Liquid-Liquid Equilibrium and Tie-Line Data for Systems of Water + Acetic Acid + Organic Solvents (Chloroform, Dichloromethane, and Cyclohexane)

Vidhya C1, a) and S. Rijith2, b)

1Department of Chemistry, Mar Ivanios College, Thiruvananthapuram
2Department of Chemistry, Sree Narayana College, Kollam
a)vidhyacobose@gmail.com
b)rijithsreenivas@gmail.com

Abstract. Recent years have observed an immense significance for the separation of acetic acid from aqueous solution in the chemical industry. The work mainly examines the potential use of a suitable solvent for the recovery of acetic acid from an aqueous solution. Liquid–Liquid Equilibrium (LLE) plays an efficient and cost-effective role in the separation process. Hence, various studies have been conducted on the LLE of this system over a range of concentrations, and temperatures. The solubility and tie-line data for the ternary systems (Water + Acetic acid + Organic solvents) were determined at a temperature, T=303K. Organic solvents such as Chloroform, Dichloromethane, and Cyclohexane were used for the study. The ternary system is observed to exhibit type-2 LLE behavior. The work also focuses on the calculation of the separation factor and distribution coefficient of the organic solvents used, thereby evaluating the extracting capability of the solvents for the separation process. The reliability of the experimental tie-line data was competently confirmed using Othmer-Tobias, Hand, and Bachman correlating equations. The experimental results indicate that cyclohexane has relatively low separation factors. However, the separation factor for CHCl3 reported in this work, implies that the extraction of acetic acid by CHCl3 is possible.

INTRODUCTION

Acetic acid (CH3-COOH) is the simplest carboxylic acid that has so many applications in various chemical industries. Several chemical compounds such as ester, vinegar, acetic anhydride, and many other polymeric materials can be produced with the help of acetic acid as a chemical reagent. It is also preferred for the preparation of pharmaceuticals, purify organic compounds, and also used as a fungicide. Acetic acid can be manufactured by synthetic methods or fermentation process. Both of these methods give dilute aqueous solutions. Hence the separation of acetic acid from dilute aqueous solution is of industrial importance [1] [2]. The separation of acetic acid and water by distillation is very difficult and it requires a column with many stages and a high reflux ratio, thus leading to high running costs. The lower energy cost of extraction allows liquid-liquid extraction (LLE) to be used as an alternative to the distillation process. Simultaneously LLE is a technique used to effectively separate acetic acid from aqueous solutions [3] [4] [5] [6].

Liquid-Liquid extraction in recent years plays an important and cost-effective role in the chemical industry as a separation process [7] [8]. LLE data is perceived to be a key factor for the proper understanding of the properties of the multi-component systems as well as the design of the efficient separation processes [9]. The work mainly concentrates to measure the LLE compositions of the ternary systems. Here for the study organic solvents such as chloroform (CHCl3), dichloromethane (CH2Cl2), and cyclohexane (C6H12) are used. H2O, 10% NaCl solution, 10% CaCl2 solution were used as aqueous solvent. To investigate the change of equilibrium characteristics, LLE data have been obtained for different systems namely: (water + acetic acid + CHCl3), (water + acetic acid + CH2Cl2), (water + acetic acid + C6H12), (10% NaCl solution + acetic acid + CHCl3), (10% NaCl solution + acetic acid + CH2Cl2), (10% NaCl solution + acetic acid + C6H12), (10% CaCl2 solution + acetic acid + CHCl3), (10% CaCl2
solution + acetic acid + CH$_2$Cl$_2$ and (10% CaCl$_2$ solution + acetic acid + C$_6$H$_{12}$) was studied at 303K and at one atmospheric pressure.

Phase equilibrium data are essential for developing the separation process. The distribution coefficients and separation factors were calculated from the experimental results, and these results were correlated. The tie-lines were constructed and analyzed the LLE data and these data were correlated using the UNIQUAC model. From the tie-line data, distribution coefficients and separation factors were determined for the immiscibility region. The quality of the experimental tie-line data was determined by the Othmer-Tobias equation [10]. The experimental LLE data were correlated using the UNIQUAC [11] and the non-random two-liquid (NRTL) [12] activity coefficient models to obtain the binary interaction parameters. The optimal values of the model parameters were determined from the data reduction. These parameters will be used in process development. The values for the binary interaction parameters were obtained for these equilibrium models. Distribution coefficients (D) and separation factors (S) were determined from the tie-line data to evaluate the extracting capability of the solvents for the separation of acetic acid from water.

**LITERATURE REVIEW**

Solvent extraction is a wide-spread technique because of its low energy consumption and high efficiency over traditional techniques. The efficiency of this technique depends on the physical and chemical properties of the organic solvent used for extracting the component contained in water. The selection of an organic solvent must be considered from the viewpoint of thermal stability, favorable density, viscosity, boiling point, and interfacial tension [13]. To design and perform solvent extraction processes, liquid-liquid equilibrium (LLE) data of ternary systems are mainly required. Ternary diagrams involving the binodal curve of solubility and tie-lines have an important role in ascertaining ternary LLE data. They can normally be obtained by direct analysis or by cloud-point titration [5].

Thermodynamic models are also important for predicting the thermodynamic properties of the ternary LLE systems, particularly the activity coefficients models. Some important LLE data on relative systems have been reported in [14] [15] [16]. Nitriles have also been time-tested to improve the extraction of this acid from water. Letcher, 2002 have studied the systems (water + carboxylic acid + benzonitrile or butanenitrile) [17].

**MATERIALS AND METHODS**

The chemicals used throughout the study were of analytical grade. Distilled and deionized water with a specific conductivity of less than 1μ/ohm/cm was used throughout the study. All the chemicals were used without further purification. Acetic acid, Chloroform, and Dichloromethane with stated mass fraction purities higher than 0.99 were purchased from Merck.

Refractive indices of the pure liquids were measured at T=303K using an Abbe Refractometer. The uncertainties in the refractive index measurements were ±0.0002. The sample weighing was carried out with an electronic analytical balance with an accuracy of ±0.001g. The temperature of the sample was measured with a precision digital thermometer. The solubility data of the ternary systems were obtained by using the cloud point method. All the binary mixtures were prepared gravimetrically and were introduced to a glass cell with a volume of about 50ml. The temperature of the cell was controlled by a water jacket and maintained within ±0.1K. The uncertainty in the mass fraction of the solubility data was estimated to be better than ±0.001. Tie-line data were determined for the ternary systems at T=303 K. Experiments were carried out in a jacketed 250ml glass cell. The temperature was estimated to be accurate to within ±0.1K. The prepared mixtures were placed in the extraction cell and were vigorously agitated by a magnetic stirrer for 4hrs. For all the mixtures, the resting time for phase separation was 4hrs. The mass fractions of the acids in both the phases were obtained by potentiometric NaOH titration. The estimated uncertainty of all measured compositions is better than ±0.001.

The concentrations of the acid in both the phases were obtained by potentiometric NaOH titration. The evaluation of the potentiometric curve was performed according to the standard analytical procedure. The water content of the organic phase was measured by the Karl-Fischer method [18]. The titrator was calibrated with a standard solution of sodium tartrate. The water content of the aqueous layer was determined using refractive index measurement method [1]. The refractive indices of the prepared standard samples lying on the binodal curves were measured and is used for building standard curves. For the studied systems, such standard curves can be made only for analysis of the aqueous phase, since the composition of data points in the organic-rich phase are close. Moreover, the experimental data on the binodal curves along the calculation procedure was used for the check of the tie-line
data. In this way, knowing the mass of the three components in the initial mixtures, the mass of separated phases, and mass of the acid in both phases, the water content in the aqueous phase, and the amount of the organic solvent in both phases were also determined by using mass balance equations.

EXPERIMENTAL RESULTS

Experimental LLE Results

Solubility and equilibrium tie-line data for the (water (1) + acetic acid (2) + organic solvent(chloroform (3), dichloromethane (4), cyclohexane (5)), ternary systems were measured at T=303K and at one atmospheric pressure. The measured solubility, the tie line data and the corresponding triangular phase diagrams for the ternary systems at temperature T=303K are also plotted in Figure 1 (a) to 1 (c). All concentrations are listed in mass fraction, I denote the mass fraction of the $i^{th}$ component, $w_{11}$ and $w_{13}$ refer to the mass fractions of the $i^{th}$ component in the aqueous and solvent phase respectively.

![Figure 1](image-url)
**Distribution Coefficient and Separation factor**

Distribution coefficient (D) and Separation factors (S) were calculated from the experimental data to evaluate the effectiveness of the acid extraction by the organic solvents. The experimental separation factor, which is a measure of the ability of a solvent to separate the acid from water, is defined as the ratio of distribution coefficient of the acid (D₂) to water (D₁) i.e.,

\[
S = \frac{D_2}{D_1} = \frac{W_{23}}{W_{13}}/\frac{W_{11}}{W_{12}}
\]

W₁₃ and W₂₃ are the mass fractions water and acetic acid in the organic phase, respectively. W₁₁ and W₂₁ are the mass fractions of water and acetic acid in the aqueous phase respectively. The distribution coefficient and separation factors, for each system are given in Table 1.

<table>
<thead>
<tr>
<th></th>
<th>CHCl₃</th>
<th>CH₂Cl₂</th>
<th>Cyclohexane</th>
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</thead>
<tbody>
<tr>
<td>D₁</td>
<td>D₂</td>
<td>S</td>
<td>D₁</td>
</tr>
<tr>
<td>0.06</td>
<td>0.78</td>
<td>13.3</td>
<td>0.08</td>
</tr>
<tr>
<td>0.07</td>
<td>0.69</td>
<td>10.1</td>
<td>0.11</td>
</tr>
<tr>
<td>0.10</td>
<td>0.69</td>
<td>6.7</td>
<td>0.13</td>
</tr>
<tr>
<td>0.13</td>
<td>0.68</td>
<td>5.3</td>
<td>0.16</td>
</tr>
<tr>
<td>0.16</td>
<td>0.70</td>
<td>4.5</td>
<td>0.19</td>
</tr>
<tr>
<td>0.18</td>
<td>0.72</td>
<td>4.0</td>
<td>0.24</td>
</tr>
</tbody>
</table>

The variation of experimental separation factor of acetic acid as a function of the mass fraction of the acid in aqueous phase for the ternary systems at T = 303K are shown in Figure 2. As can be seen, all separation factors are greater than 1 (S > 1) for the studied systems. However for these ternary systems, the separation factors changes according to the following order, i.e. CHCl₃ > CH₂Cl₂ > Cyclohexane. The experimental results indicate that CHCl₃ has a larger separation factor (varying between 13.34 and 3.97) than the others.

**FIGURE 2.** Separation factor (S) plotted against the mass fraction of acetic acid in the aqueous phase, w₂₁, at T = 303K.

The experimental results indicate the advantage of CHCl₃ as the preferred solvent for the extraction of acetic acid from its aqueous solutions. The biphasic region was found to be larger when the CHCl₃ was used as an organic solvent. The LLE data suggest that cyclohexane may serve as a very poor solvent for extracting acetic acid from its
aqueous solutions because it shows a very low separation factor. In addition, it shows solubility in water, which means the recovery of acetic acid by cyclohexane is negligible.

**Validation of Reliability for the Tie-Line Data**

The quality of the experimental tie line data was ascertained by the Othmer-Tobias [10] (Eq. (1)), Hand equation [19] (Eq. (2)) and Bachman correlation equation [20] (Eq. (3)) for the studied systems.

\[
\ln \left( \frac{1-w_{33}}{w_{33}} \right) = A + B \ln \left( \frac{1-w_{11}}{w_{11}} \right) \tag{1}
\]

\[
\ln \left( \frac{1-w_{23}}{w_{11}} \right) = A' + B' \ln \left( \frac{1-w_{23}}{w_{33}} \right) \tag{2}
\]

\[
W_{23} = A'' + B'' \frac{w_{23}}{w_{11}} \tag{3}
\]

where \( w_{11} \) is mass fraction of water in the aqueous-rich phase, and \( w_{33} \) is mass fraction of the solvent in the organic-rich phase. A, B and A’, B’ are the parameters of the Othmer–Tobias and the Bachman correlation. Where A” and B” is the Hand correlation parameters. These parameters are numerical constants which depend on degree of immiscibility and equilibrium compositions. For this investigated system, the Othmer–Tobias, Bachman and Hand plots are shown in Figure 3 (a) to (c) respectively. The correlation factor (\( R^2 \)) being approximately unity and the linearity of the plots indicate the degree of reliability of the measured tie-line data.

**FIGURE 3.** (a) Othmer–Tobias plot for ▲: (water + acetic acid + CHCl₃); ○: (water + acetic acid + CH₂Cl₂); □: (water + acetic acid + cyclohexane) ternary systems at 303 K, (b) Hand plot for ▲: (water + acetic acid + CHCl₃); ○: (water + acetic acid +
The root-mean-square deviation (RMSD) between the values was calculated from the difference in the experimental and calculated mass fractions according to the following equation:

$$\text{RMSD}\% = 100 \sqrt{\frac{\sum_{i=1}^{3} \sum_{j=1}^{3} \sum_{k=1}^{3} (x_{i,j,k} - x_{i,j,k,\text{calc}})^2}{6n}}$$

The RMSD is a measure of the agreement between the experimental and calculated data. The average root-mean-square deviations for (water + acetic acid + CHCl$_3$), (water + acetic acid + cyclohexane) and (water + acetic acid + CH$_2$Cl$_2$) were 2.15%, 2.17% and 2.16%, respectively. The experimental results indicate that CHCl$_3$ has a higher separation factor, thereby indicating the ability of CHCl$_3$ to extract acetic acid from water. This quantity for CHCl$_3$ is greater than one (separation factors varying between 1.865 and 5.783) for the system reported in this work, which means that the extraction of acetic acid using CHCl$_3$ is possible. Therefore, this solvent may be considered as a possible candidate for the recovery of acetic acid from aqueous solutions. The separation factor for cyclohexane is near one (between 1.230 and 1.358), meaning that cyclohexane is not a suitable solvent for the extraction of acetic acid from water.

CONCLUSION

The work examines the potential use of suitable solvent for the recovery of acetic acid from aqueous solutions. Studies on the LLE of these system over a range of concentration, and temperature were made. The correlation study was also investigated. LLE and dependence of various variable such as solvent polarity were analysed. The solubility and tie-line data for the (water + acetic acid + organic solvents) ternary systems were determined at T=303K. The ternary system was observed to exhibit a type-2 behaviour of the LLE. The separation factor and distribution coefficient for the organic solvents used in this work were also calculated. Othmer–Tobias, Hand and Bachman correlating equations were used for satisfactorily ascertaining the tie-line data of the system under study. The experimental results indicate that Cyclohexane has relatively low separation factors. However, this quantity is greater than one for the system reported in this work, which means that extraction of acetic acid by CHCl$_3$ is possible. The average RMSD value between the observed and calculated mass fractions was 0.66%.

REFERENCES


