Miscibility gap in a ternary system

Related concepts
Three component systems, miscibility gap, phase diagram, triangular diagram, Gibb's phase law.

Principle
A number of completely miscible two component mixtures are prepared to investigate the three component acetic acid / chloroform / water system. These mixtures are titrated with the third component until a two phase system is formed which causes turbidity. The phase diagram for the three component system is plotted in a triangular diagram.

Tasks
1. Titrate nine different acetic acid / chloroform mixtures with water until a two phase system is formed in each case.
2. Titrate six acetic acid / water mixtures with chloroform until phase separation is observed.
3. Plot the results of the titrations, expressed as molar fractions, in a triangular diagram.

Equipment
Retort stand, $h = 750$ mm 37694.00 1
Burette clamp, roller mounting 47152.01 1
Burette, 10 ml, straight stopcock, Schellbach lines 36513.01 2
Immersion thermostat, 100°C 08492.93 1
Accessory set for immersion thermostat 08492.01 1
Bath for thermostat, 6 l, Makrolon 08487.02 1
Rubber tubing, $d_i = 6$ mm 39282.00 3
Hose clip, 8…12 mm 40996.01 4
Rack for 20 test tubes 08487.03 1
Test tubes, 16/160 mm 37656.10 1
Rubber stopper, 18/20 mm 39254.00 15
Rubber stopper, 22/25 mm 39255.00 15
Long-neck flat-bottom flask, 100 ml, SB 19 36320.00 15
Funnel, glass, $d_o = 55$ mm 34457.00 1
Glass beaker, 150 ml, tall 36003.00 1
Precision balance, 620 g 48852.93 1
Wash bottle, 500 ml 33931.00 1
Pasteur pipettes 36590.00 1
Rubber bulbs 39275.03 2
Laboratory pencil, waterproof 38711.00 1
Acetic acid, 99…100%, 500 ml 31301.50 1
Chloroform, pure, 250 ml 48045.25 1
Distilled water, 5 l 31246.81 1

Set-up and procedure
Set up the experiment as shown in Fig. 1.
Prepare the chloroform / acetic acid mixtures listed in Table 1 by weighing the specified quantities of chloroform and pure acetic acid into 100 ml flat-bottomed flasks.

Table 1: Quantities and mixing proportions of chloroform / acetic acid mixtures

<table>
<thead>
<tr>
<th>Mixture</th>
<th>$n_{\text{chloroform}}/g$</th>
<th>$n_{\text{chloroform}}$</th>
<th>$n_{\text{acetic acid}}/g$</th>
<th>$n_{\text{acetic acid}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>119.5</td>
<td>1.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>B</td>
<td>107.6</td>
<td>0.9</td>
<td>6.0</td>
<td>0.1</td>
</tr>
<tr>
<td>C</td>
<td>95.6</td>
<td>0.8</td>
<td>12.0</td>
<td>0.2</td>
</tr>
<tr>
<td>D</td>
<td>83.7</td>
<td>0.7</td>
<td>18.0</td>
<td>0.3</td>
</tr>
<tr>
<td>E</td>
<td>71.7</td>
<td>0.6</td>
<td>24.0</td>
<td>0.4</td>
</tr>
<tr>
<td>F</td>
<td>59.8</td>
<td>0.5</td>
<td>30.0</td>
<td>0.5</td>
</tr>
<tr>
<td>G</td>
<td>47.8</td>
<td>0.4</td>
<td>36.0</td>
<td>0.6</td>
</tr>
<tr>
<td>H</td>
<td>35.9</td>
<td>0.3</td>
<td>42.0</td>
<td>0.7</td>
</tr>
<tr>
<td>I</td>
<td>0.0</td>
<td>0.0</td>
<td>60.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Shake the samples well and transfer 10 g of each mixture to suitably labelled test tubes. Temperature equilibrate the test tubes to 25 °C in a temperature controlled water bath. Titrate the samples with distilled water from a microburette until the liquid becomes turbid as a result of separation. Shake the test tubes from time to time to ensure good mixing of the samples (insert rubber stoppers before shaking). Record the quantity of water added (in ml) as approximation for the mass of water (in g).
Repeat the procedure for samples K to P listed in Table 2.

Table 2: Mixing proportions of water / acetic acid

<table>
<thead>
<tr>
<th>Mixture</th>
<th>$n_{\text{water}}/g$</th>
<th>$n_{\text{acetic acid}}/g$</th>
<th>$n_{\text{acetic acid}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>1.00</td>
<td>10</td>
<td>0.021</td>
</tr>
<tr>
<td>L</td>
<td>2.00</td>
<td>8.00</td>
<td>0.046</td>
</tr>
<tr>
<td>M</td>
<td>3.00</td>
<td>7.00</td>
<td>0.076</td>
</tr>
<tr>
<td>N</td>
<td>4.00</td>
<td>6.00</td>
<td>0.113</td>
</tr>
<tr>
<td>O</td>
<td>5.00</td>
<td>5.00</td>
<td>0.161</td>
</tr>
<tr>
<td>P</td>
<td>6.00</td>
<td>4.00</td>
<td>0.22</td>
</tr>
</tbody>
</table>
Again transfer 10 g of each sample to a separate test tube and temperature equilibrate them to 25 °C in the temperature controlled bath. Titrate with chloroform until turbidity occurs and record the quantity added. Calculate the mass of chloroform from the density ($\rho_{\text{chloroform}} = 1.489 \text{ g / ml}$) and the consumption (in ml). Calculate the molar fractions for all mixtures and plot the results in a phase diagram using triangular co-ordinates (see Fig. 2).

Theory and evaluation

Gibb’s phase law describes the relationship between the number of components $K$ in a system, the phases $P$ formed by the system, and the number of degrees of freedom:

$$P + F = K + 2$$

where

- $K$ Number of components
- $P$ Number of phases
- $F$ Number of degrees of freedom.

In a three component system ($K = 3$), the sum of phases and the degree of freedom is 5:

$$P + F = 5$$

In a single phase system ($P = 1$) under isothermic and isobaric conditions (= 2 degrees of freedom), two degrees of freedom remain; they characterise the composition of the system (molar fractions of two components). If the system has two phases that are under the specified conditions, only one degree of freedom remains for the composition of the system.

The solubility diagram of a ternary system is usually plotted in triangular co-ordinates with equal sides. Each apex of the triangle represents a pure component. The molar fractions of the binary mixtures are entered on the sides of the triangle. The area of the triangle represents all possible mixtures of the system. The following applies for a ternary system:

$$x_A + x_B + x_C = 1$$

where

- $x_i$ Molar fraction of component $i$

Both chloroform / acetic acid and water / acetic acid are completely miscible, but chloroform / water are not miscible in any ratio. In the chloroform / acetic acid / water triangular diagram, a straight line is drawn from a point F through the opposite apex K (water), where point F on the chloroform / acetic acid side of the diagram corresponds to a certain composition of the binary chloroform / acetic acid mixture, and point K corresponds to pure water. This straight line represents a constant composition with respect to the components chloroform and acetic acid, whereas the water content rises as one moves along line F – K.

To prepare the phase diagram of the chloroform / acetic acid / water system, first enter the molar fractions which correspond to the respective binary mixtures (points A … P) on the sides of the triangle. Then draw straight lines from these points to the opposing apices. Enter the points which correspond to the molar fraction of the third component and join them. The resulting line separates the two-phase system (below) from the single-phase one (above).

Fig. 2: Triangular diagram of the system acetic acid / chloroform / water