EBULLIOSCOPY

1. PURPOSE OF THE WORK

Determination of the boiling temperature rise (ebullioscopic effect) of a solution with respect to the pure solvent.

2. THEORETICAL NOTIONS

If a small amount of substance B, which has negligible vapor pressure, is dissolved in a pure solvent A, the decrease in vapor pressure of A can be calculated using Raoult's law, assuming ideal solvent behavior. The decrease of the vapor pressure of the solution leads, in experiment, to a rise in the boiling temperature of the solution, compared to the pure solvent. Using the Schröder-van Laar equation it follows that

$$-\ln X_A = \frac{\Delta^v H_A}{R}\left(\frac{1}{T^o_{f,A}} - \frac{1}{T}\right) = \frac{\Delta^v H_A}{R}\left(\frac{T - T^o_{f,A}}{T^o_{f,A} T}\right) \qquad \begin{matrix} Y_B \cong 0 \\ Y_A \cong 1 \end{matrix} \tag{1}$$

where $\Delta^v H_A$ represents the vapor enthalpy of solvent, $\Delta T_{eb} = T - T^o_{f,A}$ represents the raising of the boiling temperature (the ebullioscopic effect), $T^o_{f,A}$ is the boiling temperature of the pure solvent, T is the boiling temperature of the solution, X_A is the molar fraction of solvent in the mixture.

It turns out that the ebullioscopy effect has the expression:

$$\Delta T_{eb} = -\frac{R\,T\,T^o_{f,A}}{\Delta^v H_A} \ln X_A \tag{2}$$

Introducing a series of approximations valid for dilute solutions:

$$T\,T^o_{f,A} \cong (T^o_{f,A})^2 \tag{3}$$

$$-\ln X_A = -\ln(1 - X_B) \approx X_B \tag{4}$$

it turns out that

$$\Delta T_{eb} = \frac{R(T^o_{f,A})^2}{\Delta^v H_A} X_B \tag{5}$$

For dilute solutions it is advisable to use the molality, *m*, instead of the molar fraction:

$$m = \frac{g_B 1000}{M_B g_A} = \frac{X_B 1000}{M_A} \tag{6}$$

g_A and g_B are the masses of solvent, respectively of the dissolved substance, of the solution, and M_A and M_B are the molar masses of the solvent, respectively of the dissolved substance.

Thus, the relation (5) becomes:

$$\Delta T_{eb} = \frac{R(T^o_{f,A})^2}{\Delta^v H_A} \frac{M_A}{1000} m = K_{eb}\, m \tag{7}$$

$$K_{eb} = \frac{R\left(T^o_{f,A}\right)^2}{\Delta^v H_A} \frac{M_A}{1000} \tag{8}$$

The K_{eb} constant is called the ebullioscopic constant; it represents the molal rise of the boiling temperature and has specific values for each solvent. Raising the boiling temperature is a colligative property, it depends on the amount of dissolved substance and not on the nature of the substance.

To determine the molar mass of the dissolved substance, combine the relations (6) and (7):

$$M_B = \frac{g_B 1000\, K_{eb}}{g_A \Delta T_{eb}} \tag{9}$$

Thus, the molar mass of a dissolved substance (urea) in a solvent (water) can be determined experimentally by measuring the increase of the boiling temperature of the solvent as a function of the concentration of the dissolved substance.

3. EXPERIMENTAL PART

3.1. APPARATUS AND SUBSTANCES

- experimental installation for the determination of the boiling temperature, urea, distilled water, funnel, wash bottle, analytical balance.

3.2. PROCEDURE

The experimental installation for determining the boiling temperature is shown in fig. 1. The main part thereof consists of two cylindrical glass tubes, denoted 1 and 2, concentric, fixed to each other by means of a threaded assembly, as in fig. 2. The outer tube 1 acts as a protective shell and has a threaded neck provided with a plug and two tubes, one side and the other at the bottom. The inner tube 2 has a threaded neck provided with a plug, a lateral tube located just below the threaded neck and a lateral opening (a) which is continued by a narrow glass tube inward.

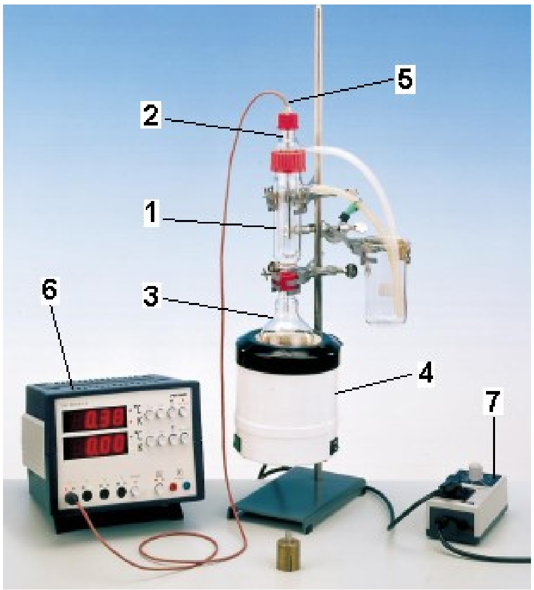

Fig. 1. Scheme of the experimental installation

1- Outer tube (protective jacket)
2- Inner tube
3- 250 mL flask
4- Heating nest
5- Temperature sensor, PT 100
6- temperature reading instrument
7- heating speed control device

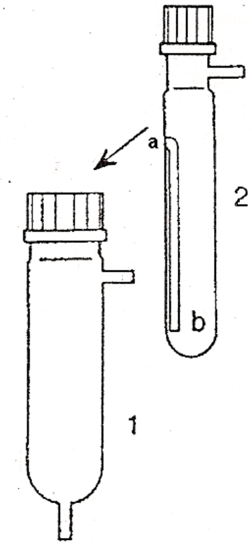

Fig. 2. The assembly of cylindrical glass tubes

***<u>Caution</u>*: When fastening tube 2 to tube 1 make sure that the opening (a) is located under the fixing gasket and is not covered by it.**

The tube 1 is then inserted into the glass flask, 3. It contains 150-200 mL of solvent (distilled water) and a few pieces of boiling chips. Place the flask in a heating system, 4 (heating nest).

About 35 mL of solvent (distilled water) is introduced into the inner vessel 2, followed by the temperature sensor, 5. It is connected to the Phywe 4-2 digital temperature reading instrument with digital display, 6.

Rubber tubes are connected to the two side openings of vessels 1 and 2. Their ends are left freely in a Berzelius glass, fixed in a stand, so that they do not touch the bottom of the glass. In this glass, some of the steam produced by boiling will condense.

A clamp is attached to the rubber hose attached to the outer tube, which is left open at the beginning.

The heating of the solvent in the flask 3 is started by operating a heating speed control device, 7. At the beginning of the heating, step 7 is selected and the Max option which ensures a rapid boiling, after which, when the temperature of the solvent in the vessel 2 reaches 87-90 ºC, the heating is switched on step 6, which ensures a uniform boiling. The vapors resulting from the boiling of the solvent in the flask ascend to the vessel 1 and thus heat the solvent in the inner tube 2. Some of the resulting vapors condense, passing again into the flask, another part passing through the rubber tube into the Berzelius glass.

Is prepared an amount of substance (urea) of about 0.7 g weighed at the analytical balance (weighing accuracy 0.1 mg) dissolved in 5 mL of water. The total mass of the solvent in inner tube will be determined precisely at the end of the experiment by weighing.

When the temperature of the solvent in the vessel 2 does not change under these conditions (this will be around 98 ° C), lower the heating nest for a short time, until the boiling stops. In this way the condensate in the outer vessel 1 passes back into the flask. Then the heating nest is raised again, and when the boiling starts again, the clamp is closed. The resulting (slightly overheated) vapors pass this time through the side opening (a) and the narrow tube into the inner vessel 2, bubbling the solvent, so it is important the opening (a) to not be closed when fixing the installation (otherwise there is a danger that the pressure in the system to grow and the weakest part will broke).

Under these conditions, the temperature of the solvent in the inner vessel rapidly reaches a constant value, which represents the boiling temperature of the solvent ($T^{o}_{f,A}$). At this point the temperature measuring instrument is set to indicate the temperature difference related to the boiling temperature of the solvent, by pressing the SET 0.00 key (accuracy in reading the temperature of 0.01 K). Check that the constant boiling temperature is reached by ± 0.03 K (if higher, set the constant temperature again by pressing the SET 0.00 key). Thus, one display will indicate the absolute temperature, and the other, the relative temperature.

It is noteworthy that the boiling happens all the time at atmospheric pressure (isobaric conditions), due to the permanent contact with the environment through the rubber connections.

After recording the boiling temperature of the solvent, open the clamp, remove the sensor, add the amount of urea dissolved in 5 mL of water through a funnel, wash the glass and the funnel with 1-2 mL of distilled water from the wash bottle and re-insert the sensor into the solution. After about 5 minutes of boiling, the clamp is closed again. At first, a decrease in temperature is observed, due to the removal of the sensor, after which it rises again, finally exceeding the boiling temperature of the solvent. When the value of the difference in temperature has become almost constant (variations of one hundredth of degrees are observed, but an average of the values is taken), this value is noted ΔT_{eb} .

The clamp is opened and the heating is switched off. Attention: first open the clamp, then turn off the heating, otherwise the solution in the vessel 2 will siphon into the outer vessel 1, and the experiment will be compromised by the impossibility of finally determining the mass of solvent in the inner vessel.

After the glass parts of the installation are cooled, the inner vessel is removed from the outer casing, the cooled solution is emptied into a glass and weighed (or weighed tube 2 with solution, having previously cooled to room temperature). The mass of solution is thus determined, m_{sol}. By the difference, $m_{sol}-m_{uree}$ results in the mass of solvent, which is required in the subsequent calculations.

The dependence of raising the boiling water temperature on the concentration of urea in the solution (linear dependence) can be demonstrated during an experiment by successively adding known quantities of the dissolved substance and measuring the temperature variation each time. In this case, the mass of solvent should be determined by weighing at the end of each addition.

4. EXPERIMENTAL DATA PROCESSING

4.1. The molar mass of the dissolved substance is determined based on the relation (9), using its value ΔT_{eb} experimentally determined and the value of the ebullioscopic constant of the water;

4.2. The result obtained is compared with the value from the literature, calculating the percentage error;

4.3. Compare its value ΔT_{eb} obtained experimentally with the value calculated with relation (2).

Note: The mass of the empty tube 2 is known (as in Fig. 2) = 76.271 g.

Data from the literature

$K_{eb,\mathrm{H_2O}} = 0,515$ K·Kg/mol ; $M_{(NH_2)_2O} = 60,06$ g/mol

$\Delta^{v}H_{H_2O} = 40680$ J/mol ; $M_{H_2O} = 18,03$ g/mol

5. QUESTIONS

5.1. What are the practical applications of the ebullioscopic phenomenon, of increasing the boiling temperature of a solution? A polymer solution in a suitable solvent is contemplated.

5.2. Can the ebullioscopic method be used in the purity analysis of some products? Give examples.