# Isobaric Vapor–Liquid Equilibrium for Methyl Acetate + Methanol + Water at 101.3 kPa

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Isobaric vapor–liquid equilibrium was measured at 101.3 kPa for the ternary system methyl acetate + methanol + water by an ebulliometric method. The results have been fitted with the van Laar, Wilson, NRTL, and NRTL-m (a modified NRTL equation) activity coefficient models. The measurements are compared with experimental data previously reported in the literature (Balashov, M. I.; Serafimov, L. A.; Bessonova, Z. V. *Zh. Fiz. Khim.* **1966**, *40*, 2294).

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## Introduction

In this paper we present vapor–liquid equilibrium (VLE) at 101.13 kPa for the ternary mixture methyl acetate (1) + methanol (2) + water (3). This work is part of a research program whose purpose is the study of the separation by a modified distillation of the azeotropic mixture methyl acetate + methanol. This mixture is involved in the industrial manufacturing process of poly(vinyl alcohol), which is obtained by alcoholysis of poly(vinyl acetate) with methanol.

In previous papers we have reported isothermal VLE for different binary mixtures involving methyl acetate or methanol and the separation agent. Several chlorinated compounds (dichloromethane, chloroform, and *trans*-1,2-dichloroethylene) were selected as azeotropic separating agents (*2*), and methoxyethanol, ethoxyethanol (*3*), and several nitrogen compounds (acetonitrile, nitromethane, and nitroethane) (*4*) as extractive distillation agents. The salt effect produced by different salts was also studied (*5*).

After these experimental VLE binary systems were measured, the effect of the separation agents on the modification of the binary azeotrope methyl acetate + methanol was predicted. The azeotropic separating agents and the nitrogen compounds decrease the composition of the ester in the azeotrope, while the opposite effect is observed for the cellosolves. However, they are not able to break the azeotrope. The best results were obtained using water as an extractive separating agent. The aim of this paper is to measure the actual ternary isobaric VLE of the system methyl acetate + methanol + water to be used in the design of an extractive distillation unit.

## Experimental Section

***Materials.*** The water used in this work was first distilled and then treated in a Milli-Q system (from Millipore). Methyl acetate and methanol used were Farmitalia Carlo Erba products, they were treated by rectification at 1 atm of pressure in a packed column with an efficiency equivalent to 25 theoretical plates, and the intermediate fraction distilling at constant temperature was collected. Gas chromatography analysis failed to show significant impurities, and the final purity was at least 99.85 mass %. Experimental liquid densities of the methyl acetate and the methanol at 298.15 K are shown in Table 1 and are in good agreement with the literature values (*6*).

**Table 1. Experimental and Literature Densities for Pure Liquids at 298.15 K**

| | $\varrho$/(g·cm$^{-3}$) | |
|---|---|---|
| | exptl | lit. |
| methyl acetate | 0.9270 | 0.9273 (*6*) |
| methanol | 0.7866 | 0.7866 (*6*) |

***Apparatus and Procedure.*** VLE was obtained by an ebullometric method using a commercial device Labodest. The evaporation of the sample is made with an electrical immersion heater, which is concentrically installed into a flow heater. Due to the regular circulation of both phases and the simultaneous mixing of the back-flowing circulation streams in a special mixing chamber, a quick adjustment of the equilibrium was obtained. Vapor and liquid samples were taken off with a gas chromatographic syringe, and they were immediately analyzed. The pressure is kept constant with an accuracy of ±10 Pa, and the temperature is measured with a Pt-100 probe with an accuracy of ±0.05 K.

The composition of both phases was determined with a KONIK KNK-2000-C gas chromatograph equipped with a thermal conductivity detector and a Hewlett-Packard electronic integrator (Model 3390). The chromatographic packed column, Porapak-Q 5 m long, was operated at 150 °C oven temperature. The chromatographic measurements present good reproducibility, and the mole fraction of the phases, accurate to within ±0.001, was calculated from the peak area ratio of the samples.

## Experimental Results

Table 2 shows the experimental $x$–$y$–$T$ data, together with the calculated values of the liquid phase activity coefficients $\gamma_i$. The vapor phase fugacity coefficients were calculated from the Peng–Robinson equation of state (*7*), where the binary interaction parameter, $\delta_{ij}$, was set as 0. The vapor pressures of the pure components were calculated by the Antoine equation using the constants given in Table 3. According to the experimental liquid phase activity coefficients, the system shows moderate positive deviations from ideality.

## Correlation

The experimental activity coefficients were correlated by the multicomponent expression of the van Laar equation

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**Table 2. Isobaric Vapor–Liquid Equilibrium Data (Liquid Phase Mole Fraction $x_i$, Vapor Phase Mole Fraction $y_i$, and Temperature $T$) and Activity Coefficients $\gamma_i$ for the Methyl Acetate (1) + Methanol (2) + Water (3) System at 101.3 kPa**

| $x_1$ | $x_2$ | $y_1$ | $y_2$ | $T$/K | $\gamma_1$ | $\gamma_2$ | $\gamma_3$ |
|---|---|---|---|---|---|---|---|
| 0.101 | 0.827 | 0.273 | 0.700 | 333.65 | 2.419 | 1.004 | 1.890 |
| 0.172 | 0.647 | 0.427 | 0.522 | 332.30 | 2.324 | 1.010 | 1.512 |
| 0.109 | 0.442 | 0.439 | 0.444 | 336.05 | 3.325 | 1.083 | 1.177 |
| 0.152 | 0.433 | 0.488 | 0.402 | 334.65 | 2.776 | 1.058 | 1.276 |
| 0.209 | 0.226 | 0.675 | 0.200 | 332.30 | 3.020 | 1.107 | 1.187 |
| 0.108 | 0.193 | 0.642 | 0.201 | 334.45 | 5.171 | 1.196 | 1.091 |
| 0.244 | 0.090 | 0.788 | 0.075 | 331.05 | 3.149 | 1.096 | 1.169 |
| 0.291 | 0.552 | 0.527 | 0.422 | 330.05 | 1.830 | 1.048 | 1.936 |
| 0.364 | 0.352 | 0.627 | 0.287 | 330.25 | 1.728 | 1.109 | 1.788 |
| 0.340 | 0.209 | 0.709 | 0.169 | 331.10 | 2.031 | 1.062 | 1.534 |
| 0.272 | 0.163 | 0.732 | 0.142 | 331.25 | 2.607 | 1.137 | 1.256 |
| 0.472 | 0.323 | 0.663 | 0.263 | 329.05 | 1.468 | 1.163 | 2.255 |
| 0.477 | 0.207 | 0.718 | 0.175 | 329.85 | 1.530 | 1.168 | 2.037 |
| 0.393 | 0.164 | 0.738 | 0.139 | 330.55 | 1.863 | 1.138 | 1.616 |
| 0.616 | 0.205 | 0.738 | 0.188 | 328.50 | 1.276 | 1.340 | 2.651 |
| 0.548 | 0.190 | 0.730 | 0.167 | 329.35 | 1.378 | 1.240 | 2.421 |
| 0.762 | 0.136 | 0.783 | 0.150 | 328.25 | 1.104 | 1.628 | 4.263 |
| 0.124 | 0.200 | 0.661 | 0.191 | 334.30 | 4.660 | 1.103 | 1.071 |

**Table 3. Antoine Constants of the Components**[a]

| component | $A$ | $B$ | $C$ |
|---|---|---|---|
| methyl acetate | 14.2533 | 2665.54 | −53.424 (*11*) |
| methanol | 15.8733 | 3242.87 | −49.550 (*11*) |
| water | 16.5699 | 3984.92 | −39.724 (*11*) |

[a] $P/\mathrm{kPa} = A - B/[(T/\mathrm{K}) + C]$.

proposed by Null (*8*), and the Wilson (*9*), NRTL (*10*), and NRTL-m (*11*) equations by a nonlinear regression method. For this purpose the following objective function, OF, was minimized:

$$\mathrm{OF} = \sum_{i=1}^{N} \sum_{j=1}^{C} \left( \frac{\gamma_{j,\mathrm{e}} - \gamma_{j,\mathrm{c}}}{\gamma_{j,\mathrm{e}}} \right)_i^2 \qquad (1)$$

where $N$ is the number of experimental data points, $C$ is the number of components, and the subscripts e and c mean experimental and calculated values, respectively.

The NRTL-m equation is a modification of the original NRTL, proposed by Mato et al. (*11*), where the nonrandomness parameter $\alpha_{ij}$ is expressed as a function of the other two binary interaction parameters $G_{ij}$ and $G_{ji}$:

$$\alpha_{ij} = \frac{1}{2 + G_{ij} G_{ji}} \qquad (2)$$

Table 4 lists the results of the correlation, where $A_{ij}$ is the fitted parameter of the corresponding model and $\Delta y_1$ and $\Delta T$ are the average absolute deviations in the vapor phase mole fraction of the ester and temperature (K), respectively. The units of the parameters $A_{ij}$ in Table 4 are kelvin for the Wilson, NRTL, and NRTL-m models, and $A_{ij}$ are dimensionless for the van Laar model.

**Table 4. Fitted Parameters $A_{ij}$ and Average Absolute Deviations in Vapor Phase Mole Fraction $\Delta y_1$ and Temperature $\Delta T$,[a] from Experimental Data**

| | Wilson | NRTL | NRTL-m | VanLaar |
|---|---|---|---|---|
| $A_{12}$ | −45.55 | 168.1 | 168.9 | 0.9183 |
| $A_{21}$ | 406.1 | 178.4 | 177.6 | 1.010 |
| $A_{13}$ | 240.5 | 368.1 | 521.3 | 2.364 |
| $A_{31}$ | 1013 | 569.5 | 667.6 | 2.077 |
| $A_{23}$ | −360.4 | 436.3 | 333.2 | 0.3105 |
| $A_{32}$ | 580.3 | −189.2 | −121.7 | 0.6515 |
| $\Delta y_1$ | 0.009 | 0.010 | 0.009 | 0.011 |
| $\Delta y_2$ | 0.006 | 0.008 | 0.007 | 0.009 |
| $\Delta y_3$ | 0.005 | 0.003 | 0.005 | 0.003 |
| $\Delta T$/K | 0.65 | 0.62 | 0.60 | 0.63 |

[a] $\Delta y_i = \sum_k |(y_{i,\mathrm{exptl}} - y_{i,\mathrm{calcd}})|_k / N$, $\Delta T = \sum_k |(T_{\mathrm{exptl}} - T_{\mathrm{calcd}})|_k / N$.

**Table 5. Average Absolute Deviations in Vapor Phase Mole Fraction $\Delta y_1$ and Temperature $\Delta T$[a] (*12*), from Literature Data (*1*)**

| | Wilson | NRTL |
|---|---|---|
| $\Delta y_1$ | 0.017 | 0.022 |
| $\Delta y_2$ | 0.016 | 0.018 |
| $\Delta y_3$ | 0.016 | 0.016 |
| $\Delta T$/K | 0.81 | 1.70 |

[a] $\Delta y_i = \sum_k |(y_{i,\mathrm{exptl}} - y_{i,\mathrm{calcd}})|_k / N$, $\Delta T = \sum_k |(T_{\mathrm{exptl}} - T_{\mathrm{calcd}})|_k / N$.

Previously published data (*1*) of the isobaric methyl acetate + methanol + water system have been correlated in the literature (*12*) using Wilson and NRTL models. The results from this correlation are presented in Table 5. The calculated deviations shown in Table 4, from experimental data here reported, are smaller than those shown in Table 5, from literature data (*1*).

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