# Theoretical Prediction and Experimental Determination of Vapour-Liquid Equilibrium for Ternary Systems Trimethyl Borate-Methanol-*N*,*N*-Dimethylformamide/*N*,*N*-Dimethylacetamide

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Vapour-liquid equilibrium prediction of ternary systems: trimethyl borate-methanol-*N*,*N*-dimethylformamide and trimethyl borate-methanol-*N*,*N*-dimethylacetamide were conducted through combined utilization of Materials Studio, COSMO-SAC program and ChemCAD. The vapour-liquid equilibrium data obtained were compared with the experimentally measured data. Results showed that predicted values were comparatively conservative than measured ones, which indicated better performance of solvents can be achieved actually. Measured data were correlated using three frequently used activity coefficient models, of which binary interaction coefficients were obtained. The solvents displayed obvious solvent effect, especially *N*,*N*-dimethylacetamide. This proves the validity of *N*,*N*-dimethylacetamide as an effective solvent.

**Keywords: Vapour-liquid equilibrium, Quantum mechanics calculation, Trimethyl borate, *N*,*N*-dimethylformamide, *N*,*N*-dimethylacetamide.**

## INTRODUCTION

Trimethyl borate [$B(OCH_3)_3$] is an essential chemical used in a variety of areas, it is the intermediate in the production of organic boride and high purity boron. However, at 101.3 kPa, it forms an azeotrope with methanol, which contains 77-78 % (wt. %) trimethyl borate[1]. An ordinary distillation column with enough trays can only get the azeotrope from the overhead, but every year in United States, almost 8600 tons of trimethyl borate needs to be produced[2], so the azeotrope must be separated in order to get high purity trimethyl borate for further utilization.

Separating the azeotrope using extractive distillation is supposed to be a convenient and efficient way to get trimethyl borate product[3]. Polar solvents are preferred as trimethyl borate can be distilled directly from the top of the extractive distillation tower. Due to the massive amount of solvent, several factors should be borne in mind. First, the solvent is a liquid which is different from salt-adding distillation. Liquid will not block the pores of trays and gaps between packings. Second, the solvent has a markedly higher boiling point than any component in the system, unlike azeotropic distillation, it will not form a new azeotrope and can be separated from other components with almost no residue inside. Third, the solvent can be recycled, which not only saves raw materials but also diminishes pollution. Therefore, extractive distillation is a green chemical process.

Solvent selection using computer-aided molecular design has been investigated by many researchers[4-6]. It connects chemical structures with macroscopic properties, softwares like Materials Studio and Gaussian provide quantum mechanics calculation of preselected group structures, desired molecules are constructed by satisfactory groups. Prediction of the vapour-liquid equilibrium by these commercial softwares can be achieved by combination of COMSO-SAC program.

After theoretical calculation, experimental determination of vapour-liquid equilibrium data of the given ternary system is necessary. The measurement is carried out with concern of practical dosage of solvents[7-9], even though the increase of solvent concentration in the liquid phase can enhance the relative volatility in a certain amount, the heat required and the solvent content in the product also increased while the unit production capacity decreased[10]. *N*,*N*-dimethylformamide and *N*,*N*-dimethylacetamide are two commonly used polar solvents. Ternary vapour-liquid equilibrium data for trimethyl borate-methanol-*N*,*N*-dimethylformamide and trimethyl borate-methanol-*N*,*N*-dimethylacetamide are not found in open literatures. In this work, ternary data of the two systems were first predicted using CAMD and then measured at 101.3 kPa, the measured data were correlated by the nonrandom two-liquid model, universal quasi-chemical model and Wilson model. The most suitable one was selected to describe the trend of the vapour-liquid equilibrium data, moreover, comparisons were made between prediction and experiment to testify the validity of CAMD.

## EXPERIMENTAL

All reagents were purchased from Tianjin Guangfu Fine Chemical Research Institute. The purity grade of anhydrous methanol was HPLC, trimethyl borate was AR, *N,N*-dimethyl-formamide and *N,N*-dimethylacetamide were GR. Their purities checked by gas chromatography were greater than 0.997 in mass fraction. All chemicals were used without further purification, but were carefully degassed using ultrasonic waves. The water mass fraction in methanol was less than 100 ppm, *N,N*-dimethylformamide and *N,N*-dimethylacetamide determined by Karl Fischer titration were less than 500 ppm.

The vapour-liquid equilibrium data were measured by a enhanced Othmer still as described by Cai *et al.*[9] and others[11]. The equilibrium temperature was measured every 15 min by a precision and calibrated thermometer with an accuracy of ± 0.01 K. On average, the system reaches equilibrium conditions after operation for 1.5-2 h. Then 0.2 µL samples were taken by syringe and were immediately analyzed. To verify the equilibrium state, samples should ensure standard deviations of less than ±0.0015 for both vapour and liquid phase. Generally, the first three samples were rejected. The whole process lasts for about 3h and the sampling process could ensure the vapour and liquid phases are in equilibrium state. The pressure was held constant at 101.3 ± 0.05 kPa throughout the experiment using an electronic manometer. The solutions were prepared gravimetrically using an electronic balance (Hengping FA1004) with a standard uncertainty of ±0.0001 g.

**Sample analysis:** Analysis of the condensed vapour and liquid phase were conducted by gas chromatography (GC). The GC (GC-2010) is equipped with a flame ionization detector (FID) and the column is SE-30 (50 m × 0.32 mm × 0.5 µm). The gas chromatograph was calibrated with a set of mixtures of known compositions that were prepared gravimetrically by the electronic balance. Calibration curves had correlation coefficients greater than 0.9992. Three samples with known compositions were used to verify the reliability of calibration curves. The results showed that the standard deviations were below ±0.001(mole fraction). The expanded uncertainty of GC's composition analysis was below ±0.007 in mole fraction (with a 95 % level of confidence).

## RESULTS AND DISCUSSION

**Predicted data:** The σ-profiles were obtained from Materials Studio, the activity coefficients of corresponding components ($\gamma_i$) at different temperatures (T) and concentrations ($x_i$) were then calculated using COSMO-SAC program. After the saturated vapour pressure ($P_i^s$) was calculated from antoine equation, P-xy data was obtained by the equation below:

$$Py_i = P_i^s \gamma_i x_i$$

The results have been plotted in Fig. 1.

Vapour-liquid equilibrium for the ternary systems of trimethyl borate (1) methanol (2) *N,N*-dimethylformamide (3) and trimethyl borate (1) methanol (2) *N,N*-dimethylacetamide (3) were measured at 101.3 kPa and the mole fraction of solvent added to the system was kept at $x_3 = 0.4$. The vapour-liquid equilibrium data are shown in Table-1.

**Correlation of the vapour-liquid equilibrium data:** The nonrandom two-liquid model, universal quasichemical model and Wilson model are the most commonly used models to correlate the vapour-liquid equilibrium data of organic systems. Correlation results have been listed in Table-2. In the table, binary interaction coefficients and nonrandomness parameter for trimethyl borate-methanol were obtained from Gmehling's handbook[12], while binary interaction coefficients and non-randomness parameter for methanol-*N,N*-dimethylformamide were obtained from ChemCAD built-in database. The other

### TABLE-1
VAPOUR-LIQUID EQUILIBRIUM DATA FOR THE TERNARY SYSTEMS TRIMETHYL BORATE (1) METHANOL (2) *N,N*-DIMETHYLFORMAMIDE (3), TRIMETHYL BORATE (1) METHANOL (2) *N,N*-DIMETHYLACETAMIDE (3) AT P = 101.3 kPa[a]

| No. | T (K) | $x_1$ | $x_2$ | $y_1$ | $y_2$ | $\gamma_1$ | $\gamma_2$ | $\gamma_3$ | $\alpha_{12}$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Trimethyl borate (1) methanol (2) *N,N*-dimethylformamide (3) | | | | | |
| 1 | 351.92 | 0.029 | 0.571 | 0.135 | 0.863 | 3.731 | 1.000 | 0.063 | 3.029 |
| 2 | 349.48 | 0.052 | 0.553 | 0.212 | 0.784 | 3.415 | 0.979 | 0.134 | 2.823 |
| 3 | 343.59 | 0.107 | 0.493 | 0.343 | 0.655 | 2.905 | 1.001 | 0.074 | 2.422 |
| 4 | 342.71 | 0.151 | 0.449 | 0.426 | 0.572 | 2.670 | 1.016 | 0.079 | 2.212 |
| 5 | 342.27 | 0.233 | 0.367 | 0.540 | 0.458 | 2.278 | 1.044 | 0.083 | 1.851 |
| 6 | 342.06 | 0.310 | 0.290 | 0.623 | 0.375 | 1.996 | 1.087 | 0.084 | 1.563 |
| 7 | 342.21 | 0.388 | 0.212 | 0.706 | 0.292 | 1.768 | 1.131 | 0.082 | 1.322 |
| 8 | 343.15 | 0.494 | 0.107 | 0.839 | 0.160 | 1.527 | 1.111 | 0.037 | 1.129 |
| 9 | 345.90 | 0.532 | 0.068 | 0.888 | 0.110 | 1.452 | 1.160 | 0.069 | 1.031 |
| 10 | 349.45 | 0.564 | 0.036 | 0.934 | 0.064 | 1.396 | 1.225 | 0.066 | 0.934 |
| | | | | Trimethyl borate (1) methanol (2) *N,N*-dimethylacetamide (3) | | | | | |
| 1 | 355.56 | 0.028 | 0.572 | 0.127 | 0.871 | 3.214 | 0.833 | 0.055 | 3.017 |
| 2 | 353.80 | 0.054 | 0.546 | 0.209 | 0.789 | 2.852 | 0.852 | 0.060 | 2.672 |
| 3 | 351.74 | 0.089 | 0.511 | 0.319 | 0.679 | 2.816 | 0.836 | 0.065 | 2.709 |
| 4 | 347.20 | 0.151 | 0.449 | 0.435 | 0.563 | 2.390 | 0.851 | 0.072 | 2.295 |
| 5 | 345.69 | 0.208 | 0.392 | 0.547 | 0.451 | 2.265 | 0.818 | 0.076 | 2.282 |
| 6 | 345.30 | 0.261 | 0.339 | 0.626 | 0.372 | 2.086 | 0.787 | 0.077 | 2.183 |
| 7 | 345.38 | 0.361 | 0.239 | 0.729 | 0.269 | 1.748 | 0.803 | 0.076 | 1.795 |
| 8 | 345.96 | 0.437 | 0.163 | 0.825 | 0.173 | 1.587 | 0.727 | 0.073 | 1.786 |
| 9 | 347.92 | 0.498 | 0.102 | 0.890 | 0.108 | 1.456 | 0.699 | 0.069 | 1.704 |
| 10 | 351.28 | 0.568 | 0.032 | 0.950 | 0.048 | 1.302 | 0.924 | 0.065 | 1.132 |

[a]Standard uncertainty of T is 0.02 K, expanded uncertainties of $x_1$, $x_2$, $y_1$ and $y_2$ are 0.007; where, $x_i$ represents the mole fraction of component i in the liquid phase; $y_i$ is the mole fraction of component i in the vapour phase; $\gamma_i$ is the activity coefficient of component i in the liquid phase; T is the equilibrium temperature, K and $\alpha_{12}$ is the relative volatility of trimethyl borate and methanol.

TABLE-2
MODEL PARAMETERS FOR NONRANDOM TWO-LIQUID, UNIVERSAL QUASICHEMICAL AND WILSON

| Nonrandom two-liquid | $B_{12}$ | $B_{21}$ | $\alpha_{12}$ | $B_{13}$ | $B_{31}$ | $\beta_{13}$ | $B_{23}$ | $B_{32}$ | $\alpha_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| | Trimethyl borate (1) methanol (2) *N,N*-dimethylformamide (3) |
| | 512.7968 | 180.0411 | 0.2903 | 485.8754 | 206.7005 | 0.3000 | -81.5114 | -5.7626 | 3.3646 |
| | Trimethyl borate (1) methanol (2) *N,N*-dimethylacetamide (3) |
| | 512.7968 | 180.0411 | 0.2903 | 561.8631 | 16.6912 | 0.3000 | -773.5314 | 1822.057 | 0.3000 |
| Universal quasichemical | $b_{12}$ | | $b_{21}$ | $b_{13}$ | | $b_{31}$ | $b_{23}$ | | $b_{32}$ |
| | Trimethyl borate (1) methanol (2) *N,N*-dimethylformamide (3) |
| | 1251.5335 | | -151.9024 | 887.1396 | | -285.1197 | -162.3507 | | 103.5814 |
| | Trimethyl borate (1) methanol (2) *N,N*-dimethylacetamide (3) |
| | 1251.5335 | | -151.9024 | 861.926 | | -314.1367 | 157.1695 | | -343.605 |
| Wilson | $A_{12}$ | | $A_{21}$ | $A_{13}$ | | $A_{31}$ | $A_{23}$ | | $A_{32}$ |
| | Trimethyl borate (1) methanol (2) *N,N*-dimethylformamide (3) |
| | 323.6090 | | 1301.9443 | -160.7785 | | 2121.769 | 393.0227 | | -648.4471 |
| | Trimethyl borate (1) methanol (2) *N,N*-dimethylacetamide (3) |
| | 323.6090 | | 1301.9443 | -298.0089 | | 2461.014 | -555.1531 | | 1135.298 |

parameters were correlated from the ternary experimental vapour-liquid equilibrium data using the maximum likelihood method (nonrand-omness parameters are chosen as 0.3000), the objective function is shown as below:

$$F = \sum_{j=1}^{N} \left( \begin{array}{c} \sum_{i=1}^{C} \left( \dfrac{y_{j,i}^{exp} - y_{j,i}^{cal}}{\sigma_y} \right)^2 + \left( \dfrac{T_j^{exp} - T_j^{cal}}{\sigma_T} \right)^2 \\ + \left( \dfrac{P_j^{exp} - P_j^{cal}}{\sigma_P} \right)^2 + \sum_{i=1}^{C} \left( \dfrac{x_{j,i}^{exp} - x_{j,i}^{cal}}{\sigma_x} \right)^2 \end{array} \right)$$

where, N is the number of data points; C is the number of components; y is the mole fraction in vapour phase; x is the mole fraction in liquid phase; T is the equilibrium temperature, K; P is the equilibrium pressure, kPa; $\sigma_y$, $\sigma_T$, $\sigma_P$ and $\sigma_x$ are estimated standard deviations for y, T, P and x, respectively ($\sigma_y = 0.007$, $\sigma_T = 0.02$ K, $\sigma_P = 0.05$ kPa, $\sigma_x = 0.007$); superscripts [exp] and [cal] denote the experimental and calculated values, respectively.

The maximum absolute deviation $\Delta_y$, mean absolute deviation $\sigma_y$ and standard deviation $\delta_y$ between the experimental and calculated values of vapour phase mole fractions are calculated by the following equation[13]:

$$\Delta y = \max|y^{exp} - y^{cal}|;$$

$$\sigma_y = \frac{1}{N} \sum_{i=1}^{N} \left| y^{exp} - y^{cal} \right|;$$

$$\delta_y = \sqrt{\frac{1}{N-1} \sum_{i=1}^{N} \left( y^{exp} - y^{cal} \right)^2}$$

Deviations of the temperature are calculated using the same method. Results of the deviations are listed in Table-3.

The Y-X phase diagram is shown in Fig. 1, where $x_1'$ is the mole fraction of trimethyl borate in liquid-phase excluding the solvent. Fig. 1 shows that the relative volatility of trimethyl borate to methanol can be obviously enhanced by *N,N*-dimethylacetamide, while *N,N*-dimethylformamide can not completely eliminate the azeotrope. Moreover, the predicted values were relatively conservative than experimental ones. The T-xy diagram is shown in Fig. 2. It can be seen that the solvents elevated the equilibrium temperature. nonrandom two-liquid model were superior to the other two models in vapour-liquid equilibrium data correlation. Fig. 3 shows the azeotrope and tie lines of the ternary system, solvent concentration in the vapour phase approximates zero.

**Conclusion**

Vapour-liquid equilibrium data were predicted and determined for the ternary system of trimethyl borate-methanol-*N,N*-dimethylformamide  and trimethyl borate-methanol-*N,N*-dimethylacetamide at 101.3 kPa. The nonrandom two-liquid model, universal quasichemical model and Wilson model were  used to correlate the data. Results showed that the nonrandom two-liquid model was rather suitable to express the phase equilibrium behavior. Prediction by quantum mechanics calculation serves to provide vapour-liquid equilibrium data conservatively. This is good information for further simulations, as simulation always overestimates separation efficiency. *N,N*-dimethylacetamide is found to be better performed as a solvent than *N,N*-dimethylformamide,

TABLE-3
MAXIMUM ABSOLUTE DEVIATION Δ, MEAN ABSOLUTE DEVIATION σ AND STANDARD DEVIATION
δ BETWEEN EXPERIMENTAL DATA AND CALCULATED VALUES BY NONRANDOM TWO-LIQUID MODEL

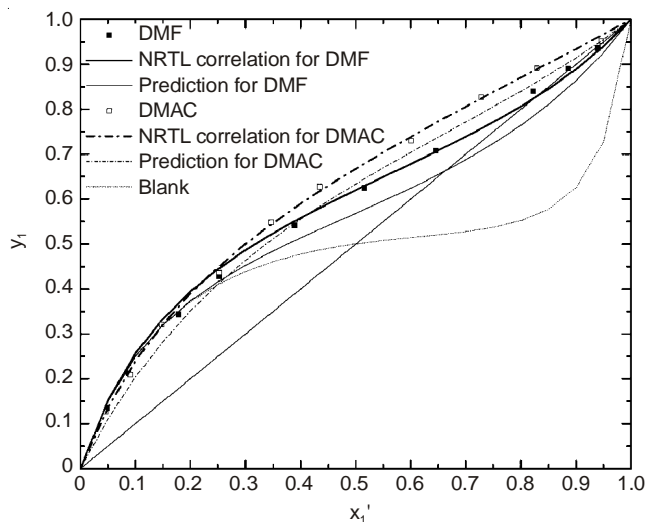| | Maximum absolute deviation (Δ) | Mean absolute deviation (σ) | Standard deviation (δ) |
|---|---|---|---|
| Trimethyl borate-methanol-*N,N*-dimethylformamide |
| Temperature (K) | 0.410 | 0.107 | 0.160 |
| y | 0.019 | 0.011 | 0.013 |
| Trimethyl borate-methanol-*N,N*-dimethylacetamide |
| Temperature (K) | 0.310 | 0.119 | 0.162 |
| y | 0.025 | 0.008 | 0.012 |

Fig. 1.  Y-X phase diagram for the ternary systems of trimethyl borate (1) methanol (2) *N,N*-dimethylformamide (3) and trimethyl borate (1) methanol (2) *N,N*-dimethylacetamide (3)
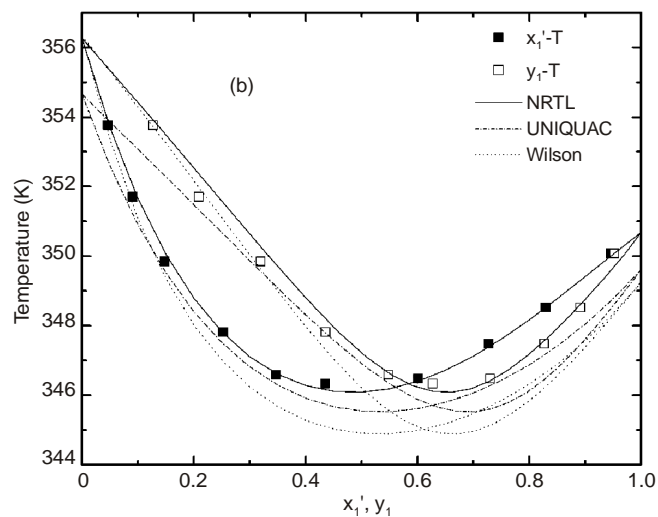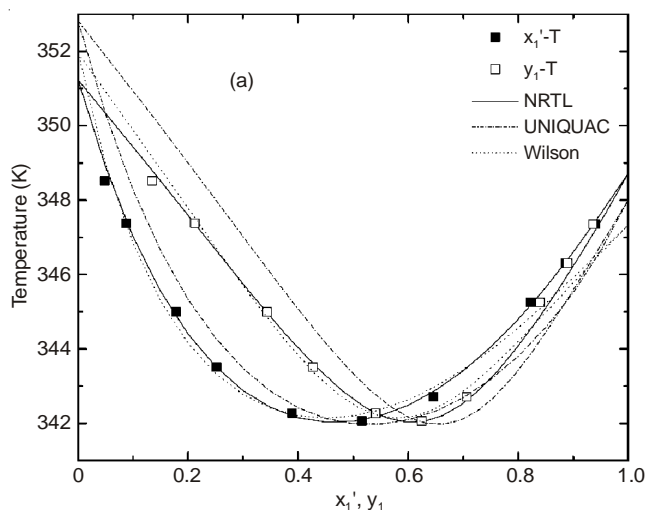


Fig. 2.  T-xy diagrams for the ternary systems of (a): trimethyl borate (1) methanol (2) *N,N*-dimethylformamide (3); (b): trimethyl borate (1) methanol (2) *N,N*-dimethylacetamide (3)
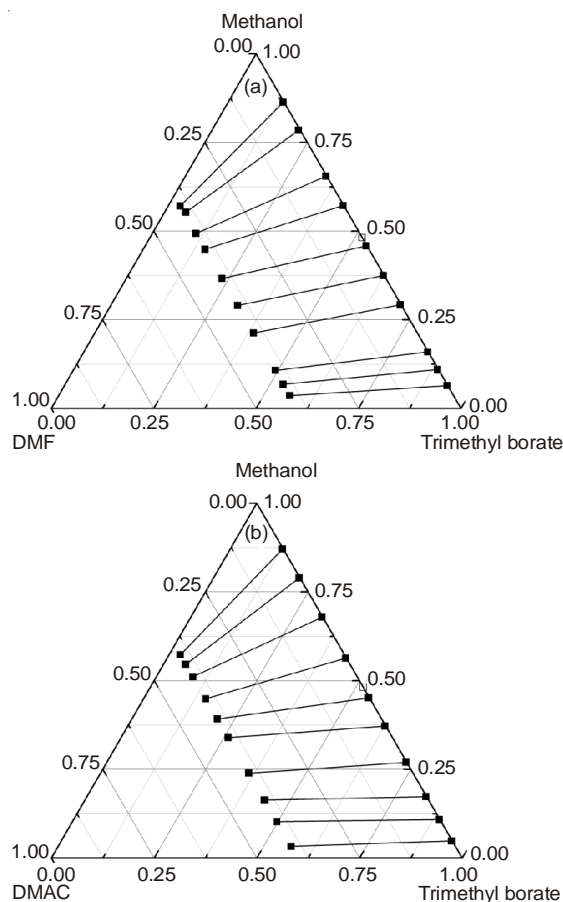


Fig. 3.  Tine lines for the ternary systems of (a): trimethyl borate (1) methanol (2) *N,N*-dimethylformamide (3); (b): trimethyl borate (1) methanol (2) *N,N*-dimethylacetamide (3)

which can be recommended to be a potential solvent applied in the separation of trimethyl borate and methanol.

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