Exercise 3 DETERMINATION OF THE LIQUID – VAPOUR EQUILIBRIUM IN A BINARY SYSTEM OF MISCIBLE LIQUIDS

Theory
A solution can be described as a homogeneous mixture of at least two substances, and in most cases, we deal with liquid solutions. The component which represents the largest portion of the solution is usually called the solvent, while the dissolved substance is referred to as the solute. However, if the solution is made of completely miscible liquids in similar portions, it is not practical to distinguish which component is the solvent and which is the solute. The solutions of miscible liquids are often called liquid mixtures.

Any liquid substance is more or less volatile; there is certain vapour pressure of this substance above the surface of the pure liquid. When the miscible liquids are mixed together, the vapour pressure of each component above the surface of the formed solution is lowered, in comparison with the pure liquid component. The quantitative expression is given by Raoult’s law, which states that the relative lowering of the vapour pressure of a given component is equal to its molar fraction in the solution. For the ideal two component system (A, B) in the thermodynamical equilibrium at constant temperature we can write the Raoult’s law in the following form:

\[ P_A = P_A^0 x_A \quad P_B = P_B^0 x_B \]  

(1)

where:
- \( P_A, P_B \) - are the partial pressures of the components above the solution surface
- \( P_A^0, P_B^0 \) - are the pressures of the pure components
- \( x_A, x_B \) - are the molar fractions

Solutions that obey Raoult’s law throughout their composition range are called ideal - Figure 1.

![Figure 1](image)

Figure 1 Isobaric phase diagram of two miscible liquids (A – toluene and B – benzene)

The total pressure of the gaseous phase is given by Dalton’s law:

\[ P = P_A + P_B = P_A^0 x_A + P_B^0 x_B \]  

(2)
\[ x_A + x_B = 1 \]  

Composition of the gaseous phase can be obtained as:

\[ y_A = \frac{P_A}{p} \quad y_B = \frac{P_B}{p} \]  

where: \( y_A, y_B \) - are the molar fractions in the gaseous phase.

**Figure 2** Graphic formulation of the Dalton’s law

If the two components (A and B) of a liquid mixture are different in character, the molecular forces between the A molecules will differ from those acting between the B molecules and the presence of B will affect the evaporation of the A, and vice versa. The observed behaviour of the solution will then differ from the Rault’s law. If the attraction between the B molecules is stronger than between the A type, the escaping tendency of the A will be increased by the presence of B. This phenomenon is known as a **positive deviation from the Rault’s law** (Figure 3), with maximum on the isothermal phase diagram (Figure 3a) and minimum on the isobaric phase diagram (Figure 3b).

**Figure 3** System with positive deviation from the Raoult’s law
If the two constituents of a liquid mixture attract one another strongly, their total vapour pressure will be less than that required by the Raoult's law. This type of nonideal behaviour is called as a negative deviation from Raoult's law (Figure 4). The vapour pressure curve may often have a minimum for a particular composition (Figure 4a) and there is a maximum on the isobaric phase diagram (Figure 4b).

![Figure 4](image)

**Figure 4** System with negative deviation from the Raoult's law

Nonideal mixtures with minimum or maximum on the phase diagram cannot be totally separated by a simple distillation. When the extreme point on the phase curve is reached the evaporation proceeds without any further change of the composition (azeotrope). The composition of the gaseous and liquid phase of the azeotrope is identical.

**Task**

Determination of liquid-vapour equilibrium for the given real system of two miscible liquids. Construction of its isobaric phase diagram $T = f(x_A, x_B)$.

**Equipments and chemicals**

Apparatus for the determination of the liquid-vapour equilibrium (Figure 5)

- Abbe’s refractometer
- Thermometer
- Pure liquid A and B
- Tubes
- Burettes

**Method**

The used apparatus (Figure 5) includes: boiling flask (1), electrical heating (2) device connected to autotransformer, vapour exhausting tubes (3), thermometer (4), cooler (5), discharging valves (7 and 9), distillation receiver, overflow tube (6).
Figure 5  Apparatus for the determination of the liquid-vapour equilibrium

Procedure
1  Prepare four solutions as a mixture of A and B pure liquids with volume concentration 20, 40, 60, 80 volumetric %. Total volume of the mixture 50 ml (samples No. 2-5 in the Table 1). Use the burette A for the liquid A, and the burette B for the liquid B to obtain the precise volumes. Samples No. 1 and No.6 represent pure liquids (100 %) A and B, respectively. Write down the volumes $V_A$ and $V_B$ to the Table 1.

Table 1  Composition of mixtures

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>$V_A$ [ml]</th>
<th>$V_B$ [ml]</th>
<th>$x_A$</th>
<th>$x_B$</th>
<th>$n^*$</th>
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$n^*$ is refractive index of mixtures before heating

2  Determine the refractive index of samples No.1-6 ($n$) using the Abbe’s refractometer. Write down the refractive indexes to the Table 1.

3  Calculate the molar fractions molar fractions – $x_A$ and $x_B$ of solvents A and B in mixture No. 1-6 according Equation 5.
\[ x_A = \frac{n_A}{n_A + n_B} \quad \text{and} \quad x_B = 1 - x_A \] (5)

4 Read the atmospheric pressure (symbol \( p \) [Pa]) from barometer and write it to the Table 2.

5 Pour the sample No.2 into the apparatus through the hole for the thermometer and close it again by the thermometer. The level of liquid should not exceed 1 cm above the heating device (2).

Set the voltage to 12-14 V on the autotransformer, and gently open the cooler's valve for appropriate cooling. Boiling hot vapour will pass around the thermometer and to condense to the receiver. When the receiver becomes full, the condensate will return to the boiling flask. After establishing the equilibrium, the composition of the phases (liquid, gas = condensate) will be equal and the temperature of the vapour will remain constant at the boiling point (\( t_i \)). Write down the equilibrium temperature to the Table 2, and switch off the electrical heating.

Withdraw the condensate (g-phase) and the liquid (l-phase) through the outlets (discharging valves 7, 9) to the test tubes.

Mark the test tubes, close and cool them down.

6 Determine the refractive indices of solvents in the test tubes (\( n_l \) and \( n_g \)) and write down their values to the Table 2.

7 Repeat steps 5 and 6 for each sample (No.2 – No.5).

8 At the end of experiment, clean test tubes with ethanol only.

**Do not use water in this experiment!**

<table>
<thead>
<tr>
<th>No.</th>
<th>( t_i ) [°C]</th>
<th>( T_i ) [K]</th>
<th>( n_l^{*\ast} )</th>
<th>( n_g^{**} )</th>
<th>( x_A )</th>
<th>( x_B )</th>
<th>( y_A )</th>
<th>( y_B )</th>
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</table>

*refractive index of liquid phase after heating of mixture

**refractive index of condensed phase

**Data treatment**

1 Use MS Excell to create a calibration curve (i.e. dependence \( n = f(x_B) \)) using data from the Table 1. Fit the experimental points with a linear function and write down its equation.

2 Determine the composition of the liquid and gas phases (\( x_A \), \( x_B \), \( y_A \), \( y_B \)) using refractive indexes \( n_l \) (for \( x_A \) and \( x_B \)) and \( n_g \) (for \( y_A \) and \( y_B \)) and the calibration curve.

3 Construct the isobaric phase diagram \( T_i = f(x_B, y_B) \) from the measured temperature and composition of mixtures (as shown in Figures 2 or 3).

Join the points referring to the liquid solution and mark it as curve 'L' – liquidus. Other
points define the curve "g" – gaseous (Figure 6). Curves start from the points $T_A^0$ and $T_B^0$, which represent the boiling points of the pure components (Table 3).

Figure 6 Isobaric phase diagram for real mixture of two miscible solvents with minimum of boiling temperature

Table 3 Boiling point ($T_i^0$) evaporated heat ($\Delta_{evap} H_i^0$), density ($\rho$) and molar mass ($M$) of used liquid

<table>
<thead>
<tr>
<th>Liquid</th>
<th>$T_i^0$ [°C]</th>
<th>$T_i^0$ [K]</th>
<th>$\Delta_{evap} H_i^0$ [kJ mol$^{-1}$]</th>
<th>$\rho$ [kg m$^{-3}$]</th>
<th>$M$ [g mol$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetone</td>
<td>56.8</td>
<td>329.7</td>
<td>30.23</td>
<td>796.0</td>
<td>58.08</td>
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<tr>
<td>amylalkohol</td>
<td>138.0</td>
<td>411.2</td>
<td>36.20</td>
<td>810.0</td>
<td>88.15</td>
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<tr>
<td>cyclohexane</td>
<td>80.7</td>
<td>353.9</td>
<td>30.16</td>
<td>779.0</td>
<td>84.16</td>
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<tr>
<td>1,4-dioxane</td>
<td>101.1</td>
<td>374.4</td>
<td>29.44</td>
<td>1035.0</td>
<td>88.11</td>
</tr>
<tr>
<td>ethylacetate</td>
<td>77.1</td>
<td>350.3</td>
<td>37.63</td>
<td>901.0</td>
<td>88.11</td>
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<tr>
<td>ethanol</td>
<td>78.4</td>
<td>351.6</td>
<td>39.39</td>
<td>789.2</td>
<td>46.07</td>
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<tr>
<td>hexane</td>
<td>68.7</td>
<td>341.9</td>
<td>29.03</td>
<td>660.3</td>
<td>86.18</td>
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<tr>
<td>tetrachlormethane</td>
<td>76.7</td>
<td>349.9</td>
<td>29.89</td>
<td>1598.0</td>
<td>153.82</td>
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<tr>
<td>trichlormethane</td>
<td>64.5</td>
<td>334.7</td>
<td>29.49</td>
<td>1498.0</td>
<td>119.38</td>
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<tr>
<td>i-propylalkohol</td>
<td>82.5</td>
<td>355.7</td>
<td>40.09</td>
<td>785.0</td>
<td>60.10</td>
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<tr>
<td>n-propylalkohol</td>
<td>97.3</td>
<td>370.5</td>
<td>41.35</td>
<td>804.4</td>
<td>60.10</td>
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<tr>
<td>water</td>
<td>100.0</td>
<td>373.2</td>
<td>40.69</td>
<td>998.2</td>
<td>18.02</td>
</tr>
</tbody>
</table>

The report must include these points

- Theory (Rault’s law, composition of solutions, ideal and non-ideal solutions)
- Equipment and chemicals
- Working procedure and measurements
- Tables of results, calculations and diagrams
- In conclusions, summarize your experiments:
  Does the isobaric phase diagram of studied mixture show a positive or a negative deviation from the Rault's law?
  What is the composition of azeotrope?
Literature

- KOPECKÝ, F., at all.: Laboratory manual for physical chemistry, Farmaceutical faculty of Comenius University in Bratislava (1996).
- OREMUSOVÁ, J., GREKSÁKOVÁ, O.: Manual for laboratory practice in physical chemistry for students of pharmacy, Department of Physical Chemistry, Faculty of Pharmacy, Comenius University in Bratislava (2007) in Slovak.
- Manual written by Ing. J. Oremusová, CSc, and PharmDr. A. Lengyel.