By introducing the following dimensionless variables

$$Y = C/C_0 \qquad X = r/r_0 \qquad \tau = tr_0^2/D$$

and considering eq 4, eq I becomes

$$\frac{\partial Y(X,\tau)}{\partial \tau} = \frac{1}{X^2}\left[2Xf(Y)\,\frac{\partial Y(X,\tau)}{\partial X} + X^2 f'(Y)\left[\frac{\partial Y(X,\tau)}{\partial X}\right]^2 + X^2 f(Y)\,\frac{\partial^2 Y}{\partial X^2}\right]$$

The function $Y(X,\tau)$ is then substituted by $\tilde{Y}(X,\tau)$ defined by a Lagrange interpolation formula

$$\tilde{Y}(X_k,\tau) = \sum_{I=1}^{N+2} l_I(X_k)Y_I(\tau)$$

where the Lagrangian coefficient functions are polinomials of n grade such as

$$l_I(X_k) = \prod_{\substack{I=1 \\ I \neq k}}^{N+2} \frac{X - X_I}{K_k - X_I}$$

$-Y_I(\tau)$ are the values of $Y(X,\tau)$ at the $N + 2$ collocation points: N points are evaluted as zeros of the Jacobi polynomial with $\alpha = 1$ and $\beta = 1$; $N = 10$ proved to be adequate to obtain sufficient accuracy. The extreme points can be evaluated from the boundary conditions (II, III):

$$Y(0,\tau) = \frac{-l_{N+2}(0) + \sum_{I=2}^{N+1} l'_I(0)\,\tilde{Y}(\tau)}{l'_I(0)}, \quad Y(1,\tau) = 1$$

In this way the examined system is transformed into a system of ordinary differential equations, which with the further condition (IV)

$$Y(X,0) = 0$$

was solved by numerical integration using a Gear method implemented in a routine of the IMSL collection.

Registry No. Propane, 74-98-6; propene, 115-07-1; butane, 106-97-8; *trans*-2-butene, 624-64-6; 1-butene, 106-98-9; *cis*-2-butene, 590-18-1.

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Vapor–Liquid Equilibria in the Systems Methyl Acetate–Methyl Methacrylate and Methyl Acetate–Propyl Bromide–Methyl Methacrylate

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

The present work was undertaken to measure VLE data for the title systems for which no isobaric data are available. Data for the two other binaries have already been measured (*1*, *2*).

Experimental Section

Purity of Materials. Methyl acetate, analytical grade (99.5%+), and propyl bromide (99.4%) were purchased from Merck; methyl methacrylate (99.4%+) was purchased from Fluka. The reagents were used without further purification after gas chromatography failed to show any significant impurities. Properties of the pure components appear in Table I.

Table I. Physical Constants of Pure Components

index	compound	refractive index (25 °C)	bp(760 mmHg), °C	purity, GLC (min) %
1	methyl acetate	1.3588[a] 1.3589[b]	56.9[a] 56.94[b]	99.5
2	propyl bromide	1.4320[a] 1.4317[b]	70.55[a] 71.00[b]	99.4
3	methyl methacrylate	1.4118[a] 1.4120[c]	100.4[a] 100.3[c]	99.4

[a] Measured value. [b] Reference 11. [c] Reference 12.

Apparatus and Procedure. An all-glass modified Dvorak and Boublik recirculation still (*3*) was used in the equilibrium determination. The experimental features have been described

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

temp, °C	x_1	y_1	temp, °C	x_1	y_1
98.30	0.025	0.084	71.85	0.487	0.789
96.96	0.039	0.125	70.09	0.540	0.826
93.95	0.078	0.229	69.34	0.555	0.835
91.08	0.120	0.333	67.82	0.605	0.862
87.55	0.175	0.443	66.96	0.635	0.876
82.89	0.251	0.557	64.43	0.707	0.908
81.51	0.276	0.588	63.33	0.750	0.927
77.98	0.345	0.668	61.95	0.801	0.945
74.70	0.415	0.736	60.85	0.838	0.957
73.09	0.454	0.774	58.68	0.927	0.982

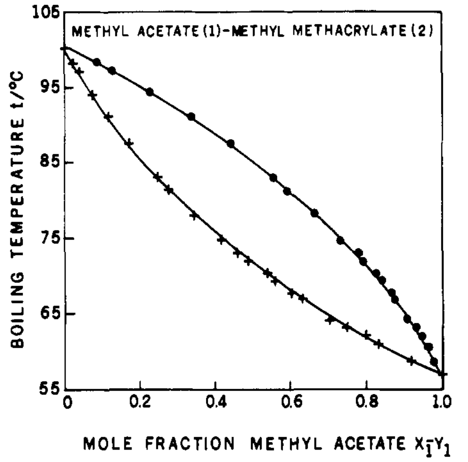

Figure 1. Boiling temperature vs mole fraction x_1 (liquid) and y_1 (vapor) for the system methyl acetate (1) + methyl methacrylate (2).

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 in length and 0.2 cm in diameter, filled with 20% OV-17, and operated at 65 °C (85 °C for the binary). 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 out to convert the peak ratio to the weight composition of the sample. Concentration measurements were accurate to better than 0.008 mole fraction unit. The accuracy in determination of pressure and temperature was at least $\Delta P = \pm 1$ mmHg and $\Delta t = \pm 0.02$ °C.

Results

The temperature–concentration measurements at 760 mmHg for the two systems are reported in Tables II and III and Figure 1, together with the activity coefficients that were calculated from the following equation (*5*):

$$\ln \gamma_1 = \ln (P y_1 / P^\circ_1 x_1) + (B_{11} - v_1^L)(P - P^\circ_1)/RT + (P/2RT) \sum_1^n \sum_1^n y_j y_k (2\delta_{ji} - \delta_{jk}) \quad (1)$$

where

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

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

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

where the constants are reported in Table IV. The molar virial coefficients B_{11}, B_{12}, and B_{22} were estimated 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. Experimental Vapor–Liquid Equilibria Data for Methyl Acetate (1)–Propyl Bromide (2)–Methyl Methacrylate (3) at 760 mmHg

temp, °C	x_1	x_2	y_1	y_2
58.28	0.760	0.142	0.840	0.133
58.53	0.840	0.100	0.891	0.093
59.34	0.720	0.201	0.800	0.177
59.90	0.707	0.178	0.801	0.168
60.62	0.651	0.212	0.760	0.200
60.78	0.688	0.172	0.795	0.164
61.10	0.606	0.264	0.712	0.251
61.27	0.521	0.366	0.654	0.316
62.16	0.712	0.080	0.858	0.079
63.52	0.460	0.381	0.606	0.348
63.55	0.411	0.450	0.553	0.404
63.69	0.640	0.100	0.809	0.107
64.45	0.530	0.217	0.700	0.221
64.60	0.455	0.315	0.618	0.304
64.74	0.308	0.588	0.438	0.527
65.17	0.435	0.317	0.610	0.309
65.75	0.386	0.366	0.548	0.359
65.84	0.540	0.124	0.743	0.128
65.93	0.240	0.675	0.369	0.601
65.93	0.596	0.062	0.808	0.071
66.10	0.211	0.715	0.328	0.645
66.50	0.450	0.242	0.638	0.254
66.62	0.303	0.492	0.460	0.468
66.70	0.172	0.768	0.284	0.695
66.78	0.175	0.760	0.289	0.688
66.94	0.400	0.281	0.594	0.297
66.99	0.353	0.381	0.510	0.389
67.12	0.292	0.491	0.444	0.474
67.18	0.351	0.367	0.510	0.384
67.63	0.123	0.831	0.230	0.750
68.32	0.104	0.857	0.190	0.794
68.36	0.350	0.324	0.540	0.339
68.72	0.327	0.357	0.490	0.386
68.85	0.527	0.051	0.752	0.065
69.93	0.105	0.757	0.194	0.750
70.00	0.148	0.657	0.265	0.658
70.16	0.321	0.289	0.513	0.336
70.26	0.129	0.704	0.231	0.700
70.47	0.329	0.270	0.530	0.325
70.71	0.231	0.442	0.389	0.480
70.92	0.216	0.454	0.375	0.489
70.94	0.057	0.834	0.116	0.838
71.10	0.423	0.085	0.690	0.109
71.11	0.202	0.470	0.352	0.510
71.56	0.257	0.344	0.439	0.392
71.71	0.084	0.730	0.167	0.751
72.28	0.365	0.127	0.620	0.169
72.84	0.311	0.199	0.540	0.254
74.63	0.166	0.423	0.296	0.519
75.00	0.068	0.617	0.151	0.706
75.19	0.148	0.427	0.286	0.512
75.66	0.301	0.104	0.570	0.149
75.95	0.219	0.274	0.409	0.350
76.59	0.227	0.162	0.493	0.219
78.18	0.188	0.212	0.388	0.312
78.80	0.052	0.478	0.126	0.644
79.48	0.201	0.186	0.404	0.266
79.72	0.265	0.034	0.554	0.052
80.18	0.235	0.075	0.488	0.124
80.45	0.123	0.255	0.289	0.383
80.75	0.187	0.121	0.423	0.190
86.60	0.114	0.081	0.302	0.144
86.87	0.060	0.195	0.165	0.347
88.35	0.012	0.249	0.036	0.458
89.25	0.067	0.108	0.196	0.210
89.80	0.086	0.062	0.246	0.122
95.41	0.027	0.045	0.092	0.102
96.06	0.024	0.040	0.077	0.091

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

Table IV. Vapor Pressure Constants

compound	α_i	β_i	δ_i
methyl acetate[a]	7.061 31	1156.43	219.69
propyl bromide[a]	6.910 65	1194.889	225.51
methyl methacrylate[b]	8.810 0	1191.818	202.921

[a] Reference 11. [b] References 1 and 14.

Table V. Redlich-Kister Correlation of Binary and Ternary Data

system[a]	B_{ij}	C_{ij}	D_{ij}
methyl acetate (1)-propyl bromide (2)*	0	0	0
methyl acetate (1)-methyl methacrylate (3)*	0	0	0
propyl bromide (2)-methyl methacrylate (3)*	0	0	0

		overall rmsd[b]	
system	C_1	γ_{ij}	y_{ij}
methyl acetate (1)-propyl bromide (2)- methyl methacrylate (3)	0 0.4396	0.11 0.12	0.024 0.028

[a] Systems marked with an asterisk are ideal. [b] Weighted average.

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

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

where B_{ij}, C_{ij}, and D_{ij} are constants for the pertinent binary 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 coefficient was obtained by a Simplex optimization technique. The differences between the values of the root mean square deviation for the weighted activity coefficient and vapor composition for the two cases—with and without the ternary constant C_1– given in Table V are statistically not significant, suggesting that ternary data can be predicted directly from the binary systems, in accordance with the fact that the three binaries exhibit ideal behavior.

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

$$
\begin{aligned}
t = {} & \sum_{i=1}^{n} x_i t^\circ_i + \sum_{i,j=1}^{l} [x_i x_j \sum_{k=0}^{1} C_k (x_i - x_j)^k] + \\
& x_1x_2x_3[A + B(x_1 - x_2) + C(x_1 - x_3) + D(x_2 - x_3) + ...] \qquad (5)
\end{aligned}
$$

In these equations t°_i is the boiling point of the pure component in °C and l 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. An equation of the same structure can be used for the direct correlation of ternary data, without use of binary data. Both forms will require about the same number of constants for similar accuracy, but the direct correlation allows an easier calculation of boiling isotherms (Figure 2). The various constants of eq 5 are reported in Table VI, which also contains information indicating the degree of goodness of the correlation.

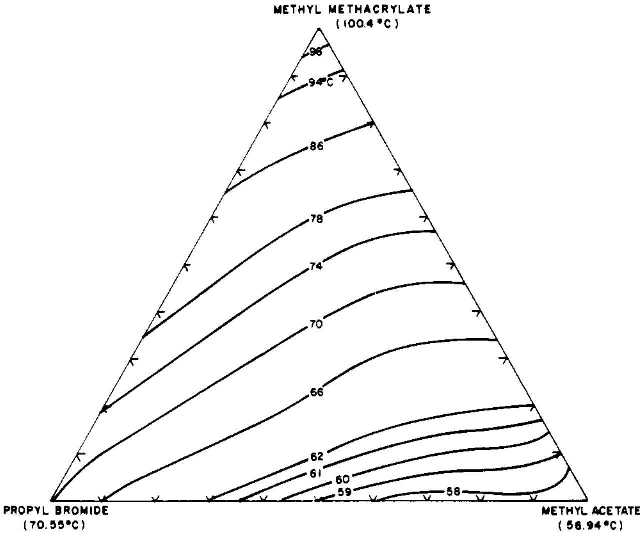

Figure 2. Isothermals for the ternary system (760 mmHg).

Table VI. Correlation of Boiling Points, Equation 5

system	C_0	C_1	rmsd
methyl acetate (1)-propyl bromide (2)	-19.555	5.4178	0.15
methyl acetate (1)-methyl methacrylate (3)	-29.331	11.566	0.13
propyl bromide (2)-methyl methacrylate (3)	-13.967	6.8844	0.13

system	A	B	rmsd
methyl acetate (1)-propyl bromide (2)-methyl methacrylate (3)	-10.833	-33.529	0.54

Acknowledgment

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

Nomenclature

α, β, δ	Antoine constants, eq 3
B_{ii}, B_{ij}	virial coefficients, eqs 1 and 2
B_{ij}, C_{ij}, D_{ij}	Redlich-Kister constants, eq 4
n	number of components (2 or 3) or number of measurements
P	total pressure, mmHg
P°_i	vapor pressure of pure component i, mmHg
R	gas constant, 62 363.3 $cm^3 \cdot mmHg \cdot g\text{-}mol^{-1} \cdot K^{-1}$
rmsd	root mean square deviation, $[\sum(T_{expt} - T_{calc})^2/n]^{0.5}$
t, T	boiling temperature of a mixture, °C, K
t°_i	boiling temperature of pure component i, °C
v_i^L	molar volume of liquid component i, $mL \cdot g\text{-}mol^{-1}$
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

Subscripts

expt	experimental value
calc	calculated value

Registry No. Methyl acetate, 79-20-9; methyl methacrylate, 80-62-6; propyl bromide, 106-94-5.

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Determination of Equilibrium Constants of a Trialkyl Borate Used in the Development of Brake Fluid Manufacturing

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For each of the three stages in the hydrolysis of tris(3,6,9-trioxadecyl) borate, the equilibrium constant is determined through aquametric analysis. It is shown that the amount of water in the equilibrium can be determined from the boiling points of mixtures made of known amounts of 3,6,9-trioxadecan-1-ol, water, and the borate ester. The equilibrium constants are then employed to calculate the composition ranges (characterized by the Karl Fischer water content and boron content) of automobile brake fluids based upon the borate ester, which obey the quality criteria set by the U. S. Department of Transportation (DOT criteria). They are also used to calculate the optimal temperature gradient in the reactor of the first industrial plant in operation producing tris(3,6,9-trioxadecyl) borate in a continuous process.

Introduction

Tris(3,6,9-trioxadecyl) borate (TMB; see nomenclature section for abbreviations), synthesized by esterification of boric acid and 3,6,9-trioxadecan-1-ol (TME) is the chief ingredient in a new type of long-life automobile brake fluid, which contributes to an increase in road safety. It does so because its hydrolysis fights water that inevitably penetrates from the atmosphere into brake systems. Brakes may not hold when water is present in the system. The specification of a brake fluid based on this principle requires the translation of the quality criteria set by the U. S. Department of Transportation (DOT criteria) into composition ranges to be expressed as the Karl Fischer water content and boron content. To do this efficiently, the equilibrium constants of the esterification/hydrolysis of TMB were determined. They also served to calculate the optimal temperature gradient in the reactor of the first industrial plant producing TMB in a continuous process, now on stream at Proviron Industries. The determination of the equilibrium constants is based on measurements of vapor pressures and boiling points. As such, it is experimentally simple and applicable to equilibria of other multistage processes in which one component is much more volatile than the others.

Hydrolysis of TMB includes the following fast equilibria

$$\mathrm{TMB} + \mathrm{H_2O} \rightleftharpoons \mathrm{DMB} + \mathrm{TME}$$

$$\mathrm{DMB} + \mathrm{H_2O} \rightleftharpoons \mathrm{MMB} + \mathrm{TME}$$

$$\mathrm{MMB} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_3BO_3} + \mathrm{TME}$$

with equilibrium constants K_1, K_2, and K_3, defined as

$$K_1 = [\mathrm{H_3BO_3}][\mathrm{TME}]/[\mathrm{MMB}][\mathrm{H_2O}],\quad K_2 = [\mathrm{MMB}][\mathrm{TME}]/[\mathrm{DMB}][\mathrm{H_2O}],\quad K_3 = [\mathrm{DMB}][\mathrm{TME}]/[\mathrm{TMB}][\mathrm{H_2O}] \tag{1}$$

In eq 1 [A] signifies the mole fraction of A in the equilibrium. Obviously, for each mol of H_2O reacting with TMB, 1 mol of TME is released, and thus

$$x^\circ(\mathrm{H_2O}) + x^\circ(\mathrm{TME}) = [\mathrm{H_2O}] + [\mathrm{TME}] \tag{2}$$

where $x^\circ(\mathrm{A})$ signifies the mole fraction of component A before any reaction has occurred.

Further straightforward mathematical manipulation leads to

$$n = K_1K_2K_3(3 - n)B^3 + K_2K_3(2 - n)B^2 + K_3(1 - n)B \tag{3}$$

with

$$n = \frac{x^\circ(\mathrm{H_2O}) - [\mathrm{H_2O}]}{x^\circ(\mathrm{TME})} \quad \text{and} \quad B = \frac{[\mathrm{H_2O}]}{[\mathrm{TME}]}$$

From eqs 2 and 3, it is clear that K_1, K_2, and K_3 follow from measurements of (at least) three values of $[\mathrm{H_2O}]$, starting from mixtures with known values of $x^\circ(\mathrm{H_2O})$, $x^\circ(\mathrm{TMB})$, and $x^\circ(\mathrm{TME})$.

Analytical methods that bind water chemically will shift the equilibria and thus cannot be used to measure $[\mathrm{H_2O}]$. Hence, physical methods are required. Despite the fact that the equilibrium mixture is complex, containing TMB, DMB, MMB, TME, H_3BO_3, and H_2O (henceforth abbreviated as the TMB/H_2O system), it proved possible to describe the system as an ideal mixture, following the simplified expression of Raoults's law:

$$p^{\mathrm{tot}} = p^\circ(\mathrm{H_2O})[\mathrm{H_2O}] + p^\circ(\mathrm{TME})[\mathrm{TME}] \tag{4}$$

Determination of $[\mathrm{H_2O}]$ then reduces to measurements of pressures, p, at known temperatures or, alternatively, measurements of boiling points at known pressures.

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