INTRODUCTION

Trimethyl borate \([\text{B(OCH}_3\text{)}_3]\) is an important reagent utilized in many fields, such as catalyst, auxiliary solvent in brass-welding and high-energy fuel in aircrafts. It is synthesized in two ways, one is reaction of boric acid and methanol, the other is reaction of borax, sulfuric acid and methanol. Both ways produce a mixture of trimethyl borate and methanol. Trimethyl borate and methanol form an azeotrope at 328.37 K at 101.3 kPa, which contains 77-78 % (wt. %) trimethyl borate\(^1\). The azeotrope must be separated in order to facilitate the reaction. Industrially, sulfuric acid is applied to dealcoholize the mixture, however, the product is impure and corrosive. New substitutive methods need to be found.

Separation of azeotropes remains a hot issue for chemical engineers, in which a multitude of methods are used, such as, extractive distillation, pressure swing distillation, azeotropic distillation. Extractive distillation is superior to pressure swing distillation when utilized in pressure-insensitive mixtures, which is superior to azeotropic distillation in solvent recovery process as no new azeotrope is formed. However, solvent selection is the main concern for extractive distillation process. More recently, computer-aided molecular design (CAMD) is developed as a novel tool in solvent selection\(^4\). Usually, performance of selected solvents need to be assessed in order to prevent major flaws produced by computer-aided molecular design.

The assessment includes experimental determination of vapour-liquid equilibrium data of the given ternary system. This is achieved by fixing the proper solvent concentration in the mixture and comparing the relative volatility that altered\(^5\). The measurement is easy to carry out, meanwhile, it is a mature technique that has been reported by many researchers recently\(^6-8\).

Dimethyl sulfoxide and \(N\)-methyl-2-pyrrolidinone are two commonly used polar solvents. vapour-liquid equilibrium data for trimethyl borate-methanol-dimethyl sulfoxide and trimethyl borate-methanol-\(N\)-methyl-2-pyrrolidinone are not found in open literatures. In this work, ternary data of the two systems were measured at 101.3 kPa and were correlated by the non-random two-liquid model, universal quasichemical model and Wilson model. Binary interaction parameters were obtained.

EXPERIMENTAL

All reagents were purchased from Tianjin Guangfu Fine Chemical Research Institute. The purity grade of anhydrous methanol was HPLC, trimethyl borate and \(N\)-methyl-2-pyrrolidinone were AR, dimethyl sulfoxide was GR. Their purities checked by gas chromatography were all 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, dimethyl sulfoxide and \(N\)-methyl-2-pyrrolidinone determined by Karl Fischer titration were all less than 500 ppm.

The vapour-liquid equilibrium data were measured by a enhanced method as described\(^9\). The equilibrium temperature was measured by a precision and calibrated thermometer with

Vapour-liquid equilibrium data for trimethyl borate-methanol-dimethyl sulfoxide and trimethyl borate-methanol-\(N\)-methyl-2-pyrrolidinone were measured at 101.3 kPa. The data were fitted to the frequently used models: non-random two-liquid, universal quasichemical and Wilson. Results proved that the vapour-liquid equilibrium data agreed well with the non-random two-liquid model. Addition of both solvents produced notable effect on the relative volatility of trimethyl borate to methanol. An interesting phenomenon is that the optimum solvent performance occurs at totally different concentration of trimethyl borate. This indicates an enhancing solvent effect could be brought about by combination of the two solvents.

Keywords: Vapour-liquid equilibrium, Azeotrope, Trimethyl borate, Methanol, Dimethyl sulfoxide, \(N\)-methyl-2-pyrrolidinone.
an accuracy of ± 0.01 K. Phase equilibrium was supposed to be achieved when constant boiling temperature was gained for about 30 min. Then vapour and liquid samples were simultaneously taken every 20 min and the temperature was recorded. To verify the equilibrium state, samples were taken until the compositions of the last five samples have standard deviations of less than ±0.0015 for both vapour and liquid phase. The whole process lasts for about 3 h 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 by means of a buffer bottle and a three-way valve pressure controller. The solutions were prepared gravimetrically using an electronic balance (Hengping FA1004) with a standard uncertainty of ±0.0001 g.

**Sample analysis:** The compositions of the condensed vapour and liquid phase were analyzed by gas chromatography (GC). The GC (GC-2010) is equipped with a flame ionization detector (FID) and the column is SE-30 (50m × 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. Assessments of the calibration curves were done using three samples with known compositions. 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 95% confidence).

**RESULTS AND DISCUSSION**

Vapour-liquid equilibrium for the ternary systems of trimethyl borate (1) methanol (2) dimethyl sulfoxide (3) and trimethyl borate (1) methanol (2) N-methyl-2-pyrrolidinone (3) were measured at 101.3 kPa and the mole fraction of solvent added to the system was kept at x₃ = 0.4. The vapour-liquid equilibrium data are shown in Table-1.

**Correlation of the vapour-liquid equilibrium data:** The non-random two-liquid model, universal quasichemical model and Wilson model were chosen to correlate the experimental vapour-liquid equilibrium data. The results have been listed in Table-2. In the table, binary interaction coefficients and non-randomness parameter for trimethyl borate-methanol were obtained from Gmehling’s handbook, while binary interaction coefficients and non-randomness parameter for methanol-DMSO were obtained from ChemCAD build-in database. The other parameters were correlated from the ternary experimental vapour-liquid equilibrium data using the maximum likelihood method, the objective function is shown as below:

\[
F = \frac{1}{N} \sum_{i,j} \left( \frac{(y_{ij}^{exp} - y_{ij}^{cal})^2}{\sigma_{y_{ij}}} + \frac{(T_i^{exp} - T_i^{cal})^2}{\sigma_{T_i}} + \frac{(P_i^{exp} - P_i^{cal})^2}{\sigma_{P_i}} + \frac{(x_{ij}^{exp} - x_{ij}^{cal})^2}{\sigma_{x_{ij}}} \right)
\]

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); \(\sigma_{y_{ij}}\), \(\sigma_{T_i}\), \(\sigma_{P_i}\) and \(\sigma_{x_{ij}}\) are estimated standard deviations for y, T, P and x, respectively (\(\sigma_{y_{ij}} = 0.007\), \(\sigma_{T_i} = 0.02\ K\), \(\sigma_{P_i} = 0.05\ kPa\), \(\sigma_{x_{ij}} = 0.007\); superscripts exp and cal denote the experimental and calculated values, respectively.

| No. | T (K) | x₁ | x₂ | x₃ | y₁ | y₂ | y₃ | y₁⁺ | y₂⁺ | y₃⁺ |
|-----|-------|----|----|----|----|----|----|-----|-----|-----|
| Trimethyl borate (1) methanol (2) dimethyl sulfoxide (3) | | | | | | | | | | |
| 1   | 353.34| 0.029| 0.571| 0.173| 0.825| 4.346| 0.260| 4.060 |
| 2   | 351.39| 0.061| 0.539| 0.289| 0.709| 3.752| 0.365| 3.506 |
| 3   | 346.65| 0.119| 0.481| 0.463| 0.535| 3.455| 0.189| 3.430 |
| 4   | 342.60| 0.184| 0.416| 0.601| 0.397| 3.108| 0.765| 3.430 |
| 5   | 341.21| 0.278| 0.322| 0.681| 0.318| 2.455| 0.843| 2.487 |
| 6   | 341.01| 0.374| 0.226| 0.762| 0.237| 2.023| 0.885| 2.194 |
| 7   | 341.23| 0.451| 0.149| 0.837| 0.162| 1.791| 0.866| 1.715 |
| 8   | 342.00| 0.523| 0.077| 0.902| 0.206| 1.571| 0.947| 1.382 |
| 9   | 343.90| 0.531| 0.069| 0.912| 0.206| 1.552| 0.938| 1.376 |
| 10  | 350.68| 0.562| 0.038| 0.947| 0.051| 1.469| 0.966| 1.272 |

| No. | T (K) | x₁ | x₂ | x₃ | y₁ | y₂ | y₃ | y₁⁺ | y₂⁺ | y₃⁺ |
|-----|-------|----|----|----|----|----|----|-----|-----|-----|
| Trimethyl borate (1) methanol (2) N-methyl-2-pyrrolidinone (3) | | | | | | | | | | |
| 1   | 359.51| 0.031| 0.569| 0.144| 0.855| 3.203| 0.795| 3.130 |
| 2   | 356.03| 0.119| 0.481| 0.394| 0.605| 2.530| 0.774| 2.617 |
| 3   | 353.40| 0.184| 0.416| 0.507| 0.492| 2.219| 0.772| 2.328 |
| 4   | 350.16| 0.266| 0.334| 0.637| 0.362| 1.979| 0.728| 2.216 |
| 5   | 347.19| 0.343| 0.257| 0.713| 0.286| 1.703| 0.743| 1.866 |
| 6   | 346.21| 0.389| 0.211| 0.796| 0.203| 1.660| 0.635| 1.213 |
| 7   | 345.70| 0.449| 0.151| 0.806| 0.136| 1.513| 0.608| 2.014 |
| 8   | 345.68| 0.479| 0.121| 0.897| 0.102| 1.483| 0.537| 2.229 |
| 9   | 346.25| 0.520| 0.080| 0.925| 0.074| 1.397| 0.581| 1.935 |
| 10  | 348.56| 0.571| 0.029| 0.963| 0.036| 1.295| 0.767| 1.351 |

*Standard uncertainty of T is 0.02 K, expanded uncertainties of x₁, x₂, y₁ and y₂ are 0.007; where, xᵢ represents the mole fraction of component i in the liquid phase; yᵢ is the mole fraction of component i in the vapour phase; γᵢ is the activity coefficient of component i in the liquid phase; T is the equilibrium temperature (K); aᵢ is the relative volatility of trimethyl borate and methanol.*
Experimental data and the correlation curves have been plotted in Figs. 1-3. The correlation curves agree well with the experimental values. 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 equations:

$$
\Delta_y = \max |y_{\text{exp}} - y_{\text{cal}}|;
$$

$$
\sigma_y = \frac{1}{N} \sum_{i=1}^{N} |y_{\text{exp}}(i) - y_{\text{cal}}(i)|;
$$

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

Deviation of the temperature was 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. The azeotrope has been totally eliminated when mole fraction of the solvent is 0.4, which proves that dimethyl sulfoxide and N-methyl-2-pyrrolidinone are rather effective solvents. The same result can be observed from the $\alpha_{12}$ values in Table-1. The relative volatility of trimethyl borate to methanol can be enhanced by both solvents. This is due to the different polarity of the components. The interaction of methanol and the solvent is much stronger than that of trimethyl borate and the solvent. Thus, trimethyl borate becomes more volatile and the product of extractive column is trimethyl borate. The T-xy diagrams are shown in Fig. 2a b. It can be seen that the azeotrope is a minimum boiling point, with the addition of solvents, the boiling points increase, especially DMSO.

Tie lines for the ternary systems have been plotted in Fig. 3a b. Since $y_2$ is low enough ($y_2 \leq 0.002$), we may assume that the solvents are non-volatile, which is a favorable feature in separation practice. Moreover, the vapour phase points on the tie lines are expected to be close to the trimethyl borate point, which means more trimethyl borate enters vapour phase. Thus, tie lines that are horizontal even with negative slopes are preferred. In Fig. 3a b, both solvents have these types of tie lines, but the corresponding $x_1$ is lower for dimethyl sulfoxide than N-methyl-2-pyrrolidinone. This represents dimethyl sulfoxide

\begin{table}[h]
\centering
\caption{Model Parameters for Nonrandom Two-Liquid, Universal Quasichemical, and Wilson}
\begin{tabular}{ccccc}
\hline
 & $B_{12}$ & $B_{21}$ & $\alpha_{12}$ & $B_{13}$ & $B_{23}$ & $\alpha_{13}$ \\
\hline
Nonrandom & & & & & & \\
two-liquid & & & & & & \\
Trimethyl borate (1) methanol (2) DMSO (3) & 512.7968 & 180.0411 & 0.2903 & 675.8059 & 153.5397 & 0.3000 & -84.7012 & -250.3110 & 0.3079 \\
Trimethyl borate (1) methanol (2) N-methyl-2-pyrrolidinone (3) & 512.7968 & 180.0411 & 0.2903 & 699.5534 & -50.2283 & 0.3000 & -925.7337 & 1739.892 & 0.3000 \\
\hline
Universal & & & & & & \\
quasichemical & & & & & & \\
Trimethyl borate (1) methanol (2) DMSO (3) & 1251.5335 & -151.9024 & 914.1472 & 212.0281 & -336.7607 & 84.4189 \\
Trimethyl borate (1) methanol (2) N-methyl-2-pyrrolidinone (3) & 1251.5335 & -151.9024 & 856.6082 & -341.2015 & -916.1893 & 2265.926 \\
\hline
Wilson & & & & & & \\
& & & & & & \\
Trimethyl borate (1) methanol (2) DMSO (3) & 323.6090 & 1301.9443 & 21.0919 & 2459.702 & -75.9373 & -575.122 \\
Trimethyl borate (1) methanol (2) N-methyl-2-pyrrolidinone (3) & 323.6090 & 1301.9443 & -103.0976 & 1472.089 & -605.4467 & 1514.387 \\
\hline
\end{tabular}
\end{table}

\begin{table}[h]
\centering
\caption{Maximum Absolute Deviation $\Delta$, Mean Absolute Deviation $\sigma$ and Standard Deviation $\delta$ Between Experimental Data and Calculated Values by Nonrandom Two-Liquid Model}
\begin{tabular}{ccc}
\hline
 & Maximum absolute deviation $\Delta$ & Mean absolute deviation $\sigma$ & Standard deviation $\delta$ \\
\hline
Trimethyl borate-methanol DMSO & & & \\
Temperature (K) & 0.286 & 0.167 & 0.202 \\
y & 0.082 & 0.044 & 0.063 \\
Trimethyl borate-methanol N-methyl-2-pyrrolidinone & & & \\
Temperature (K) & 0.544 & 0.213 & 0.268 \\
y & 0.029 & 0.015 & 0.019 \\
\hline
\end{tabular}
\end{table}
sulfoxide leads to a large $\alpha_1$ at low $x_1$, while $N$-methyl-2-pyrrolidinone brings about high separation efficiency at high $x_1$. This conclusion is also proved by Fig. 1. We would suppose that the mixture of dimethyl sulfoxide and $N$-methyl-2-pyrrolidinone could probably produce more satisfactory separation effect.

**Conclusion**

Vapour-liquid equilibrium data were determined for the ternary system of trimethyl borate-methanol-dimethyl sulfoxide and trimethyl borate-methanol-$N$-methyl-2-pyrrolidinone at 101.3 kPa. The non-random two-liquid model, universal quasichemical model and Wilson model were used to correlate the data. Results showed that non-random two-liquid model was rather suitable to express the phase equilibrium behavior. Both solvents can greatly enhance the relative volatility of trimethyl borate to methanol. Specifically, dimethyl sulfoxide leads to a large relative volatility at low trimethyl borate concentrations, while $N$-methyl-2-pyrrolidinone brings about high separation efficiency at high trimethyl borate concentrations.

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