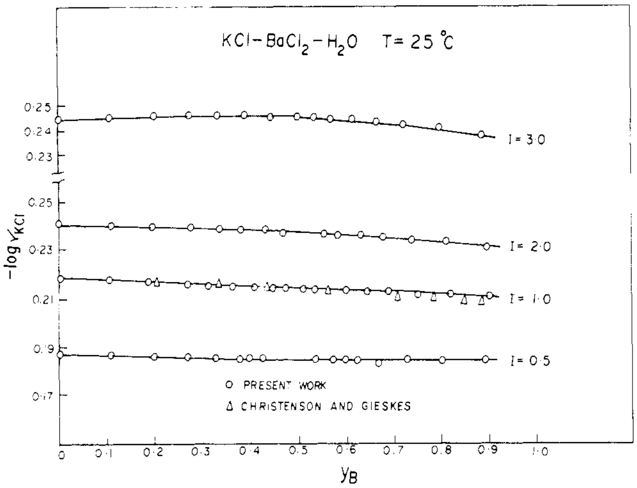

Figure 1. Plot of $-\log \gamma_{KCl}$ against y_{BaCl_2} at different ionic strengths.

(α_{AB} and β_{AB}) values are listed in Table II.

The activity coefficients of KCl in constant ionic strength mixtures of $KCl-BaCl_2-H_2O$ are described by the Pitzer equation, which is given in the literature (*8-10*). The experimental activity coefficient data was fitted to this equation to calculate the binary interaction coefficients (${}^s\Theta_{KBa}$) and ternary interaction coefficients (Ψ_{KBaCl}) at every ionic strength. These ${}^s\Theta$ and Ψ values are also listed in Table II along with the corresponding root mean square deviation (RMSD) values. Next, the common ${}^s\Theta$ and Ψ values were calculated at each of the ionic strengths and temperatures studied with use of a linear least-squares program. From Table II, it is evident that these common ${}^s\Theta$ and Ψ values are nearly constant at each temperature and are independent of ionic strength as expected according to the Pitzer formalism (*8*). These ${}^s\Theta = 0.034$ and $\Psi = -0.027$ values obtained in the present work at 25 °C are in reasonable agreement with the values (${}^s\Theta = 0.01$ and $\Psi = -0.017$) reported by Pitzer (*11*) using the isopiestic data of Robinson and Bower (*2*). The ${}^s\Theta$ and Ψ values (cf. Table II) at 25, 35, and 45 °C give the temperature derivatives of ${}^s\Theta$ and Ψ as $\partial {}^s\Theta/\partial T = (2.0 \pm 0.2) \times 10^{-4}$ and $\partial\Psi/\partial T = (3.3 \pm 0.2) \times 10^{-4}$. These values are in the same range as reported by Pitzer (*12*) for the similar systems. Next, with these common ${}^s\Theta$ and Ψ values, the osmotic coefficients of the mixtures were calculated at each of the ionic strengths and temperatures studied with use of the Pitzer equation (*13*). These osmotic coefficients are listed in Table III. These osmotic coefficients are in agreement with the experimental data of Robinson and Bower (*2*) with an RMSD of 9.1×10^{-3}. Also, the activity coefficients of the second component, i.e., $BaCl_2$, were calculated at each of the ionic strengths and temperatures studied with the respective ${}^s\Theta$ and Ψ values in the appropriate Pitzer equation (*8*, *9*). These values are also listed in Table III.

The excess Gibbs free energies of mixing for $KCl-BaCl_2-H_2O$ system were calculated with the equation

$$\Delta_m G^E = Y_A[\ln(\gamma_A/\gamma_A^\circ) + (\Phi_A - \Phi_m)] + Y_B[\ln(\gamma_B/\gamma_B^\circ) + (\Phi_B - \Phi_m)] \quad (6)$$

where $Y_A = \nu_A y_A m_A RT$: $Y_B = \nu_B y_B m_B RT$, and the other symbols have their usual significance (*9*). These values are also listed in Table III. These excess Gibbs free energies were fitted to the Friedman equation (*14*)

$$\Delta_m G^E = I^2RTy(1 - y)[g_0 + (1 - 2y)g_1] \quad (7)$$

The Friedman parameters g_0 and g_1 were evaluated by a least-squares regression procedure, and the values are listed in Table II. As the ionic strength and also temperature are increasing, the $\Delta_m G^E$ values are changing in both magnitude and sign.

Acknowledgment

We express our deep sense of gratitude to Professor T. Navaneeth Rao, Vice-Chancellor, Osmania University, India, and Professor G. Atkinson, University of Oklahoma, Norman, OK, for constant encouragement and many helpful discussions.

Registry No. KCl, 7447-40-7; $BaCl_2$, 10361-37-2.

Literature Cited

(1) Christenson, P. G.; Gieskes, J. M. *J. Chem. Eng. Data* **1971**, *16*, 388.
(2) Robinson, R. A. Bower, V. E. *J. Res. Natl. Bur. Stand.* **1965**, *69A*, 439.
(3) Ives, D. J.; Janz, G. J. *Reference Electrodes*; Academic Press: New York, 1961; Chapter 4.
(4) Holmes, H. F.; Mesmer, R. E. *J. Phys. Chem.* **1983**, *87*, 1242.
(5) Kim, H. T.; Frederick, W. J., Jr. *J. Chem. Eng. Data* **1988**, *33*, 177.
(6) Silvester, L. F.; Pitzer, K. S. *J. Solution Chem.* **1978**, *7*, 326.
(7) Harned, H. S.; Owen, B. B. *The Physical Chemistry of Electrolyte Solutions*, 3rd ed.; Reinhold: New York, 1958, Chapter 14.
(8) Pitzer, K. S. *Pure Appl. Chem.* **1986**, *58*, 1599.
(9) Ananthaswamy, J.; Atkinson, G. *J. Solution Chem.* **1982**, *11*, 509.
(10) Ananthaswamy, J.; Atkinson, G. *J. Chem. Eng. Data* **1984**, *29*, 81.
(11) Pitzer, K. S. *J. Solution Chem.* **1975**, *4*, 249.
(12) Pitzer, K. S. *J. Phys. Chem.* **1983**, *87*, 2360.
(13) Pitzer, K. S.; Kim, J. J. *J. Am. Chem. Soc.* **1974**, *96*, 5701.
(14) Friedman, H. L. *Ionic Solution Theory*; Interscience: New York, 1962.

Received for review April 12, 1989. Accepted November 20, 1989.

Isobaric Vapor–Liquid Equilibria in the Systems Propyl Bromide–Methyl Ethyl Ketone, Methyl Ethyl Ketone–*p*-Xylene, and Vinyl Acetate–Methyl Methacrylate

Jaime Wisniak* and Abraham Tamir

Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel 84105

Vapor-liquid equilibria for the title systems have been determined at 760 mmHg. The two methyl ethyl ketone systems exhibit positive deviations from ideal behavior, no azeotropes are present, and the third system behaves ideally. An empirical equation was used to correlate the boiling points with the composition of the liquid phase.

The present work is part of our program for determining vapor–liquid equilibrium (VLE) data for organic systems in which one of the components is a bromide. The only literature reference is that of Chandrashekara and Seshadri (*1*) who measured the vapor–liquid equilibria of methyl ethyl ketone (MEK) and *p*-xylene at 685 mmHg. We claim that their data are not acceptable because they show that the activity coefficients of

Table I. Refractive Index n_D and Normal Boiling Points t_b of Pure Components

compound (supplier; GLC purity, mole %)	n_D(25 °C)	t_b/°C
propyl bromide	1.4320[a]	70.55[a]
(bromine compounds; 99.6)	1.4317[b]	71.00[b]
vinyl acetate	1.3932[a]	72.56[a]
(Fluka; 99.0)	1.3934[c]	72.49[c]
methyl ethyl ketone	1.3764[a]	79.56[a]
(Fluka; 99.6)	1.3764[b]	79.64[b]
methyl methacrylate	1.4118[a]	100.4[a]
(Fluka; 99.4)	1.4120[d]	100.3[c]
p-xylene	1.4935[a]	138.20[a]
(Merck; 99.3)	1.4933[b]	138.36[b]

[a] This work. [b] Reference 13. [c] Reference 14. [d] Reference 15.

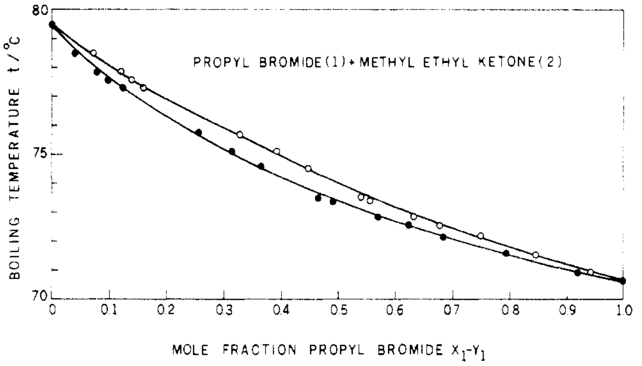

Figure 1. Boiling temperature vs mole fraction x_1 (liquid) and y_1 (vapor) for the system propyl bromide (1) + MEK (2).

p-xylene are larger than unity in part of the concentration range and smaller than unity in the rest; in addition they go through a minimum value, without a corresponding thermodynamic behavior of the activity coefficients of MEK. The absence of a maximum value in the activity coefficient of MEK can be hardly ascribed to the change in temperature. This kind of behavior reflects data that are inconsistent from a thermodynamic point of view.

Experimental Section

Materials. Properties of the components appear in Table I. The reagents were used without further purification after gas chromatography analysis failed to show any significant impurities (none higher than 0.2 mol %).

Apparatus and Procedure. An all-glass modified Dvorak–Boublik recirculation still (*2*) was used in the equilibrium determinations. The experimental details have been described in a previous publication (*3*). In order to avoid the polymerization of methyl methacrylate, up to 0.2 wt % of hydroquinone monomethyl ether was added to the original reagent. After equilibrium was attained, the vapor and liquid samples were withdrawn for analysis without disturbing the operation of the still. All analyses were carried out by gas chromatography on a Packard-Becker Model 417 chromatograph 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 SE30 for the systems MEK + *p*-xylene and MEK + propyl bromide and OV-17 for the system vinyl acetate + methyl methacrylate. Operating conditions were (in the order of the title systems) column, 130, 45, 80 °C; injector, 210, 90, 220 °C; and detector, 220, 180, 230 °C. Very good separation was achieved with helium as the gas carrier, and calibration analyses were carried to convert the peak area ratio to the composition of the sample. Concentration measurements were accurate to better than 0.008 mole concentration unit. The accuracy in the determination of pressure and temperature was at least $\Delta P = \pm 2$ mmHg and $\Delta T = \pm 0.02$ °C.

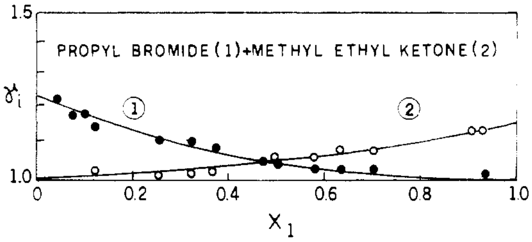

Figure 2. Activity coefficients for the system propyl bromide (1) + MEK (2).

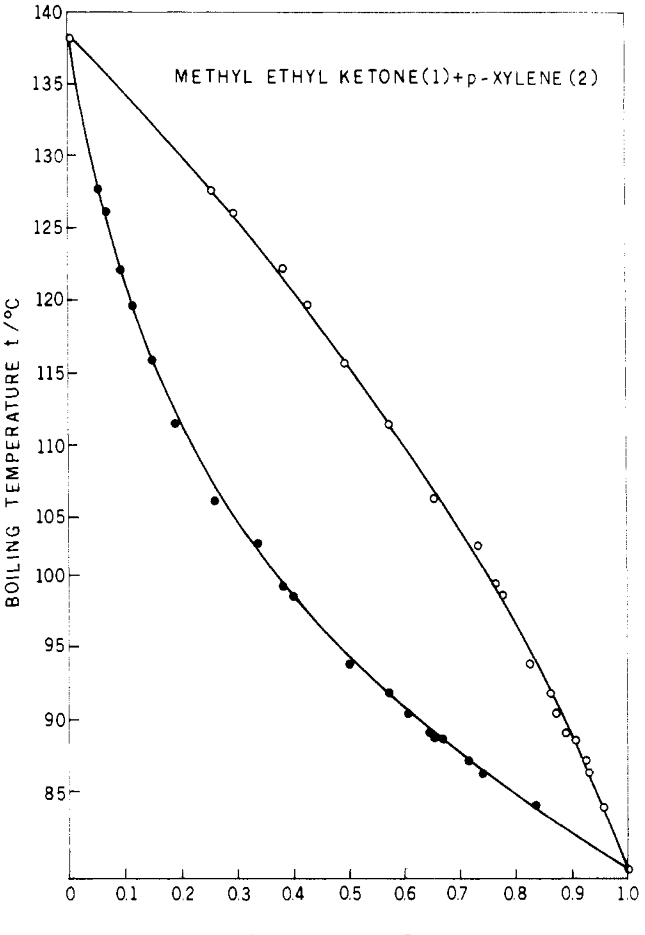

Figure 3. Boiling temperature vs mole fraction x_1 (liquid) and y_1 (vapor) for the system MEK (1) + *p*-xylene (2).

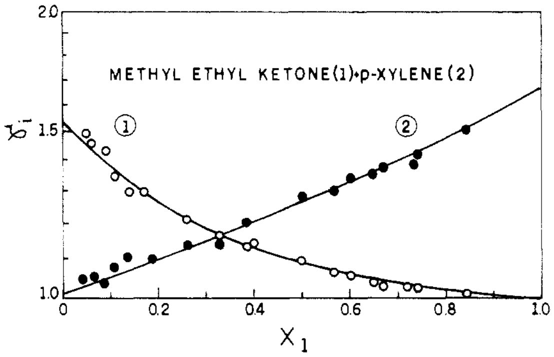

Figure 4. Activity coefficients for the system MEK (1) + *p*-xylene (2).

Results

The temperature–concentration measurements at 760 mmHg are reported in Table II and Figures 1, 3, and 5. The activity

Table II. Temperature t, Liquid Mole Fraction x_1, and Vapor Mole Fraction y_1 at 760 mmHg

propyl bromide (1) + methyl ethyl ketone (2)			methyl ethyl ketone (1) + p-xylene (2)			vinyl acetate (1) + methyl methacrylate (2)		
t/°C	x_1	y_1	t/°C	x_1	y_1	t/°C	x_1	y_1
78.50	0.042	0.073	127.67	0.049	0.249	99.04	0.039	0.086
77.93	0.083	0.120	126.12	0.060	0.287	97.68	0.067	0.145
77.56	0.098	0.140	122.22	0.088	0.381	96.64	0.098	0.205
77.30	0.120	0.165	119.70	0.110	0.420	95.54	0.127	0.258
75.81	0.256	0.331	115.90	0.139	0.489	95.50	0.124	0.257
75.12	0.315	0.392	106.18	0.258	0.660	94.12	0.165	0.325
74.54	0.369	0.447	102.16	0.335	0.728	93.60	0.183	0.348
73.50	0.466	0.532	99.19	0.385	0.762	92.86	0.205	0.385
73.40	0.494	0.555	98.63	0.394	0.772	90.11	0.283	0.493
72.88	0.577	0.634	93.91	0.502	0.828	88.48	0.335	0.548
72.55	0.629	0.676	91.76	0.571	0.861	87.90	0.354	0.567
72.20	0.700	0.740	90.43	0.604	0.874	86.22	0.412	0.627
71.60	0.810	0.830	89.02	0.650	0.893	85.46	0.447	0.663
70.90	0.924	0.934	88.74	0.672	0.900	82.80	0.535	0.739
			87.12	0.716	0.917	82.42	0.555	0.755
			86.30	0.739	0.924	81.67	0.582	0.775
			83.76	0.840	0.955	80.35	0.644	0.821
						80.35	0.647	0.823
						79.13	0.693	0.851
						78.38	0.725	0.869
						77.43	0.779	0.899
						76.50	0.808	0.916
						75.85	0.853	0.937
						74.77	0.907	0.961
						74.50	0.918	0.971
						74.08	0.946	0.979

Table III. Antoine Constants, Equation 1

compound	α_i	β_i	δ_i
propyl bromide[a]	6.910 65	1194.889	225.51
vinyl acetate[c]	6.992 27	1191.99	217.01
methyl ethyl ketone[a]	7.208 67	1368.21	236.50
methyl methacrylate[b]	7.109 00	1387.86	226.15
p-xylene	6.990 52	1453.43	215.307

[a] Reference 13. [b] Reference 4. [c] Reference 16.

coefficients (Figures 2 and 4) were calculated as in a previous publication (*4*). The molar virial coefficients were estimated by the method of Tsonopoulos (*5*, *6*) with the parameters suggested by the author. The virial terms contributed less than 2% to the activity coefficient, and their influence was important only at very dilute concentrations.

Vapor pressures of the pure components, $P°_1$, were calculated according to Antoine's equation:

$$\log (P°_i/\text{mmHg}) = \alpha_i - \beta_i/((t/°\text{C}) + \delta_i) \qquad (1)$$

where the constants appear in Table III.

The calculated activity coefficients for the binary propyl bromide + MEK are thermodynamically consistent by the area and Herington (*7*) tests and exhibit positive deviations from Raoult's law. The binary system MEK + p-xylene shows positive deviations from Raoult's law but clearly does not satisfy the area consistency test. One possibility for the inconsistency is the presence of a heat of mixing effect large enough to explain the difference in areas, in which case we can apply the Herington (*7*) consistency test. The quantities D and J defined in ref 7 are, respectively, 28.8 and 24.9; hence, the data may be considered thermodynamically consistent.

The system vinyl acetate + methyl methacrylate appears to be practically ideal.

Activity coefficients of the first two binaries were correlated by the Redlich-Kister expansion (*8*):

$$\log (\gamma_1/\gamma_2) = B(x_2 - x_1) + C(6x_1x_2 - 1) + D(x_2 - x_1)(1 - 8x_1x_2) + E(x_2 - x_1)^2(2x_1x_2 - 1) \qquad (2)$$

The pertinent parameters and coefficients of determination R^2 (*9*) appear in Table IV.

Table IV. Redlich-Kister Constants, Equation 2

system	B	C	D	E	R^2
propyl bromide (1) + methyl ethyl ketone (2)	0.078				0.961
methyl ethyl ketone (1) + p-xylene (2)	0.199	-0.138	0.044	0.218	0.990

Table V. Wilson Constants, Equations 3 and 4

system	A_{12}	A_{21}	Δy_1[a]	Δy_2[a]
propyl bromide (1) + MEK (2)	0.7504	1.0644	0.005	0.003
MEK (1) + p-xylene (2)	0.4437	0.9721	0.095	0.022

[a] $\Delta y_i = \sum|y_{i,\text{calc}} - y_{\text{exptl}}|/n$.

Table VI. Boiling Point Constants, C_i, Equation 5, and Root Mean Square Deviation, rmsd

system	C_0	C_1	C_2	C_3	rmsd/ °C
propyl bromide (1) + methyl ethyl ketone (2)	-6.69	-4.10			0.19
methyl ethyl ketone (1) + p-xylene (2)	-57.97	37.49	-34.48	36.87	0.28
vinyl acetate (1) + methyl methacrylate (2)	-9.19	2.62			0.18

The binary data were also correlated with use of the Wilson model (*10*)

$$\ln \gamma_1 = -\ln (x_1 + A_{12}x_2) + x_2\left[\frac{A_{12}}{x_1 + A_{12}x_2} - \frac{A_{21}}{A_{21}x_1 + x_2}\right] \qquad (3)$$

$$\ln \gamma_2 = -\ln (x_2 + A_{21}x_1) - x_1\left[\frac{A_{12}}{x_1 + A_{12}x_2} - \frac{A_{21}}{A_{21}x_1 + x_2}\right] \qquad (4)$$

The constants A_{12} and A_{21} were determined by the all-points-one-point (APOP) simplified method proposed by Apelblat and Wisniak (*11*) and are reported in Table V together with the mean deviation errors for the composition of the vapor phase y_1 and y_2.

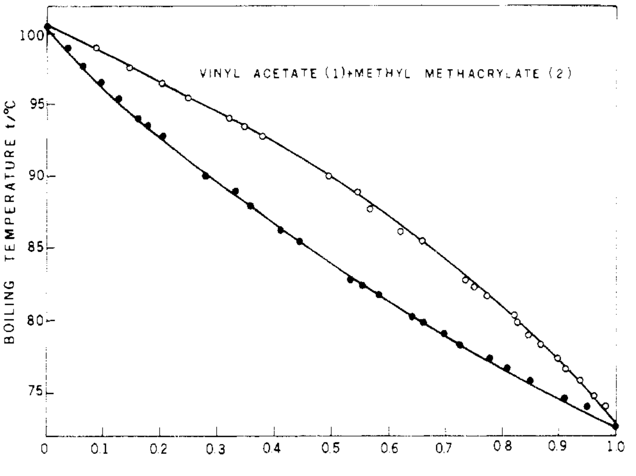

Figure 5. Boiling temperature vs mole fraction x_1 (liquid) and y_1 (vapor) for the system vinyl acetate (1) + methyl methacrylate (2).

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

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

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 $\{\sum(T_{\mathrm{expt}} - T_{\mathrm{calc}})^2/n\}^{0.5}$
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.

Literature Cited

(1) Chandrashekara, M. N.; Seshadri, D. N. *J. Chem. Eng. Data* **1979**, *24*, 6.
(2) Boublikova, L.; Lu, B. C.-Y. *J. Appl. Chem.* **1969**, *19*, 89.
(3) Wisniak, J.; Tamir, A. *J. Chem. Eng. Data* **1975**, *20*, 168.
(4) Wisniak, J.; Tamir, A. *J. Chem. Eng. Data* **1989**, *34*, 14.
(5) Tsonopoulos, C. *AIChE J.* **1974**, *20*, 263.
(6) Tsonopoulos, C. *AIChE J.* **1975**, *21*, 827.
(7) Herington, E. F. G. *J. Inst. Pet.* **1951**, *30*, 457.
(8) Redlich, O.; Kister, A. T. *Ind. Eng. Chem.* **1948**, *40*, 345.
(9) Montgomery, D. C.; Peck, E. A. *Introduction to Linear Regression Analysis*; Wiley: New York, 1985.
(10) Wilson, G. H. *J. Am. Chem. Soc.* **1964**, *86*, 127.
(11) Apelblat, A.; Wisniak, J. *Ind. Eng. Chem. Res.* **1989**, *28*, 324.
(12) Wisniak, J.; Tamir, A. *Chem. Eng. Sci.* **1975**, *30*, 335.
(13) TRC—Thermodynamic Tables—Hydrocarbons, Thermodynamics Research Center, The Texas A&M University System: College Station, TX, 1985; p a-3290, *p*-xylene (loose-leaf data sheets). TRC—Thermodynamic Tables—Nonhydrocarbons; Thermodynamic Research Center, The Texas A&M University System: College Station, TX, 1958, p a-7460 and 1956, p k-7430, propyl bromide; 1965, p 5370 and 1981, p k-5920, MEK (loose-leaf data sheets).
(14) Daubert, T. E.; Danner, R. P. *Data Compilation Tables of Properties of Pure Compounds*; Design Institute for Physical Properties, AIChE: New York, 1985.
(15) Perry, R. H. *Perry's Chemical Engineer's Handbook*, 6th ed.; McGraw-Hill: New York, 1984; p 3-58.
(16) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Physical Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill: New York, 1977.

Received for review April 13, 1989. Revised October 2, 1989. Accepted November 13, 1989.

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

Jaime Wisniak* and Abraham Tamir

Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel 84105

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] 1.3934[c]	72.56[a] 72.49[c]	99
2	propyl bromide	1.4320[a] 1.4317[b]	70.55[a] 70.80[b]	99.4
3	methyl methacrylate	1.4118[a] 1.4120[d]	100.4[a] 100.3[c]	99.4

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