*Subscripts*

| | |
|---|---|
| 1 | *o*-dichlorobenzene |
| 2 | aromatic hydrocarbon |

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# Vapor–Liquid Equilibria of the Ternary System Methyl Borate–Methyl Alcohol–Carbon Tetrachloride

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**Vapor–liquid equilibrium measurements at 760 Torr are reported for the methyl borate–methyl alcohol–carbon tetrachloride system. Analysis of the results shows that the ternary system can be adequately represented from binary data by means of the van Laar correlations (average error 2.2%) and well represented by the Wilson equation (average error 0.9%).**

The vapor–liquid equilibria have been measured for the ternary system methyl borate–methyl alcohol–carbon tetrachloride at a pressure of 760 ± 1 Torr. An Altsheler (circulation type) still was used and is described in detail by Hala et al. (*3*). The methyl borate used was purchased from Apache Chemicals, Inc., at a nominal 98% purity and was further purified by successive fractional distillation to 99.9+%. Analysis of the borate was by the standard mannitol–sodium hydroxide titration (*6*). Methyl alcohol ("absolute") and carbon tetrachloride were used as purchased. Properties of these compounds compared with literature values are shown in Table I.

Mixture analyses were made by a combination of chemical analysis and physical property measurements. Measurements necessary were the weight fraction of methyl borate, which was again determined by the mannitol–sodium hydroxide titration, refractive indices, and densities of both the pure components and the mixtures. Once the weight fraction of methyl borate was known, the Lorentz–Lorenz equation (*8*)

$$\frac{(\eta^2-1)}{(\eta^2+2)\rho} = \sum_{1}^{3} (\omega_i)\frac{(\eta_i^2-1)}{(\eta_i^2+2)\rho_i} \qquad (1)$$

and

$$\sum_{1}^{3} \omega_i = 1 \qquad (2)$$

were used to obtain the weight fraction of the other two components. To verify this procedure, several mixtures of known composition were assayed and the results were to within ±0.1% of the known values. Experimental evidence showed no necessity of including a liquid volume correction term to eq 1. Refractive indices were measured with a Bausch and Lomb Model 33-45-03 refractometer capable of precision to ±0.000 03 RI units. The sodium D line at 25.0 ± 0.1 °C was used. Densities were determined by means of a pycnometer, with a nominal volume of 10 mL, at 25.0 ± 0.05 °C. The pycnometer was calibrated with deionized water, specific resistance approximately 450 000 Ω, and weighed to ±0.0001 g.

Experimental data are tabulated in Table II and the tie lines are also shown in Figure 1. Three-dimensional models representing the temperature–vapor and temperature–liquid compositions were constructed from these data. Estimated isotherms on these surfaces have been projected as shown in Figures 2 and 3.

For the liquid surface, a sharp temperature drop occurs from the methyl borate–carbon tetrachloride binary as a small amount of methyl alcohol is added. The decline is less severe at high methyl borate concentrations. A nearly flat interior is seen at all points reasonably removed from the pure components. The flat interior rises quickly to a point as pure methyl alcohol is approached. The vapor surface shows a trough connecting the two binary azeotropes (methyl borate–methyl alcohol and methyl alcohol–carbon tetrachloride) which is nearly linear. The surfaces rising from the trough to pure methyl alcohol and also to the methyl borate–carbon tetrachloride binary show slight outward curvature. There is no evidence of a ternary azeotrope.

Activity coefficients of the components were calculated from the equation

$$\gamma_i = \frac{y_i P}{x_i P_i^0} \qquad (3)$$

Table I

| Compound | Bp, °C | | Refractive index, 25 °C sodium D line | | Density 25 °C, g mL$^{-1}$ | |
|---|---|---|---|---|---|---|
| | This work | Lit. | This work | Lit. | This work | Lit. |
| Methyl borate | 68.6 ± 0.1 | 68.7 (*7*) | 1.35504 | — | 0.9273 | 0.9273 (*2*) |
| Methyl alcohol | 64.6 ± 0.1 | 64.51 (*1*) | 1.3268 | 1.326 (*4*) | 0.7867 | 0.7867 (*7*) |
| Carbon tetrachloride | 76.7 ± 0.1 | 76.54 (*4*) | 1.4575 | 1.459 (*4*) | 1.5843 | 1.5867 (*7*) |

**Table II**

| | | Mole fraction liquid | | | Mole fraction vapor | | | Activity coefficients | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Point | Temp, °C | $(CH_3O)_3B$ | $CH_3OH$ | $CCl_4$ | $(CH_3O)_3B$ | $CH_3OH$ | $CCl_4$ | $(CH_3O)_3B$ | $CH_3OH$ | $CCl_4$ |
| 1 | 57.5 | 0.083 | 0.125 | 0.792 | 0.051 | 0.491 | 0.458 | 0.890 | 5.254 | 1.073 |
| 2 | 56.3 | 0.079 | 0.430 | 0.491 | 0.065 | 0.538 | 0.397 | 1.244 | 1.759 | 1.564 |
| 3 | 56.3 | 0.069 | 0.716 | 0.215 | 0.100 | 0.577 | 0.323 | 2.191 | 1.133 | 2.906 |
| 4 | 57.3 | 0.049 | 0.831 | 0.120 | 0.110 | 0.645 | 0.245 | 3.275 | 1.047 | 3.814 |
| 5 | 56.2 | 0.048 | 0.672 | 0.280 | 0.064 | 0.576 | 0.360 | 2.023 | 1.210 | 2.496 |
| 6 | 56.6 | 0.079 | 0.770 | 0.151 | 0.142 | 0.608 | 0.250 | 2.688 | 1.096 | 3.169 |
| 7 | 55.1 | 0.527 | 0.443 | 0.030 | 0.471 | 0.507 | 0.022 | 1.410 | 1.691 | 1.479 |
| 8 | 55.2 | 0.575 | 0.391 | 0.034 | 0.479 | 0.498 | 0.023 | 1.310 | 1.874 | 1.360 |
| 9 | 55.6 | 0.432 | 0.407 | 0.161 | 0.371 | 0.509 | 0.120 | 1.331 | 1.810 | 1.477 |
| 10 | 55.5 | 0.563 | 0.333 | 0.104 | 0.439 | 0.492 | 0.069 | 1.213 | 2.147 | 1.320 |
| 11 | 55.5 | 0.623 | 0.259 | 0.118 | 0.453 | 0.475 | 0.072 | 1.131 | 2.665 | 1.214 |
| 12 | 56.2 | 0.556 | 0.226 | 0.218 | 0.395 | 0.474 | 0.131 | 1.078 | 2.960 | 1.166 |
| 13 | 65.6 | 0.966 | 0.015 | 0.019 | 0.839 | 0.149 | 0.012 | 1.018 | 9.617 | 0.892 |
| 14 | 64.0 | 0.824 | 0.029 | 0.147 | 0.690 | 0.215 | 0.095 | 0.972 | 7.640 | 0.962 |
| 15 | 63.1 | 0.686 | 0.041 | 0.273 | 0.551 | 0.275 | 0.174 | 0.961 | 7.162 | 0.978 |
| 16 | 61.5 | 0.536 | 0.054 | 0.410 | 0.402 | 0.346 | 0.252 | 0.946 | 7.290 | 0.995 |
| 17 | 62.0 | 0.329 | 0.048 | 0.623 | 0.245 | 0.363 | 0.392 | 0.924 | 8.434 | 1.001 |
| 18 | 56.4 | 0.396 | 0.262 | 0.342 | 0.284 | 0.498 | 0.218 | 1.080 | 2.660 | 1.229 |
| 19 | 56.8 | 0.232 | 0.216 | 0.552 | 0.155 | 0.505 | 0.340 | 0.992 | 3.219 | 1.171 |
| 20 | 55.6 | 0.245 | 0.522 | 0.233 | 0.243 | 0.546 | 0.211 | 1.537 | 1.513 | 1.795 |
| 21 | 55.2 | 0.352 | 0.598 | 0.050 | 0.412 | 0.538 | 0.050 | 1.840 | 1.324 | 2.010 |
| 22 | 56.3 | 0.157 | 0.819 | 0.024 | 0.333 | 0.622 | 0.045 | 3.206 | 1.067 | 3.627 |
| 23 | 55.8 | 0.195 | 0.640 | 0.165 | 0.247 | 0.562 | 0.191 | 1.949 | 1.260 | 2.279 |
| 24 | 55.9 | 0.139 | 0.716 | 0.145 | 0.212 | 0.583 | 0.205 | 2.339 | 1.164 | 2.773 |
| 25 | 61.7 | 0.020 | 0.960 | 0.020 | 0.079 | 0.846 | 0.075 | 4.951 | 0.995 | 6.029 |

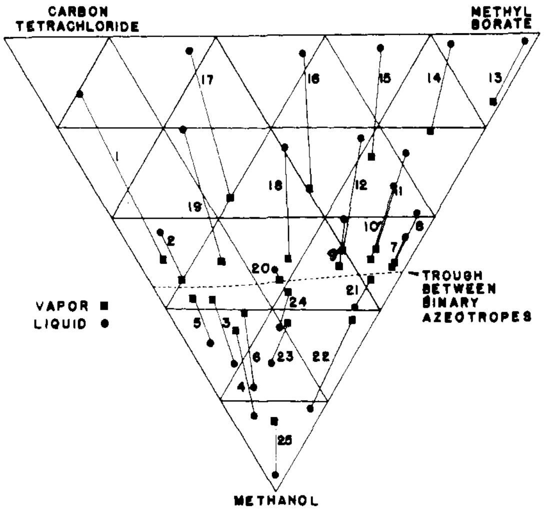

Figure 1. Equilibrium tie lines.

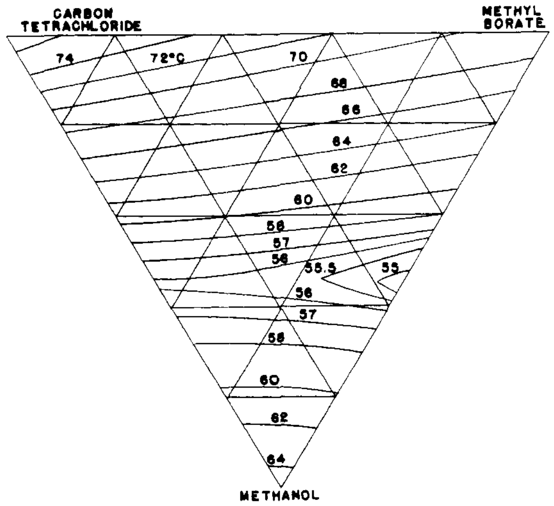

Figure 2. Isotherms on the vapor surface of the system methyl borate-methanol-carbon tetrachloride.

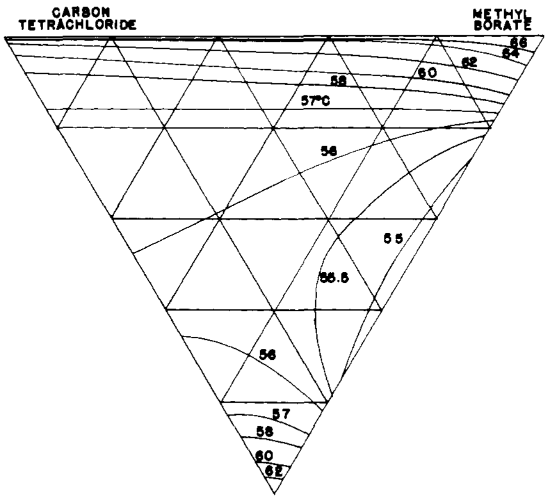

Figure 3. Isotherms on the liquid surface of the system methyl borate-methanol-carbon tetrachloride.

Estimations of nonideality of the vapor phase fugacity coefficients were made using techniques associated with the second virial coefficients and suitable mixing rules as described in Smith and Van Ness (*12*). These estimations were hampered by the lack of suitable physical property data for methyl borate, but indicated values of the vapor phase fugacity coefficients of 0.97–1.0. Because of this small deviation and approximations necessary, the small vapor phase imperfections were absorbed in the calculation of the liquid phase activity coefficients. Equations used for the vapor pressures of the pure components are reported in ref 7 and 9.

Data for the three binary systems which compose this ternary have been reported previously (*5, 9, 11*). The systems methyl borate-methyl alcohol and methyl alcohol-carbon tetrachloride have minimum boiling azeotropes, whereas methyl borate-carbon tetrachloride exhibits ideal behavior. From these binary data, constants for the Van Laar equations and also the Wilson equations (*12*) were evaluated and are shown in Table III.

**Table III**

| System (component $i$–component $j$) | Van Laar constants $A_{ij}$ | $A_{ji}$ | Wilson constants $G_{ij}$ | $G_{ji}$ |
|---|---|---|---|---|
| $(CH_3O)_3B$-$CH_3OH$ | 1.8184 | 1.8179 | 0.25718 | 0.16781 |
| $(CH_3O)_3B$-$CCl_4$ | 0 | 0 | 1 | 1 |
| $CH_3OH$-$CCl_4$ | 1.4313 | 1.9236 | 0.08705 | 0.31203 |

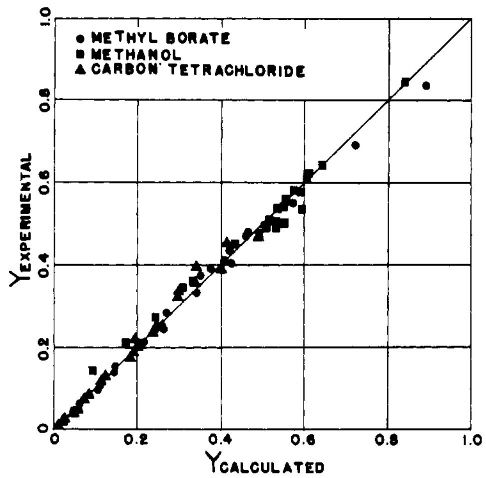

**Figure 4.** Comparison of calculated and experimental results for the ternary Van Laar equation.

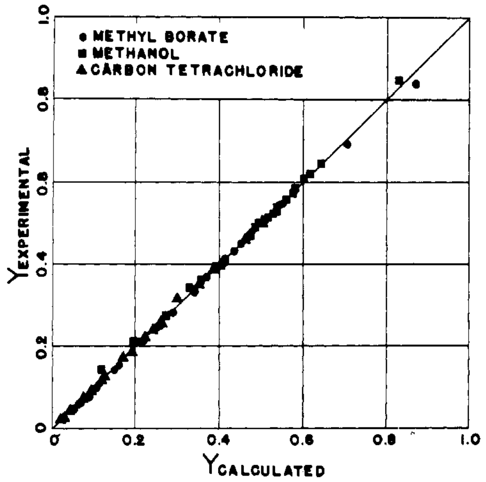

**Figure 5.** Comparison of calculated and experimental results for the ternary Wilson equation.

Ternary vapor phase compositions and equilibrium temperature were estimated for the measured liquid compositions using both Van Laar (*3*) and Wilson (*12*) expansions for the liquid phase activity coefficients. These expansions involve only concentrations and the six constants derived from binary data. Values for the activity coefficient as calculated from the Van Laar form can be obtained from

$$\ln \gamma_i = \frac{x_j{}^2 A_{ij}\left(\frac{A_{ji}}{A_{ij}}\right)^2 + x_k{}^2 A_{ik}\left(\frac{A_{ki}}{A_{ik}}\right)^2 + x_j x_k\left(\frac{A_{ji}}{A_{ij}}\right)\left(\frac{A_{ki}}{A_{ik}}\right)\left[A_{ij} + A_{ik} - A_{kj}\left(\frac{A_{ik}}{A_{ki}}\right)\right]}{\left[x_i + x_j\left(\frac{A_{ji}}{A_{ij}}\right) + x_k\left(\frac{A_{ki}}{A_{ik}}\right)\right]^2} \tag{4}$$

where $i = 1$, $j = 2$, and $k = 3$. Expressions for $\gamma_2$ and $\gamma_3$ are the same as $\gamma_1$. To obtain $\gamma_2$, eq 4 should have subscripts of $i = 2$, $j = 3$, and $k = 1$ while for $\gamma_3$, $i = 3$, $j = 1$, $k = 2$.

The Wilson expansion for $\ln \gamma_i$ is

$$\ln \gamma_i = 1 - \ln\left(\sum_j x_j G_{ij}\right) - \sum_k \left(\frac{x_k G_{ki}}{\sum_j x_j G_{kj}}\right) \tag{5}$$

Results of the predictions for the vapor compositions are shown in Figures 4 and 5. Predictions by the Van Laar method showed approximately ±2.2% average deviation (max 5.8%) from measured values while the predictions from the Wilson equation represented the data with an average error of ±0.9% (max 3.6%). These errors are essentially of the same magnitude as found in the binary predictions; therefore no loss in accuracy was observed in going from the binary to the ternary data. The largest errors arise at small methyl alcohol liquid phase concentrations since the vapor phase changes markedly with slight changes in the liquid composition. Tabular comparisons of the estimations along with computer programs for the various calculations may be found in ref 10.

## Glossary

| | |
|---|---|
| $A_{ij}$ | constant in the Van Laar equation |
| $G_{ij}$ | constant in the Wilson equation |
| $P$ | total pressure, mmHg |
| $P^0$ | vapor pressure, mmHg |
| $x$ | mole fraction, liquid |
| $\omega$ | weight fraction, liquid |
| $y$ | mole fraction, vapor |
| $\eta$ | refractive index |
| $\gamma$ | activity coefficient, dimensionless |
| $\rho$ | density |

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