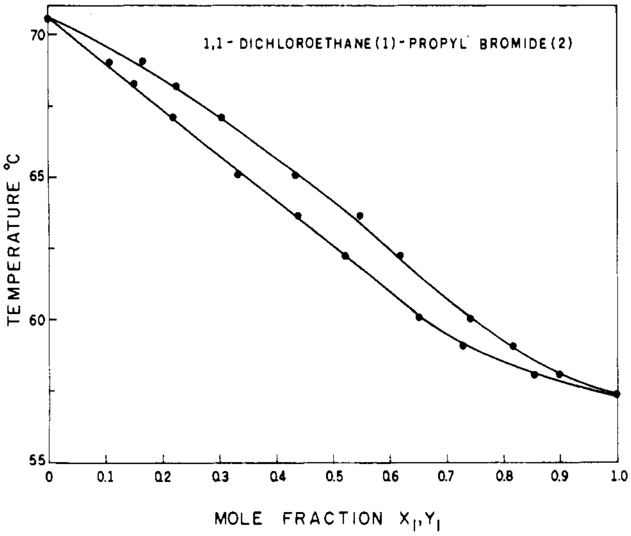

Figure 1. Boiling point diagram.

Table III. Antoine Constants[a]

	α_i	β_i	δ_i
propyl bromide	6.910 65	1194.889	225.51
1,1-dichloroethane	6.985 30	1171.42	228.12

[a] Reference 3.

Results

The temperature–concentration measurements are reported in Table II and Figure 1. The activity coefficients were calculated from the following equations:

$$\ln \gamma_1 = \ln (Py_1/P_1^0x_1) + (B_{11} - v_1^L)(P - P_1^0)/RT + P(1 - y_1)^2\delta_{12}/RT \quad (1)$$

$$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj} \quad (2)$$

Vapor pressures of the pure components, P_i^0, were calculated according to Antoine's equation

$$\log P_i^0 = \alpha_i - \beta_i/(t + \delta_i) \quad (3)$$

the constants of which appear in Table III (*3*). The virial coefficients B_{11}, B_{22}, and B_{12} were estimated by the method of Tsonopoulos (*4*, *5*) using the molar parameters suggested by the author.

The activity coefficients reported in Table II are thermodynamically consistent and show that the system behaves almost ideally.

Boiling points of the binary system were correlated by the equation suggested by Wisniak and Tamir (*6*):

$$T = x_1T_1 + x_2T_2 + x_1x_2[C_0 + C_1(x_1 - x_2) + C_2(x_1 - x_2)^2 + ...] \quad (4)$$

An optimization technique yielded the following values for the constants: $C_0 = -5.811$, $C_1 = -5.373$, $C_2 = 0$, with an rmsd of 0.14.

The ideality of the system permitted correlating the boiling points by the simpler equation

$$t = 70.6 \exp(-0.2304x_1) \quad (5)$$

with an rmsd of 0.20.

Acknowledgment

Yehudit Reizner and Moshe Golden helped in the experimental and numerical calculations.

Glossary

α, β, δ	constants
B_{ii}, B_{ij}	virial coefficients
n	number of experimental points
P	overall pressure, mmHg
P_i^0	vapor pressure of pure component, mmHg
R	gas constant
rmsd	root mean square deviation $(\sum(T_{exptl} - T_{calcd})^2/n)^{1/2}$
t, T	temperature, °C, K
v_i^L	molar volume of pure liquid i, mL/mol
x_i, y_i	molar fraction of component i in the liquid and vapor phases
γ_i	activity coefficient of component i

Subscripts

calcd	calculated
exptl	experimental
i, j, k	component i, j, k

Registry No. 1,1-Dichloroethane, 75-34-3; propyl bromide, 106-94-5.

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(1) Boublikova, L.; Lu, B. C. Y. *J. Appl. Chem.* **1969**, *19*, 89.
(2) Wisniak, J.; Tamir, A. *J. Chem. Eng. Data* **1975**, *20*, 168.
(3) TRC Tables; "Selected Values of Properties of Chemical Compounds"; Thermodynamic Research Center Data Project, College Station, TX, 1974.
(4) Tsonopoulos, C. *AIChE J.* **1974**, *20*, 263.
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Vapor–Liquid Equilibria at 760 mmHg in the System Methanol–1,1-Dichloroethane

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Vapor–liquid equilibria for the title system have been determined at 760 mmHg. The methanol–1,1-dichloroethane system shows positive deviations from ideal behavior and presents a minimum boiling point azeotrope at 48.94 °C with 34 mol % methanol. The boiling points were well correlated with the composition of the liquid phase.

Experimental Section

Purity of Materials. Analytical grade methanol (99.6+%) was supplied by BDH and 1,1-dichloroethane analytical grade (99.6%+) was purchased from Merck. The reagents were used without further purification after gas chromatography analysis failed to show any significant impurities. Properties of the components appear in Table I.

Table I. Physical Properties of Pure Components

compound	refract index (25 °C)	normal bp, °C
methanol	1.3280[a]	64.68[a]
	1.3284[b]	64.70[b]
1,1-dichloroethane	1.4138[a]	57.29[a]
	1.4135[b]	57.28[b]

[a] This work. [b] Reference 3.

Table II. Experimental Vapor-Liquid Equilibria Data for Methanol (1)-1,1-Dichloroethane (2) at 760 mmHg

temp, °C	x_1	y_1	γ_1	γ_2
53.20	0.025	0.135	8.3974	1.0002
52.68	0.029	0.145	7.9424	1.0178
51.16	0.060	0.205	5.7814	1.0321
50.23	0.090	0.245	4.7898	1.0443
49.92	0.110	0.240	3.8881	1.0861
49.41	0.160	0.280	3.1877	1.1088
49.39	0.180	0.295	2.9887	1.1128
49.15	0.240	0.300	2.3026	1.2018
48.95	0.270	0.320	2.2023	1.2235
48.93	0.315	0.325	1.9189	1.2951
48.99	0.380	0.350	1.7096	1.3748
48.96	0.400	0.350	1.6261	1.4221
49.02	0.450	0.365	1.5040	1.5122
49.22	0.515	0.375	1.3392	1.6764
49.44	0.555	0.385	1.2644	1.7843
49.70	0.610	0.405	1.1976	1.9521
51.23	0.745	0.475	1.0807	2.5008
52.45	0.795	0.510	1.0348	2.7872
53.55	0.840	0.555	1.0197	3.1263
54.00	0.850	0.573	1.0208	3.1557
55.52	0.890	0.640	1.0260	3.4471
55.86	0.895	0.645	1.0144	3.5222
57.25	0.918	0.705	1.0233	3.5821
58.66	0.938	0.760	1.0216	3.6835
60.02	0.956	0.810	1.0133	3.9353
61.48	0.973	0.875	1.0167	4.0290
62.04	0.979	0.900	1.0172	4.0721

Apparatus and Procedure. An all-glass modified Dvorak–Boublik recirculation still (*1*) was used in the equilibrium determinations. The experimental details have been described previously (*2*). All analyses were carried out by gas chromatography on a Packard-Becker 417 apparatus provided with thermal conductivity detector and a Spectra Physics Model SP 4290 electronic integrator. The column was 200 cm long and 0.2 cm in diameter and was packed with 20% OV-17 and was operated isothermally at 80 °C. Injector and detector temperatures were 230 and 222 °C, respectively. Very good separation was achieved with helium as the gas carrier, and calibration analyses were carried to convert the peak area ratio to composition of the sample. Concentration measurements were accurate to better than ±1%. The accuracy in determination of pressure and temperature was $\Delta P = \pm 2$ mmHg and $\Delta T = \pm 0.02$ °C.

Results

The temperature–concentration measurements are reported in Table II and Figures 1 and 2. The activity coefficients were calculated from the following equations:

$$\ln \gamma_1 = \ln (Py_1/P_1^0 x_1) + (B_{11} - v_1^L)(P - P_1^0)/RT + P(1 - y_1)^2 \delta_{12}/RT \quad (1)$$

$$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj} \quad (2)$$

Vapor pressures of the pure components, P_i^0, were calculated according to Antoine's equation

$$\log P_i^0 = \alpha_i - \beta_i/(t + \delta_i) \quad (3)$$

the constants of which appear in Table III (*3*). The virial coefficients B_{11}, B_{22}, and B_{12} were estimated by the method of Tsonopoulos (*4*, *5*) using the molar parameters suggested by the author.

The activity coefficients reported in Table II are thermodynamically consistent and show that the system exhibits positive deviations from Raoult's law. They were well correlated by the following Redlich–Kister (*6*) equation

$$\log \gamma_1/\gamma_2 = 0.705\,(x_2 - x_1) - 0.152(6x_1x_2 - 1) + 0.103(x_2 - x_1)(1 - 8x_1x_2) \quad (4)$$

with a coefficient of determination of 0.997.

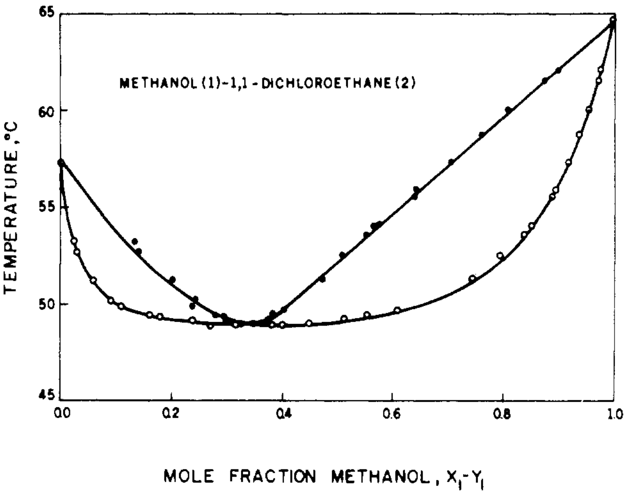

Figure 1. Boiling point diagram.

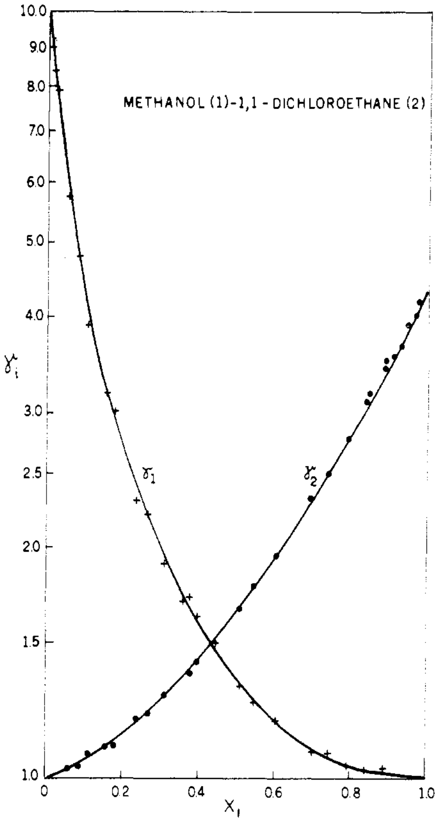

Figure 2. Activity coefficients.

Table III. Antoine Constants[a]

	α_i	β_i	δ_i
methanol	7.897 50	1474.08	229.13
1,1-dichloroethane	6.985 30	1171.42	228.12

[a] Reference 3.

J. Chem. Eng. Data 1988, 33, 111-115

Boiling points of the binary system were correlated by the equation suggested by Wisniak and Tamir (7):

$$T = x_1T_1 + x_2T_2 + x_1x_2[C_0 + C_1(x_1 - x_2) + C_2(x_1 - x_2)^2 + ...] \quad (5)$$

An optimization technique yielded the following values for the constants: $C_0 = -51.325$, $C_1 = 29.786$, $C_2 = 22.484$, $C_3 = 60.637$, $C_4 = 134.786$, with a coefficient of determination of 0.970.

Acknowledgment

Yehudit Reizner and Moshe Golden helped in the experimental and numerical calculations.

Glossary

α, β, δ	constants
B_{ii}, B_{ij}	virial coefficient
P	overall pressure, mmHg
P_i^0	vapor pressure of pure component, mmHg
R	gas constant
t, T	temperature, °C, K
v_i^L	molar volume of pure liquid i, mL/mol
x_i, y_i	molar fraction of component i in the liquid and vapor phases
γ_i	activity coefficient of component i

Subscripts

i, j, k	component i, j, k

Registry No. Methanol, 67-56-1; 1,1-dichloroethane, 75-34-3.

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Vapor–Liquid Equilibria for the Ethane–Propane System at Low Temperature

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Vapor–liquid equilibrium data for the ethane–propane mixture at 270, 255.4, 245, 235, 210, and 195 K are reported. These data have been correlated with good accuracy by the Soave, Redlich–Kwong, and Peng–Robinson equations of state, allowing a variation with temperature of the binary interaction parameter. Variation of equimolar excess Gibbs energy with temperature is also reported.

Introduction

This experimental study is a part of an extensive research program on natural gas liquefaction and cryogenic treatments. Accurate data on ethane–propane equilibria at low temperature are necessary in several fields: prediction of the behavior of mixed refrigerant cycles in gas liquefaction units; heavy hydrocarbon removal from natural gas to be liquefied; ethane extraction from natural gas for ethylene production.

The data obtained complement those published by Djordjevich and Budenholzer (1) who performed 47 equilibria determinations at various temperatures with a large internal between there (25 K). Hirata et al. (2) and Skripka et al. (3) have also published some equilibrium values at low temperature.

Equipment and Experiment

The closed-loop vapor recirculation apparatus is of the type described by Kidnay et al. (4). The equilibrium cell and close surroundings are shown in Figure 1. The external and internal diameters of the equilibrium cell, realized in sapphire, are respectively 6.5 and 4.5 cm; the height is 9.5 cm. Available volume for liquid and vapor phases is about 140 cm^3. This original apparatus has been manufactured by Société des Matériels Cryogéniques (SMC) based on laboratory specifications.

Temperature is measured by platinum resistance thermometers at four different locations in the equilibrium cell. They are calibrated every 2 months with pure methane. Vapor pressure versus temperature data used are those published by the National Bureau of Standards (5, 6). Accuracy is within 0.015 K. Pressure is measured by a Mensor-QM quartz gauge accurate to 0.5 kPa for a 5 MPa pressure value.

All samples are analyzed by gas chromatography using a 2.2-m column packed with 60/80 mesh silica gel at 120 °C. For the vapor phase, a cylindrical container mounted on the recirculation system is used. When equilibrium is reached, this container is isolated and then connected to chromatograph through valves. For the liquid, a sample less than 0.1 cm^3 is taken from the bulk, using a 0.02 cm diameter capillary tube, and entirely vaporized into an exhausted container where it is homogenized by a magnetically driven turbine.

Chromatographic peaks are then processed by a Hewlett-Packard 3354 integrating computer. The gases used were supplied by L'Air Liquide. The purity was 99.95%. Further purification has been applied to propane by flowing it through dried 5A molecular sieve.

Results and Discussion

The unsmoothed 152 data obtained at seven different temperatures ranging from 270 to 195 K are reported in Tables I–VII. In addition to the pressure and mole fractions X and Y of the lighter constituent in liquid and vapor phases, respectively, the K values of the two components are also reported.

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