Liquid-liquid Equilibrium Data for the Ternary Systems of Propionic Acid-Water-Solvents

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Abstract: Liquid-liquid equilibrium data for propionic acid with water and solvents (methyl butyl ketone, methyl isopropyl ketone and methyl isobutyl ketone) are presented at 25-26°C and used to evaluate the possibility of employing distribution of propionic acid between water and these solvents as a means of separation of propionic acid from its aqueous solution. Mutual solubility curves, tie-line data, distribution coefficient, selectivity diagrams and separation factor data were determined for these systems. The thermodynamic consistency of the tie-line data was ascertained by Othmer-Tobias plots as well as by Hand plots. From these data it has been concluded that all these solvents are suitable separating agents for propionic acid from its dilute aqueous solution, but of these solvents methyl isobutyl ketone offers the best hope of achieving separation of propionic acid by distribution between methyl isobutyl ketone and water as it has the highest separation factor value than those of other two solvents.

Key words: Liquid-liquid equilibrium, ternary system, separation factor, distribution coefficient, tie-line

INTRODUCTION

Liquid-liquid extraction is a process in which a solution is brought into contact with a second liquid (solvent) essentially immiscible or partially miscible with the first one in order to bring about transfer of one or more components from the solution into the second solvent. The solvent phase is usually termed as extract phase and another phase from where the solute is extracted, called diluent or raffinate phase. It is an effective alternative method to distillation process. Liquid-liquid extraction process is the most useful method for purification, enriching and separation of components of very close volatility and of heat sensitive. Extraction of constituents by using solvent is a very common practice in chemical processing where a mixture containing separable components is treated with a solvent in which one or more of the desired components are preferentially soluble.

With an increase in demand for environmentally friendly chemicals, the efficient separation of carboxylic acids from dilute solutions resulting from fermentation processes is an important where many solvents have been tested to improve such separation\(^5\). The extractive recovery of propionic acid by selective solvent systems from aqueous solutions, such as fermentation broth has received increasing interest. Propionic acid is an important laboratory reagent as well as solvent for carrying reactions since it remains unchanged by oxidizing and reducing agents. It is used as a cellulose-solvent in pharmaceutical industries and also can be used to provide propionates, which are used as fungicides\(^6\). Propionic acid can be used in electroplating industry and to prepare perfume esters. Thus, the study of propionic acid extraction from its aqueous solution is fascinating all the time.

In this study, liquid-liquid equilibrium data as well as the mutual solubility data for the ternary systems of propionic acid + water + methyl butyl ketone, propionic acid + water + methyl isopropyl ketone and propionic acid + water + methyl isobutyl ketone were determined at 25-26°C in order to find out the proper solvent for the separation of propionic acid from aqueous solution. Complete ternary phase diagram was obtained by evaluating the solubility and the tie line data for these systems. Separation factor which is a quantitative index of effectiveness of separation has been computed from these data. To compare the selectivity advantages of these solvents, solvent free-based selectivity diagrams were plotted. In addition, the thermodynamic consistency of the tie-line data were correlated by making Othmer-Tobias plots\(^7\) and also by making Hand plots\(^8\).

MATERIALS AND METHODS

All the materials used were of laboratory reagent grade as shown in Table 1. The method that was used for the determination of mutual solubility and tie-line data the present study was the titration method of Othmer et al.\(^9\). All the measurements were carried out at 25-26°C
in May to July, 2005. The mutual solubility curves for each system were obtained by titrating known mixture of two components with the third one to the point of first appearance of permanent turbidity (cloud point) and the tie-line data determination was performed by taking various mixtures of known compositions within the heterogeneous region were prepared, brought to equilibrium and the compositions of the conjugate phases were determined by measurement of refractive index as our previous study[9].

**Determination of mutual solubility curves:** Twenty microliter of water (diluent) was measured into a 150 mL Erlenmayer flask and methyl butyl ketone (solvent) was added from a micro-burette and the content of the flask was constantly agitated until the solution became just turbid. The mixture temperatures were regulated by a thermostat water bath. The amounts added were recorded as the maximum solubility of solvent in the diluent, since the appearance of the turbidity indicated the formation of second phase, the solvent layer. The compositions of the mixture at the maximum solubility were expressed in weight percent, (W). Now 2 drops of water was added to this mixture and because of its consolate effect, a clear solution resulted. Then an arbitrarily chosen amount of propionic acid (solute) was added so that the compositions of the resulting mixture moved out side the solubility curve and the solvent was again added until turbidity resulted, a second point on the mutual solubility curve was obtained. Two drops of diluent was again added and the above operation of successive addition of solute and solvent were repeated, gave the diluent branch of the mutual solubility curve. To obtain the solute branch of the mutual solubility curve, 20 mL of solvent was taken into a flask and the diluent was added from the micro-burette until turbidity was obtained. Successive addition of solute and diluent in a manner similar to that for diluent branch gave solvent branch of the mutual solubility curve. Diluent branch and solvent branch of the mutual solubility curve together appeared as a hump and described the complete mutual solubility curve for the system propionic acid-water-methyl butyl ketone.

Similarly, mutual solubility curves for propionic acid-water-methyl isopropyl ketone and propionic acid-water-methyl isobutyl ketone systems were also obtained. The refractive index of each mutual solubility point was measured by Abbe Refractometer to construct calibration curves of equilibrium compositions versus refractive index for each system[9].

**RESULTS AND DISCUSSION**

Liquid-liquid mutual solubility data and curves for the ternary systems of propionic acid + water + methyl butyl ketone, propionic acid + water + methyl isopropyl ketone and propionic acid + water + methyl isobutyl ketone are reported in Table 2 and Fig. 1, respectively. The compositions of mutual solubility data in Table 2 and in Fig. 1 are expressed in weight percent and in weight fraction, respectively. It is evident from the Fig. 1 that the area of heterogeneity increased for the systems studied in the order methyl isopropyl ketone, methyl butyl ketone and methyl isobutyl ketone. This is because of higher mutual solubilities of water and methyl isopropyl ketone when compared with those of water and methyl butyl ketone and water and methyl isobutyl ketone. It is also concluded that the solvent that shows low solubility against water is the superior to use as a extracting solvent for separating propionic acid from its aqueous solution.

**Tie-line data:** Tie-line data of each of these systems were obtained by taking about 20 mL of solvent and 20 mL of diluent (water) in a flask and 2 to 5 mL of solute was added to give a ternary mixture of known compositions within the heterogeneous region of the mutual solubility curve in Fig. 1, brought to equilibrium and the refractive indices of these two coexisting phases were measured by Abbe Refractometer. The compositions of the two coexisting phases in the ternary mixture were read off from the calibration curves constructed from the mutual solubility ternary compositions and their respective refractive index as our previous study[9]. Successive addition of solute in this ternary mixture gave the other tie-line data for these systems and continued until a single phase existed. Tie-line data for these systems are shown in the Table 3 on the basis of weight percent, which represents the equilibrium ternary compositions of two phases (aqueous and solvent) while they are in equilibrium stage. According to Table 3, the equilibrium distribution compositions of propionic acid (1) in solvent phase (3) and in water phase (2) are shown in Fig. 2.
Figure 2 indicated that the solubility of propionic acid in solvent against that in water for the systems studied is higher in order methyl isobutyl ketone, methyl butyl ketone and methyl isobutyl ketone.

**Distribution coefficient and separation factor:** The separation factor (S) and the distribution coefficient of propionic acid, \((D_i)\) between water and solvents were determined numerically \(^{10}\) from the experimental tie-line data. The ratio of weight percent of propionic acid in solvent phase \((W_{1s})\) to the weight percent of propionic acid in diluent phase \((W_{1d})\) for each tie-line gives the distribution coefficients of propionic acid \((D_i)\) are shown in Table 4. The obtained highest value of \((D_i)\) is 18.146 for the system propionic acid + water + methyl isobutyl ketone while for the systems of propionic acid + water + methyl butyl ketone and propionic acid + water + methyl isopropyl ketone are 9.166 and 8.04, respectively. This indicates that all the solvents are suitable for this extraction, having the distribution coefficient values much greater than unity but methyl isobutyl ketone is the best efficient solvent among them having highest distribution coefficient value, 18.146 which is the key factor in the extraction process.

Separation factor \((S)\) is a ratio of distribution coefficient of propionic acid \((D_i)\) to the distribution coefficient of water \((D_w)\). Hence the separation factor, \(S = D_i/D_w\). The distribution coefficient of water, \((D_w)\) is the ratio of the weight percent of water in solvent phase \((W_{sw})\) to that in water phase \((W_{sw})\). It is also observed from the Table 4 that the separation factor \((S)\) for the system propionic

<table>
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<tr>
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<th>W2</th>
<th>W3</th>
<th>W1</th>
<th>W2</th>
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Table 3: Tie-line data for Propionic acid(1) - Water(2) - Solvent(3) systems at 25-36°C

<table>
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<th>Solvent-rich phase</th>
<th>Water-rich phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>W1</td>
<td>W2</td>
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</table>

Propionic acid (1) - Water(2) - Methyl butyl ketone(3)
7.46 18.30 74.24 0.85 97.65 1.50
11.00 21.00 68.00 1.20 90.80 2.00
15.10 23.50 61.40 1.75 95.25 2.00
22.50 31.20 46.20 3.00 94.50 2.50
24.60 47.60 28.80 5.35 91.65 3.50

Propionic acid (1) - Water(2) - Methyl isopropyl ketone(3)
4.02 22.00 73.98 0.50 98.00 1.50
7.23 26.30 66.47 1.00 97.50 1.50
10.90 31.10 58.00 1.50 96.70 1.80
15.62 41.30 42.88 2.50 95.00 2.50
18.45 49.86 31.69 4.00 93.50 2.50

Propionic acid (1) - Water(2) - Methyl isobutyl ketone(3)
9.50 6.50 84.00 0.60 97.50 1.90
16.83 7.75 75.42 1.00 96.50 2.50
27.22 10.63 62.18 1.00 94.70 3.80
35.00 15.23 49.76 2.25 93.75 4.00
38.00 21.43 46.57 3.00 93.50 4.50
38.80 38.12 25.68 4.50 88.00 7.50

Fig. 3: Selectivity diagram for systems propionic acid-water-solvents

acid+water+methyl isobutyl ketone is the highest, 237 that is about 5 times and 6.6 times higher than those of methyl butyl ketone and methyl isopropyl ketone, respectively. Separation factor is a measure of the solubility of solvents to separate propionic acid from aqueous solution.

Selectivity diagram: This was constructed by plotting weight percent of propionic acid in the solvent phase against that in the diluent phase both on solvent free basis. Selectivity diagrams of all the systems are shown in Fig. 3, which reveals that methyl isobutyl ketone shows the highest selectivity and methyl butyl ketone and methyl isopropyl ketone give almost the same selectivity but less than that of methyl isobutyl ketone.

Othmer-Tobias and hand correlations: The reliability of experimentally measured tie line data on the basis of weight percent for these three systems is ascertained by applying Othmer-Tobias Eq. 1 and Hand Eq. 2.

\[
\ln \left( \frac{100 - W_n}{W_n} \right) = a + b \ln \left( \frac{100 - W_n}{W_n} \right) \tag{1}
\]

\[
\ln \left( \frac{W_n}{W_n} \right) = a + b \ln \left( \frac{W_n}{W_n} \right) \tag{2}
\]

Othmer-Tobias plots and Hands plots for the correlations of experimental tie line data are shown in Fig. 4 and 5, respectively, while the correlation
Table 4: Distribution coefficients of propionic acid (D<sub>i</sub>) and that of water (D<sub>w</sub>) and separation factors (S) for propionic acid(1)-Water(2)-Solvents(3) systems at 25-26°C

<table>
<thead>
<tr>
<th></th>
<th>(1)-(2)-methyl ketone (3) system</th>
<th>(1)-(2)-methyl isobutyl ketone (3) system</th>
<th>(1)-(2)-methyl isopropyl ketone (3) system</th>
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<tbody>
<tr>
<td></td>
<td>D&lt;sub&gt;i&lt;/sub&gt;</td>
<td>D&lt;sub&gt;W&lt;/sub&gt;</td>
<td>D&lt;sub&gt;W&lt;/sub&gt;</td>
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8.1777 0.4331 18.87

Table 5: Correlation coefficients and factors for the Othmer-Tobias and Hand Equations for the Propionic acid(1)-Water(2)-Solvents (3) systems

<table>
<thead>
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<th>a</th>
<th>b</th>
<th>R²</th>
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<td>MIPK</td>
<td>4.594</td>
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<tr>
<td>Hand</td>
<td>MBK</td>
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<td>1.225</td>
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<tr>
<td></td>
<td>MIPK</td>
<td>3.907</td>
<td>1.145</td>
<td>0.996</td>
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</table>

MBK: Methyl butyl ketone; MIBK: Methyl isobutyl ketone; MIPK: Methyl isopropyl ketone

coefficients (a) and (b) and correlation factor (R²) values were calculated from their respective correlation curve by the least-squares method, given in Table 5. Going through Fig. 4 and 5, the linearity of the plot indicates the degree of consistency of the related data. It is also observed from Table 5 that the correlation factor (R²) close to unity suggests a high degree of consistency of the related data.

CONCLUSIONS

For the separation of propionic acid from its aqueous solution by using solvents (methyl butyl ketone, methyl isobutyl ketone and methyl isopropyl ketone), liquid-liquid equilibrium data, mutual solubility data, distribution coefficient, separation factor data and selectivity diagram of these systems were studied at 25-26°C and thus it can be said after considering all the findings, all three solvents, showing low solubility against water, may serve as adequate solvents to extract propionic acid from its dilute solutions. But methyl isobutyl ketone is the most selective, having the highest distribution coefficient, separation factor as well as selectivity, among these three solvents.

Both the Othmer-Tobias and the Hand equations show a good correlation and straight lines for each ternary system.

REFERENCES