotrope–CH_3SiHCl_2, within the limits of the accuracy of our measurements (1-2%), obey Raoult' s law over the entire concentration range. Fig. 3 shows the isobars of the solutions investigated by us at $P = 760$ mm.

Moscow State University
named after M. V. Lomonosov

Received
2 IV 1960

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Fig. 3

Figure 3: Fig. 3