X	mole fraction
R	gas constant
Subscripts	
1,2	component number in mixtures
Superscript	
E	excess

Registry No. PA, 79-09-4; A, 62-53-3; MA, 26915-12-8; EA, 103-69-5.

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Vapor–Liquid Equilibria at 760 mmHg in the Systems Propyl Bromide–*tert*-Butyl Alcohol and Propyl Bromide–*p*-Xylene

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Vapor–liquid equilibria for the title systems have been determined at 760 mmHg. The propyl bromide–*tert*-butyl alcohol system shows positive deviations from ideal behavior and presents a minimum boiling point azeotrope at 68.55 °C with 23.5 mol % propyl bromide. The system propyl bromide–*p*-xylene behaves 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 analytical grade *tert*-butyl alcohol (99.5%+) and *p*-xylene (99.3%+) were 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 operated isothermally at 80 °C for separating *tert*-butyl alcohol and 100 °C for separating *p*-xylene. Injector and detector temperatures were (220, 240 °C) and (220, 230 °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

propyl bromide	refract. index (25 °C)	normal bp, °C
propyl bromide	1.4300[a]	70.55[a]
	1.4302[b]	70.80[c]
tert-butyl alcohol	1.3853[a]	82.50[a]
	1.3851[b]	82.42[b]
p-xylene	1.4935[a]	138.20[a]
	1.4933[b]	138.36[b]

[a] This work. [b] Reference *3*. [c] Reference *4*.

Table II. Experimental Vapor–Liquid Equilibria Data for *tert*-Butyl Alcohol (1)–Propyl Bromide (2) at 760 mmHg

temp, °C	x_1	y_1	γ_1	γ_2
69.00	0.080	0.125	2.6586	1.0105
68.65	0.140	0.170	2.0978	1.0363
68.66	0.170	0.185	1.8795	1.0540
68.54	0.204	0.205	1.7447	1.0760
68.55	0.230	0.220	1.6602	1.0909
68.43	0.280	0.245	1.5268	1.1334
68.52	0.290	0.243	1.4565	1.1493
69.03	0.405	0.305	1.2819	1.2393
69.60	0.515	0.370	1.2031	1.3612
70.40	0.610	0.430	1.1421	1.4944
71.15	0.650	0.465	1.1158	1.5199
71.35	0.665	0.455	1.0583	1.6081
71.50	0.680	0.470	1.0474	1.6127
71.80	0.695	0.500	1.0660	1.5700
71.90	0.700	0.510	1.1157	1.6020
75.80	0.870	0.700	1.0333	1.9884
76.91	0.900	0.755	1.0377	2.0553
77.80	0.925	0.805	1.0395	2.1231
78.39	0.933	0.820	1.0259	2.1570
78.30	0.941	0.835	1.0394	2.2508
79.10	0.957	0.870	1.0323	2.3780
79.65	0.970	0.905	1.0371	2.4517
80.50	0.980	0.935	1.0339	2.4694

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Table III. Experimental Vapor–Liquid Equilibria Data for Propyl Bromide (1)-*p*-Xylene (2) at 760 mmHg

temp, °C	x_1	y_1	γ_1	γ_2
73.78	0.905	0.988	1.0056	0.9872
74.10	0.900	0.987	0.9997	0.9973
74.44	0.890	0.985	0.9988	1.0323
78.48	0.775	0.965	0.9992	1.0089
81.68	0.720	0.945	0.9619	1.1302
86.10	0.600	0.915	0.9894	1.0408
89.47	0.530	0.885	0.9896	1.0632
90.10	0.525	0.885	0.9825	1.0291
92.83	0.475	0.860	0.9825	1.0312
93.15	0.470	0.860	0.9848	1.0104
93.46	0.465	0.845	0.9702	1.0962
97.20	0.415	0.825	0.9649	0.9979
101.67	0.335	0.770	0.9987	0.9960
107.70	0.280	0.710	0.9724	0.9908
112.30	0.220	0.630	0.9691	0.9745
115.70	0.180	0.570	0.9930	0.9781
123.40	0.081	0.405	1.0524	0.9775
127.67	0.067	0.285	1.0348	1.0163
134.08	0.024	0.110	0.9814	1.0185

Table IV. Antoine Constants[a]

	α_i	β_i	δ_i
propyl bromide	6.910 65	1194.889	225.51
tert-butyl alcohol	7.319 94	1154.48	177.65
p-xylene	6.990 52	1453.43	215.307

[a] Reference *3*.

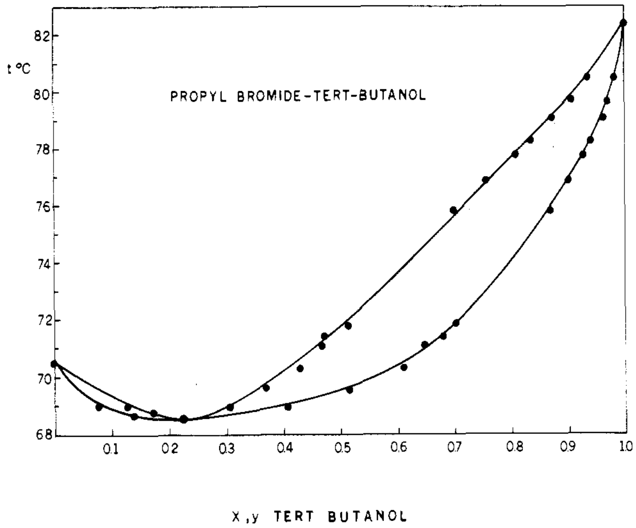

Figure 1. Temperature–composition diagram: propyl bromide-*tert*-butyl alcohol.

Results

The temperature–concentration measurements are reported in Tables II and III and Figures 1–3. 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

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

where the constants appear in Table IV (*3*, *4*). The virial coefficients B_{11}, B_{22}, and B_{12} were estimated by the method of Tsonopoulos (*5*, *6*) using the molar parameters suggested by the author.

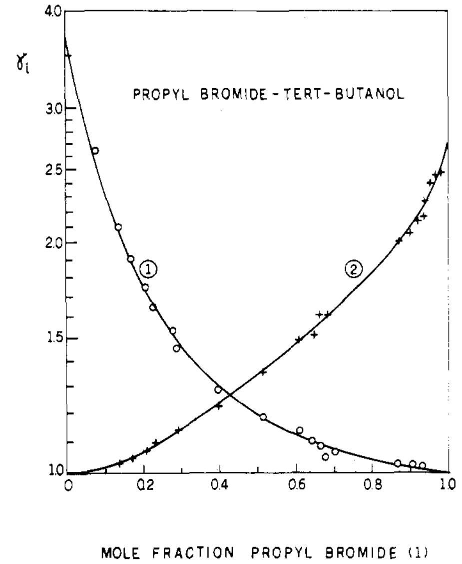

Figure 2. Activity coefficients for the system propyl bromide-*tert*-butyl alcohol.

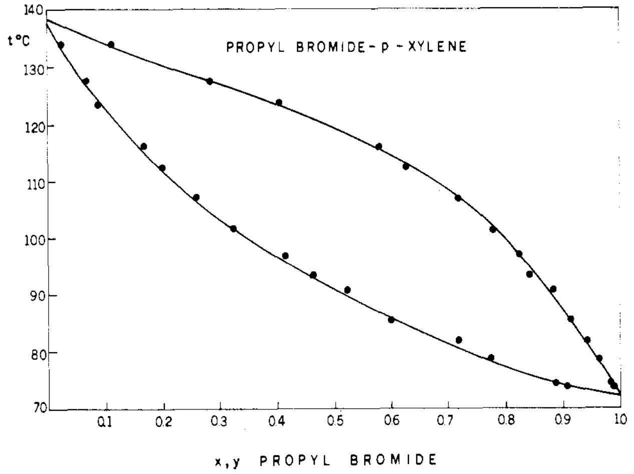

Figure 3. Temperature–composition diagram: propyl bromide-*p*-xylene.

The activity coefficients reported in Table II and III are thermodynamically consistent and show that the system propyl bromide-*tert*-butyl alcohol has positive deviation from Raoult's law while the system propyl bromide-*p*-xylene behaves ideally.

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

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

An optimization technique yielded the following values for the constants:

propyl bromide-*tert*-butyl alcohol:
$C_0 = -26.61$, $C_1 = -9.600$, $C_2 = -21.48$;
rmsd = 0.37

propyl bromide-*p*-xylene:
$C_0 = -49.75$, $C_1 = 25.24$, $C_2 = 15.48$;
rmsd = 0.54

Boiling points for the system propyl bromide-*p*-xylene were also correlated by another equation proposed by Wisniak (*8*):

$$T = x_1T_1 + x_2T_2 + Ax_1x_2(-Bx_1) \quad (5)$$

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 $\mathrm{cm^3/(g{\cdot}mol{\cdot}K)}$
rmsd	root mean square deviation, $[\sum(T_{\mathrm{exptl}} - T_{\mathrm{calcd}})^2/n]^{1/2}$
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
exptl	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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