Isobaric vapor-liquid equilibrium for methyldichlorosilane-methyltrichlorosilane-dimethyldichlorosilane system[*]

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Abstract: This paper describes measurement of vapor-liquid equilibrium (VLE) data of methyldichlorosilane-methyltrichlorosilane-dimethyldichlorosilane system and that of the three binary systems at 101.325 kPa with a new pump-ebulliometer. The equilibrium composition of the vapor phase was calculated from *pTx* by indirect method. The model parameters of the liquid activity coefficient of the Wilson, NRTL, Margules and van Laar equations was corrected by the least square method. The ternary system VLE data were predicted by the Wilson equation, with the calculated boiling points showing good agreement with the experimental data.

INTRODUCTION

Vapor-liquid equilibrium (VLE) data are very important in the design and operation of separation processes in chemical industry. Such information can be obtained experimentally or estimated by using generalized methods for calculation of the properties of mixtures. For ideal system, it is relatively easy to estimate vapor-liquid equilibrium. However, most systems of industrial interest show deviations from the ideal behavior.

The methyldichlorosilane-methyltrichlorosilane-dimethyldichlorosilane and constituent binary system are of importance in the production of silicon, while VLE data of these systems are very scarce in the literature. Only in the past several years did some researchers (Ana *et al.*, 1995; Liviu *et al.*, 1995; Wu and Cai, 1997; Xie *et al*., 1998) begin to study isobaric vapor-liquid equilibrium for multicomponent systems containing halogenated silane. In order to provide some necessary basic data on silicon derivatives, these systems are selected for study. The VLE data are measured by the total pressure-temperature-liquid composition (*pTx*) method. In this study, the VLE data are determined at 101.325 kPa for methyldichloroslane-methyltrichlorosilane-dimethyldichlorosilane and constituent binary system. The results calculated by the activity coefficient models were shown to be in good agreement with the experimental data.

EXPERIMENTAL

Materials

Methyldichlorosilane, methyltrichlorosilane and dimethyldichlorosilane were obtained from Xinhuo Chemical Factory, Jiangxi. All the chemicals were purified by distillation in a laboratory column to a purity of more than 99.5% by gas chromatography

(GC) analysis. Methyldichlorosilane, methyltrichlorosilane and dimethyldichlorosilane should be purified just before measurement because they may easily react with water when exposed to the air. Comparison between some of the measured data and literature data is given Table 1.

Table 1 Boiling point of pure component

Component	Boiling point (K)	
	Lit.	Exp.
Methyldichlorosilane	314.15 (Dean, 2003)	314.41
Methyltrichlorosilane	339.55 (Dean, 2003)	339.50
Dimethyldichlorosilane	343.15 (Dean, 2003)	343.46

Apparatus and procedure

A new type of magnetical pump-ebulliometer, described in detail by Qiu *et al.*(1995) was used for measuring the boiling points with different liquid phase compositions (Qiu *et al.*, 1997). The apparatus was an all-glass dynamic recirculation still with total volume of about 1.00×10^{-4} m^3. During the run, the still was submerged in a constant temperature bath about 3 °C below the equilibrium boiling point. The atmospheric pressure, *P*, was measured by a Fortin-type mercury barometer. Since the barometric pressure changed slightly, the experimental temperatures were automatically corrected to that at 101.325 kPa. The equilibrium temperature, *T*, was measured using a standard mercury thermometer with accuracy of 0.1 K. In each experiment, a known mass of the material was introduced into the still from the injector and was heated at a fixed pressure of 101.325 kPa by an automatic regulation system. The accuracy of the liquid and vapor phase was constant. The liquid compositions component was added into the still. The vapor compositions, y_i, were calculated from the experimental *pTx* data by an indirect method (Qiu *et al.*, 1994). This *pTx* method was based on the *Q* function (The function of molar excess Gibbs energy) and had rigorous thermodynamic consistency (Hu, 1982).

RESULTS AND DISCUSSION

At low and moderate pressures, the pointing factor is negligible, so the equilibrium relations is as follows

$$Py_i\hat{\varphi}_i = P_i^s \varphi_i^s x_i \gamma_i \qquad (1)$$

where y_i is the mole fraction of component *i* in the vapor phase, $\hat{\varphi}_i$ is the fugacity coefficient of component *i* in the vapor phase, *P* is the total pressure, γ_i is the activity coefficient of component *i* in the vapor phase, x_i is the mole fraction of component *i* in the liquid phase, φ_i^s is the pure component fugacity coefficient at saturation, and P_i^s is the vapor pressure of pure component *i*. The coefficients of $\hat{\varphi}_i$ and φ_i^s were evaluated using the second virial coefficients from the critical data, respectively. The vapor pressure of pure component, P_i^s is calculated by the Antoine equation. The critical data and Antoine constants of the pure component are given in Table 2.

The experimental data were correlated using the Wilson, NRTL, Margules and van Laar equations *f*. The optimal parameters were obtained by minimization of the objective function *F* (Qiu *et al.*, 1994).

$$F = \sum | \ln(r_1)_{\text{cal}} - f_1(\overline{a_i})|_k^2 + \sum | \ln(r_2)_{\text{cal}} - f_2(\overline{a_i})|_k^2 \quad (2)$$

where γ_1, γ_2 are the activity coefficient of component 1and component 2 in the liquid phase, $\overline{a_i}$ is model parameter. *k* is the point of difference.

The binary systems VLE data were used to plot the three graphs in Fig.1.

The model parameters of liquid activity coefficient and the absolute average deviations are listed in Table 3 showing that the deviations of Wilson, NRTL, Margules equations are reasonably small, especially

Table 2 Antoine constants, critical temperature, pressure and volume of the pure components*

Component	*A*	*B*	*C*	T_c(K)	P_c (kPa)	V_c (10^{-6} m^3/mol)
Methyldichlorosilane (Rugina and Sacarescu, 1992)	7.0484	1179	242	475	3901.1	290
Methyltrichlorosilane (Rugina and Sacarescu, 1992)	6.8721	1167	226	518	5562.7	339
Dimethyldichlorosilane (Rugina and Sacarescu, 1992)	7.1435	1328	241	520	3485.6	350

*A, B, C: Antoine constants; P_c: Critical temperature; P_c: Critical pressure; V_c: Critical volume
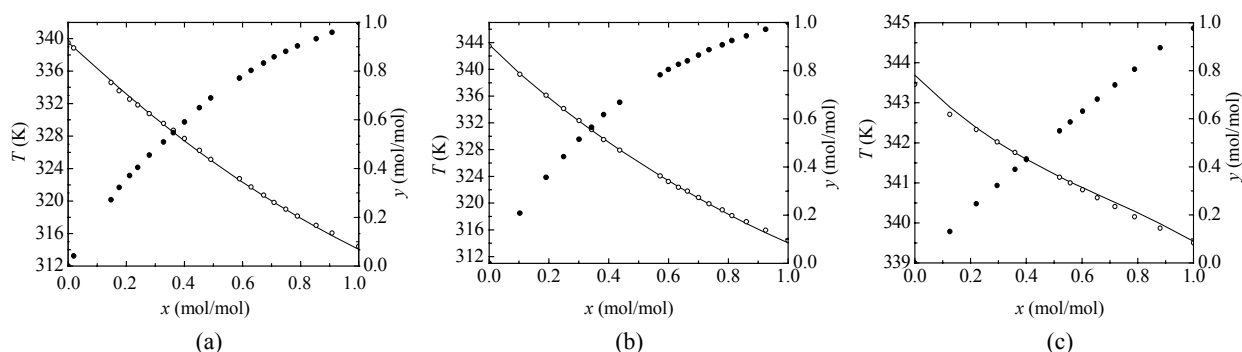
Fig.1 VLE curve of (a) methyldichlorosilane+methyltrichlorosilane; (b) methyldichlorosilane+dimethyldichlorosilane; (c) methyltrichlorosilane+dimethyldichlorosilane
• Calculated vapor phase points; − Calculated temperature curve; ◦ Experimental temperature data

that of the Wilson equation, while the deviations of the van Laar equation is a little bigger. So the activity coefficient models are suitable for representing the binary experimental data. The binary parameters of the Wilson model given in Table 3 were used to predict the VLE data of the ternary system. The results were satisfactory. The VLE data of the ternary system and the average deviation in boiling temperatures are listed in Table 4.

CONCLUSION

Vapor-liquid equilibrium for a ternary system of methyldichloroslane-methyltrichlorosilane-dimethyl-dichlorosilane and constituent binary systems were measured at 101.325 kPa. The equilibrium composition of the vapor phase was calculated from pTx by the indirect method. The experimental data were correlated using the Wilson, NRTL, Margules and van Laar equations. It was shown that the deviations of the Wilson, NRTL, Margules equations were reasonably small, while the deviation of the van Laar equation was a little bigger. Ternary system VLE data were predicted by the Wilson equation; the calculated boiling points accorded well with experimental data. The results showed that the calculated boiling point is fitted by the models which satisfied the need for the design and operation of separation processes.

Table 3 Model parameters and the absolute average deviations

Equation	Parameters and deviations	Methyldichlorosilane (1)+ methyltrichlorosilane (2)	Methyldichlorosilane (1)+ dimethyldichlorosilane (2)	Methyltrichloroslane (1)+ dimethyldichloroslane (2)
Wilson	A	−38.1	−120.1	−28.9
	B	0.05	0.1	0.11
	d_t^*	0.17	0.14	0.07
	d_y^{**}	0.004	0.0089	0.006
NRTL	A	−66.5	−0.1	−142.2
	B	0.01	−148.7	−1.4
	A_{ij}	0.05	0.3	0.08
	d_t	0.14	0.15	0.09
	d_y	0.0038	0.0081	0.0039
Margules	A	−0.125	−0.41	−0.34
	B	−0.11	−0.12	−0.13
	d_t	0.15	0.5	0.28
	d_y	0.0039	0.0042	0.007
van Laar	A	0.001	0.0001	0.0001
	B	0.003	0.05	0.03
	d_t	0.61	1.34	1.15
	d_y	0.0074	0.0157	0.0155

*$d_t=\Sigma |T-T_{mod}|/N$, **$d_y=\Sigma |y_{cal}-y_{mod}|/N$, N=Number of data points; T_{mod}: Calculated boiling point from model (K); y_{cal}: Calculated vapor phase mole fraction from pTx; y_{mol}: Calculated vapor phase mole fraction from mode

Table 4 Experimental VLE data and calculated results from the ternary system methyldichlorosiane (1)-methyltrichlorosilane (2)-dimethyldichlorosilane (3) at 101.325 kPa[*]

No.	T_{mod} (K)	T_{exp} (K)	x_1	x_2	x_3	$y_{1,cal}$	$y_{2,cal}$	$y_{3,cal}$
1	318.36	318.67	0.7488	0.2253	0.0259	0.8638	0.1255	0.0107
2	319.01	319.22	0.7226	0.2174	0.0600	0.8505	0.1238	0.0257
3	319.73	320.03	0.6948	0.2091	0.0961	0.8353	0.1219	0.0428
4	320.41	320.61	0.6689	0.2012	0.1299	0.8202	0.1199	0.0599
5	320.90	321.10	0.6509	0.1959	0.1532	0.8092	0.1185	0.0723
6	321.56	321.78	0.6269	0.1886	0.1845	0.7938	0.1165	0.0898
7	321.98	322.40	0.6118	0.1841	0.2041	0.7837	0.1152	0.1012
8	322.57	323.37	0.5910	0.1778	0.2312	0.7692	0.1132	0.1176
9	323.12	323.81	0.5717	0.1720	0.2563	0.7553	0.1113	0.1334
10	323.74	324.18	0.5504	0.1656	0.2840	0.7393	0.1092	0.1515
11	325.04	325.60	0.5327	0.0268	0.4405	0.7326	0.0186	0.2488
12	325.61	326.02	0.5000	0.0865	0.4135	0.7018	0.0606	0.2376
13	326.03	326.34	0.4774	0.1278	0.3948	0.6802	0.0902	0.2296
14	326.26	327.03	0.4651	0.1503	0.3846	0.6682	0.1065	0.2253
15	326.52	327.12	0.4518	0.1746	0.3736	0.6552	0.1243	0.2205
16	326.93	327.38	0.4314	0.2118	0.3568	0.6348	0.1520	0.2132
17	327.20	327.50	0.4181	0.2361	0.3458	0.6213	0.1704	0.2083
18	327.55	328.02	0.4017	0.2661	0.3322	0.6044	0.1935	0.2021
19	327.80	328.18	0.3901	0.2872	0.3227	0.5922	0.2099	0.1978
20	328.07	329.03	0.3780	0.3095	0.3125	0.5794	0.2275	0.1931
21	328.19	329.08	0.3725	0.3195	0.3080	0.5734	0.2355	0.1910
22	339.34	340.78	0.0242	0.7459	0.2299	0.0544	0.7391	0.2065
23	337.44	338.58	0.0711	0.7101	0.2188	0.1498	0.6665	0.1838
24	335.40	336.04	0.1248	0.6690	0.2062	0.2457	0.5931	0.1612
25	334.06	334.86	0.1621	0.6405	0.1974	0.3055	0.5472	0.1473
26	332.90	333.80	0.1956	0.6149	0.1895	0.3552	0.5090	0.1358
27	331.88	332.98	0.2264	0.5913	0.1823	0.3979	0.4761	0.1260
28	330.44	331.61	0.2713	0.5570	0.1717	0.4558	0.4313	0.1129
29	329.76	330.53	0.2933	0.5402	0.1665	0.4824	0.4107	0.1069
30	328.84	329.87	0.3239	0.5180	0.1593	0.5177	0.3834	0.0990

Deviations: d_t=0.63; d_t (max)=1.44

[*]$d_t = \sum |T_{exp} - T_{mod}|/N$; T_{mod}: Calculated boiling point from model ; T_{exp}: Experimental boiling point; x_1, x_2, x_3: Liquid-phase mole fraction of (1) (2) (3); $y_{1,cal}$, $y_{2,cal}$, $y_{3,cal}$: Calculated vapor-phase mole fraction of (1) (2) (3) from pTx; N: Number of data point

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