Vapor–Liquid Equilibria at 760 mmHg in the Systems Acetonitrile–Methyl Methacrylate, Acetonitrile–Vinyl Acetate, and Methyl Acetate–Vinyl Acetate

Jaime Wisniak* and Abraham Tamir

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

Vapor–liquid equilibria for the title systems have been determined at 760 mmHg. The systems acetonitrile–methyl methacrylate and acetonitrile–vinyl acetate exhibit positive deviations from ideal solution behavior and a minimum boiling point azeotrope. The system methyl acetate–vinyl acetate shows ideal behavior. Activity coefficients and boiling points were well correlated with the composition of the liquid phase.

The data reported here are not available in the literature and were determined as part of a project on UNIFAC parameters.

Experimental Section

Purity of Materials. Acetonitrile (99.5%+) was purchased from H.P.L.C. Bio-Lab, methyl acetate (99.2+%) was purchased from Merck, and methyl methacrylate, analytical grade (99.4+%), and vinyl acetate, analytical grade (99%+), were purchased from Fluka. The reagents were used without further purification after gas chromatographic 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. A vacuum system controlled by a Cartesian manostat connected the vapor condenser with a Swietoslawski ebulliometer and allowed total pressure regulation. The total pressure of the system was determined from the boiling point temperature of the distilled water in the ebulliometer. Temperatures were measured with a Hewlett-Packard quartz thermometer, Model 2801A. The experimental details have been described in a previous publication (*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 apparatus provided with a 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 operating conditions for the various systems are reported in Table II. 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%. The accuracy in determination of pressure and temperature was $\Delta P = \pm 2$ mmHg and $\Delta T = \pm 0.01$ °C.

All solvents used in this work should be handled with proper care since they are flammable, form explosive mixtures, and can be toxic.

Results

The temperature–concentration measurements at 760 mmHg are reported in Tables III–V and Figures 1, 3, and 5. The activity coefficients (Figures 2 and 4) were calculated from the equations

$$\ln \gamma_1 = \ln (Py_1/P^\circ_1/P^\circ_1x_1) + (B_{11} - v^L_1)(P - P^\circ_1)/RT + P(1 - y_1)^2\delta_{12}/RT \quad (1)$$

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

Table I. Physical Properties of Pure Components

compound	refract. index (25 °C)	normal bp, °C
acetonitrile	1.3410[a]	81.1[a]
	1.3416[b]	81.3[b]
methyl methacrylate	1.4118[a]	100.4[a]
	1.4120[c]	100.3[d]
vinyl acetate	1.3932[a]	72.56[a]
	1.3934[d]	72.53[b]
methyl acetate	1.3588[a]	56.94[a]
	1.3589[b]	56.94[b]

[a] This work. [b] Reference *10*. [c] Reference *11*. [d] Reference *12*.

Table II. Gas Chromatography Conditions

system	column	temperature, °C		
		column	injector	detector
acetonitrile–methyl methacrylate	20% OV-17	110	220	210
acetonitrile–vinyl acetate	SE30	55	90	190
vinyl acetate–methyl acetate	20% OV-17	60	90	190

Table III. Experimental Vapor–Liquid Equilibria Data for Acetonitrile (1)–Methyl Methacrylate (2) at 760 mmHg

temp, °C	x_1	y_1	γ_1	γ_2
97.62	0.045	0.125	1.6933	1.0476
97.06	0.054	0.145	1.6632	1.0512
96.20	0.070	0.180	1.6324	1.0528
95.48	0.083	0.205	1.6007	1.0584
94.30	0.115	0.260	1.5161	1.0587
93.14	0.150	0.310	1.4334	1.0657
91.50	0.190	0.370	1.4174	1.0751
89.80	0.250	0.420	1.2861	1.1283
89.73	0.265	0.435	1.2593	1.1241
88.87	0.300	0.470	1.2332	1.1381
87.11	0.380	0.550	1.2015	1.1549
85.65	0.460	0.605	1.1416	1.2207
84.61	0.545	0.670	1.1018	1.2525
83.47	0.640	0.735	1.0662	1.3202
83.36	0.650	0.745	1.0678	1.3115
82.34	0.770	0.815	1.0180	1.4981
82.03	0.810	0.850	1.0191	1.4858
81.88	0.855	0.875	0.9986	1.6306
81.72	0.890	0.905	0.9972	1.6423
81.29	0.980	0.975	0.9890	2.4118
81.27	0.985	0.980	0.9896	2.5743
81.28	0.988	0.981	0.9873	3.0560
81.30	0.995	0.990	0.9875	3.8523

For all systems the last two 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°_i, were calculated according to Antoine's equation:

$$\log P^0_i = \alpha_i - \beta_i/(t + \delta_i) \quad (3)$$

where the constants appear in Table VI. The virial coefficients B_{11}, B_{22}, and B_{12} were estimated by the method of Tsono-

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Table IV. Experimental Vapor–Liquid Equilibria Data for Acetonitrile (1)–Vinyl Acetate (2) at 760 mmHg

temp, °C	x_1	y_1	γ_1	γ_2
72.36	0.059	0.070	1.5357	0.9901
72.18	0.080	0.088	1.4300	0.9988
72.18	0.108	0.116	1.3947	0.9986
72.11	0.122	0.130	1.3856	1.0001
72.08	0.169	0.174	1.3377	1.0005
72.10	0.193	0.192	1.2910	1.0112
72.15	0.275	0.257	1.2083	1.0349
72.34	0.372	0.327	1.1280	1.0767
72.47	0.407	0.354	1.1111	1.0905
72.80	0.456	0.394	1.0925	1.1044
73.16	0.521	0.444	1.0654	1.1390
73.30	0.542	0.462	1.0610	1.1481
73.78	0.593	0.494	1.0225	1.1979
74.10	0.630	0.538	1.0379	1.1924
74.61	0.681	0.584	1.0268	1.2271
74.84	0.695	0.590	1.0010	1.2562
74.96	0.710	0.603	1.0068	1.2750
75.95	0.781	0.678	1.0004	1.3309
76.40	0.810	0.701	0.9989	1.4059
76.63	0.819	0.707	0.9999	1.4363
77.24	0.857	0.766	0.9993	1.4276
77.88	0.878	0.793	0.9986	1.4529
78.94	0.930	0.872	1.0009	1.5203
80.20	0.965	0.931	0.9993	1.5813

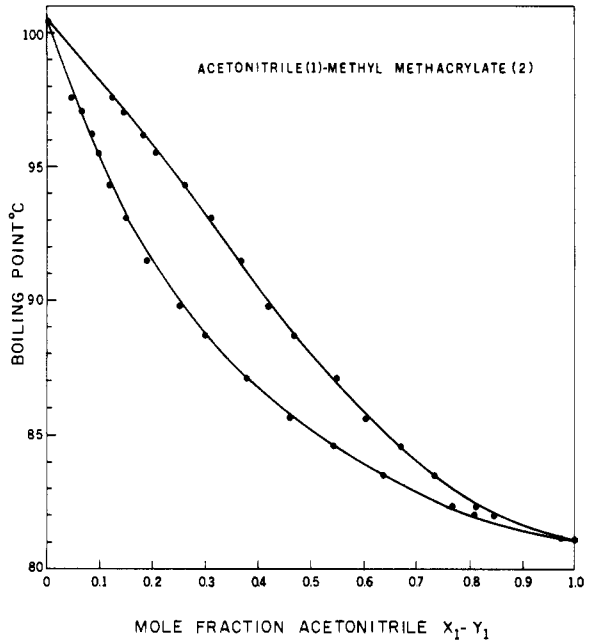

Figure 1. Boiling point diagram for the system acetonitrile (1)–methyl methacrylate (2).

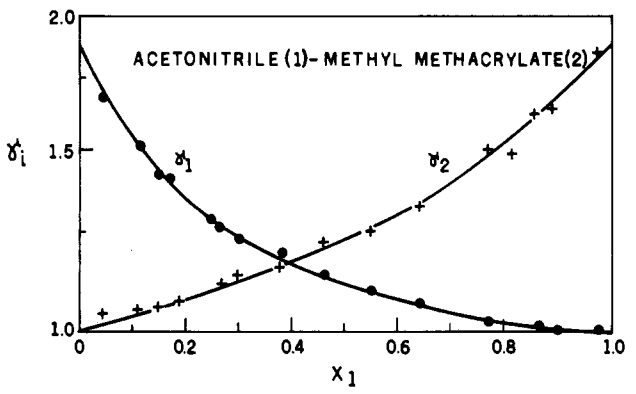

Figure 2. Activity coefficients for the system acetonitrile (1)–methyl methacrylate (2).

Table V. Experimental Vapor–Liquid Equilibria Data for Methyl Acetate (1)–Vinyl Acetate (2) at 760 mmHg

temp, °C	x_1	y_1	γ_1	γ_2
71.28	0.074	0.117	1.005	0.9991
71.03	0.088	0.137	0.9971	0.9983
69.78	0.158	0.224	1.000	1.001
69.14	0.196	0.282	0.9976	0.9904
68.35	0.247	0.343	0.9965	1.002
67.36	0.301	0.412	1.000	0.9988
66.72	0.338	0.451	0.9974	0.9945
66.33	0.353	0.480	1.005	0.9976
65.78	0.396	0.518	0.9984	0.9987
64.83	0.456	0.580	1.000	1.000
64.03	0.506	0.631	1.000	1.000
62.55	0.603	0.723	0.9998	0.9961
61.41	0.682	0.786	1.000	0.9962
60.54	0.743	0.834	0.9970	0.9952
59.88	0.781	0.861	1.001	1.002
58.92	0.861	0.917	0.9973	0.9930
58.48	0.892	0.935	1.000	0.9952
58.42	0.917	0.950	0.9986	1.000

Table VI. Antoine Constants

	α_i	β_i	δ_i
acetonitrile[a]	7.073 52	1279.20	224.00
methyl methacrylate[b]	7.109 0	1387.86	226.15
vinyl acetate[a]	6.992 20	1191.99	217.51
methyl acetate[a]	7.061 31	1156.43	219.69

[a] Reference *10*. [b] Reference *13*.

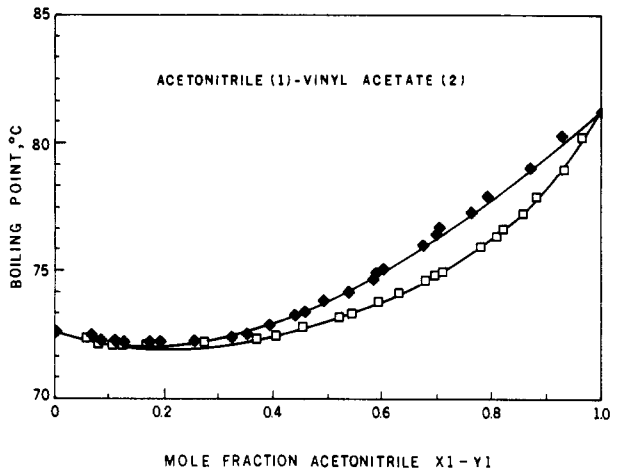

Figure 3. Boiling point diagram for the system acetonitrile (1)–vinyl acetate (2).

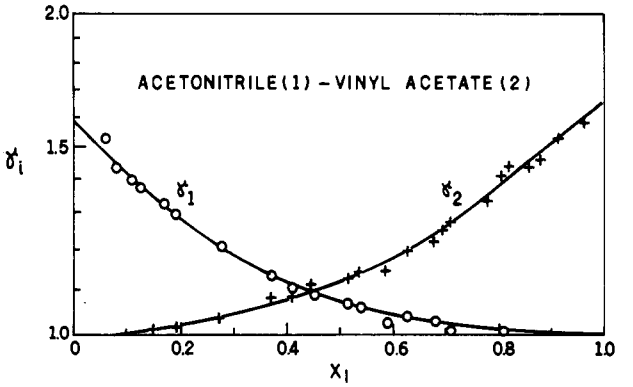

Figure 4. Activity coefficients for the system acetonitrile (1)–vinyl acetate (2).

poulos (*3*, *4*) using the molar parameters suggested by the author.

The activity coefficients reported in Tables III and IV for the binaries acetonitrile–methyl methacrylate and acetonitrile–vinyl

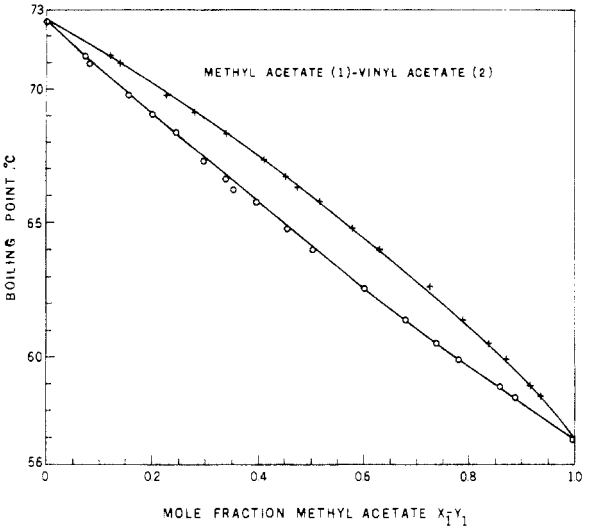

Figure 5. Boiling point diagram for the system methyl acetate (1)–vinyl acetate (2).

Table VII. Redlich–Kister Constants, Eq 4

system	B	C	D	E	R^2
acetonitrile (1)–methyl methacrylate (2)	0.250	−0.068	0.129	0.183	0.979
acetonitrile (1)–vinyl acetate (2)	0.206	−0.013	0	0	0.978

acetate are thermodynamically consistent by the area and Herington (*5*) tests and exhibit positive deviations from Raoult's law. The acetonitrile–methyl methacrylate system has a minimum boiling point azeotrope containing close to 100 mol% methyl methacrylate; no effort was made to determine its exact composition because the experimental error is about the difference of composition against the pure component. The binary acetonitrile–vinyl acetate has a minimum boiling point azeotrope that boils at 72.1 °C and contains 19.2 mol % acetonitrile. The binary system methyl acetate–vinyl acetate behaves like an ideal solution.

Activity coefficients of the binaries of acetonitrile were correlated by the Redlich–Kister expansion (*6*):

$$\log \gamma_1/\gamma_2 = B(x_2 - x_1) + C(6x_1x_2 - 1) + D(x_2 - x_1)(1 - 8x_1x_2) + E(x_2 - x_1)^2(2x_1x_2 - 1) \quad (4)$$

The pertinent parameters and coefficients of determination R^2 appear in Table VII.

The activity coefficients of the acetonitrile binaries were also correlated by the Wilson equations (*7*):

$$\ln \gamma_1 = -\ln (x_1 + A_{12}x_2) + x_2\left[\frac{A_{12}}{x_1 + A_{12}x_2} - \frac{A_{21}}{A_{21}x_1 + x_2}\right] \quad (5)$$

$$\ln \gamma_2 = -\ln (x_2 + A_{21}x_1) - x_1\left[\frac{A_{12}}{x_1 + A_{12}x_2} - \frac{A_{21}}{A_{21}x_1 + x_2}\right] \quad (6)$$

The constants A_{12} and A_{21} were determined by using the simplified method suggested by Apelblat and Wisniak (*8*) and appear in Table VIII.

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

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

Table VIII. Wilson Constants, Eq 4 and 5

	A_{12}	A_{21}	$\%\Delta y_1$[a]	$\%\Delta y_2$[a]
acetonitrile–methyl methacrylate	0.48805	0.96000	1.8	1.6
acetonitrile–vinyl acetate	0.85748	0.78171	0.5	1.1

[a] $\%\Delta y_i = 100\sum|y_{i,exp} - y_{i,calc}|/n$.

Table IX. Boiling Point Constants, Eq 7

system	C_0	C_1	C_2	rmsd
acetonitrile (1)–methyl methacrylate (2)	−22.427	12.257	−6.3995	0.15
acetonitrile (1)–vinyl acetate (2)	−15.236	−4.5423	−3.2858	0.09
methyl acetate (1)–vinyl acetate (2)	−2.6480	0.28966	1.7775	0.09

An optimization technique yielded the values for the constants reported in Table IX.

Acknowledgment

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

Glossary

α, β, δ	constants
A_{ij}	Wilson constants, eq 5 and 6
B_{ii}, B_{ij}	virial coefficients
B, C, D, E	Redlich–Kister constants, eq 4
C_i	constants in eq 7
n	number of experimental points
P	total pressure, mmHg
P°_i	vapor pressure of pure component, mmHg
R	gas constant, 82.06 cm^3/(mol·K)
rmsd	root mean square deviation $[\sum(T_{exp} - T_{calc})^2/n]^{0.5}$
t, T	temperature, °C, K
T_i	boiling point of pure component, K
v^L_i	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

calc	calculated
exp	experimental
i, j	component i, j

Registry No. Acetonitrile, 75-05-8; methyl methacrylate, 80-62-6; vinyl acetate, 108-05-4; methyl acetate, 79-20-9.

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