Vapor–Liquid Equilibria at 760 mmHg in the Systems Propyl Bromide–Methyl Methacrylate and Vinyl Acetate–Propyl Bromide

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Vapor–liquid equilibria for the title systems have been determined at 760 mmHg. The propyl bromide–methyl methacrylate system behaves essentially in an ideal form while the vinyl acetate–propyl bromide system behaves like a regular solution with positive deviations from ideal behavior and exhibits a minimum boiling point azeotrope at 69.16 °C containing 37.5 mol % vinyl acetate. The boiling points of each system were well correlated with the composition of the liquid phase, using an empirical correlation developed by the authors.

The present work is part of our program for determining VLE data for organic systems in which one of the components is a bromide. No experimental data are available in the literature on systems of this nature.

Experimental Section

Purity of Materials. Propyl bromide (99.6+%) was supplied by Bromine compounds Ltd., Beer-Sheva, and methyl methacrylate, analytical grade (99+%), and vinyl acetate, analytical grade (99+%), were purchased from Fluka. The reagents were used without further purification after gas chromatography analysis failed to show any significant impurities (less than 0.03%). 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. A vacuum system connected the vapor condenser with a Swietoslawski ebulliometer and allowed total pressure regulation. The total pressure of the system was determined from the boiling temperature of the distilled water in the ebulliometer. Temperatures were measured with a Hewlett-Packard quartz thermometer. Other experimental details have been described in previous publications (*2*). In order to reduce the polymerization of methyl methacrylate up to 0.2 wt % of hydroquinone monomthyl ether was added to the original reagent. 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 operated isothermally at 90 °C (propyl bromide–methyl methacrylate) or 70 °C (propyl bromide–vinyl acetate). Injector and detector temperatures were 220 and 230 °C, respectively. Very good separation was achieved with helium as the gas carrier, and calibration analyses were carried out to convert the peak area ratio to composition of the sample. Concentration measurements were accurate to better than ±1% (repeatitive measurements). The accuracy in determination of pressure and temperature was $\Delta P = \pm 2$ mmHg and $\Delta T = \pm 0.02$ °C. No special handling or safety-associated problems were connected with the handling of these systems.

Results

The temperature–concentration measurements at 760 mmHg are reported in Tables II and III and Figures 1 and 2. The activity coefficients were calculated from the equations

Table I. Physical Properties of Pure Components

compound	refract. index (25 °C)	normal bp, °C
propyl bromide	1.4300[a]	70.55[a]
	1.4302[b]	70.80[c]
methyl methacrylate	1.4118[a]	100.4[a]
	1.4120[d]	100.3[d]
vinyl acetate	1.3932[a]	72.56[a]
	1.3934[d]	72.53[d]

[a] This work. [b] Reference *10*. [c] Reference *3*. [d] Reference *11*.

Table II. Experimental Vapor-Liquid Equilibria Data for Propyl Bromide (1)–Methyl Methacrylate (2) at 760 mmHg

temp, °C	x_1	y_1	γ_1	γ_2
97.70	0.055	0.120	1.0534	1.0629
95.65	0.096	0.200	1.0587	1.0674
95.15	0.110	0.225	1.0527	1.0730
92.99	0.165	0.320	1.0545	1.0403
90.72	0.220	0.405	1.0614	1.0678
89.79	0.250	0.435	1.0279	1.0852
87.14	0.330	0.540	1.0369	1.0740
85.62	0.370	0.595	1.0614	1.0550
83.98	0.425	0.650	1.0554	1.0525
82.93	0.460	0.680	1.0499	1.0599
81.96	0.495	0.720	1.0611	1.0234
81.67	0.510	0.730	1.0526	1.0266
80.62	0.560	0.760	1.0276	1.0517
80.50	0.570	0.765	1.0197	1.0579
79.51	0.600	0.790	1.0285	1.0499
77.63	0.675	0.845	1.0314	1.0152
77.28	0.690	0.850	1.0252	1.0422
76.17	0.740	0.880	1.0217	1.0319
74.35	0.825	0.926	1.0149	1.0006
73.32	0.880	0.951	1.0069	1.0061

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

temp, °C	x_1	y_1	γ_1	γ_2
70.40	0.079	0.097	1.3308	0.9994
70.20	0.109	0.131	1.3109	1.0013
70.02	0.137	0.161	1.2892	1.0036
69.62	0.206	0.230	1.2377	1.0076
69.48	0.243	0.262	1.2034	1.0206
69.40	0.268	0.285	1.1902	1.0251
69.28	0.326	0.337	1.1612	1.0361
69.23	0.361	0.366	1.1407	1.0466
69.16	0.374	0.376	1.1336	1.0537
69.26	0.479	0.463	1.0863	1.0863
69.32	0.504	0.493	1.0972	1.0754
69.39	0.532	0.515	1.0834	1.0880
69.48	0.581	0.553	1.0621	1.1170
69.58	0.607	0.571	1.0463	1.1395
69.95	0.700	0.649	1.0292	1.1534
70.00	0.690	0.664	1.0438	1.1469
70.25	0.758	0.710	1.0263	1.1770
70.48	0.777	0.731	1.0165	1.2257
70.80	0.847	0.795	1.0097	1.2646
71.00	0.869	0.827	1.0112	1.3213
71.34	0.902	0.868	1.0115	1.3341
71.65	0.933	0.908	1.0129	1.3476
71.78	0.942	0.918	1.0101	1.3822
71.99	0.973	0.936	0.9976	0.4523
72.13	0.985	0.951	0.9968	1.4693

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$$\ln y_i = \ln (Py_i/P_i^\circ x_i) + (B_{ii} - v_i^L)(P - P_i^\circ)/RT + P(1 - y_i)^2\delta_{ij}/RT \quad (1)$$

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

The last two terms in eq 2 contributed between 2 and 4% to the activity coefficient, and their influence was important only at very dilute concentrations.

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

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

where the constants appear in Table IV. The coefficients for methyl methacrylate were obtained by reduction of the data reported in Perry (*3*) since the equations reported by Boublik et al. (*4*) and Ohe (*5*) are in error at temperatures close to the boiling point of methyl methacrylate. The reported Antoine equation with the fitted data represents the data given in Perry with a coefficient of determination of 0.997 and an rmsd of 10.6. The virial coefficients B_{11}, B_{22}, and B_{12} were estimated by the method of Tsonopoulos (*6*, *7*) using the molar parameters suggested by the author.

The activity coefficients reported in Tables II and III are thermodynamically consistent by the area test and show that the system propyl bromide–methyl methacrylate behaves essentially ideally, while the vinyl acetate–propyl bromide system presents positive deviations from ideal behavior and exhibits a minimum boiling point azeotrope at 69.16 °C containing 37.5% mol % vinyl acetate. The slight deviations from ideality presented by the propyl bromide–methyl acrylate system, particularly at the dilute ends, can be attributed to the combined influence of the analytical error and the errors in the Antoine correlation.

The data in Table III were also correlated using the Redlich–Kister (*8*) equation

$$\log (\gamma_1/\gamma_2) = A(x_2 - x_1) + B(6x_2x_1 - 1) + C(x_2 - x_1)(1 - 8x_2x_1) \quad (4)$$

The results that appear in Figure 3 show that $\log (\gamma_1/\gamma_2)$ varies linearly with x_1 so that

$$\log (\gamma_1/\gamma_2) = 0.151(1 - 2x_1) \quad (5)$$

with a coefficient of determination 0.989 and an rmsd of 0.004. Equation 5 indicates that solutions of vinyl acetate and propyl bromide behave like regular solutions so that

$$\Delta G^E = 226.450x_1x_2 \text{ cal/(g·mol)} \quad (6)$$

with a coefficient of determination of 0.965 and an rmsd of 3.0.

Boiling points of the binary system were correlated by the equation suggested by Wisniak and Tamir (*9*):

$$T = x_1T_1 + x_2T_2 + x_1x_2[C_0 + C_1(x_1 - x_2) + C_2(x_1 - x_2)^2 + ...] \quad (7)$$

An optimization technique yielded the values for the constants given in Table V.

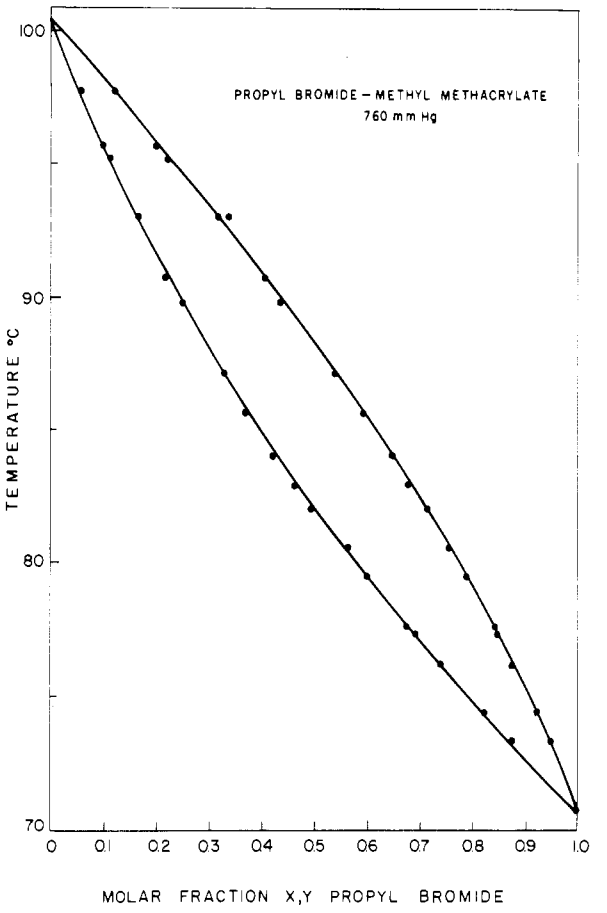

Figure 1. Propyl bromide–methyl methacrylate: boiling point diagram.

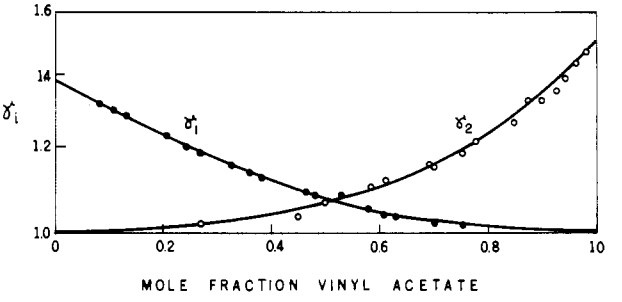

Figure 2. Vinyl acetate–propyl bromide: activity coefficients as a function of composition.

Table IV. Antoine Constants

	α_i	β_i	δ_i
propyl bromide[a]	6.91065	1194.889	225.51
methyl methacrylate	7.1090	1387.86	226.15
vinyl acetate[a]	6.99220	1191.99	217.51

[a] Reference *3*.

Table V. Constants in Eq 7

system	C_0	C_1	rmsd
propyl bromide–methyl methacrylate	−1.0459	1.9020	0.16
vinyl acetate–propyl bromide	−9.8680	−2.564	0.16

The almost ideal nature of the system propyl bromide–methyl methacrylate also allows correlation of the boiling points with the simple expression

$$\ln (t) = 4.6060 - 0.4628x_1 + 0.1266x_1^2 \quad (8)$$

with a coefficient of determination of 0.99 and an rmsd of 0.17.

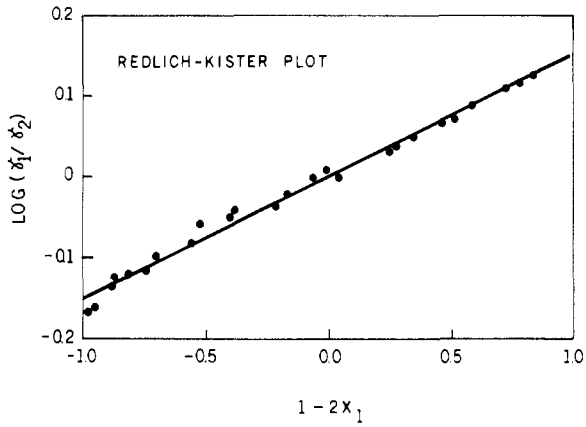

Figure 3. Test of eq 4.

Acknowledgment

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

Glossary

α, β, δ	constants
B_{ii}, B_{ij}	virial coefficients
ΔG^E	excess of the Gibbs function
n	number of experimental points
P	total pressure, mmHg
P_i°	vapor pressure of pure component, mmHg
R	gas constant, 82.06 cm^3/(g·mol·K)
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	components i, j

Registry No. Propyl bromide, 106-94-5; vinyl acetate, 108-05-4; methyl methacrylate, 80-62-6.

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Vapor–Liquid Equilibria at 760 mmHg in the Systems Methyl Acetate–Propyl Bromide, Methyl Acetate–Toluene, and Methyl Methacrylate–Toluene

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Vapor–liquid equilibria for the title systems have been determined at 760 mmHg. The three systems exhibit positive deviations from ideal behavior. 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. No literature data are available for comparison purposes.

Experimental Section

Purity of Materials. Propyl bromide (99.4+%) and methyl acetate (99.2+%) were supplied by Merck, analytical grade methyl methacrylate (99.4+%) was supplied by Fluka, and toluene (99.6+%) was supplied by Frutarom. The reagents were used without further purification after gas chromatography analysis failed to show any significant impurities (none higher than 0.2 mol %). 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 in previous publications (*2*). In order to reduce the polymerization of methyl methacrylate, up to 0.2 wt % of hydroquinone monomethyl ether was added to the original reagent. All analyses were carried out by gas chromatography on a Packard-Becker 417 chromatograph provided with thermal conductivity detector and an Spectra Physics Model SP 4290 electronic integrator. The column was 200 cm long and 0.2 cm in diameter and packed with 20% OV-17. Temperatures were column, 90 °C (120 °C for methyl acetate–toluene); injector, 220 °C; and detector, 230 °C. Very good separation was achieved with helium as the gas carrier, and calibration analyses were carried

Table I. Physical Properties of Pure Components

compound	refractive index (25 °C)	normal bp, °C
propyl bromide	1.4320[a]	70.55[a]
	1.4317[b]	70.80[c]
methyl acetate	1.3588[a]	56.94[a]
	1.3589[b]	56.94[b]
methyl methacrylate	1.4118[a]	100.4[a]
	1.4120[c]	100.3[d]
toluene	1.4926[a]	110.70[a]
	1.4941[b]	110.80[b]

[a] This work. [b] Reference 8. [c] Reference 9. [d] Reference 10.

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