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K	vaporization equilibrium ratio, y/x
k	binary interaction parameter
n	number of moles
P	pressure
R	universal gas constant
T	temperature
V	total volume
v	molar volume
$\bar{v}$	partial molar volume
x	mole fraction in the liquid phase
y	mole fraction in the vapor phase
z	mole fraction (liquid or vapor phase)

Greek Letters

Φ	fugacity coefficient
ω	acentric factor

Superscripts

L	liquid phase
s	saturated property
∞	infinite dilution

Subscripts

1	component 1 (solvent)
2	component 2 (solute)
c	critical property
i,j	components i and j
r	reduced property

Registry No. CO_2, 124-38-9; phenol, 108-95-2; catechol, 120-80-9.

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Isobaric Vapor–Liquid Equilibria for the Binary Systems CH_3SiHCl_2 with $(CH_3)_3SiCl$, $(CH_3)_2SiCl_2$, CH_3SiCl_3, or $SiCl_4$

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This paper reports isobaric vapor–liquid equilibrium (VLE) data for four binary systems containing dichloromethylsilane, CH_3SiHCl_2, and chlorotrimethyl-, dichlorodimethyl-, trichloromethyl-, or tetrachlorosilane, $(CH_3)_{4-n}SiCl_n$ (n = 1–4). The VLE data were determined ebulliometrically at atmospheric pressure, and the experimental temperatures were corrected for 760 mmHg. The pure component vapor pressures were calculated using literature Antoine constants. The VLE data were then correlated by means of the Wilson, nonrandom two-liquid (NRTL), and Gothard equations.

Introduction

Vapor–liquid equilibrium (VLE) data for binary methylchlorosilane systems are scarce. In view of the importance of these data for the design of rectification columns in manufacturing silicon derivatives, we developed a data base for this class of substances. All the VLE data published until now on methylchlorosilanes were tested using a rectification process computer simulator and were verified on an industrial pilot plant.

Experimental Section

Materials. The methylchlorosilanes were Fluka products with 98% stated purity. They were purified by distillation on a laboratory column until no impurities were chromatographically detectable.

The physicochemical constants of the purified substances are compared with literature data in Table I.

Apparatus and Procedure. The experimental apparatus was a Swietoslawski-type ebulliometer (*1*).

The experimental boiling temperatures, t^*, were measured to within 5.10^{-2} °C with a Beckmann thermometer calibrated in our laboratory with benzene for high boiling points and CH_3HSiCl_2 for low boiling points. The atmospheric pressure, P^*, was read on a Hg barometer to within 0.1 mmHg. The liquid, x_i, and vapor, y_i, mole fraction compositions of the two phases at equilibrium were determined by means of a gas chromatograph (*2*) packed with a mixture of 70% FS 1265 + 30% SE-30 on AW/DHCS Chromosorb P, 60–80 mesh. The overall uncertainty in the equilibrium mole fractions is estimated to be $(0.1–1) \times 10^{-2}$. The t^* values at pressure P^* were corrected for normal pressure, $P° = 760$ mmHg, using the following equation (*3*):

$$t = t^* + ((dt_1/dP)x_1 + (dt_2/dP)x_2)(P° - P^*) \qquad (1)$$

where t_i is the boiling temperature of pure component i calculated with the Antoine equation from

$$t_i/°C = B_i/[A_i - \log (P°/mmHg)] - C_i \qquad (2)$$

The experimental data are shown in Tables II–V.

Results

The liquid-phase activity coefficients, γ_i, were calculated from the experimental P–x–y data at each temperature. The

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Table I. Densities, Normal Boiling Points *t*, and Antoine Coefficients *A*, *B*, and *C*, Equation 2 (*3*), for Methylchlorosilanes

	ρ(20 °C)/(g cm^{-3})		t/°C				
component	exptl	lit. (*8*, *9*)	exptl	lit. (*8*, *9*)	A	B	C
CH_3SiHCl_2	1.110	1.1069	41.60	41.0	7.0484	1179	242.00
$SiCl_4$	1.479	1.483	56.63	57.2	6.9728	1200	235.96
$(CH_3)_3SiCl$	0.859	0.858	57.14	57.2	6.9505	1191	235.05
CH_3SiCl_3	1.273	1.276	65.38	65.34	6.8721	1167	226.00
$(CH_3)_2SiCl_2$	1.069	1.0663	69.37	70.00	7.1435	1328	241.05

Table II. Experimental Boiling Temperature t^* at Pressure P^*, Corrected Boiling Temperature t at Normal Pressure (P = 760 mmHg), Equation 1, Activity Coefficients γ_i, Liquid-Phase Mole Fraction x_1, and Vapor-Phase Mole Fraction y_1 for the Binary System CH_3SiHCl_2 (1)–$SiCl_4$ (2)

t^*/°C	P^*/mmHg	t/°C	x_1	y_1	γ_1	γ_2	t^*/°C	P^*/mmHg	t/°C	x_1	y_1	γ_1	γ_2
54.44	745.5	55.03	0.0204	0.0461	1.4687	1.0445	46.13	745.5	46.71	0.4103	0.5583	1.1321	1.0531
54.30	745.5	54.89	0.0253	0.0567	1.4612	1.0427	44.72	745.5	45.30	0.5082	0.6369	1.0892	1.0890
53.94	745.5	54.43	0.0426	0.0923	1.4311	1.0364	44.29	745.5	44.87	0.5431	0.6634	1.0761	1.1026
53.34	745.5	53.93	0.0618	0.1294	1.4038	1.0305	43.77	745.5	44.34	0.5898	0.6981	1.0603	1.1217
52.47	745.5	53.06	0.0962	0.1917	1.3701	1.0211	42.54	745.5	43.11	0.7274	0.7923	1.0144	1.2121
51.40	745.5	51.99	0.1402	0.2611	1.3215	1.0154	41.78	745.5	42.35	0.7697	0.8244	1.0220	1.2454
50.86	745.5	51.45	0.1637	0.2944	1.2966	1.0144	41.33	745.5	41.90	0.8680	0.9001	1.0038	1.2565
50.35	745.5	50.94	0.1868	0.3259	1.2766	1.0134	41.30	744.8	41.89	0.8695	0.9015	1.0040	1.2536
48.29	745.5	48.87	0.2867	0.4416	1.1995	1.0241	40.70	744.8	41.29	0.9385	0.9539	1.0035	1.2719
47.43	745.5	48.01	0.3335	0.4894	1.1732	1.0315							

Table III. Experimental Boiling Temperature t^* at Pressure P^*, Corrected Boiling Temperature t at Normal Pressure (P = 760 mmHg), Equation 1, Activity Coefficients γ_i, Liquid-Phase Mole Fraction x_1, and Vapor-Phase Mole Fraction y_1 for the Binary System CH_3SiHCl_2 (1)–$(CH_3)_3SiCl$ (2)

t^*/°C	P^*/mmHg	t/°C	x_1	y_1	γ_1	γ_2	t^*/°C	P^*/mmHg	t/°C	x_1	y_1	γ_1	γ_2
77.20	750.6	57.58	0.0522	0.0751	0.8212	0.9796	47.73	751.6	48.03	0.6537	0.7737	0.9445	0.8882
56.30	750.6	56.68	0.0997	0.1366	0.8482	0.9866	46.40	751.6	46.73	0.7419	0.8424	0.9432	0.8670
55.90	750.6	56.28	0.1490	0.2045	0.8590	0.9737	45.30	751.6	45.63	0.7876	0.8749	0.9550	0.8679
55.30	750.7	55.68	0.2029	0.2777	0.8711	0.9618	44.00	751.6	44.33	0.8624	0.9235	0.9591	0.8563
54.50	750.7	54.88	0.2616	0.3551	0.8838	0.9506	43.50	751.6	43.83	0.8990	0.9454	0.9569	0.8471
53.90	751.2	54.30	0.3167	0.4248	0.8879	0.9333	42.85	751.6	43.18	0.9323	0.9643	0.9609	0.8450
52.70	751.2	53.05	0.4055	0.5301	0.8973	0.9120	42.50	751.5	42.83	0.9345	0.9655	0.9706	0.8542
51.90	751.2	52.25	0.4720	0.6027	0.8972	0.8910	42.30	751.5	42.63	0.9463	0.9720	0.9712	0.8515
50.80	751.6	51.14	0.5139	0.6458	0.9127	0.8943	41.85	751.5	42.18	0.9822	0.9910	0.9679	0.8388
48.90	751.6	49.23	0.6065	0.7331	0.9299	0.8861							

Table IV. Experimental Boiling Temperature t^* at Pressure P^*, Corrected Boiling Temperature t at Normal Pressure (P = 760 mmHg), Equation 1, Activity Coefficients γ_i, Liquid-Phase Mole Fraction x_1, and Vapor-Phase Mole Fraction y_1 for the Binary System CH_3SiHCl_2 (1)–CH_3SiCl_3 (2)

t^*/°C	P^*/mmHg	t/°C	x_1	y_1	γ_1	γ_2	t^*/°C	P^*/mmHg	t/°C	x_1	y_1	γ_1	γ_2
66.04	753.0	66.33	0.0102	0.0188	0.8734	0.9930	53.35	754.1	53.59	0.5227	0.7119	0.9193	0.9070
65.52	753.0	65.81	0.0263	0.0481	0.8786	0.9948	48.78	753.8	49.03	0.6953	0.8444	0.9397	0.8962
64.45	753.6	65.72	0.0337	0.0615	0.8787	0.9910	46.80	753.4	74.06	0.7712	0.8912	0.9501	0.8939
64.67	753.6	64.87	0.0629	0.1135	0.8870	0.9907	44.95	753.4	45.21	0.8438	0.9305	0.9605	0.8930
63.79	754.1	64.04	0.0952	0.1689	0.8932	0.9865	44.16	753.4	44.42	0.8795	0.9481	0.9627	0.8892
61.40	754.1	61.64	0.1801	0.3055	0.9113	0.9801	43.02	745.7	43.58	0.9150	0.9645	0.9668	0.8887
59.80	754.1	60.04	0.2492	0.4057	0.9139	0.9635	42.32	746.1	42.86	0.9393	0.9753	0.9743	0.8917
56.40	754.1	56.64	0.3787	0.5679	0.9265	0.9446	41.80	746.5	42.33	0.9608	0.9843	0.9780	0.8917
55.40	754.1	55.64	0.4419	0.6351	0.9138	0.9178							

Table V. Experimental Boiling Temperature t^* at Pressure P^*, Corrected Boiling Temperature t at Normal Pressure (P = 760 mmHg), Equation 1, Activity Coefficients γ_i, Liquid-Phase Mole Fraction x_1, and Vapor-Phase Mole Fraction y_1 for the Binary System CH_3SiHCl_2 (1)–$(CH_3)_2SiCl_2$ (2)

t^*/°C	P^*/mmHg	t/°C	x_1	y_1	γ_1	γ_2	t^*/°C	P^*/mmHg	t/°C	x_1	y_1	γ_1	γ_2
69.51	751.1	69.88	0.0284	0.0546	0.8293	0.9911	52.85	753.4	53.12	0.5048	0.7232	0.8902	0.8762
69.14	750.9	69.52	0.0384	0.0736	0.8344	0.9921	50.72	755.9	50.88	0.6098	0.8075	0.9060	0.8652
68.70	750.9	69.08	0.0552	0.1052	0.8390	0.9885	48.41	756.2	48.56	0.6920	0.8616	0.9108	0.8518
67.06	751.2	67.42	0.1118	0.2081	0.8554	0.9793	46.47	756.3	46.62	0.7756	0.9078	0.9187	0.8452
66.37	751.7	66.71	0.1354	0.2491	0.8613	0.9752	45.39	756.9	45.51	0.8383	0.9382	0.9327	0.8427
64.61	752.2	64.93	0.1988	0.3531	0.8716	0.9587	44.52	757.3	44.63	0.8744	0.9538	0.9412	0.8443
64.61	752.2	64.93	0.2019	0.3579	0.8699	0.9553	43.71	757.7	43.80	0.9116	0.9687	0.9427	0.8392
60.47	753.4	60.74	0.2239	0.3916	0.8724	0.9490	43.21	757.7	43.30	0.9369	0.9783	0.9510	0.8403
59.66	753.4	59.93	0.3489	0.5609	0.8842	0.9161	42.80	757.5	42.90	0.9511	0.9834	0.9568	0.8448
58.11	753.4	58.38	0.3751	0.5918	0.8875	0.9112	42.10	757.5	42.30	0.9668	0.9889	0.9588	0.8445
56.15	753.4	56.42	0.4269	0.6485	0.8926	0.9004							

nonideality of the vapor phase and the Poynting factor were taken into account in terms of the second virial coefficients of the pure components estimated from critical data (*4*) (Table VI).

The excess virial coefficients and the excess molar volumes

Table VI. Critical Temperature, T^c, Pressure, P^c, and Molar Volume, V^c, of the Pure Components (*9*)

component	T^c/K	P^c/atm	V^c/(cm^3 mol^{-1})
CH_3SiHCl_2	475	38.5	290
$SiCl_4$	507	37.0	330
CH_3SiCl	498	31.6	363
$(CH_3)_3SiCl_3$	518	54.9	339
$(CH_3)_2SiCl_2$	520	34.4	350

Table VII. Root Mean Square Deviations of g^E/RT, $\sigma^2(g^E)$, and y, $\sigma^2(y)$, Obtained from the Correlations

model parameter	CH_3SiHCl_2 +			
	$SiCl_4$	$(CH_3)_3SiCl$	CH_3SiCl_3	$(CH_3)_2SiCl_2$
	Wilson, Equation 3			
$(\lambda_{12} - \lambda_{11})$/(J mol^{-1})	−709.563	614.5	304.5	332.0
$(\lambda_{21} - \lambda_{22})$/(J mol^{-1})	1427.938	739.5	947	918.875
$\sigma^2(g^E)/10^2$	2.0	1.5	2.3	2.0
$\sigma^2(y)/10^2$	1.7	3.4	3.3	4.8
	NRTL, Equation 6			
α_{ij}	0.3	0.3	0.3	0.3
$(g_{12} - g_{11})$/(J mol^{-1})	169.578	−149.563	−97.688	−183.625
$(g_{21} - g_{22})$/(J mol^{-1})	62.469	−94.875	−93.625	−79.563
$\sigma^2(g^E)/10^2$	1.9	1.3	2.3	1.9
$\sigma^2(y)/10^2$	0.46	2.4	2.5	3.9
	Gothard, Equation 8			
n_1	0.903	0.805	1.05	
n_2	1.175	0.766	0.65	
$\sigma^2(g^E)/10^2$	1.9	1.5	2.1	1.3
$\sigma^2(y)/10^2$	0.96	2.2	2.0	1.9

of the mixtures were assumed to be zero.

The experimental data were correlated using the following equations (*5*).

(a) Wilson (*4*):

$$(g^E/RT)_{calc} = -\sum_i x_i \ln\left(\sum_j x_i \Lambda_{ij}\right) \tag{3}$$

$$g^E/RT = \sum_i x_i \ln \gamma_i \tag{4}$$

$$\Lambda_{ij} = v_j/v_i \exp[(\lambda_{ij} - \lambda_{ii})/RT] \tag{5}$$

(b) NRTL (*6*):

$$g^E/RT = \sum_i x_i\left(\sum_j \zeta_{ij} G_{ij} x_j \Big/ \sum_k G_{ki} x_k\right) \tag{6}$$

$$G_{ij} = \exp(-\alpha_{ij}\zeta_{ij}) \qquad \zeta_{ij} = (g_{ij} - g_{ii})/RT \tag{7}$$

(c) Gothard (*7*):

$$(g^E/RT)_{calc} = (1/K) \ln[n(n-1)/2] \tag{8}$$

$$2/n = \sum_i x_i \Big/ \sum_j n_{ij} x_j \tag{9}$$

$K = 4$ for systems without miscibility gaps

The optimal parameters were obtained by minimization of the objective function:

$$Q = \sum_N [(g^E/RT)_{exptl} - (g^E/RT)_{calc}]^2 \tag{10}$$

Table VII presents the root mean square deviations, $\sigma^2(g^E)$ and $\sigma^2(y)$, of g^E/RT and y_i for the studied binary systems. From this table one can see that the three models reproduce the binary systems equally well.

The results presented in Tables II–V show that the deviations from ideality are small. The system $MeHSiCl_2$–$SiCl_4$ has a slight positive deviation; for all the other systems the deviations are negative.

Glossary

g^E	experimental boiling temperature at pressure P^*, °C
g_{ij}, g_{ii}	corrected boiling temperature at normal pressure $P°$ = 760 mmHg
n	liquid-phase mole fraction
R	vapor-phase mole fraction
t^*	molar gas constant, 4.187 J mol^{-1} K^{-1}
t	molar volume, cm^3 mol^{-1}
v_i	molar excess Gibbs energy, J mol^{-1}
x	NRTL model parameters, J mol^{-1}
y	Gothard model parameters

Greek Letters

α_{ij}	third parameter in NRTL equation
γ_i	activity coefficient in liquid phase
λ_{ii}, λ_{ij}	Wilson parameters, J mol^{-1}

Subscripts

i, j	components

Registry No. CH_3SiHCl_2, 75-54-7; $(CH_3)_3SiCl$, 75-77-4; $(CH_3)_2SiCl_2$, 75-78-5; CH_3SiCl_3, 75-79-6; $SiCl_4$, 10026-04-7.

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