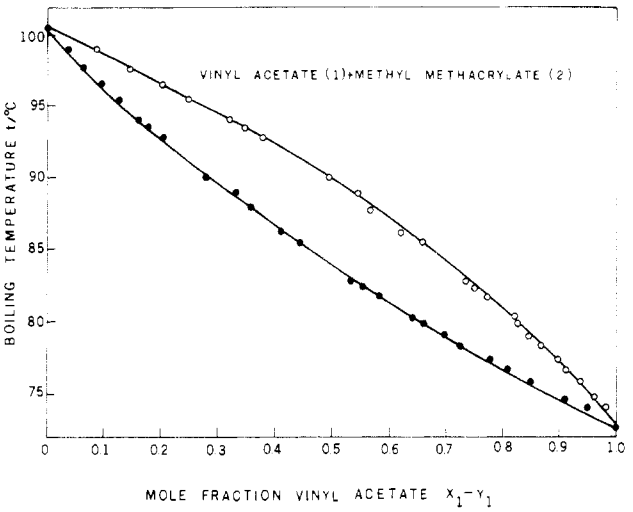

Figure 5. Boiling temperature vs mole fraction x_1 (liquid) and y_1 (vapor) for the system vinyl acetate (1) + methyl methacrylate (2).

Boiling points of the binary system were correlated by the equation suggested by Wisniak and Tamir (*12*):

$$t/°C = x_1(t°_1/°C) + x_2(t°_2/°C) + x_1x_2[C_0 + C_1(x_1 - x_2) + C_2(x_1 - x_2)^2 + ...] \quad (5)$$

A simplex optimization technique yielded the values for the constants reported in Table VI.

Acknowledgment

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

Glossary

α,β,δ	Antoine constants, eq 1
A_{ij},A_{ji}	Wilson constants
B,C,D,E	Redlich-Kister coefficients, eq 2
C_i	coefficients in eq 5
n	number of experimental points
rmsd	root mean square deviation $\{\sum(T_{expt} - T_{calc})^2/n\}^{0.5}$
t	temperature, °C
$t°_i$	boiling temperature of pure component i, °C
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	component i,j
calc	calculated
expt	experimental

Registry No. Propyl bromide, 106-94-5; 2-butanone, 78-93-3; *p*-xylene, 106-42-3; vinyl acetate, 108-05-4; methyl methacrylate, 80-62-6.

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Vapor–Liquid Equilibria in the System Vinyl Acetate–Propyl Bromide–Methyl Methacrylate

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Vapor–liquid equilibrium at 760 mmHg has been determined for the title system. The ternary data were correlated by various equations, and the appropriate parameters are reported. No azeotrope is present.

The present work was undertaken to measure vapor–liquid equilibrium (VLE) data for the title system for which no isobaric data are available. Data for the three other binaries have already been measured (*1*, *2*).

Experimental Section

Purity of Materials. Vinyl acetate analytical grade (99%+) and methyl methacrylate (99.4%+) were purchased from Fluka, propyl bromide (99.4%) from Merck. The reagents were used without further purification after gas chromatography failed to show any significant impurities. Properties of the pure

Table I. Physical Constants of Pure Components

index	compound	refractive index (25 °C)	bp(760 mmH), °C	purity GLC (min), %
1	vinyl acetate	1.3932[a]	72.56[a]	99
		1.3934[c]	72.49[c]	
2	propyl bromide	1.4320[a]	70.55[a]	99.4
		1.4317[b]	70.80[b]	
3	methyl methacrylate	1.4118[a]	100.4[a]	99.4
		1.4120[d]	100.3[c]	

[a] Measured. [b] Reference 11. [c] Reference 12. [d] Reference 14.

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Table II. Experimental Vapor–Liquid Equilibria Data for Vinyl Acetate (1)–Propyl Bromide (2)–Methyl Methacrylate (3) at 760 mmHg

temp, °C	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3	temp, °C	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
70.80	0.257	0.693	0.280	0.700	1.145	1.015	1.062	77.90	0.650	0.076	0.751	0.114	0.977	1.277	1.036
71.00	0.323	0.608	0.348	0.625	1.126	1.028	1.034	78.10	0.450	0.200	0.538	0.287	1.003	1.165	1.046
71.10	0.380	0.541	0.393	0.577	1.079	1.064	1.001	78.20	0.251	0.381	0.311	0.500	1.037	1.063	1.073
71.70	0.600	0.331	0.580	0.394	0.990	1.164	0.973	78.20	0.111	0.527	0.149	0.667	1.123	1.025	1.061
71.70	0.496	0.420	0.500	0.467	1.032	1.090	1.015	78.50	0.431	0.217	0.517	0.306	0.995	1.133	1.040
71.70	0.460	0.441	0.471	0.490	1.047	1.088	1.017	78.50	0.476	0.168	0.578	0.244	1.006	1.166	1.032
71.70	0.674	0.272	0.665	0.314	1.009	1.131	1.002	79.40	0.353	0.253	0.435	0.356	0.993	1.100	1.064
71.80	0.715	0.237	0.696	0.288	0.991	1.185	0.854	79.60	0.391	0.197	0.498	0.290	1.021	1.145	1.026
71.90	0.097	0.846	0.118	0.856	1.238	0.986	1.170	79.80	0.436	0.166	0.539	0.245	0.983	1.140	1.073
72.00	0.792	0.183	0.777	0.215	0.994	1.140	0.815	79.90	0.582	0.052	0.726	0.079	0.991	1.171	1.050
72.10	0.086	0.806	0.147	0.820	1.726	0.985	0.777	80.00	0.333	0.250	0.420	0.361	0.999	1.110	1.033
72.50	0.165	0.729	0.192	0.763	1.161	1.001	1.067	80.40	0.348	0.209	0.452	0.306	1.015	1.112	1.062
72.60	0.184	0.699	0.210	0.746	1.135	1.018	0.941	80.60	0.041	0.550	0.055	0.697	1.043	0.958	1.172
72.60	0.610	0.282	0.619	0.336	1.009	1.136	1.043	81.00	0.207	0.317	0.286	0.460	1.061	1.084	1.018
72.70	0.530	0.345	0.538	0.410	1.007	1.131	1.040	82.30	0.135	0.351	0.191	0.510	1.047	1.047	1.067
72.70	0.600	0.287	0.621	0.336	1.025	1.112	0.948	82.50	0.220	0.263	0.309	0.396	1.032	1.079	1.038
72.70	0.662	0.239	0.671	0.290	1.004	1.152	0.981	83.00	0.206	0.248	0.299	0.389	1.049	1.106	1.022
72.80	0.548	0.324	0.550	0.402	0.992	1.177	0.933	83.20	0.289	0.207	0.380	0.306	0.45	1.037	1.108
72.80	0.756	0.168	0.756	0.215	0.987	1.212	0.946	83.70	0.450	0.056	0.609	0.082	0.959	1.014	1.094
72.90	0.799	0.140	0.792	0.181	0.977	1.223	1.095	84.70	0.447	0.018	0.631	0.032	0.972	1.198	1.068
72.90	0.031	0.883	0.040	0.922	1.269	0.986	1.092	84.90	0.339	0.100	0.486	0.160	0.981	1.071	1.063
73.20	0.044	0.834	0.056	0.887	1.240	0.995	1.144	85.00	0.146	0.264	0.217	0.406	1.013	1.026	1.075
73.30	0.036	0.866	0.46	0.908	1.245	0.981	1.148	85.10	0.383	0.046	0.568	0.064	1.008	0.926	1.080
73.50	0.050	0.804	0.065	0.866	1.256	0.999	1.148	85.90	0.380	0.043	0.557	0.073	0.976	1.107	1.048
73.60	0.144	0.681	0.167	0.756	1.116	1.027	1.065	86.20	0.260	0.115	0.389	0.197	0.986	1.107	1.075
73.80	0.041	0.879	0.054	0.913	1.262	0.957	0.989	86.20	0.146	0.227	0.218	0.370	0.983	1.052	1.064
73.90	0.632	0.220	0.660	0.280	0.996	1.167	0.970	86.30	0.136	0.231	0.211	0.380	1.018	1.058	1.042
74.00	0.580	0.255	0.612	0.320	1.006	1.150	0.986	86.90	0.274	0.094	0.412	0.165	0.969	1.111	1.059
74.00	0.233	0.561	0.272	0.639	1.112	1.043	1.035	88.70	0.227	0.086	0.361	0.154	0.972	1.078	1.056
74.40	0.679	0.162	0.717	0.215	0.994	1.201	1.009	90.70	0.077	0.193	0.118	0.312	0.885	0.921	1.101
74.60	0.277	0.483	0.321	0.573	1.082	1.066	1.037	90.90	0.175	0.061	0.305	0.120	1.000	1.114	1.054
74.80	0.442	0.342	0.485	0.420	1.018	1.097	1.024	91.10	0.227	0.030	0.365	0.053	0.917	0.995	1.090
75.00	0.628	0.182	0.674	0.243	0.989	1.185	1.008	91.50	0.197	0.040	0.339	0.080	0.971	1.115	1.046
75.10	0.146	0.629	0.177	0.715	1.115	1.007	1.107	92.20	0.102	0.095	0.183	0.188	0.992	1.082	1.055
75.20	0.327	0.412	0.380	0.505	1.065	1.082	1.014	92.40	0.144	0.064	0.251	0.120	0.960	1.022	1.065
75.30	0.480	0.294	0.516	0.380	0.982	1.137	1.053	92.40	0.126	0.081	0.223	0.161	0.975	1.083	1.040
75.70	0.700	0.105	0.765	0.146	0.986	1.209	1.028	92.40	0.201	0.015	0.343	0.030	0.939	1.088	1.070
76.50	0.586	0.153	0.663	0.215	0.996	1.195	1.028	95.30	0.094	0.030	0.180	0.066	0.969	1.106	1.055
76.80	0.737	0.059	0.826	0.080	0.980	1.145	1.002	95.40	0.051	0.080	0.099	0.163	0.981	1.022	1.037
76.90	0.615	0.119	0.704	0.172	0.997	1.216	1.013	95.90	0.063	0.057	0.108	0.105	0.852	0.910	1.076
77.00	0.570	0.167	0.636	0.233	0.967	1.169	1.077	97.60	0.065	0.020	0.111	0.037	0.810	0.874	1.065
77.70	0.530	0.154	0.626	0.224	1.003	1.195	1.005	98.00	0.016	0.041	0.033	0.090	0.966	1.025	1.050

components appear in Table I.

Apparatus and Procedure. An all-glass modified Dvorak and Boublik recirculation still (*3*) was used in the equilibrium determination. 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. The experimental features have been described in a previous publication (*4*). All analyses were carried out by gas chromatography on a Packard-Becker Model 417 apparatus provided with a thermal conductivity detector and a Spectra Physics Model SP 4290 electronic integrator. The column was 3 m long and 0.2 cm in diameter and was filled with 20% SP 2100 and operated at 65 °C. The temperatures at the detector and injector were 210 and 120 °C, respectively. Very good separation was achieved under these conditions, and calibration analyses were carried to convert the peak ratio to the weight composition of the sample. Concentration measurements were accurate to better than ±1%. The accuracy in the determination of pressure and temperature was $\Delta P = \pm 1$ mmHg and $\Delta t = \pm 0.02$ °C.

Results

The temperature–concentration measurements at 760 mmHg for the ternary system are reported in Table II, together with the activity coefficients that were calculated from the following equation (*5*):

$$\ln \gamma_i = \ln (Py_i/P_i^\circ x_i) + (B_{ii} - V_i^L)(P - P_i^\circ)/RT + (P/2RT)\sum\sum y_j y_k (2\delta_{ji} - \delta_{jk}) \quad (1)$$

where

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

Vapor pressures P_i° were calculated according to Antoine's equation:

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

where the constants are reported in Table III. The molar virial coefficients B_{ii} and the molar mixed coefficient B_{ij} were calculated by the method of Tsonopoulos (*6*) using the molecular parameters suggested by the same author. The last two terms contributed between 1% and 2% to the activity coefficient, and their influence was important only at very dilute concentrations.

Table III. Vapor-Pressure Constants

compound	α_i	β_i	δ_i
vinyl acetate[a]	6.99227	1191.99	217.01
propyl bromide[b]	6.91065	1194.889	225.51
methyl methacrylate[c]	7.1090	1387.86	226.15

[a] Reference 13. [b] Reference 11. [c] Reference 2.

Table IV. Redlich–Kister Correlation of Ternary Data, Equation 4

system	B_{ij}	C_{ij}	D_{ij}	rmsd[a] γ_1	rmsd[a] γ_2
vinyl acetate (1)–propyl bromide (2)	0.27051	−0.010220	0.13950	0.025	0.39
vinyl acetate (1)–methyl methacrylate (3)[b]					
propyl bromide (2)–methyl methacrylate (3)[b]					

system	C_1	overall rmsd[c] γ_{ij}	overall rmsd[c] y_{ij}
vinyl acetate (1)–propyl bromide (2) methyl methacrylate (3)	0	0.17	0.023
	−2.2543	0.17	0.023

[a] rmsd = room mean square deviations. [b] Ideal system. [c] Weighted average.

Table V. Correlation of Boiling Points, Equation 5

system	C_0	C_1	C_2	rmsd[a]
vinyl acetate (1)–propyl bromide (2)	−9.0730	0.50615	0.22946	0.066
vinyl acetate (1)–methyl methacrylate (3)	−9.1901	2.6248		0.18
propyl bromide (2)–methyl methacrylate (3)	−13.973	6.8921		0.13

system	A	B	rmsd[a]
vinyl acetate (1)–propyl bromide (2)–methyl methacrylate (3)	0.87533	−2.7274	0.401

[a] rmsd = room mean square deviation.

The ternary data reported in Table II were found to be thermodynamically consistent as tested by the McDermot–Ellis method (*7*) modified by Wisniak and Tamir (*8*).

The activity coefficients for the ternary system were correlated by the following Redlich–Kister expansion (*9*):

$$\ln \gamma_1 = x_2x_3[(B_{12} + B_{13} - B_{23}) + C_{12}(2x_1 - x_2) + C_{13}(2x_1 - x_3) + 2C_{23}(x_3 - x_2) + D_{12}(x_1 - x_2)(3x_1 - x_2) + D_{13}(x_1 - x_3)(3x_1 - x_2) - 3D_{23}(x_3 - x_2)^2 + C_1(1 - 2x_1)] + x_2^2[B_{12} + C_{12}(3x_1 - x_2) + D_{12}(x_1 - x_2)(5x_1 - x_2)] + x_3^2[B_{13} + C_{13}(3x_1 - x_3) + D_{13}(x_1 - x_3)(5x_1 - x_3)] \quad (4)$$

where B_{ij}, C_{ij}, and D_{ij} are the binary constants and C_1 is a ternary constant. The equations for two other activity coefficients were obtained by cyclic rotation of the indices. The binary data used for calculating the binary constants have been reported elsewhere (*1*, *2*).

The ternary Redlich–Kister coefficients were obtained by a Simplex optimization technique and are reported in Table IV. The relative values of the root mean square deviation and the ternary constant C_1 suggest that ternary data can be predicted directly from the binary systems.

Boiling points of system were correlated by the equation suggested by Wisniak and Tamir (*10*), based solely in the liquid composition:

$$T = \sum_{i=1}^{3} x_i T_i^{\circ} + \sum_{i,j=1}^{i} [x_i x_j \sum_{k=0}^{1} C_k (x_i - x_j)^k] + x_1x_2x_3[A + B(x_1 - x_2) + C(x_1 - x_3) + D(x_2 - x_3) + \ldots] \quad (5)$$

In these equations, T_i° is the boiling point of the pure component in kelvin, and i is the number of terms in the series expansion of $x_i - x_j$. C_k are the binary constants where A, B, C, D are ternary constants (Figure 1). The various constants of eq 5 are reported in Table V, which also contains information indicating the degree of goodness of the correlation.

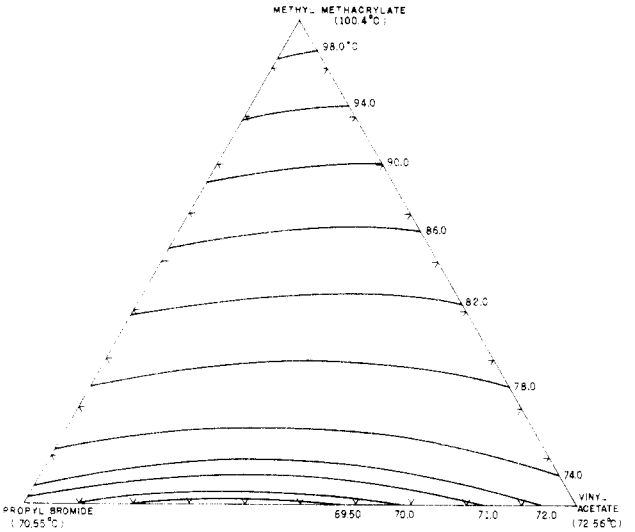

Figure 1. Isothermals for the ternary system (760 mmHg).

Acknowledgment

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

Glossary

B_{ij}, C_{ij}	virial coefficients, eqs 1,2
B_{ij}, C_{ij}, D_{ij}	Redlich–Kister constants, eq 4
n	number of components
P	total pressure, mmHg
P_i°	vapor pressure of pure component i, mmHg
R	gas constant, 62 363.3 cm^3·mmHg·g-mol^{-1}·K^{-1}
T	boiling temperature of a mixture, K
T_i°	boiling temperature of pure component, i, K
t	temperature, °C
v_i^L	molar volume of liquid component i, mL·g-mol^{-1}
x_i, y_i	mole fraction of component i in the liquid and vapor phases
α_i	coefficient, Antoine equation
β_i	coefficient, Antoine equation
γ_i	activity coefficient of component i
δ_i	coefficient, Antoine equation
δ_{ij}	virial coefficient parameter, eq 2

Registry No. 1, 108-05-4; 2, 106-94-5; 3, 80-62-6.

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