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Vapor-Liquid Equilibrium at Atmospheric Pressure

Carbon Disulfide–Methanol System

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Isobaric vapor-liquid equilibrium was established for the heterogeneous system carbon disulfide–methanol at 760 mm of Hg pressure, using a modified Smith-Bonner still. Liquid-phase activity coefficients were calculated; the data were thermodynamically consistent. The binary constants for the NRTL (nonrandom, two-liquid) equation of Renon and Prausnitz were determined.

SEVERAL industrial processes, particularly those for manufacturing rayon, pulp, and related products, require separating carbon disulfide from methanol. Vapor-liquid equilibrium values of this system, however, have been reported only at 20°C (*3*). Therefore, vapor-liquid equilibrium data at atmospheric pressure and the boiling point were determined.

MATERIALS

A commercially available 99.9 mole % carbon disulfide was used. Chromatographic analysis was carried out on a 6-foot column of Porapak Type Q (120- to 150-mesh) (*1*) at 100°C. Analysis indicated three trace impurities. The methanol, commercial practical grade, was dried over calcium chloride and distilled three times. The distillate was 99.9 mole % methanol; the impurity was less than 0.10 mole % water. Table I compares the literature and experimental values of the physical properties of these materials.

EXPERIMENTAL PROCEDURE AND ANALYSIS

The vapor-liquid experimental procedure was reported by Smith and Bonner (*7*). Samples of carbon disulfide and methanol were weighed and mixed in various concentrations. These heterogeneous samples were made homogeneous by adding an equal volume of dry 2-propanol. The calibration curve of carbon disulfide–methanol was determined by gas chromatography.

Approximately 500 ml of a carbon disulfide–methanol mixture were weighed into the still. The still was allowed to operate for about 1 hour, the 5°C differential between liquid and vapor temperature being maintained as closely as possible. The temperature was recorded and a 2-ml condensate sample drawn off through an auxiliary cooler, with an equal volume of dry 2-propanol added to make the samples homogeneous for gas chromatographic analysis. The composition of the liquid phase was assumed that of the still. Between runs, the still was cleaned by refluxing acetone in it for 20 minutes and then drying it under vacuum.

The experimental results are given in Table II and presented in Figure 1 as a *T-x-y* diagram. The vapor condensate samples were analyzed with a Shimazu GC-3AH gas chromatograph equipped with a Model 250A011, 1-mv recorder. A Porapak Type Q column under isothermal operation yielded excellent separations for the ternary samples, including 2-propanol. The analysis data are accurate to ±0.002 mole fraction. The accuracy of the equilibrium temperature, measured by the calibrated thermometer, is ±0.1° C. All the experiments were run at 760 mm of Hg pressure, kept constant within 1 mm of Hg with a mercury manostat, and measured with an ordinary mercury manometer.

Table I. Properties of Materials

	Carbon Disulfide		Methanol	
	Exptl.	Lit. (*8*)	Exptl.	Lit. (*8*)
Refractive index, n_D^{25}	1.62781	1.62794	1.32657	1.32663
Density, d_4^{25}	1.25578	1.25585	0.78681	0.78675
Boiling point, 760 mm of Hg, ° C	46.3	46.25	64.7	64.51
Antoine constants				
A		6.85145		7.87863
B		1122.50		1473.11
C		236.46		230.0

$\log P^\circ = A - [B/(C + t)]$, P° mm of Hg, t = ° C

Table II. Vapor-Liquid Equilibrium of Carbon Disulfide–Methanol System under 760-Mm Absolute Pressure

Boiling Temp., ° C	x_1	y_1	$y_{1\ \text{calcd}}$	γ_1	γ_2
58.8	0.013	0.206	0.218	11.04	1.04
53.0	0.025	0.349	0.347	11.26	1.13
47.8	0.045	0.487	0.482	10.46	1.13
43.5	0.099	0.653	0.642	7.32	0.98
42.8	0.106	0.659	0.653	7.09	1.00
40.0	0.151	0.676	0.700	5.62	1.14
38.9	0.194	0.701	0.723	4.71	1.15
38.5	0.200	0.691	0.726	4.57	1.22
38.0	0.340	0.698	0.742	2.74	1.48
37.8	0.649	0.701	0.703	1.44	2.76
37.6	0.700	0.701	0.695	1.37	3.04
37.9	0.757	0.705	0.688	1.24	3.93
37.8	0.903	0.723	0.719	1.07	9.24
37.7	0.916	0.734	0.731	1.07	10.24
37.8	0.928	0.727	0.745	1.03	12.71
38.2	0.930	0.729	0.748	1.03	13.02
41.0	0.990	0.844	0.927	1.04	44.77
44.1	0.997	0.995	0.975	1.05	33.51

Table III. Experimental Boiling Point–Composition Data for System Carbon Disulfide–Methanol under 760-Mm Absolute Pressure

Mole Fraction Carbon Disulfide, x_1	Boiling Point, ° C
0.174	39.7
0.230	38.1
0.307	37.7
0.400	37.5
0.451	37.5
0.502	37.4
0.728	37.5
0.814	37.5
0.832	37.5
0.886	37.5
0.940	37.8
0.971	38.8

The activity coefficients (Figure 2) were calculated from the equation $\gamma = (y\pi/xP^\circ)$. P° was calculated for different temperatures from the Antoine equation. The boiling point for this system was determined with a Swietoslawski-type ebulliometer. Twelve determinations were made, covering a concentration range of 0.15 to 0.98 mole fraction of carbon disulfide (Table III).

The composition of the minimum boiling type azeotrope as determined from experimental data is 0.700 mole fraction of carbon disulfide at 37.5° C. Horsley (*2*) reported no separation obtainable at a concentration above 0.6950 mole fraction of carbon disulfide at 37.65° C. This is consistent with the observations made in this investigation.

THERMODYNAMIC CONSISTENCY

The experimentally determined values of γ are in general agreement with the thermodynamically correct values, as shown by the NRTL equation curve (*6*) (Figure 2). The values of τ_{12} and τ_{21} resulting from NRTL equation curves were 2.0031 and 1.4031, using a nonlinear least-squares fitting program to minimize the sum of squares of deviations in the vapor-phase mole fraction for all data points. The nonrandomness constant, α_{12}, was assumed to be 0.30 (*6*)

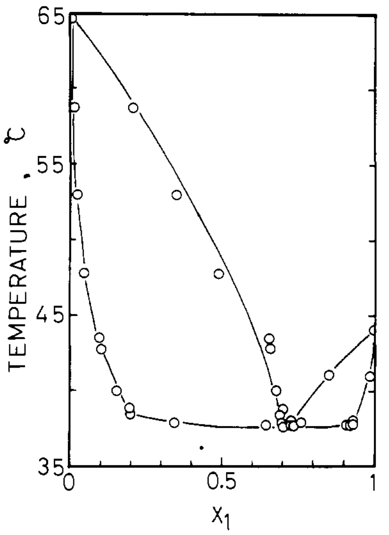

Figure 1. Boiling point–composition curve for carbon disulfide–methanol system

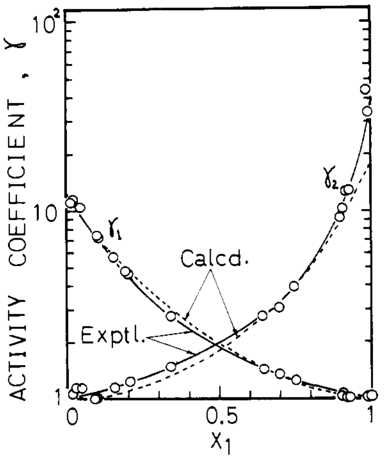

Figure 2. Activity coefficient curves for carbon disulfide–methanol system

for the system reported here. The calculation method used is similar to the one suggested by Prausnitz *et al.* (*4*).

$$\ln \gamma_1 = x_2^2 \left\{ \tau_{21} \frac{\exp(-2\alpha_{12}\tau_{21})}{[x_1 + x_2 \exp(-\alpha_{12}\tau_{21})]^2} + \tau_{12} \frac{\exp(-\alpha_{12}\tau_{12})}{[x_2 + x_1 \exp(-\alpha_{12}\tau_{12})]^2} \right\} \quad (1)$$

$$\ln \gamma_2 = x_1^2 \left\{ \tau_{12} \frac{\exp(-2\alpha_{12}\tau_{12})}{[x_2 + x_1 \exp(-\alpha_{12}\tau_{12})]^2} + \tau_{21} \frac{\exp(-\alpha_{12}\tau_{21})}{[x_1 + x_2 \exp(-\alpha_{12}\tau_{21})]^2} \right\} \quad (2)$$

where

$$\begin{aligned} \tau_{12} &= (g_{12} - g_{22})/RT \\ \tau_{21} &= (g_{21} - g_{11})/RT \\ \alpha_{12} &= 0.30 \\ g_{12} &= g_{21} \end{aligned} \quad (3)$$

Calculated values of y_1 based on τ_{12} and τ_{21} are given in Table II ($y_{1\ \text{calcd}}$). The maximum percentage deviation between $y_{1\ \text{exptl}}$ and $y_{1\ \text{calcd}} = (100\Delta y/y_{1\ \text{exptl}})$ is less than 3.03%. Plots of log (γ_1/γ_2) *vs.* x_1 in accordance with the Redlich and Kister equation (*5*) showed the integrated value was 0.417 and the absolute value was 4.075. The small integrated value showed that the data were consistent.

NOMENCLATURE

g_{ij} = energies of interaction between an *i-j* pair of molecules
P° = vapor pressure, mm of Hg
x = mole fraction in liquid phase
y = mole fraction in vapor phase
α_{ij} = nonrandomness constant for binary *i -j* interactions
Δy = ($y_{1\ \text{exptl}} - y_{1\ \text{calcd}}$)
γ = activity coefficient
π = total pressure, mm of Hg
τ_{ij} = coefficient defined in Equation 3

Subscripts

1 = carbon disulfide
2 = methanol

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Solubility Isotherm of the $FeCl_2$-$MgCl_2$-HCl-H_2O System

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The $FeCl_2$-$MgCl_2$-HCl-H_2O system at 50° C was studied at HCl concentrations of 2, 4, and 11 weight % by using a vacuum evaporation method. Experimental results were shown in a diagram by projecting the data points on the $FeCl_2$-$MgCl_2$-H_2O face, using the HCl vertex as the projection center. Within the HCl concentration ranges investigated, the solid phases existing in the system are $FeCl_2 \cdot 4H_2O$ and $MgCl_2 \cdot 6H_2O$. No double or complex salts were found.

SOLUBILITY isotherms of the $FeCl_2$-HCl-H_2O system at 40° and 60° C (*5*), the $MgCl_2$-HCl-H_2O system at 25° C (*1, 2*), and the $FeCl_2$-$MgCl_2$-H_2O system at 15° and 40° C (*3, 4*) are available in the literature. However, no data on the $FeCl_2$-$MgCl_2$-HCl-H_2O system have been reported. The present work investigated this quaternary system at 50° C.

EXPERIMENTAL

The apparatus used is shown schematically in Figure 1. An aqueous solution with the desired composition of $MgCl_2$ and HCl was saturated with $FeCl_2 \cdot 4H_2O$ at 50° ± 0.5° C. The solution was charged into flask *A* and agitated, and the pressure in the system was adjusted so that

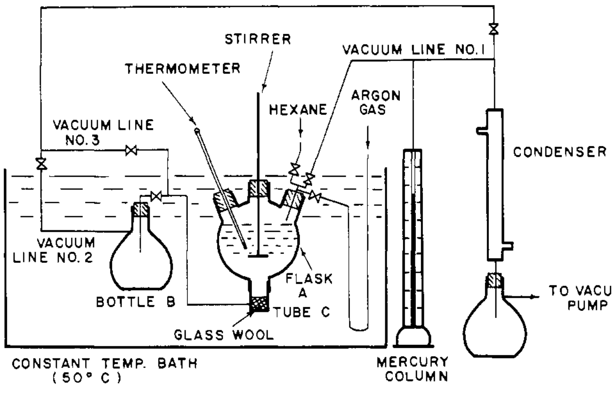

Figure 1. Schematic diagram of experimental apparatus

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