Liquid–liquid equilibrium data and correlation for quaternary systems of acetic acid + water + methyl acetate + p-xylene at 313.2 K

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The experimental liquid–liquid equilibrium (LLE) data of the quaternary (acetic acid + water + p- xylene + methyl acetate) system was investigated at 313.2 K and atmospheric pressure. This research is aimed to examine the potential of the mixture of methyl acetate and p-xylene, which available as the remaining substances in terephthalic acid production, to be prospective extracting solvent for the acetic acid dehydration. LLE phase diagrams at different ratio of p-xylene to methyl acetate were presented for this quaternary system. The results showed that an enlargement of the LLE two-phase region occurred with increasing p-xylene to methyl acetate mass ratio in the initial solvent phase. The distribution coefficient and selectivity for the extraction of acetic acid were also obtained to evaluate the capability of solvent. LLE data were sufficiently correlated by Othmer-Tobias and Bachman equations. The experimental results were used to obtain binary interaction parameters as correlated by the non-random two liquid (NRTL) and universal quasi-chemical theory (UNIQUAC) equation models. The root mean square deviations (RMSD) values as low as 0.0119 and 0.0128 were calculated for NRTL and UNIQUAC, respectively; indicating excellent results for both models were suitable for the determination of LLE data of this quaternary system.

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Introduction

Acetic acid (HAc) is a vital chemical material with a wide range of applications in the production of acetic anhydride, terephthalic acid, vinyl acetate, vitamins, and other chemicals [1–3]. In terms of these applications, high purity HAc is essential. Thus, the extraction of HAc from its aqueous mixtures is an important project. The economics of the process are contingent on the development of an effective recovery system. In particular, in the industrial HAc dehydration system of a terephthalic acid (TPA) plant, there is unreacted p-xylene (PX) and by-product methyl acetate (MA) in the feed in addition to just HAc and water. Consequently, this system contains four components, including MA, PX, HAc, and water. The physical quaternary system is complex because of its multi-boiling point, homogeneous azeotropes and heterogeneous azeotropes, particularly its strong non-ideality of the vapor phase caused by the association of HAc [4,5].

Furthermore, to solve the problem of HAc dehydration, this study evaluates fundamental stage for the possibility of hybrid liquid–liquid extraction and distillation as an effective method for HAc extraction from an aqueous solution, containing water, HAc, MA, and PX. A stringent analysis is crucial for choosing the appropriate solvent in the extraction process. Isopropenyl acetate [6], cyclohexanone [7], cyclohexane [8], ethyl heptanoate [9], 2-ethyl hexyl acetate [10] have been suggested to extract HAc from the water. On the other hand, MA, which previously occurred in the system, is expected to be used as a mixed solvent with PX. An evaluation of the mixed solvent for HAc extraction is essential because of the simplicity of the subsequent separation process. In TPA production plants, this mixed solvent can reduce the cost and the complexity of the process by having no further separation of HAc from the solvent. Therefore, the use of MA and PX produced in an earlier process can take an important advantage for HAc extraction from water than using other solvents.

In the quaternary system of the HAc dehydration process, atmospheric pressure is applied. The isobaric binary vapor-liquid

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equilibrium (VLE) data at atmospheric pressure has been measured by several authors, such as HAc + PX, MA + PX by Huang et al. [11], HAc + Water by Vercher et al. and Toikka et al. [12,13], HAc + PX by Marek [14], HAc + MA by Sawistowski and Pilavakis [15], Water + MA by Perelygin [16], and Water + PX by Xiao et al. [17]. Therefore, for distillation purposes using the VLE data of six binary mixtures, the data currently available can be used to design a distillation process.

Moreover, liquid–liquid equilibrium (LLE) investigations for ternary and quaternary mixtures have been performed in numerous industrial separation processes [18–25], particularly for the liquid–liquid extraction process. Liquid–liquid phase equilibrium investigations of this quaternary system have attracted considerable interest because there is no report of LLE data and binary parameters of this quaternary system. As this study proposes four components mixed together as a quaternary system, the LLE data obtained will be compatible with actual plant conditions.

The design of an apparatus and determining the optimal operating conditions of liquid–liquid extractor require knowledge of the LLE data. The LLE binary parameters in the non-random two-liquid (NRTL) and universal quasichemical activity coefficient (UNIQUAC) models of this quaternary system are unavailable in the commercial process simulator. These two activity coefficient models were used to demonstrate their predictive capacities for the resulting data behavior.

This study was carried out to provide essential LLE data and model related to HAc dehydration at a pilot extractor. Therefore, the experimental data of each quaternary system were obtained at 313.2 K and atmospheric pressure based on the real operating condition. The experimental results on the composition of the coexisting phases of a series of quaternary mixtures of the components were acquired. Quantitative analysis was performed by gas chromatography and the Karl Fischer titration method. The resulting experimental data was regressed using both models to obtain the binary parameters. The binary parameter data of this quaternary system is essential in the simulation, design, and optimization of this hybrid extraction and distillation process.

**Experimental**

**Materials**

Methyl acetate (>99.5%), acetic acid (>99.5%) and p-xylene (>99%) were obtained from ACROS. The purity of the chemicals was confirmed by gas chromatography, and all chemicals were used as received. Table 1 lists the purity of the chemicals produced by the company. In addition, HPLC grade water was purchased from Duksan.

**Apparatus and experimental procedure**

The apparatus used to obtain the experimental tie-line data consisted of a 50 ml glass round-bottomed flask (SIMAX) and a separating funnel (LK Lab Korea 100 ml). Each component was added to the vessel by mass at known ratios. The quaternary mixtures samples were weighed on an analytical balance (AnD fx-200i) with an estimated uncertainty of 0.001 g.

According to results from the preliminary tests, at a constant temperature (313.2 K) and atmospheric pressure, the heterogeneous mixtures were stirred (1100 rpm) for at least 8 h with a magnetic stirrer and allowed to settle for a minimum of 15 h in the oven (WiseVen) at the same temperature to reach complete phase separation. The stirring and settlement times were determined when the composition of the solvent-rich phase and water-rich phase remained largely unchanged. During the agitation process, the temperature was measured with a mercury-in-glass thermometer with the uncertainty of ±0.1 K, and for the settlement, the separatory funnel was remained inside of the oven to preserve a constant temperature within ±0.1 K.

In this study, quaternary mixtures were prepared by combining mixtures of PX and MA as a mixed solvent, whose compositions were R1, R2, R3, R4, and R5, with water followed by the addition of HAc. The values of R1, R2, R3, R4, and R5 are approximately 4:1, 3:2, 1:1, 2:3, and 1:4 in PX to MA mass ratios. Fig. 1 presents an illustration of the mass ratio used in this quaternary system.

**Analytical methods**

Samples from both layers were taken carefully and analyzed by gas chromatography (GC, Agilent 6890 N) with a flame ionization detector (FID). Chromatography separation of the mixture constituents was achieved using a capillary column Agilent DB-Wax with a 30 m × 0.25 mm. The inlet pressure of the carrier nitrogen gas was set to 1.5 bar and the temperatures of both the detector and injector were set to 553.2 K and 523.2 K, respectively. In this mixture, the oven temperature was programmed as follows: the initial temperature was set to 313.2 K for 4 min, followed by a constant heating rate of 8 K/min until a final temperature of 423.2 K. The final temperature was kept for 3.5 min and the cycle was repeated. The method of internal normalization and relative calibration were used to calculate compositions of equilibrium liquid phases. The standard uncertainty for the component mass fractions is estimated as follows, \( u(W_{HAc}) = 0.0021, u(W_{PX}) = 0.0017, \) and \( u(W_{MA}) = 0.0015 \).

Water analysis was performed using a Karl Fischer coulometer (Model-KF 831, Metrohm, Switzerland) with the uncertainty of ±0.01 g/kg. By using oven auto-sampler (Mettler Toledo), a small amount of sample (0.01–0.1 g) was added to an isolated glass chamber containing the Karl Fischer solvent HYDRANAL™ (Sigma-Aldrich). Under the atmospheric pressure, the isolated glass chamber was heated to 433.2 K to vaporize all the components. The high purity air was supplied in that closed system at a flow rate 50 ml/min. The

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**Table 1**

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Source</th>
<th>Purity(%)mass</th>
<th>UNIQUAC parameters [26]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>r</td>
</tr>
<tr>
<td>Methyl acetate</td>
<td>ACROS</td>
<td>&gt;99.5</td>
<td>2.80422</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>ACROS</td>
<td>&gt;99.5</td>
<td>2.19512</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>ACROS</td>
<td>&gt;99.0</td>
<td>4.65788</td>
</tr>
<tr>
<td>Water</td>
<td>Duksan</td>
<td></td>
<td>0.92</td>
</tr>
</tbody>
</table>

**Fig. 1.** Quaternary diagram of acetic acid (HAc) + water + p-xylene (PX) + methyl acetate (MA) illustrating the mass ratios used at 313.2 K for the tie-line measurements.
standard uncertainty for the water mass fractions measured was estimated as $\nu(W_{\text{water}}) = 0.0012$. All GC and Karl Fischer measurements were carried out in triplicate. Owing to the combination of analysis equipment, mathematical manipulation was needed to calculate the mass ratio of all components.

**Data regression and correlation**

The Aspen Plus physical parameter regression system has been proven to be a powerful simulator to regress and correlate the experimental data for obtaining binary parameters [27–34]. In this study, Aspen Plus v8.4 simulator was used for mathematical modeling to build up the regression parameter. This software was used because of its flexibility in performing the simulation in further steps. Six effective NRTL and UNIQUAC binary interaction parameters are determined for a quaternary system at a constant temperature. Fig. 2 shows a flow chart of data regression from the LLE experiments to obtain the predicted data, and the reliability of experimental and correlation data with numerous mathematical equations.

**Results and discussion**

**Experimental results**

The extraction temperature of HAC extraction subsequent to TPA production is desired at 313.2 K and atmospheric pressure. This condition was selected because the aqueous solution fed to the extractor column previously comes from the top product of a distillation column in the upstream process, and its temperature needs to maintain at 313.2 K to avoid the possible crystallization of HAC during the process. Therefore, the experimental liquid–liquid equilibrium data for the quaternary system involving MA + PX + water + HAC at a desired temperature and pressure were performed, as shown in Table 2. The data given in Table 2 were shown as a mass fraction. The compositions of the feed mixtures for examining the LLE were chosen so that the compositions of the organic and aqueous phases (tie-lines) could be well-ordered consistently on an LLE triangular diagram. To achieve the proper analysis using a mixed solvent of PX and MA, the experimental data were also displayed in a triangular diagram, as shown in Fig. 3. The area sizes of immiscibility in the quaternary system increased while the PX to MA mass ratio increased. Most of the water occurred in the aqueous phase and PX was observed in the organic phase. This shows that PX must be in excess compared to MA to achieve high separation efficiency.

The distribution coefficient and selectivity equation were used as preliminary data to evaluate PX+MA as a mixed solvent to separate water from HAC, and the values are listed in Table 2. These calculations are important parameters for liquid–liquid extraction to emphasize the effects of the mixed PX to MA ratio on the phase distribution of HAC and water. The respective equations are as follows:

$$D_1 = \frac{w_1^f}{w_1^i}; \quad D_2 = \frac{w_2^f}{w_2^i}; \quad S_{1.2} = \frac{D_1}{D_2}$$

where $D_1$ and $D_2$ are the distribution coefficient of HAC and water, respectively, $w_1^f$ and $w_2^f$ are the mass fraction of HAC and water in the aqueous phase, respectively, $w_1^i$ and $w_2^i$ are the mass fraction of HAC and water in the organic phase, respectively, and $S_{1.2}$ is the selectivity of HAC from the water. To indicate the separation effect for different ratio of PX to MA more clearly, Fig. 4 shows the dependence of selectivity on the water/HAC mass ratio in the initial mixture for various ratios of PX to MA in the initial mixture. In general, as the new mixed solvent proposed here, the value of its selectivity is higher than other solvents that proposed earlier by Demirel and Cehreli [9] and also from Ince and Lalikогlu [10]. These results reveal the general capability of mixed solvent to extract HAC from the aqueous phase at different feed composition. As mentioned earlier, MA has been put up in this industrial operation, since it was available as the byproduct of TPA production. As can be seen in Fig. 4, a higher ratio of PX to MA can produce higher selectivity of HAC against water. It showed the positive influence of the high amounts of PX on the selectivity. This is coherent with the idea that adding PX into MA as a mixed solvent could lead to enhance the values of capacity of extraction and selectivity of HAC against water. This result showed PX is powerful enough to be considered as the feasible solvent when mixed with MA. Likewise, the use of PX as solvent for the particular application of the industrial TPA production is expected to offer extra benefits since this substance already present in the process as main reactant.

Reliable phase equilibrium data are the key to the design and assessment of industrial unit operations in extraction processes. Up to now, the reliability of the experimental data can be determined by applying the well-known Othmer-Tobias [35] and Bachman [36] correlations. The correlations are given by Eqs. (2) and (3), respectively. Table 3 lists the parameters for each plot correlation ($a$ and $b$) together in those equations and the regression coefficients ($R^2$) which were taken as a means to estimate the reliability of the experimental data are listed in Table 2. The $R^2$ values, which indicate the degree of consistency of the measured LLE data, were $\geq 0.95$. This highlights the good consistency and high reliability of the experimental data.

**Othmer-Tobias equation:**

$$\ln \left( \frac{1-W_{\text{HAC}}}{W_{\text{water}}} \right) = a + b \ln \left( \frac{W_{\text{HAC}}}{W_{\text{water}}} \right)$$

**Bachman equation:**

$$W_{\text{HAC}} = a + b \left( \frac{W_{\text{HAC}}}{W_{\text{water}}} \right)$$

where I: organic phase, II: aqueous phase.

**Data regression and correlation**

Reliable thermodynamic methods are extremely important for process simulation and design of this extraction process. This LLE experimental data was used to assess the LLE predictive capability of some liquid–phase models. The mathematical models used in this study were NRTL [37] and UNIQUAC [38]. Both models were used as programmed into the Aspen Plus simulator. The adjustable parameters of those two models are defined as follows:
Table 2
LLE experimental data (mass fraction), values of the distribution coefficients ($D_i$ and $D_j$), and selectivity ($S_{i,j}$) for the quarternary system, HAc + PX + MA + Water, at 313.2 K under atmospheric pressure$^a$.

<table>
<thead>
<tr>
<th>Set</th>
<th>Organic phase</th>
<th>Aqueous phase</th>
<th>Calculation parameters</th>
</tr>
</thead>
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<tr>
<td></td>
<td>$W_{Wa}$</td>
<td>$W_{Wa}$</td>
<td>$W_{Pi}$</td>
</tr>
<tr>
<td></td>
<td>R1</td>
<td>0.0003</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>R2</td>
<td>0.0008</td>
<td>0.0117</td>
</tr>
<tr>
<td></td>
<td>R3</td>
<td>0.0009</td>
<td>0.0048</td>
</tr>
<tr>
<td></td>
<td>R4</td>
<td>0.0024</td>
<td>0.0036</td>
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<td></td>
<td>R5</td>
<td>0.0018</td>
<td>0.0015</td>
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<tr>
<td></td>
<td>R6</td>
<td>0.0085</td>
<td>0.0011</td>
</tr>
<tr>
<td></td>
<td>R7</td>
<td>0.0043</td>
<td>0.0013</td>
</tr>
<tr>
<td></td>
<td>R8</td>
<td>0.0023</td>
<td>0.0012</td>
</tr>
<tr>
<td></td>
<td>R9</td>
<td>0.0063</td>
<td>0.0029</td>
</tr>
<tr>
<td></td>
<td>R10</td>
<td>0.0009</td>
<td>0.0037</td>
</tr>
</tbody>
</table>

$^a$ Standard uncertainties u are u(T)=0.1 K, u(p)=1 kPa, u($W_{Wa}$)=0.0012, u($W_{Pi}$)=0.0021 u($W_{Pi}$)=0.0017, and u($W_{MA}$)=0.0015.

**NRTL equation:**

$$\ln y_i = \sum_{j} x_j \frac{G_{ij}}{G_{ij}} - \left( \sum_{j} x_j \frac{G_{ij}}{G_{ij}} \right) + \sum_{j} \frac{x_j G_{ij}}{x_j G_{ij}} \left( \frac{\sum x_k G_{kj}}{x_k G_{kj}} \right)$$

**UNIQUAC equation:**

$$\ln y_i' = \ln \frac{\Phi_i}{x_i} + \frac{x_i}{2} q_i \ln \frac{\Phi_i}{q_i} - q_i' \ln t_i' - q_i' \sum_j \theta_j q_i j$$

**Equations:**

1. $G_{ij} = \exp(-\alpha_i \tau_{ij})$
2. $\tau_{ij} = a_{ij} + \frac{b_{ij}}{T}$
3. $\alpha_i = 0$
4. $G_{ii} = 1$

where $x$ is the mole fraction, $\tau_{ij} (\neq \tau_{ji})$ is the interaction parameter, $\alpha_i$ is the non-randomness parameter.

Fig. 3. LLE phase diagram for the system mixed solvent (PX + MA) + HAc + Water at 313.2 K (○—experimental, ▲—NRTL model): (a) $R_1 = 4:1$, (b) $R_2 = 3:2$, (c) $R_3 = 1:1$, (d) $R_4 = 2:3$, (e) $R_5 = 1:4$. Standard uncertainties for the mass fraction of four components $u$ are $u(T) = 0.1$ K, $u(p) = 1$ kPa, $u(W_{\text{HAc}}) = 0.0012$, $u(W_{\text{MA}}) = 0.0021$ $u(W_{\text{PX}}) = 0.0017$, and $u(W_{\text{HAc}}) = 0.0015$. 
Fig. 4. The selectivity of acetic acid against water (Sij) vs water/acetic acid mass ratio in the initial mixture phase for different ratio of PX to MA (R₁ to R₃) at 313.2 K and under atmospheric pressure.

\[ l_i = \frac{Z}{2} (r_i - q_i) + 1 - r_i \]  
\[ c'_{ij} = \sum k \theta_{ji} \]  
\[ r_{ij} = \exp \left( a_{ij} + \frac{b_{ij}}{T} + c_{ij} \ln T \right) \]

where \( \Phi \) is the segment fraction; \( \theta \) is the area fraction; \( r \) and \( q \) are the pure component relative volume and surface area parameters, respectively; \( r_{ij} \) is the interaction parameter; \( z \) is the number of close interacting molecules around a central molecule and was set to 10.

The binary interaction parameters of NRTL and UNIQUAC models were obtained using the data regression of the Aspen Plus simulator. Since the experiment was carried out at a single temperature point; the \( a_{ij} \) parameter of those two models was set to zero in the process of regression calculations. Particularly for UNIQUAC activity model, the value of UNIQUAC structural parameters \( (r \text{ and } q) \) of this quaternary system can be seen in Table 1. These binary interaction parameters were determined by minimizing the deviation between the experimental data and model-calculated values. The minimization process involves calculating the mass fraction for a given set of parameters from which a new set of parameters will arise. The computation is continued until the value of the objective function is smaller than a prescribed tolerance. The following objective function (OF) was used:

\[ OF = \sum_{i=1}^{m} \sum_{j=1}^{n} \left( \frac{T_{ij}^{\text{cal}} - T_{ij}^{\text{exp}}}{\sigma^2_{T}} \right)^2 + \left( \frac{w_{ij}^{\text{cal}} - w_{ij}^{\text{exp}}}{\sigma^2_{w}} \right)^2 \]

Table 3
<table>
<thead>
<tr>
<th>PX:MA</th>
<th>Otherm-Tobias</th>
<th>Bachman</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( a )</td>
<td>( b )</td>
</tr>
<tr>
<td>4:1</td>
<td>-0.8083</td>
<td>3.2967</td>
</tr>
<tr>
<td>2:2</td>
<td>-0.8203</td>
<td>3.3908</td>
</tr>
<tr>
<td>3:1</td>
<td>-0.8616</td>
<td>3.4863</td>
</tr>
<tr>
<td>2:3</td>
<td>-1.0286</td>
<td>4.0102</td>
</tr>
<tr>
<td>1:4</td>
<td>-1.1115</td>
<td>4.1697</td>
</tr>
</tbody>
</table>

where \( m \) and \( n \) are the number of components and the number of tie-lines, respectively, \( w_{\text{cal}} \) and \( T_{\text{cal}} \) are the experimental mass fraction and temperature, respectively, and \( w_{\text{cal}} \) and \( T_{\text{cal}} \) are the calculated mass fraction and temperature, respectively. The subscripts \( i, j \) and \( k \) denote the component, phase and tie-line, respectively. \( \sigma_T \) and \( \sigma_w \) refer to the standard deviation of the temperature and mass fraction, respectively.

Table 4 lists the binary parameters retrieved from Aspen Plus, resulting from the NRTL and UNIQUAC models, respectively. The new Britt-Luecke [39] algorithm was used in Aspen Plus to obtain the NRTL and UNIQUAC model parameters. The regression convergence tolerance was set to 0.0001. In the NRTL model, the non-randomness parameters, \( c_{ij} \), were chosen to 0.3 as recommended commonly while those for the liquid–liquid immiscible binaries such as water-PX and water-MA were set to 0.2. The regression method used in the Aspen Plus simulator is the generalized least-squares method based on the maximum likelihood principle.

The quality of experimental LLE data and the calculated results for each activity model was measured by root mean square deviations (RMSD). The RMSD values were calculated from the difference between the experimental and calculated mass percentages. Therefore, to illustrate the accuracy of the models, Table 4 lists RMSD values calculated using both models at \( T = 313.2 \) K. The RMSD is defined as follows:

\[ \text{RMSD} = \sqrt{\frac{\sum_{i=1}^{n} \sum_{j=1}^{2} \sum_{k=1}^{3} \left( \frac{w_{ij}^{\text{cal}} - w_{ij}^{\text{exp}}}{\delta n} \right)^2}{\delta n}} \]

Low RMSD values indicate that both models accurately correlated the experimental tie-line data and exhibits acceptable agreement. Particularly the correlation of the NRTL model was superior to that of the UNIQUAC model. Fig. 3 also presents the comparison of the curves calculated from the NRTL model with the experimental results for the quaternary system. In addition, the low RMSD values for NRTL and UNIQUAC confirm the ability of these models provide the LLE data in this work. The proper activity coefficient model is extremely needed for the process simulation in the future [40]. Furthermore, successful correlation using the obtained binary interaction parameters by the simultaneous correlations (NRTL and UNIQUAC) of all the experimental LLE data of this quaternary system contributes to generating a reliable conceptual design and process simulation and optimization of HAc extraction from the water.

Conclusions

In this work, the LLE data of quaternary systems, HAc, water, MA, and PX were investigated at 313.2 K and under atmospheric pressure. The reliability of the LLE data of the quaternary system was evaluated using the Otherm-Tobias and Bachman correlations, and good consistency was achieved. The obtained equilibrium
phase diagrams of a mixed solvent (MA and PX), HAc and water have been shown. It was found that the immiscible area sizes in the quaternary system increased once the PX to MA mass ratio increased. The result showed this mixed solvent is powerful enough to be considered as the feasible solvent for HAc extraction because it also offers more benefits considering its availability as the main reactant and by-product in TPA production. Furthermore, the distribution coefficient and selectivity of the solvent were calculated to assess the ability of mixed solvent for HAc extraction from the aqueous phase. Both the NRTL and UNIQUAC models were applied to correlate the LLE data and the model parameters calculated. The calculated results by both models showed a good match with the experimental data. The results produced using the NRTL model was slightly better than those from the UNIQUAC model. Both models showed a low RMSD (0.0119 and 0.0128 for NRTL and UNIQUAC, respectively); indicating the validity of a simulation of extraction process in this quaternary system based on the NRTL and UNIQUAC models. Finally, the relevant binary parameters of this work will be used as essential data for the design of a multi-stage extractor column to extract HAc from water in the hybrid extraction and distillation process involving this quaternary system.

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