Vapor/Liquid/Liquid Equilibrium. Total-Pressure Data and G^E for Water/Methyl Acetate at 50 °C

Joseph R. Loehe, Hendrick C. Van Ness,* and Michael M. Abbott*

Chemical and Environmental Engineering Department, Rensselaer Polytechnic Institute, Troy, New York 12181

Isothermal P-x data for the binary system water/methyl acetate at 50 °C are reported. Reduction of data by a modification of Barker's method allows calculation of G^E.

We previously have reported experimental and correlated vapor/liquid equilibrium (VLE) data taken on an isothermal static total-pressure device. However, none of these studies dealt with systems which form two liquid phases. Herein are results of our first investigation of a binary system exhibiting vapor/liquid/liquid equilibrium (VLLE): water (1)/methyl acetate (2) at 50 °C.

Data were taken on the total-pressure apparatus described by Gibbs and Van Ness (*1*), as modified by DiElsi et al. (*2*). The water was doubly deionized with conductivity less than 1 × 10^{-6} Ω^{-1}. The methyl acetate was chromatoquality reagent supplied by Matheson Coleman and Bell, with a stated purity of 99.7 mol %. Both reagents were thoroughly degassed.

Results and Data Reduction

Table I contains experimental total-pressure data for the two regions of VLE. For liquid compositions in the region designated "miscibility gap", the observed pressure was essentially constant, indicating the presence of two liquid phases in equilibrium with a vapor phase. Nine measurements in this region yielded a three-phase equilibrium pressure P^* of 78.30 ± 0.02 kPa. Observed trends of P with x outside the two-liquid region imply a P-x-y diagram of "peritectic" type, for which the three-phase equilibrium compositions follow the order $y_1^* < x_1^\alpha < x_1^\beta$. A maximum-pressure homogeneous azeotrope occurs in the methyl acetate-rich region of VLE.

The P-x data were reduced by a modification of Barker's method. Barker's method (*3*) involves minimization of the sum of squares of pressure residuals. For binary VLE, the residuals are defined with respect to pressures computed from the equilibrium equation

$$P = x_1\gamma_1 P_1^{\text{sat}}/\Phi_1 + x_2\gamma_2 P_2^{\text{sat}}/\Phi_2$$

Here, the Φ_i are correction factors, of order unity, which incorporate vapor-phase fugacity coefficients and the effect of pressure on liquid fugacities. Liquid-phase nonidealities are represented by an assumed expression for g ($\equiv G^E/RT$), whence follow expressions for the activity coefficients γ_i; values for parameters in the assumed expression for g are determined by nonlinear regression of the P-x data.

Barker's method is applicable in principle to systems exhibiting VLLE. At least two general approaches may be taken. In the first (unconstrained) approach, one fits simultaneously P-x data for the two regions of VLE. The resulting numerical expressions for the γ_i can then be used to compute the liquid miscibility limits x_1^α and x_1^β via solution of the equations for LLE:

$$x_i^\alpha\gamma_i^\alpha = x_i^\beta\gamma_i^\beta \qquad (i = 1, 2) \tag{1}$$

The three-phase pressure P^* is found from

$$P^* = x_1^p\gamma_1^p P_1^{\text{sat}}/\Phi_1^* + x_2^p\gamma_2^p P_2^{\text{sat}}/\Phi_2^* \qquad (p = \alpha \text{ or } \beta)$$

Table I. Total-Pressure Data for Water (1)/Methyl Acetate (2) at 50 °C

x_1	x_2	P, kPa	x_1	x_2	P, kPa
0.0000	1.0000	79.162	0.2502	0.7498	79.218
0.1041	0.8959	80.530	0.2877	0.7123	78.757
0.1521	0.8479	80.191	0.3257	0.6743	78.362
0.1909	0.8091	79.847			
Miscibility Gap					
0.9317	0.0683	78.512	0.9703	0.0297	59.173
0.9346	0.0654	77.719	0.9741	0.0259	55.216
0.9348	0.0652	77.743	0.9750	0.0250	54.182
0.9399	0.0601	76.541	0.9789	0.0211	49.546
0.9445	0.0555	75.014	0.9800	0.0200	47.934
0.9448	0.0552	74.996	0.9839	0.0161	42.284
0.9499	0.0501	72.968	0.9851	0.0149	40.482
0.9544	0.0456	70.857	0.9894	0.0106	33.274
0.9550	0.0450	70.429	0.9902	0.0098	32.138
0.9600	0.0400	67.471	0.9947	0.0053	23.275
0.9630	0.0370	65.397	0.9952	0.0048	22.691
0.9653	0.0347	63.562	1.0000	0.0000	12.328
0.9683	0.0317	61.055			

By this approach, no use whatsoever is made of the VLLE data. However, the computed values of x_1^α, x_1^β, and P^* may be compared with experiment, and thereby checked for reasonableness.

In the second (constrained) approach, one again applies Barker's method to the regions of VLE, but eq 1 is incorporated into the regression as a constraint. Here, one requires predetermined values for the miscibility limits, which are built into the correlation of g. This procedure in effect reduces by two the number of independent parameters in the assumed expression for g.

Our data proved resistant to the approaches just described. In the absence of LLE constraints, we obtained acceptable correlations of the VLE data, but the calculated miscibility limits were very poor. With the second approach, no expression for g of reasonable complexity seemed capable of fitting all of the data to within their precision, with a single set of parameters. We finally adopted a combination of the two approaches, incorporating eq 1 into the regression procedure, but using separate sets of parameters in representing g for the two regions of VLE. For this purpose, we employed a modified Margules equation:

$$g \equiv G^E/RT = \{A_{21}x_1 + A_{12}x_2 - \alpha_{12}\alpha_{21}x_1x_2/(\alpha_{12}x_1 + \alpha_{21}x_2)\}x_1x_2 \tag{2}$$

An unconstrained fit of the VLE data for water-rich mixtures implied a miscibility limit $x_1^\beta = 0.9313$ at the specified three-phase pressure $P^* = 78.30$ kPa and gave the following values of activities for VLLE:

$$\hat{a}_1^\beta \equiv x_1^\beta\gamma_1^\beta = 0.9613$$

$$\hat{a}_2^\beta \equiv x_2^\beta\gamma_2^\beta = 0.8372$$

The VLE data for methyl acetate-rich mixtures were fitted separately, with eq 1 and the numerical values of the $\hat{a}_i$ incorporated as constraints. Here, the three-parameter version of eq 2 sufficed, implying a miscibility limit $x_1^\alpha = 0.3400$ for mixtures rich in methyl acetate at pressure P^*.

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Table II. Properties Used in the Data Reduction[a]

P_1^{sat}, kPa	12.328
P_2^{sat}, kPa	79.162
V_1^L, cm^3/mol	18
V_2^L, cm^3/mol	80
B_{11}, cm^3/mol	−1120
B_{22}, cm^3/mol	−1260
B_{12}, cm^3/mol	−970

[a] Species 1 is water; species 2 is methyl acetate.

Table III. Results of the Data Reduction[a]

	for $x_1 \leqslant$ 0.3400	for $x_1 \geqslant$ 0.9313
A_{21}	2.80588	3.34109
A_{12}	2.24614	−0.61329
α_{12}	0.72339	−0.09936
α_{21}	0.72339	−6.35286
rms δP, kPa	0.048	0.102
max $\vert\delta P\vert$, kPa	0.081	0.251

[a] Values of parameters in eq 2, and statistics. Species 1 is water, species 2 is methyl acetate.

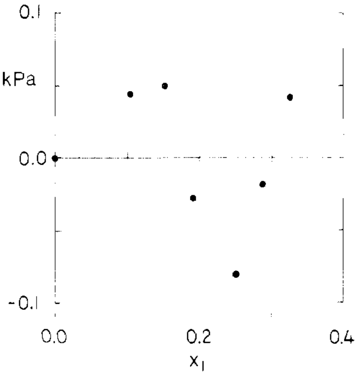

Figure 1. Pressure residuals for VLE: $x_1 < 0.3400$. Species 1 is water.

Table II contains ancillary information employed in the regressions. The pure-component vapor pressures P_i^{sat} are the end points of the data set; second virial coefficients B_{ij} were estimated from the Hayden–O'Connell correlation (*4*). Table III contains values of the correlating parameters in eq 2, and statistics for the regressions. Figures 1 and 2 are plots of pressure residuals, illustrating the goodness of fit for the two regions of VLE.

Discussion

The only published isothermal VLE data directly comparable with ours are those of Perelygin and Volkov, tabulated by Gmehling and Onken (*5*). Gmehling and Onken do not cite vapor pressures for the pure materials, but the trends of the mixture data suggest a value of P_2^{sat} no greater than about 77 kPa, a full 2 kPa lower than ours and other values from the literature. Hence, not surprisingly, the total pressures of Perelygin and Volkov are uniformly smaller than ours. The best that can be said is that the general features of P–x–y behavior are similar for their study and for ours.

Skrzecz and Maczynska (*6*) determined three-phase pressures at four temperatures by ebulliometry and correlated their results with an Antoine equation. At 50 °C, this equation gives a value for P^* of 78.74 kPa, which may be compared with the figure of 78.30 kPa found in our investigation. The discrepancy may be attributable to differences in purities of the reagents, or to differences in temperature or pressure standards; in neither case does the value for P^* depend upon measurement of composition.

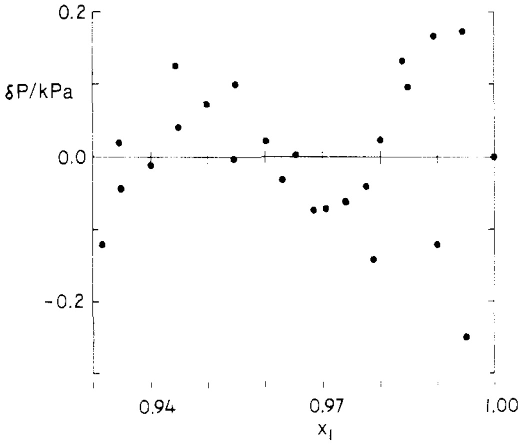

Figure 2. Pressure residuals for VLE: $x_1 > 0.9313$. Species 1 is water.

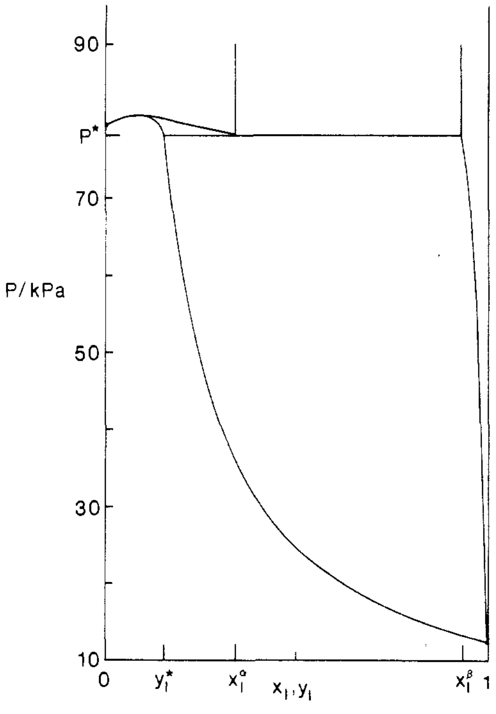

Figure 3. P–x–y diagram for water (1)/methyl acetate (2) at 50 °C.

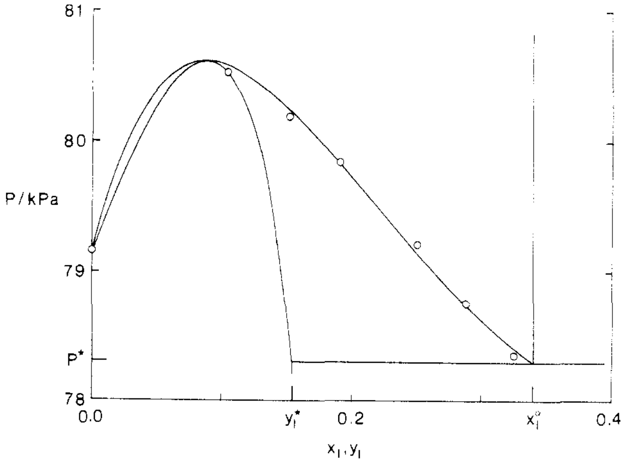

Figure 4. Detailed view of Figure 3, for region of homogeneous azeotropy. Circles are P–x data points.

The results of this study are depicted graphically in Figures 3 and 4. Figure 3 is the complete P–x–y diagram, and Figure 4 is a detailed view of the region of homogeneous azeotropy.

Table IV. Coordinates of Three-Phase Equilibrium and of Homogeneous Azeotropy for Water (1)/Methyl Acetate (2) at 50 °C

P^*, kPa (measured)	78.30
x_1^α (calculated)	0.3400
x_1^β (calculated)	0.9313
y_1^* (calculated)	0.1542
P^{az}, kPa (calculated)	80.604
x_1^{az} (calculated)	0.0876

All curves were generated from the equilibrium equations, with parameters for eq 2 as given in Table III. Values of significant pressure and composition coordinates are summarized in Table IV.

Glossary

A_{12}, A_{21}	parameters in eq 2
$\hat{a}_i^\alpha$, $\hat{a}_i^\beta$	liquid-phase activities at miscibility limits
B_{11}, B_{22}, B_{12}	second virial coefficients
G^E	excess Gibbs function, liquid phase
g	G^E/RT
P	total pressure
P^{az}	azeotropic pressure
P^*	three-phase equilibrium pressure
P_i^{sat}	vapor pressure of pure i
R	universal gas constant
T	absolute temperature
V_i^L	molar volume of pure liquid i
x_i	mole fraction, liquid phase
x_i^{az}	azeotropic composition
x_i^α, x_i^β	liquid miscibility limits
y_i^*	vapor-phase mole fraction at three-phase equilibrium

Greek Letters

α_{12}, α_{21}	parameters in eq 2
γ_i	activity coefficient, liquid phase
γ_i^α, γ_i^β	liquid-phase activity coefficients at miscibility limits
δ	denotes the difference, calculated − experimental
Φ_i	correction factors in the equation for VLE
Φ_i^*	Φ_i, evaluated at conditions of three-phase equilibrium

Registry No. Methyl acetate, 79-20-9.

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Excess Thermodynamic Functions for Ternary Systems. 8. Total-Pressure Data and G^E for Ethanol/Chloroform/1,4-Dioxane at 50 °C

Carlos Gonzalez and Hendrick C. Van Ness*

Chemical and Environmental Engineering Department, Rensselaer Polytechnic Institute, Troy, New York 12181

Isothermal P–x data for the ternary system ethanol/chloroform/1,4-dioxane at 50 °C are reported, together with data for the constituent binaries. Data reduction by Barker's method provides a correlation for G^E.

Reported here are vapor/liquid equilibrium (VLE) measurements for the ethanol (1)/chloroform (2)/1,4-dioxane (3) system at 50 °C. Experimental values of total vapor pressure are presented for the full composition range of the three constituent binaries and for five runs with ternary mixtures formed by addition of a pure species to mixtures of the other two. The apparatus is that of Gibbs and Van Ness (*1*) as modified by DiElsi et al. (*2*).

Reagent-quality ethanol was supplied by U.S. Industrial Chemicals and chromatoquality chloroform and dioxane came from Matheson Coleman and Bell. Except for thorough degassing, all were used as received with minimum indicated purity of 99.9 mol %.

Table I. P–x Data for Ethanol (1)/Chloroform (2) at 50 °C

x_1	x_2	P, kPa	x_1	x_2	P, kPa
0.0208	0.9792	70.783	0.5505	0.4495	65.106
0.1017	0.8983	72.808	0.6004	0.3996	62.858
0.1523	0.8477	72.883	0.6508	0.3492	60.115
0.2029	0.7971	72.639	0.7010	0.2990	56.862
0.2532	0.7468	72.152	0.7512	0.2488	52.985
0.3036	0.6964	71.485	0.7984	0.2016	48.888
0.3536	0.6464	70.653	0.8517	0.1483	43.829
0.4032	0.5968	69.627	0.9014	0.0986	38.849
0.4532	0.5468	68.367	0.9481	0.0519	34.254
0.4998	0.5002	66.978	0.9805	0.0195	31.237
0.5026	0.4974	66.856			

Results and Correlations

Tables I–III give experimental values of total pressure for the three constituent binary systems, and Table IV shows the data for ternary mixtures. Data reduction is by Barker's method, as described earlier (*3*, *4*). For the binary systems, the

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