J. Chem. Eng. Data **1995**, *40*, 71−73

Vapor−Liquid Equilibria for Dichlorodimethylsilane + Heptane

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Isobaric vapor−liquid equilibria (VLE) were measured with a small Swietoslawsky still for dichlorodimethylsilane + heptane. The measurements were made at atmospheric pressure. Activity coefficients were calculated after accounting for the nonideality of the vapor phase, using calculated virial coefficients. The vapor pressures of the pure components were obtained using Antoine constants from the literature. The results obtained were correlated in terms of liquid activity coefficients calculated from the Wilson, NRTL, and Gothard equations.

Introduction

Vapor−liquid equilibria are required both for practical use such as in the design and operation of distillation equipment and for theoretical use to determine the thermodynamic properties of binary mixtures. We have selected this system to initiate a study on the properties of silane + hydrocarbon binary (polar + nonpolar) mixtures.

Prediction of the behavior of systems containing organochlorosilanes is known to require modification of the mixing rules used for solution models. To evaluate the parameters for the characterization of the silane + hydrocarbon interactions requires measurements on such systems. These studies can form a data base for generalization of the interaction parameters in silane mixtures. The equations used in this work to predict the activity coefficients of the liquid phase were the Wilson, NRTL, and Gothard equations.

Experimental Section

Materials. Dimethyldichlorosilane (Fluka, >99 mass %) was distilled before use. *n*-Heptane (Carlo Erba, >99.5 mass %) was distilled over phosphorous pentoxide. Densities, boiling points, and Antoine constants of the substances are displayed in Table 1.

Apparatus and Procedure. Vapor−liquid equilibria were measured in a modified Swietoslawski equilibrium still (*1*). An electric heater was inserted into the boiling flask, and some glass dust was placed on the heat-transfer surface to stabilize the boiling. Thermal isolation was made with insulation covering the entire apparatus except the condenser.

All samples were prepared by weighing under a dry nitrogen atmosphere just before use. The required amount was 15 g of mixture for each measurement.

The boiling points, *t*, were read with a Beckmann thermometer which was calibrated with water + benzene using two ebulloscopes and a mercury manometer (the comparative measurement method (*1*)). In this case the experimental precision limit was 0.01 K.

The mole fraction compositions of the liquid phase, *x*, and vapor phase, *y*, at equilibrium were determined by gas-chromatographic analysis. Every sample was sealed and ice-cooled to prevent evaporation. Each composition was analyzed four times to obtain a precision within (0.1−1.0) × 10^{-2} (*2*).

The barometric pressure, *p*, was determined from the boiling points of water in an ebulloscope adapted to the equipment. The experimental error was less than 13.3 10^{-3} kPa in each point.

The *t* values at pressure *p* were corrected to normal pressure (101.3 kPa) using a method described in a previous paper (*3*).

The experimental results are shown in Table 2.

Table 1. Densities ϱ, Normal Boiling Points t, and Antoine Coefficients A, B, and C for Dimethyldichlorosilane (1) and Heptane (2)

component	ϱ(20 °C/(g·cm^{-3})) exptl	lit.	t/°C exptl	lit.	A	B	C
1	1.069	1.066 (*11*)	69.37	70.00 (*11*)	4.2627	1328	−32.10 (*11*)
2	0.733	0.730 (*12*)	98.30	98.00 (*12*)	4.0221	1268	−56.25 (*12*)

Table 2. Boiling Temperature t at Pressure p and at 101.3 kPa, Liquid-Phase Mole Fraction x_1, Vapor-Phase Mole Fraction y_1, and Activity Coefficients γ_1 and γ_2 for $(CH_3)_2SiCl_2$ (1) + C_7H_{16} (2)

t/°C	p/kPa	t(101.3 kPa)/°C	x_1	y_1	γ_1	γ_2
86.35	100.98	86.57	0.1392	0.3339	1.5338	1.0819
84.81	100.60	85.4	0.2004	0.4062	1.3353	1.0758
86.76	100.56	87.4	0.2101	0.4069	1.2087	1.0258
84.35	100.51	85.08	0.2242	0.4565	1.3514	1.0255
85.44	100.81	85.91	0.2405	0.4404	1.1887	1.0521
82.96	100.47	83.89	0.2986	0.5085	1.1662	1.0639
83.15	100.73	83.82	0.3250	0.5263	1.1107	1.0682
84.26	100.77	84.89	0.3250	0.5222	1.0704	1.0435
81.96	100.39	83.04	0.3306	0.5210	1.1045	1.1148
79.51	99.97	81.55	0.4549	0.6294	1.0085	1.1112
74.66	99.01	78.19	0.4579	0.6450	1.1283	1.1873
75.36	99.67	77.93	0.4727	0.6499	1.1094	1.2138
76.36	100.33	78.14	0.5705	0.7344	1.0312	1.1264
74.16	100.38	75.94	0.6101	0.7205	1.0079	1.3984
74.46	100.45	76.27	0.6749	0.8203	1.0262	1.0714
72.96	99.90	75.97	0.6855	0.8195	1.0182	1.1230
72.45	100.37	74.54	0.7287	0.8529	1.0388	1.1121
72.91	100.45	74.9	0.7517	0.8670	1.0129	1.0868
73.21	100.43	75.25	0.7584	0.8725	1.0000	1.0591

Results

The liquid-phase activity coefficients were estimated from the results after accounting for the nonideality of the vapor phase by employing the following equation:

$$\ln \gamma_i = \ln y_i p / x_i p_i + (B_{ii} - v_i)(p - p_i)/RT + (1 - y_i)^2 p\delta/RT \quad (1)$$

where

$$\delta = 2B_{12} - B_{11} - B_{22} \quad (2)$$

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Table 3. Critical Temperature, T_c, Pressure, P_c, and Molar Volume, V_c, of the Pure Components

component	T_c/K	P_c/MPa	V_c/(cm^3·mol^{-1})
$(CH_3)_2SiCl_2$	523.48 (*11*)	3.44 (*11*)	317.46 (*11*)
C_7H_{16}	540.16 (*12*)	2.74 (*12*)	426.04 (*12*)

The virial coefficients B_{ii} were computed from the Tsonopoulos correlation (*4*). The constants a and b for heptane were obtained from the Dymond and Smith compilation of experimental data sets with the smallest deviations (*5*):

$$a = 0.016\,533$$

$$b = 0.028\,54$$

The constants a and b for dimethyldichlorosilane were assumed to be 0.

The interaction virial coefficients B_{ij} were estimated from critical data (Table 3) using the mixing rules of Prausnitz et al. (*6*).

A conventional thermodynamic consistency area test was applied:

$$c\int_0^1 \ln(\gamma_1/\gamma_2)\,\mathrm{d}x_1 = 0 \qquad (3)$$

Practically, a given set of data is consistent if (*7*)

$$A = \frac{|\text{area above } x \text{ axis} - \text{area below } x \text{ axis}|}{|\text{area above } x \text{ axis} + \text{area below } x \text{ axis}|} < 0.02 \qquad (4)$$

For these measurements $A = 0.017$.

Using a nonlinear least-squares regression, which minimized the deviations between calculated and experimental excess Gibbs free energies, values of the optimal parameters were calculated for the Wilson, NRTL, and Gothard equations:

(a) Wilson (*8*)

$$(G^E/RT)_{\mathrm{calc}} = -\sum_i x_i \ln(\sum_\gamma x_i\Lambda_{ij}) \qquad (5)$$

$$G^E/RT = \sum_i x_i \ln \gamma_i \qquad (6)$$

$$\Lambda_{ij} = v_j/v_i \exp[(\lambda_{ij} - \lambda_{ii})/RT] \qquad (7)$$

(b) NRTL (*9*)

$$(G^E/RT)_{\mathrm{calc}} = \sum_i x_i(\sum_j \zeta_{ij}G_{ij}x_j/\sum_k G_{ki}x_k) \qquad (8)$$

$$G_{ij} = \exp(-\alpha_{ij}\zeta_{ij}) \quad \text{and} \quad \zeta_{ij} = (g_{ij} - g_{ii})/RT \qquad (9)$$

(c) Gothard (*10*)

$$(G^E/RT)_{\mathrm{calc}} = (1/K)\ln[n(n-1)/2] \qquad (10)$$

$$2/n = \sum_i x_i/\sum_j n_{ij}x_j \qquad (11)$$

and $K = 4$ for systems without miscibility gaps.

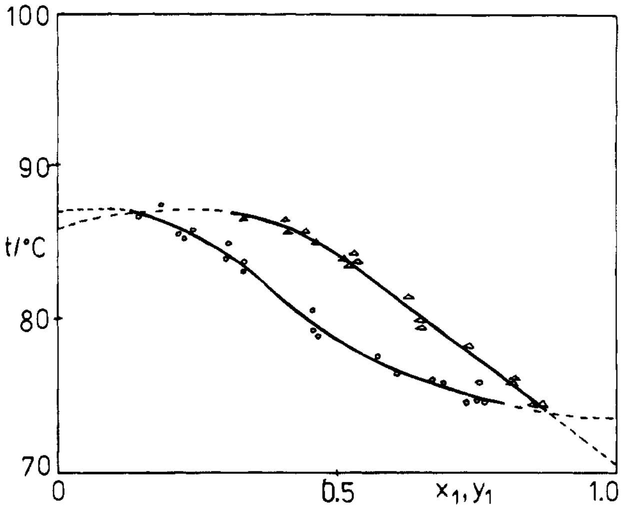

Figure 1. Corrected boiling points against the mole fraction of dimethyldichlorosilane in the liquid and vapor phases for dimethyldichlorosilane (1) + heptane (2): (○) $t(x_1)$ experimental points, (△) $t(y_1)$ experimental points.

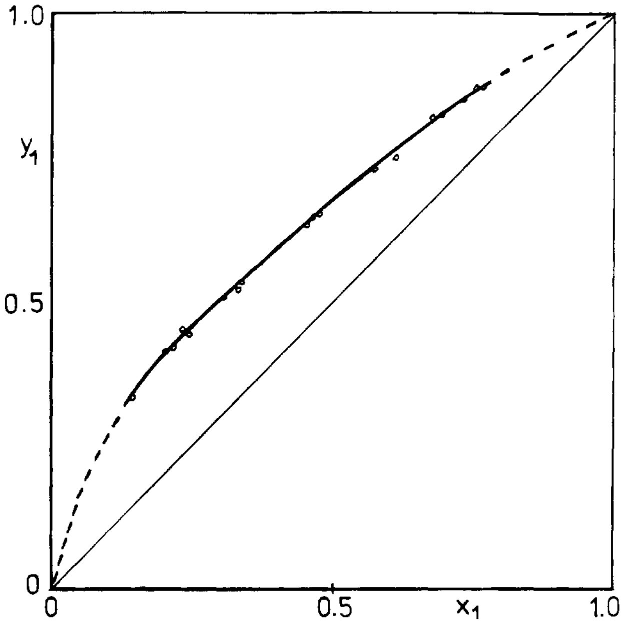

Figure 2. Mole fraction of the vapor phase (y_1) against the mole fraction of the liquid phase (x_1) for dimethyldichlorosilane (1) + heptane (2): (○) $y_1(x_1)$ experimental points.

Table 4. Root-Mean-Square Deviations of G^E/RT, $\sigma^2(G^E)$, and y, $\sigma^2(y)$, Obtained from the Correlations

parameter		parameter	
	Wilson, Eq 5		
$(\lambda_{12} - \lambda_{11})$/(J·mol^{-1})	155.00	$\sigma^2(G^E)$/100	3.6
$(\lambda_{21} - \lambda_{22})$/(J·mol^{-1})	65.00	$\sigma^2(y)$/100	6.7
	NRTL, Eq 8		
α_{ij}	0.3	$\sigma^2(G^E)$/100	3.6
$(g_{12} - g_{11})$/(J·mol^{-1})	91.75	$\sigma^2(y)$/100	4.6
$(g_{21} - g_{22})$/(J·mol^{-1})	104.00		
	Gothard, Eq 10		
n_{12}	0.763	$\sigma^2(G^E)$/100	2.7
n_{21}	2.139	$\sigma^2(y)$/100	6.6

Figure 1 shows the corrected boiling points, t, of the mixture. Figure 2 shows the mole fraction of dimethyldichlorosilane in the vapor phase against the mole fraction of dimethyldichlorosilane in the liquid phase. Table 4 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 system.

Glossary

t	experimental boiling temperature at pressure p, °C
x	liquid-phase mole fraction
y	vapor-phase mole fraction
p	vapor pressure, kPa
γ_i	activity coefficient in the liquid phase
R	gas constant, 8.319 $\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$
B_{ii}	gas-phase second virial coefficient, $\mathrm{m^3{\cdot}mol^{-1}}$
B_{ij}	gas-phase second cross virial coefficients, $\mathrm{m^3{\cdot}mol^{-1}}$
v_i	molar volume, $\mathrm{m^3{\cdot}mol^{-1}}$
a, b	Tsonopoulos constants for heptane
G^E	molar excess Gibbs energy, $\mathrm{J{\cdot}mol^{-1}}$
λ_{ii}, λ_{ij}	Wilson parameters, $\mathrm{J{\cdot}mol^{-1}}$
$g_{ij}-g_{jj}$	NRTL model parameters, $\mathrm{J{\cdot}mol^{-1}}$
α_{ji}	third parameter in the NRTL equation
n	Gothard model parameters

Subscripts

i, j	components

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Received for review November 19, 1993. Revised May 13, 1994. Accepted July 7, 1994.⊗

⊗ Abstract published in *Advance ACS Abstracts,* September 1, 1994.