CRYOSCOPY

1. PURPOSE OF THE WORK

Determination of the reduction of the solidification temperature (cryoscopic effect) of a solution with respect to the pure solvent.

2. THEORETICAL NOTIONS

If a small amount of substance B is dissolved in a pure solvent A, the solidification temperature (freezing, crystallization) of the solution drops below the temperature of the pure solvent. Assuming that A and B do not mix in the solid phase (which means that $X_A^s = X_B^s \cong 1$), using the Schröder-van Laar equation it follows that

$$\ln X_A^l = \frac{\Delta^t H_A}{R}\left(\frac{1}{T_{t,A}^o} - \frac{1}{T}\right) = -\frac{\Delta^t H_A}{R}\left(\frac{T_{t,A}^o - T}{T_{t,A}^o T}\right) \tag{1}$$

where $\Delta^t H_A$ represents the melting enthalpy of the solvent, $\Delta T_{cr} = T_{t,A}^o - T$ represents the lowering of the solidification temperature (cryoscopic effect), $T_{t,A}^o$ is the solidification / melting temperature of the pure solvent, T is the solidification / melting temperature of the solution, X_A^l is the molar fraction of the solvent in solution. It turns out that the cryoscopic effect has the expression:

$$\Delta T_{cr} = -\frac{R\,T\,T_{t,A}^o}{\Delta^t H_A}\ln X_A^l \tag{2}$$

Introducing a series of approximations valid for dilute solutions

$$T\,T_{t,A}^o \cong \left(T_{t,A}^o\right)^2 \tag{3}$$

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

it turns out that

$$\Delta T_{cr} = \frac{R\left(T_{t,A}^o\right)^2}{\Delta^t H_A} X_B^l \tag{5}$$

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

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

where g_A and g_B are the masses of solvent, respectively of 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

$$\Delta T_{cr} = \frac{R\left(T_{t,A}^o\right)^2}{\Delta^t H_A} \frac{M_A}{1000} m = K_{cr}\, m \tag{7}$$

$$K_{cr} = \frac{R\left(T_{t,A}^o\right)^2}{\Delta^t H_A} \frac{M_A}{1000} \tag{8}$$

The constant K_{cr} is called the cryoscopic constant; it represents the molal lowering of the solidification temperature, having specific values for each solvent. The lowering of the solidification temperature is a colligative property, it depends on the amount of dissolved substance and not on its nature.

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

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

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

If the dissolved substance dissociates into ions, equation (7) is written:

$$\Delta T_{cr} = i\, K_{cr}\, m \tag{10}$$

where i is Van´t Hoff's factor, which depends on the degree of dissociation of the electrolyte.

3. EXPERIMENTAL PART

3.1. APPARATUS AND SUBSTANCES

- experimental plant for determining the solidification temperature, urea, NaCl, distilled water, graduated cylinder, Berzelius glasses, kitchen salt, ice, analytical balance.

The experimental installation for determining the solidification temperature is shown in fig. 1.

The main part of it is the assembly of two cylindrical glass tubes, concentric, 1 and 2, fixed to each other by means of a threaded stopper with gasket, marked with a in figure 2. The outer tube 1 acts as a protective casing for tube 2 and can be used as such, filled with air, but it is preferable to be filled with 35-40 mL ethanol, which provides better heat transfer. The inner tube 2 has a threaded neck provided with a plug through which the temperature sensor is inserted and a side tube for introducing the solutions. This is the vessel in which the solidification temperature of the solvent and solutions is determined. The base of the vessel is flat, allowing a magnetic stirrer to rotate.

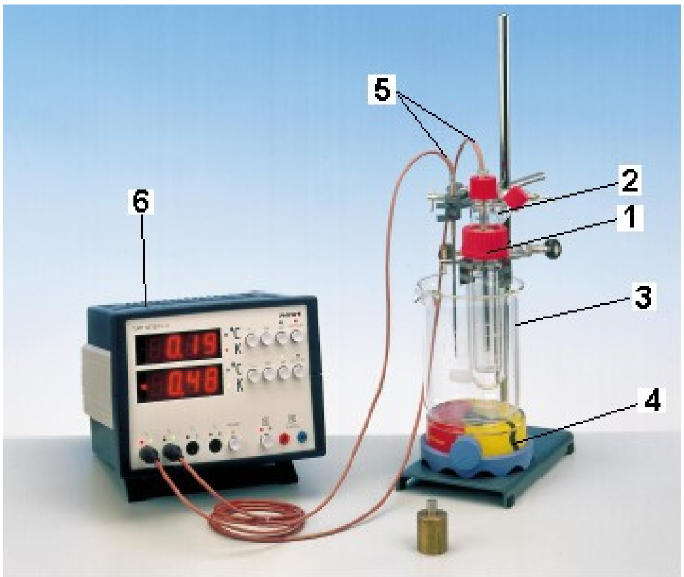

Fig. 1. Scheme of the experimental installation

1- Outer tube (protective cover)
2- Inner tube
3- Berzelius 1000 mL beaker
4- Magnetic stirrer
5- Temperature sensors, PT 100
6- Temperature reading instrument

3.2. PROCEDURE

The assembly of the two tubes is centrally fixed, by means of clips, in a Berzelius beaker, 3, which is placed on a magnetic stirrer, 4. The Berzelius beaker contains cooling mixture ice and kitchen salt (generally 3 parts ice and a salt part of the kitchen ensures a temperature of about -20 ºC).

Through the threaded plug the temperature sensor is inserted, PT 100 (protected by a glass tube) connected to the Phywe 4-2 temperature display instrument, 6, so on one of the displays the sample temperature of the inner tube is read. A second sensor is introduced into the cooling mixture, its (control) temperature being read on the other display.

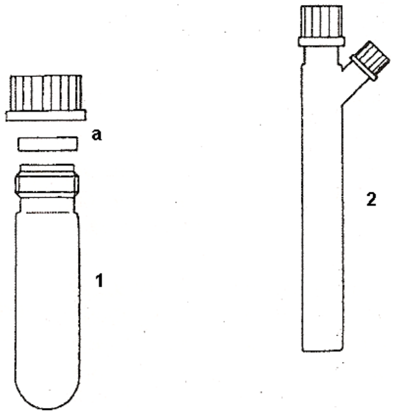

Fig. 2. The assembly of cylindrical glass tubes

Under the conditions of the work, the temperature of the cooling mixture should be around -10 ºC, which is obtained from filling the vessel 3 with two-thirds of ice, over which 2-4 spatulas of salt are added. The contents of the Berzelius glass (ice + salt) are mixed throughout the experiment carefully to avoid breaking the glass tubes and the magnetic stirrer must be switched on. If necessary (the temperature does not drop below -10 ° C after a few minutes of stirring) add more salt. This temperature will allow the contents of tube 2 to cool rapidly in about 15 minutes.

The measurements are made in two stages, but following the same experimental protocol:

a) determining the water solidification temperature - when the distilled water is cooled;

b) determination of the solidification temperature of the urea solution, respectively of NaCl - when the solutions are cooled one by one.

For this, the temperature is recorded each 15 seconds for the pure water, respectively for the solutions (of urea and NaCl), from the moment the temperature displayed by the internal sensor is 2 ° C, until the constant value is established (as in figure 3) . As the figure shows, at first the temperature decreases in time, passes through a minimum (metastable phase) and then when the crystallization begins, the temperature rises slightly, then reaching a constant value (in the case of water there is a possibility that the minimum is not observed). Cooling curves must be measured for a sufficiently long period to determine the plateau, which represents the solidification temperature of the solvent, $T^{o}_{t,A}$, respectively of the solution, *T*.

To measure the solvent cooling curve, tube 2 is charged with 25 mL of water, mounted in the system and cooled to temperature.

After determining the solvent cooling curve, lift the tubes from the cooling mixture to replace the solvent with the urea solution, respectively NaCl.

Prepare solutions of about 0.2 molal by dissolving in 25 mL of distilled water 0.3 g urea, respectively NaCl, weighed at the analytical balance (weighing accuracy 0.1 mg). Replace the water with the prepared solution, then re-enter the installation in the cooling mixture and follow the variation of the temperature of the solution over time, starting at about 2° C. A cooling curve similar to the solvent is obtained, resulting in the solidification temperature of the solution, *T*.

The ice formed in the vessel 2 is melted by the addition of (warmer) water or the passage of tube 2 under a stream of water.

Caution: Do not throw ethanol between the tubes or the glycerin in the sensor pads!

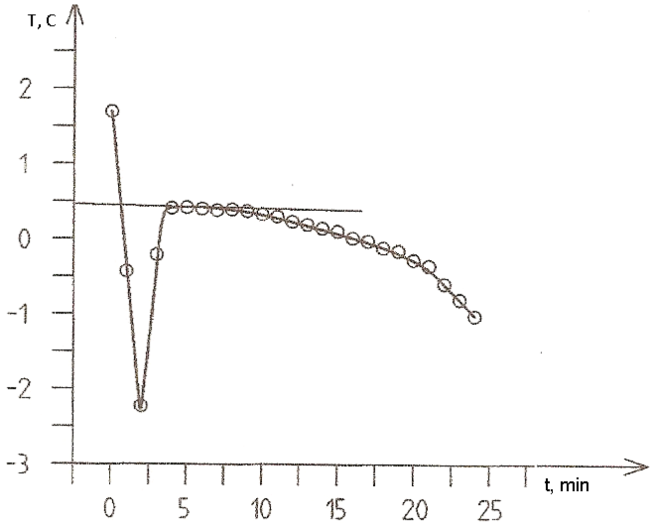

Fig. 3. Cooling curve for solvent / solution

4. EXPERIMENTAL DATA PROCESSING

4.1. The experimental data are recorded as a table:

Time, min	t, °C, Water	t, °C, NaCl solution	t, °C, Urea solution
0			
0.25			
0.5			
0.75			
…			

4.2. Draw the cooling curves for both solvent and urea and / or NaCl solutions; by extrapolation the solidification temperatures of the solvent are determined, $T^{o}_{t,A}$, respectively the solution, *T;*

4.3. The molar mass of the dissolved substance is determined based on the relation (9), using the value $\Delta T_{cr} = T^{o}_{t,A} - T$ and cryoscopic constant of water;

4.4. The molar masses obtained are compared with the literature values, calculating the percentage errors;

4.5. Compare its value $\varDelta T_{cr}$ obtained experimentally with the value calculated with relation (2);

4.6. Determine the *i* van't Hoff factor for urea and sodium chloride (*i* = *Mlit / Mexp*) and discuss the results.

Data from the literature

$K_{cr,H_2O} = 1{,}86$ K Kg/mol ; $M_{(NH_2)_2O} = 60{,}06$ g/mol

$\Delta^{t}H_{H_2O} = 6014$ J/mol ; $M_{NaCl} = 58{,}44$ g/mol

5. QUESTIONS

5.1. What are the practical applications of the cryoscopic phenomenon, of lowering the freezing temperature of a solution? Applications are considered in the food field, but also in everyday life.

5.2. How the cryoscopic method is used in the purity analysis of some products. Give examples.