The constants were determined to be $A = -79.12$ and $B = 0.844$, with $r^2 = 0.963$.

Acknowledgment

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

Glossary

α, β, δ	constants
B_{ii}, B_{ij}	virial coefficients
n	number of experimental points
P	total pressure, mmHg
P_i^0	vapor pressure of pure component, mmHg
R	gas constant, 82.06 cm^3/(g·mol·K)
rmsd	root mean square deviation, $[\sum(T_{expti} - T_{calcd})^2/n]^{1/2}$
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
δ_i	activity coefficient of component i

Subscripts

calcd	calculated
expti	experimental
i, j	component i, j

Registry No. Propyl bromide, 106-94-5; *tert*-butyl alcohol, 75-65-0; *p*-xylene, 106-42-3.

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Vapor–Liquid Equilibria at 760 mmHg for the System 1,1-Dichloroethane–Propyl Bromide

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Vapor–liquid equilibria for the title system have been determined at 760 mmHg. The system behaves almost ideally. The boiling points were well correlated with the composition of the liquid phase.

The present work is part of our program for determining VLE data for organic systems in which one of the components is a bromide.

Experimental Section

Purity of Materials. Propyl bromide (99.6+%) was supplied by Bromine Compounds Ltd., Beer-Sheva, 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.

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 an Autolab Model 6300 electronic integrator. The column was 200 cm long and 0.2 cm in diameter and was packed with OV-17 and was operated isothermally at 80 °C. Injector and detector temperatures were 230 and 240 °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.

Table I. Physical Properties of Pure Components

compd	refractive index (25 °C)	normal bp, °C
propyl bromide	1.4300[a]	70.55[a]
	1.4302[b]	70.80[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 Equilibrium Data for 1,1-Dichloroethane (1)-Propyl Bromide (2) at 760 mmHg

temp, °C	x_1	y_1	γ_1	γ_2
70.00	0.061	0.095	1.0576	0.9935
69.09	0.111	0.165	1.0365	0.9955
68.80	0.115	0.175	1.0702	0.9968
68.20	0.150	0.224	1.0688	0.9944
67.55	0.204	0.279	0.9978	1.0066
67.38	0.208	0.284	1.0012	1.0100
67.08	0.220	0.303	1.0189	1.0077
65.11	0.332	0.437	1.0328	1.0109
63.62	0.441	0.551	1.0255	1.0100
63.55	0.442	0.545	1.0142	1.0276
62.17	0.515	0.617	1.0280	1.0402
60.33	0.652	0.741	1.0323	1.0407
59.59	0.697	0.781	1.0416	1.0354
59.00	0.732	0.816	1.0556	1.0028
58.62	0.805	0.859	1.0227	1.0695
58.22	0.830	0.877	1.0259	1.0848
58.00	0.856	0.900	1.0276	1.0485

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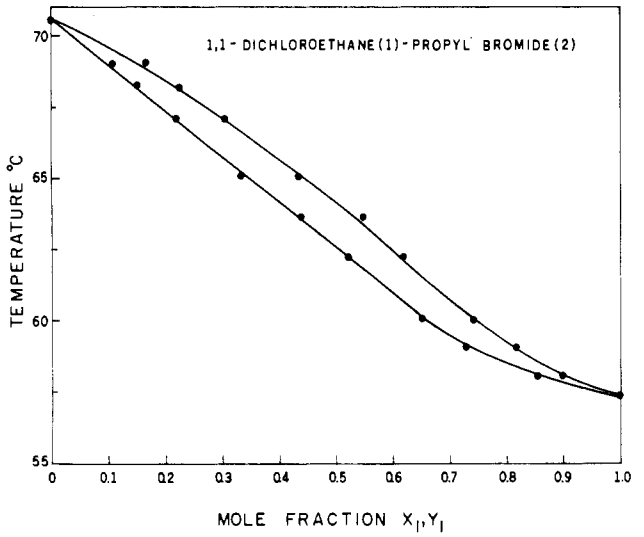

Figure 1. Boiling point diagram.

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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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.

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