

6. SOLID-LIQUID EQUILIBRIUMS IN AQUEOUS SOLUTIONS

GOALS

- Check the formation of a solid phase as an aqueous solution cools.
- Verify that the equilibrium temperature of an aqueous solution mixed with ice in an adiabatic container depends on the solute concentration.
- Verify that the freezing-point depression of an aqueous solution provoked by different solutes, with identical molality, is different respect to the one predicted by the ideal law, and also different from each other.
- Use concepts such as the activity, the activity coefficient or the osmotic coefficient as a way of quantifying these deviations.

THEORETICAL BACKGROUND

The freezing-point depression of a liquid due to the presence of a solute (lower cryoscopic constant) is one of what are known as the colligative properties of solutions (such as the rise in the ebullioscopic constant, the vapour pressure decrease or osmotic pressure). Historically this has been very useful when determining the molecular weights of unknown solutes, as was shown in an experiment from the Experimental Methodology in Chemistry course during 1st year Chemistry.

The equation that describes the freezing-point depression in a solution that is sufficiently diluted is:

$$\Delta T_c = K_c m$$

where this decrease (ΔT_c) is expressed as a function of the molality (mols of solute per kilogram of solvent) and a constant that is characteristic of each solvent, K_c , the cryoscopic or freezing-point constant. For water, this constant is 1.86.

It was soon experimentally shown that this law was not met at very high concentrations and that, particularly in the case of ionic solutions, solutions with equal molality but a different solute caused a freezing depression that could be substantially different.

One way of expressing these deviations, in the case of non-ionic solutions, is to determine the solvent's activity (a_1) or its activity coefficient (γ_1), which can be calculated with the following expressions:

$$\ln a_1 = \frac{\Delta_{fus} H_m}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right)$$

$$\gamma_1 = a_1 / x_1$$

where T_0 is the pure solvent freezing temperature (water in this case) and T the freezing temperature of water in the solution. $\Delta_{fus}H_m$ is the molar enthalpy of water fusion (6002 J/mol) and x_1 the molar fraction of the solvent in the solution.

Another way of quantifying these deviations was the so called van't Hoff factor defined as:

$$i = \frac{\Delta T_c \text{ (experimental)}}{K_c m}$$

Soon it was proven experimentally that the van't Hoff factor increases as the concentration decreases. Non-ionic solutes tend towards one with an asymptotic shape, while ionic solutions tended towards a number (ν) that corresponds to the number of ions that the ionic substance generates in the solution (for example, $\nu=2$ in the case of NaCl and equal to 3 in the case of CaCl_2).

In order to take into account all these factors, the osmotic coefficient (ϕ) was entered, as a function of the molality, as:

$$\phi(m) = \frac{\Delta T_c \text{ (experimental)}}{\nu K_c m}$$

It is clear that for a certain molality:

$$i = \nu \phi$$

with ϕ tending towards 1 and i tending towards ν when the molality is tending towards zero. This type of behaviour of ionic solutions can be explained using the Debye-Hückel theory that will be covered in Physical Chemistry I.

Given that ϕ is a measurement of the deviation from the ideal nature of the ionic solutions, it has to be related to the activity and the activity coefficient of these solutions. It can be demonstrated that there is a relationship between ϕ and the average ionic activity coefficient γ_{\pm} , that we will see in Physical Chemistry I, by means of the equation:

$$\ln(\gamma_{\pm}) = (\phi - 1) + \int_0^m \frac{(\phi - 1)}{m} dm$$

although evaluating γ_{\pm} from this equation requires very precise measurements of cryoscopic constant drops for the equipment that you have in the Lab. However, it is easier to corroborate that ϕ follows an equation derived from the Debye-Hückel theory:

$$\phi = 1 - 0.38\sigma m^{1/2}$$

where σ is a function of the type of ionic solution.

EXPERIMENTAL PROCEDURE

Equipment	Reactants
A cooling Bath	NaCl to cool down the dissolution
A Thermometer with centesimal resolution	Ethanol
A Dewar flask	Potassium hydrogen phthalate
Two metallic stirrers (large and small)	CaCl ₂ anhydrous
Test-tubes to freeze the dissolutions	NaOH
100 mL two graduated cylinders	phenolphthalein
A 250 mL Volumetric Flask	
2 100 mL Beakers	

Water/sodium chloride equilibrium

In the experiments explained below, you are going to use what is known as the **cooling bath mixture** to cool our solutions. It comprises a mixture of liquid water and ice to which common salt (NaCl) is added. The actual mixture that you are using to cool solutions is in itself a very interesting system to understand solid/liquid equilibriums in solutions.

In a Dewar flask, add ice right up to the top and then add water until you get a mixture than can be moved easily with a metal stirrer that you will be given. Add a little more ice so that the Dewar flask is almost full. Insert the probe from a thermometer measuring in hundredths and check the temperature after stirring the water and ice mixture intensely. Explain your result.

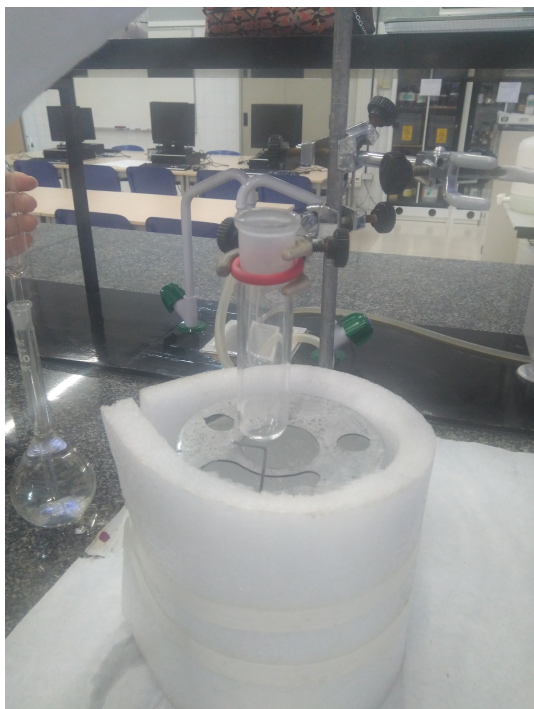
Add 6 grams of common salt to the Dewar flask. Stir intensely and check that it reaches a new equilibrium temperature. Note it down and add 6 grams of salt twice, repeating the process and noting down the temperature it reaches each time. Discuss the results.

When you have finished, do not throw the mixture, as you will use it in the next step.

Drop in cryoscopic constant in aqueous sucrose solutions

Sucrose or conventional sugar is an organic substance with the molecular formula C₁₂H₂₂O₁₁ that dissolves in water but does not ionise in the process.

Prepare a 0.6 M aqueous solution, using a 250 ml volumetric flask. Determine its freezing point using a burette to take off 50 cc of this solution in one of the tubes provided. The tube will be inserted in a cooling bath mixture of water, ice and salt that has reached at least -5°C , using the most of the mixture from the previous experiment. The thermometer probe will be inserted in the tube. It should not touch the walls of the tube or the metal stirrers (see pictures 1 and 2 below). Check the temperature every 30 seconds; it will decrease quite quickly, which will cause what is known as the over-cooling effect. After reaching a certain low temperature, you will see that it starts to go up until it stabilises at a value that is the value you take as the freezing point of your solution.



Picture 1: The cooling bath mixture before the tube is inserted

Repeat the process another five times, preparing 50 ml of new solutions, diluting 37.5, 25, 19, 12.5 and 6 ml of the starting solution with the corresponding volumes of water. Use the two burettes provided for this purpose.

Remember that students need to know the molality of the solutions and not the molarity. Explain how you are going to calculate it and propose any extra measurements that you need for it.

Be careful: the cooling bath mixture shouldn't be below -5.5° .

Freezing-Point depression in ionic aqueous solutions

This involves repeating the sucrose experiments with an ionic substance, CaCl_2 anhydrous. The procedure is similar to what was used for the sucrose, also considering

that the CaCl_2 anhydrous is sufficiently stable to be able to prepare solutions with accurate concentrations merely by weighing. In this case, the cooling bath mixture of water, ice and salt should have reached at least -8°C before starting the experiment.

Be careful: the cooling bath mixture shouldn't be below -8.5° .

Questions to be resolved

- Draw a graph in Excel that, while representing decreases in water freezing temperature against the molality, includes data from sucrose, from the ionic substance that you have been offered and data that would be obtained in the case that the ideal law was met ($\Delta T_c = K_c m$). Explain the results obtained.
- In the case of the sucrose solutions, determine the water activity in each of them, and the activity coefficient. Explain the results.
- With data from concentrations and freezing temperature depressions, determine the osmotic coefficient value ϕ for each of the experiments. Compare the results from the sucrose solutions and the ionic substance that you have used.