LIQUID-VAPOR DIAGRAM (T-x-y) OF A BINARY MIXTURE

1. PURPOSE OF THE WORK

The determination of the boiling diagram of a binary system (cyclohexane-ethyl acetate) at constant pressure.

2. INTRODUCTIVE NOTIONS

A phase diagram represents the boiling temperatures of a binary mixture as a function of vapor / liquid composition at equilibrium at constant pressure. The boiling temperatures for different mixtures of cyclohexane and ethyl acetate are measured and the composition of both phases is determined using a refractometer and a calibration curve.

The boiling diagram graphically illustrates the dependence of the boiling temperature on the composition of the liquid phase at constant pressure. The boiling temperature curve results from the measurement of the temperature at which the mixtures begin to boil. The composition of the vapor phase is usually different from that of the boiling liquid from which it is vaporized (in this experiment, the composition of the vapor phase is determined at the beginning of the boiling of each mixture). Therefore, in the phase diagram, two curves are drawn, the boiling point curve (liquid curve) and the condensate curve (vapor curve). The liquid curve represents the composition of the mixture that begins to boil at a certain temperature, and the vapor curve represents the composition of the vapors that are in equilibrium with the liquid mixture at the same temperature. For an ideal mixture, the boiling temperature decreases continuously, with the molar fraction of the more volatile component increasing. The vapor phase is always enriched with the more volatile component. When a mixture has a maximum vapor pressure, it corresponds to a minimum boiling temperature. The lower the boiling temperature, the higher the vapor pressure. The boiling curve and the condensation curve coincide at this minimum point, which indicates the same composition for the liquid and vapor phase. Such mixtures, which do not change their composition during boiling, are called azeotropic mixtures ($X_1 = Y_1$).

For an ideal binary mixture, Raoult's law is written:

$$X_i \cdot P_i^0 = Y_i \cdot P \quad ; \quad X_1 + X_2 = 1 \quad ; \quad Y_1 + Y_2 = 1$$

The system chosen for the study, cyclohexane (1) + ethyl acetate (2), is a real system, which has azeotropes with minimum temperature.

3. THE EXPERIMENTAL PART

3.1. APPARATUS AND SUBSTANCES

- Ball with round bottom and with two necks
- Thermocouple
- Condenser Dimroth
- Heating nest
- Refractometer
- Voltage regulator
- Device for temperature measurement
- Pt100 temperature sensor
- Cyclohexane
- Ethyl acetate
- Solutions cyclohexane + ethyl acetate

Fig. 1. The experimental installation

3.2. PROCEDURE

The experimental installation is shown in fig. 1. Pour from the first mixture into the two-necked flask ~ 50 mL (about half full), place a few boiling chips (to initiate the boiling) and turn on the heating. Adjust the heating to the MAX option and by turning the heating regulator power knob to 6 so that there is a liquid reflux on the thermocouple protection tube a few minutes before the first drops reach the Dimroth. In order not to change the molar fraction (composition) of the vapor phase, the heating is stopped as soon as a minimum amount of product (up to the sign) is distilled. Collect the few drops of distillate (by turning the blue valve) into a Berzelius beaker to determine the refractive index (drop the distillate with a Pasteur pipette or by pouring it on the prism of the refractometer) and read the boiling temperature. The refractive index is used to determine the vapor phase composition of the calibration curve.

Turn off the heating, lower the heating nest on the stem of the stand and wait a few minutes for the balloon to cool. Carefully pour this mixture into the vial from which it was taken.

CAREFUL! The mixtures are hot and there is a risk of burns!

The procedure described above is repeated for the other mixtures and for the pure substances.

4. EXPERIMENTAL DATA PROCESSING

4.1. The data obtained are presented in a table of the form:

No. crt.	Solution	n_D inițial	X_1	X_2	n_D distillate	Y_1	Y_2	t, °C
1.								
2.								
3.								
4.								
5.								
6.								
7								

4.2. The boiling temperatures of the five mixtures cyclohexane (1) + ethyl acetate (2) are noted.

4.3. The refractive indices of the pure components and of the mixtures are determined, both for the liquid phase and for the vapor phase.

4.4. Calculate the compositions of the two phases (liquid, X_1, respectively of vapors, Y_1) from the equation of the calibration curve of the refractive indices according to the composition:

$$X_1(Y_1) = 1283,42232 \cdot n^3 - 5466,68377 \cdot n^2 + 7777,85811 \cdot n - 3695,41085;$$

4.5. Draw the boiling diagram of the cyclohexane binary mixture (1) + ethyl acetate (2).

Data from the literature

$M_1 = 84,16$ g/mol ; $M_2 = 88,1$ g/mol

$\rho_1 = 0,779$ g/cm^3 ; $\rho_2 = 0,897$ g/cm^3

$t_{az} = 70,95$ °C ; ; $X_1^{az} = Y_1^{az} = 0,4065$

$t_1^0 = 78,37°C$; ; $t_2^0 = 77,10°C$

5. QUESTIONS

5.1. What is the liquid curve? And what is the vapor curve?

5.2. Does the studied system exhibit a positive or negative deviation from ideality?

5.3. Is the vapor pressure at the azeotropic composition lower or higher than that predicted by Raoult's law? Explain.

5.4. In the case of an azeotropic binary mixture, is fractional distillation an appropriate separation method? Why?