

Journal of Zhejiang University SCIENCE  
ISSN 1009-3095  
http://www.zju.edu.cn/jzus  
E-mail: jzus@zju.edu.cn



## Isobaric vapor-liquid equilibrium for methylchlorosilane-dimethylchlorosilane-benzene system\*

QIU Zu-min (邱祖民)<sup>†1,2</sup>, XIE Xin-liang (谢心亮)<sup>1</sup>, YU Shu-xian (余淑娴)<sup>3</sup>,  
CHEN Wen-you (陈文有)<sup>3</sup>, XIE Feng-xia (谢凤霞)<sup>1</sup>, LIU Juan (刘娟)<sup>1</sup>

(<sup>1</sup>School of Environmental Science and Engineering, Nanchang University, Nanchang 330029, China)

(<sup>2</sup>Key Laboratory of Poyang Lake Ecology and Bio-resource Utilization, Nanchang University, Nanchang 330029, China)

(<sup>3</sup>Editorial Department of Journal of Nanchang University, Nanchang 330029, China)

<sup>†</sup>E-mail: qiuzm@ncu.edu.cn

Received June 1, 2005; revision accepted Aug. 11, 2005

**Abstract:** The elucidation of vapor-liquid equilibrium (VLE) of the halogenated silane was necessary for the production of silicon derivatives, especially for methylvinylchlorosilane, due to the lack of the relevant reports. Isobaric VLE for the system methylchlorosilane-dimethylchlorosilane-benzene and isobaric VLE of the three binary systems were measured with a new pump-ebullimeter at the pressure of 101.325 kPa. These binary compositions of the equilibrium vapor were calculated according to the  $Q$  function of molar excess Gibbs energy by the indirect method and the resulted VLE data agreed well with the thermodynamic consistency. Moreover, the experimental data were correlated with the Wilson, NRTL, Margules and van Laar equations by means of the least-squares fit, the acquired optimal interaction parameters were fitted to experimental vapor-liquid equilibrium data for binary systems. The binary parameters of Wilson equation were also used to calculate the bubble point temperature and the vapor phase composition for the ternary mixtures without any additional adjustment. The predicted vapor-liquid equilibrium for the ternary system was in a good agreement with the experimental results. The VLE of binary and multilateral systems provided essential theory for the production of the halogenated silane.

**Key words:** Ebullimeter, Vapor-liquid equilibrium, Methylchlorosilane, Dimethylchlorosilane, Benzene

doi:10.1631/jzus.2005.B1033

Document code: A

CLC number: O642.4<sup>+2</sup>

### INTRODUCTION

Vapor-liquid equilibrium (VLE) data are very important in the design and operation of separation processes in the 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 methylchlorosilane-dimethylchlorosilane-benzene and constituent binary system are of importance in the production of halogen silanes, while VLE data on these systems are very scarce in the literature. Only in the past several years did some researchers (Ana *et al.*, 1995; Sacarescu *et al.*, 1995; Wu and Cai, 1997; Xie *et al.*, 1998) begin to study isobaric vapor-liquid equilibrium of multicomponent systems containing halogenated silane. Yu *et al.* (2000; 2003a; 2003b) and Qiu *et al.* (2005) also have done some works on this problem. 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

\* Project supported by the Foundation of Science and Technology of the Ministry of Education (No. 03071) and the Natural Science Foundation of Jiangxi Province (No. 0320013), China

data are determined at 101.325 kPa for methyl-dichlorosilane-dimethyldichlorosilane-benzene and constituent binary system. The results calculated by the activity coefficient models agreed well with the experimental data.

## EXPERIMENTAL DETAILS

### Materials

Methyldichlorosilane, dimethyldichlorosilane and benzene were obtained from Xinhua Chemical Factory, Jiangxi, China. All the chemicals were purified by distillation in a laboratory column to a purity of more than 99.5% as verified by gas chromatography (GC) analysis. Methyldichlorosilane and dimethyldichlorosilane and benzene should be purified just before measurement because they easily react with water when exposed to the air. Comparison between some measured data and data in literature is given in Table 1.

**Table 1 Boiling point of pure component**

Component	Boiling point (K)	
	Lit.	Exp.
Methyldichlorosilane	314.15 (Dean, 2003)	314.41
Dimethyldichlorosilane	343.15 (Dean, 2003)	343.46
Benzene	353.15 (Dean, 2003)	353.16

### Apparatus and procedure

A new type of magnetic pump-bullimeter 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  $1.00 \times 10^{-4} \text{ m}^3$ . During the run, the still was submerged in a constant temperature bath at 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 from the injector into the still and heated at a fixed pressure of 101.325 kPa by an automatic pressure regulation system. Liquid com-

positions component,  $x_i$ , were added into the still. Vapor compositions,  $y_i$ , were calculated from the experimental  $pTx$  data by an indirect method (Qiu *et al.*, 1994) 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 relation is as follows

$$Py_i \hat{\phi}_i = P_i^s \phi_i^s x_i \gamma_i \quad (1)$$

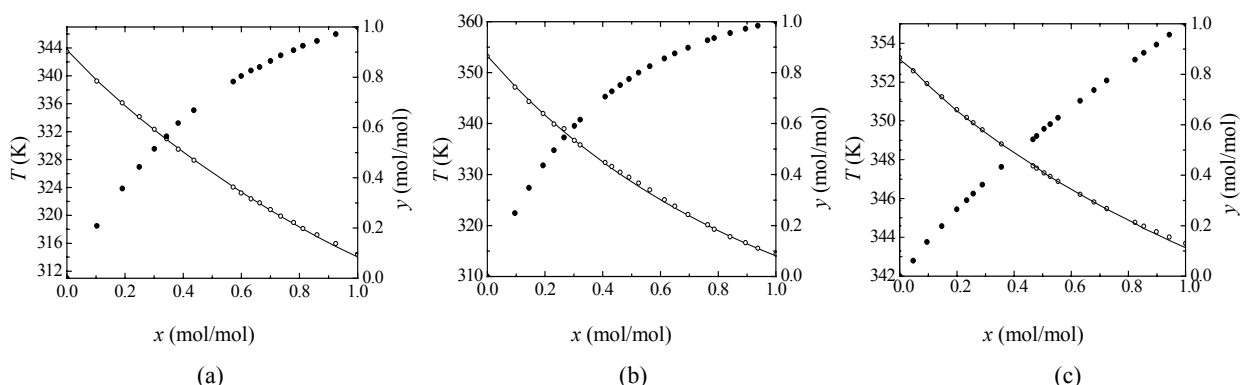
where  $y_i$  is the mole fraction of component  $i$  in the vapor phase,  $\hat{\phi}_i$  is the fugacity coefficient of component  $i$  in the vapor phase,  $P$  is the total pressure,  $\gamma_i$  is the activity coefficient of component  $i$  in the liquid phase,  $x_i$  is the mole fraction of component  $i$  in the liquid phase,  $\phi_i^s$  is the pure component fugacity coefficient at saturation, and  $P_i^s$  is the vapor pressure of pure component  $i$  at saturation. The coefficients  $\hat{\phi}_i$  and  $\phi_i^s$  were evaluated using the second virial coefficient equation, 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. The optimal interaction parameters were obtained by minimization of the objective function  $F$  (Qiu *et al.*, 1994) by means of the least-squares fit.

$$F = \sum |\ln(\gamma_1)_{\text{cal}} - f_1(\bar{a}_i)|_k^2 + \sum |\ln(\gamma_2)_{\text{cal}} - f_2(\bar{a}_i)|_k^2 \quad (2)$$

where  $\gamma_1, \gamma_2$  are the activity coefficients of component 1 and component 2 in the liquid phase,  $\bar{a}_i$  is model interaction parameter,  $f_1, f_2$  are model equation calculated the activity coefficients of component 1 and component 2, respectively.  $k$  is the inflexion point to calculate.

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



**Fig.1** VLE curve of (a) methylchlorosilane+dimethylchlorosilane; (b) methylchlorosilane+benzene; (c) dimethylchlorosilane+benzene

• Calculated vapor phase points; – Calculated temperature curve; ° Experimental temperature data

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

Component	A	B	C	$T_c$ (K)	$P_c$ (kPa)	$V_c$ ( $\times 10^{-6} \text{ m}^3/\text{mol}$ )
Methylchlorosilane (Rugina and Sacarescu, 1992)	7.0484	1179	242	475	3901.1	290
Dimethylchlorosilane (Rugina and Sacarescu, 1992)	7.1435	1328	241	520	3485.6	350
Benzene (Dean, 2003)	6.90565	1211.033	220.79	562.05	4895	255

A, B, C: Antoine constants;  $T_c$ : Critical temperature;  $P_c$ : Critical pressure;  $V_c$ : Critical volume

**Table 3** Model interaction parameters and the absolute average deviations

Equation	Parameters and deviations	Methylchlorosilane (1)+ dimethylchlorosilane (2)	Methylchlorosilane (1)+ benzene (2)	Dimethylchlorosilane (1)+ benzene (2)
Wilson	A	-120.1	-62.8	-22.4
	B	0.1	1.2	0.005
	$d_t^*$	0.14	0.27	0.05
	$d_y^{**}$	0.0089	0.0039	0.0052
NRTL	A	-0.1	-65.6	-42.2
	B	-148.7	1.1	0.8
	$A_{ij}$	0.3	0.27	0.3
	$d_t$	0.15	0.26	0.05
	$d_y$	0.0081	0.004	0.0053
Margules	A	-0.41	-0.1	-0.117
	B	-0.12	-0.13	-0.01
	$d_t$	0.5	0.27	0.11
	$d_y$	0.0042	0.0042	0.0037
van Laar	A	0.0001	0.0001	0.0001
	B	0.05	0.01	0.02
	$d_t$	1.34	0.49	0.34
	$d_y$	0.0157	0.0046	0.0061

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

The model interaction parameters of liquid activity coefficient and the absolute average deviations are listed in Table 3 (in the preceding page) showing that the deviations of Wilson, NRTL, Margules equations are reasonably small, especially that of the Wilson equation, while the deviation of the van Laar equation is a little bigger. So the activity coefficient

models are suitable for representing the binary experimental data. The binary interaction 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 the bubble temperatures are listed in Table 4.

**Table 4** Experimental VLE data and calculated results from the ternary system methylchlorosilane (1)-dimethylchlorosilane (2)-benzene (3) at 101.325 kPa\*

No.	$T_{\text{mod}}$ (K)	$T_{\text{exp}}$ (K)	$x_1$	$x_2$	$x_3$	$y_{1,\text{cal}}$	$y_{2,\text{cal}}$	$y_{3,\text{cal}}$
1	330.92	331.93	0.3144	0.6058	0.0798	0.5392	0.4200	0.0408
2	331.75	332.28	0.2979	0.5740	0.1281	0.5235	0.4093	0.0672
3	333.15	333.79	0.2715	0.5232	0.2053	0.4968	0.3907	0.1125
4	333.76	334.41	0.2602	0.5013	0.2385	0.4847	0.3821	0.1332
5	334.52	334.88	0.2467	0.4753	0.2780	0.4696	0.3715	0.1589
6	335.35	335.50	0.2323	0.4476	0.3201	0.4529	0.3595	0.1877
7	336.04	336.05	0.2207	0.4253	0.3540	0.4388	0.3493	0.2119
8	336.61	336.77	0.2114	0.4074	0.3812	0.4271	0.3408	0.2321
9	347.04	346.20	0.0236	0.3777	0.5987	0.0655	0.4305	0.5040
10	346.15	345.60	0.0388	0.3718	0.5894	0.1047	0.4130	0.4823
11	344.03	344.47	0.0766	0.3572	0.5662	0.1932	0.3733	0.4335
12	342.07	342.21	0.1138	0.3428	0.5434	0.2700	0.3388	0.3912
13	341.04	340.68	0.1342	0.3349	0.5309	0.3085	0.3214	0.3701
14	339.96	339.34	0.1564	0.3263	0.5173	0.3478	0.3037	0.3485
15	338.35	338.82	0.1906	0.3131	0.4963	0.4037	0.2784	0.3179
16	337.34	337.97	0.2131	0.3044	0.4825	0.4377	0.2630	0.2994
17	336.12	336.43	0.2411	0.2935	0.4654	0.4773	0.2449	0.2778
18	335.29	335.23	0.2609	0.2859	0.4532	0.5036	0.2329	0.2635
19	334.42	334.17	0.2820	0.2777	0.4403	0.5303	0.2207	0.2490
20	334.04	333.47	0.2915	0.2741	0.4344	0.5419	0.2154	0.2427
21	325.93	325.95	0.5502	0.0370	0.4128	0.8001	0.0232	0.1767
22	326.31	326.49	0.5333	0.0665	0.4002	0.7844	0.0422	0.1734
23	326.36	327.34	0.5307	0.0711	0.3982	0.7820	0.0451	0.1729
24	326.94	327.71	0.5051	0.1158	0.3791	0.7577	0.0745	0.1679
25	327.33	327.56	0.4884	0.1452	0.3664	0.7414	0.0943	0.1643
26	327.71	328.04	0.4720	0.1738	0.3542	0.7252	0.1139	0.1610
27	327.93	328.16	0.4630	0.1895	0.3475	0.7161	0.1248	0.1591
28	328.22	328.51	0.4511	0.2104	0.3385	0.7040	0.1395	0.1565
29	328.55	329.02	0.4374	0.2343	0.3283	0.6899	0.1566	0.1535

Deviations:  $d_T=0.42$ ;  $d_T$  (max)=1.01

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

## CONCLUSION

VLE of the ternary system of methylchlorosilane-dimethylchlorosilane-benzene and constituent binary systems were measured at 101.325 kPa. The eq-

ilibrium 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 equa-

tions 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 bubble points accorded well with experimental data. The results showing that the calculated bubble point is fitted by the models satisfy the need for the design and operation of separation processes.

## References

- Ana, D., Rosa, M., Margarita, S., 1995. Isobaric vapor-liquid equilibria of tetrachloroethylene with 1-butanol and 2-butanol at 6 and 20 kPa. *J. Chem. Eng. Data*, **40**(1):290-292.
- Dean, J.A., 2003. Lange's Handbook of Chemistry, 2nd Ed. Science Press, Beijing (in Chinese).
- Hu, Y., 1982. Fluid Molecule Thermodynamic. Higher Education Press, Beijing (in Chinese).
- Qiu, Z.M., Luo, Z.C., Hu, Y., 1994. Vapor-liquid equilibria of two binary systems containing methylal. *Journal of Chemical Engineering of Chinese Universities*, **8**(2):106-110 (in Chinese).
- Qiu, Z.M., Luo, Z.C., Hu, Y., 1995. The new motive cottrell pump ebulliometer. *Journal of Nanchang University (Engineering & Technology)*, **17**(4):6-11 (in Chinese).
- Qiu, Z.M., Luo, Z.C., Hu, Y., 1997. The pump ebulliometer. *Journal of Chemical Engineering of Chinese Universities*, **11**(1):74-77 (in Chinese).
- Qiu, Z.M., Xie, X.L., Luo, M., Xie, F.X., 2005. Isobaric vapor-liquid equilibrium for methyldichlorosilane-dimethyldichlorosilane-benzene system. *J. Zhejiang Univ. SCI*, **6B**(6):559-562.
- Rugina, T., Sacarescu, L., 1992. Isobaric vapor-liquid equilibrium for the binary systems  $\text{CH}_3\text{SiHCl}_2$  with  $(\text{CH}_3)_3\text{SiCl}$ ,  $(\text{CH}_3)_2\text{SiCl}_2$ ,  $\text{CH}_3\text{SiCl}_3$ , or  $\text{SiCl}_4$ . *J. Chem. Eng. Data*, **37**:143-145.
- Sacarescu, L., Marcu, M., Luchian, N., Sacarescu, G., 1995. Vapor-liquid equilibria for dichlorodimethylsilane plus heptane. *J. Chem. Eng. Data*, **40**(1):71-73.
- Wu, Q., Cai, M.L., 1997. Relative volatility and separation for halogenosilanes. *Chemical Engineering*, **25**(2):57-62 (in Chinese).
- Xie, J.J., Pan, Q.M., Pan, Z.R., 1998. Study of vapor-liquid equilibria for polydimethylsiloxane/solvents by using gas-liquid chromatography. *Chemical Engineering*, **26**(3):49-54 (in Chinese).
- Yu, S.X., Yu, Z.B., Qiu, Z.M., 2000. Isobaric vapor-liquid equilibrium for methyldichlorosilane-methyltrichlorosilane-toluene system. *J. Chem. Indu. Eng.*, **51**(6):844-847 (in Chinese).
- Yu, S.X., Qiu, Z.M., Li, F.Y., Yu, Z.B., Sun, W., 2003a. Isobaric vapor-liquid equilibrium of binary and ternary systems for methyltrichlorosilane-methylvinylidichlorosilane-toluene. *J. Chem. Indu. Eng.*, **54**(6):846-849 (in Chinese).
- Yu, S.X., Yu, Z.B., Qiu, Z.M., Sun, W., 2003b. Isobaric vapor-liquid equilibrium for methyldichlorosilane-methylvinylidichlorosilane-toluene and constituent binary systems. *J. Chem. Eng.*, **11**(2):213-216.

## Welcome Contributions to JZUS-B

### ➤ Welcome Your Contributions to JZUS-B

Journal of Zhejiang University SCIENCE B warmly and sincerely welcome scientists all over the world to contribute to JZUS-B in the form of Review, Article and Science Letters focused on **biomedicine and biotechnology areas**. Especially, Science Letters (3–4 pages) would be published as soon as about 30 days (Note: detailed research articles can still be published in the professional journals in the future after Science Letters are published by JZUS-B).

### ➤ Contributions requests

- (1) Electronic manuscript should be sent to [jzus@zju.edu.cn](mailto:jzus@zju.edu.cn) only. If you have any question, please feel free to visit our website: <http://www.zju.edu.cn/jzus>, and hit "For Authors".
- (2) English abstract should include Objective, Method, Result and Conclusion.
- (3) Tables and figures could be used to prove your research result.
- (4) Full text of the Science Letters should be in 3–4 pages. The length of articles and reviews are not limited.
- (5) Please visit our website (<http://www.zju.edu.cn/jzus/pformat.htm>) to see paper format.