KEMS448 Physical Chemistry
Advanced Laboratory Work

Freezing Point Depression

1   Introduction

Colligative properties are properties of liquids that depend only on the amount of dissolved matter (concentration), not its quality. Colligative properties are the decrease in vapour pressure, boiling point elevation, freezing point depression, and osmotic pressure. Measuring colligative properties is therefore basically comparing the solution's quantity to a pure solvent's. Familiar examples include the use of ethylene (or propylene) glycol as coolants in cars, salting roads during the winter, or the osmotic pressure responsible for fluid balance in cells. The properties are also used to determine the molecular masses of organic compounds. In electrolytic solutions, the colligative properties do not behave ideally, which led to the definition of activity coefficients, and the development of the theory concerning interactions between ions.

2   Theory

2.1   Thermodynamics

Let us first examine a solution in which the solute vapour pressure is zero, i.e. the solute is non-vaporizable. The solvent on the other hand has a vapour pressure. According to Raoult's law, an ideal solution has a vapour pressure dependent on the composition of the solution.

$$p = \chi_{solvent} p^*_{solvent} + \chi_{solute} p^*_{solute}, \tag{1}$$

where χ is the mole fraction of the solvent (or solute) and p^* is the pure solvent's (or solute's) vapour pressure. Because it is assumed that the solute is non-vaporizable, the latter term in equation (1) is zero. In an ideal solution there are no attractive forces between the solvent and the solute, and the solvatation enthalpy $\Delta H_{solv} = 0$. An example of a nearly ideal mixture is toluene in benzene. Normally, all dilute solutions have near ideal behaviour, i.e. they behave according to Raoult's law. According to the law, the solution's vapour pressure decreases when an alien substance is added into a pure solvent (see Figure 1). Because the vapour pressure of the solution is lower, the temperature needs to be raised higher for boiling to begin. In other words, the solution's boiling point has elevated compared to a pure solvent. On the other hand, solvent molecules are more frequently transferred from the solid into the liquid phase, so the melting (freezing) point decreases.

The chemical potential of a solution is

$$\mu = \mu^* + RT \ln \chi_{solvent}, \tag{2}$$

where μ^* is the chemical potential of a pure solvent. Because $\chi_{solvent} < 1$, the chemical potential of a solution, μ, is always lower than a pure solvent's. Let's assume only the chemical potential of the liquid phase decreases because of the effect of the dissolved matter. In other words, the dissolved matter does not vapourize during boiling, or crystallize when the solution freezes.
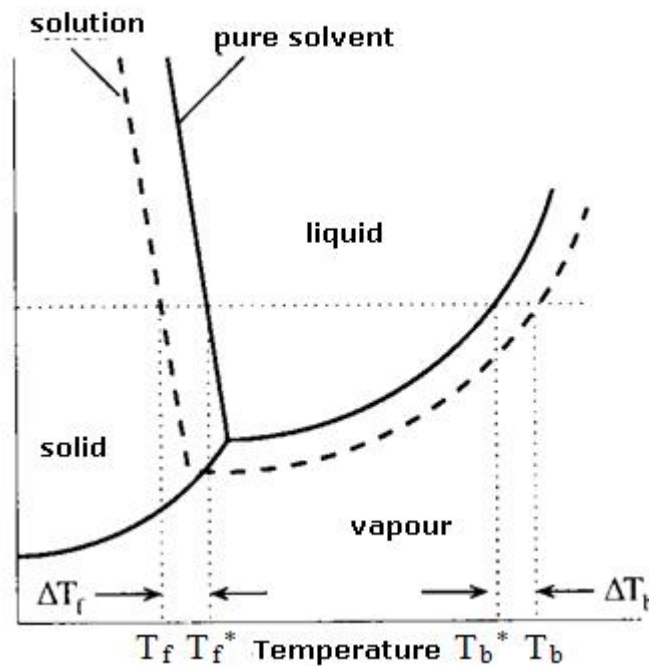

Figure 1: *The phase diagrams of a pure solvent and a solution. Adding impurities into the solvent decreases vapour pressure, which lowers the freezing point and raises the boiling point.*

In Figure 2, the chemical potential of a solution is presented as a function of temperature. The slope represents the molar Gibbs free energy of the system, which is always larger for vapours than liquids. In a given temperature, the stable phase is the one with the lowest chemical potential. When an another substance is added to a pure solvent, the chemical potential decreases, which lowers the freezing point and raises the boiling point. This is also shown in Figure 2.

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In addition to the decrease in vapour pressure, the raise in boiling point and the decrease of freezing point, the osmotic pressure is a colligative property. The solution is separated from a pure solvent with a semipermeable membrane, through which the solvent molecules can travel through, but the dissolved molecules cannot. Spontaneous solvent molecule current through the membrane is called osmosis. For the solvent current to disappear, a pressure has to be applied to the solution. This pressure is called the osmotic pressure Π. The chemical potential of a pure solvent in a pressure p is μ^*. As previously noted, in a solution the chemical potential is lower, so the system tends to approach an equilibrium, in which the chemical potential is the same on both sides of the membrane. This is achieved when the solution's pressure reaches $p + \Pi$, because of the pressure
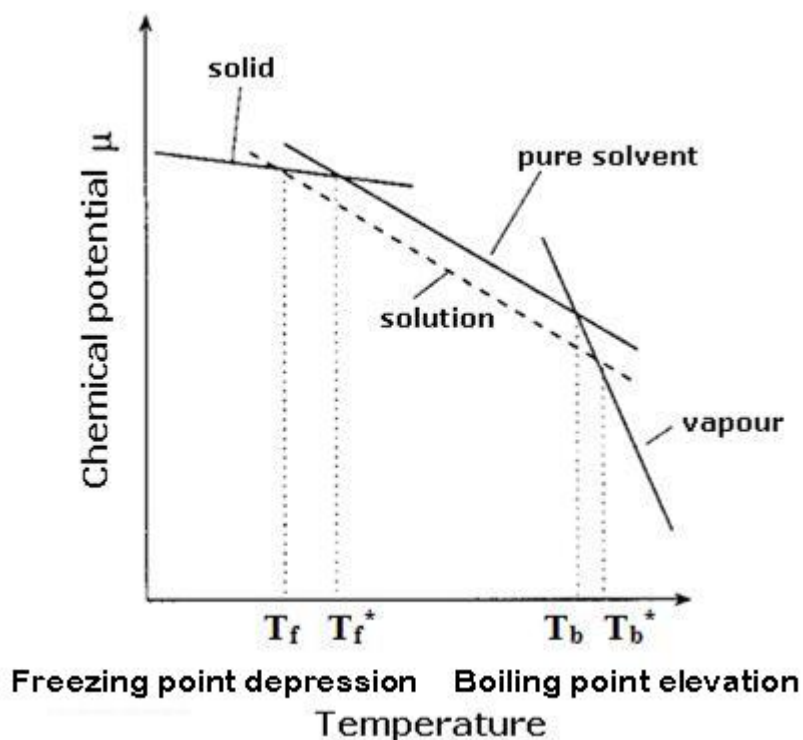
Figure 2: *The chemical potential as a function of temperature. In any temperature, the stable phase is the one with the smallest chemical potential. When impurities are added to a pure solvent, the chemical potential of the liquid decreases resulting in elevation of the boiling point, and decrease of the freezing point.*

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dependence of the chemical potential.

2.2 Molecular interpretation

The vapour pressure of a liquid represents the tendency of the molecules in the liquid to transfer into the gas phase, striving for a greater entropy in the system. If the liquid is a solution of a solvent and a dissolved substance, less solvent molecules are able to transfer into the gas phase from the liquid (Figure 3). From this, it follows that the vapour pressure decreases compared to a pure solvent. On the other hand, the dissolved matter increases the entropy in the solution (also in ideal cases), which leads to a decrease in the liquid's tendency to transfer into the gas phase, raising the boiling temperature. Respectively, the increased disorder in the solution lowers the tendency to freeze, i.e. lowers the freezing temperature.
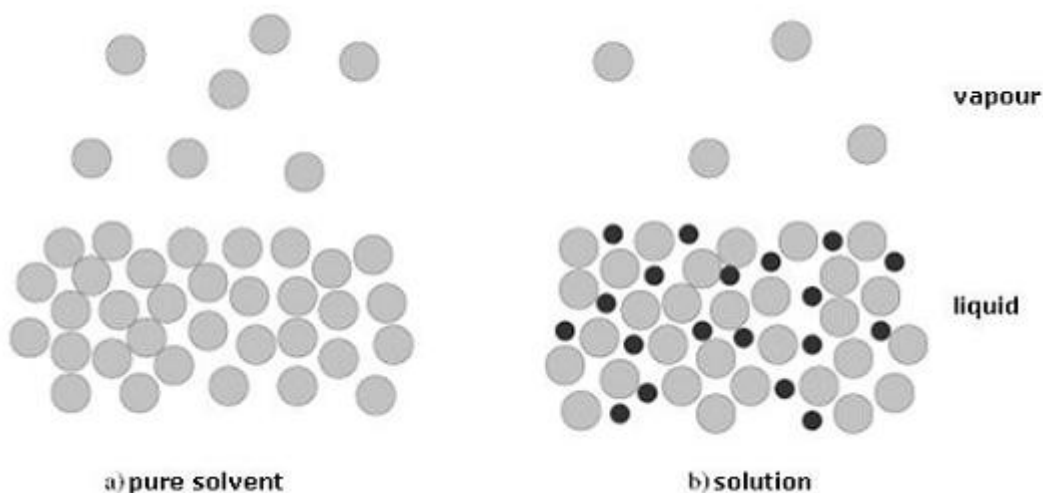

Figure 3: *The effects of impurities on the vapour pressure.*

2.3 Freezing point depression of electrolytic solutions

For non-electrolytic solutions the freezing point depression is

$$\Delta T_f = K_f b, \tag{3}$$

where b is the molality of the solution and K_f a cryoscopic constant characteristic of the solvent:

$$K_f = \frac{M_{w(solvent)}RT_f^2}{1000\Delta H_f}, \tag{4}$$

where $M_{w(solvent)}$ is the solvent's molecular mass, R the molar gas constant, T_f the freezing temperature and ΔH_f the melting heat. The factor 1000 is meant for transforming grams into kilograms for molality. For water, the cryoscopic constant is 1,860 $\frac{K \cdot kg}{mol}$.

Compounds that form ions when dissolved produce several particles into the solution. For example NaCl produces two and $FeCl_3$ four ions. Therefore, the colligative properties of electrolytic solutions are always greater than for what could be expected. When dealing with electrolytic solutions and their colligative properties, the so called van't Hoff coefficient i is introduced

$$i = \frac{\Delta T_f}{(\Delta T_f)_0}, \tag{5}$$

where ΔT_f is the freezing point depression (or some other colligative property) and $(\Delta T_f)_0$ is the non-electrolytic decrease in the freezing point in the same concentration. Therefore, the freezing point depression for an electrolytic solution is

$$\Delta T_f = iK_f b. \tag{6}$$

In dilute solutions, the van't Hoff coefficient increases, when molality decreases, reaching a limit value of 2 for electrolytes such as NaCl, HNO_3 or $MgSO_4$, the limit value of 3 for $CaCl_3$, H_2SO_4, etc. In other words, in a dilute solution, the van't Hoff coefficient is the same as the number of ions ν formed when the substance dissolves. In addition, defining the osmotic coefficient g tells us how much the colligative properties of a solution differ from those of a strong, completely dissociated electrolyte.

$$i = \nu g \tag{7}$$

Experimentally, the values of i and ν are usually not integers, which is due to interactions between ions in the solution. In an infinitesimally dilute solution, the osmotic coefficient gets the value of one, because of no intermolecular interactions. In that situation, the osmotic coefficient represents the difference of the colligative properties in pure and impure solutions. Through the osmotic coefficient, the activity coefficient of the solvent can be determined, and vice versa. The more

Table 1: Theoretical and experimental values for the van't Hoff coefficient

Electrolyte ($0,05\ M$)	i_{exp}	i_{calc}
HCl	1,9	2,0
NaCl	1,9	2,0
$MgSO_4$	1,3	2,0
$MgCl_2$	2,7	3,0
$FeCl_3$	3,4	4,0

potent the solution is concentration-wise, the more ion pairs are formed and all ions do not behave like they were completely separate from each other. When a part of the ions receive a pair ion of opposite electric charge, they start acting like one particle, decreasing the van't Hoff coefficient. Table 1 gives some van't Hoff coefficients, both calculated and experimental for some electrolytes.

Because the molality (the weight concentration) is determined through the ratio of the reagent and solvent masses, with equation (6) the molecular mass can be determined as

$$M_B = K_f \frac{im_B}{\Delta T_f m_A},\tag{8}$$

where m_A is the solvent's mass and m_B the mass of the dissolved electrolyte.

3   Experimental methods

Weigh salt (NaCl and $MgSO_4$) so that the temperature of the water is decreased by two degrees when the salt is dissolved into the water. The amount needed can be calculate from equation (8). A reasonable amount of solution in the sample chamber is about 20 ml.

Prepare a mixture of sea salt and ice (ratio 1:4) into a plastic beaker, which will be the cooler of the system. Fill the beaker and bury the outer glass tube as deep as possible into the mixture. Place the beaker in an isolating styrofoam box, so the solution stays cool enough ($-10 - -15\ ^oC$) for the duration of measurements.

In this laboratory work, the temperature with respect to time is observed. First cool the sample tube in a regular ice bath, until its temperature is about three

degrees above zero, and then place the sample tube inside the outer glass tube placed in the salt-ice mixture. Stir the sample solution efficiently enough, so that the temperature inside it stays evenly distributed.

First, the stage of decreasing temperature is observed (when the liquid's heat capacity is constant) well past the freezing point. After freezing, a group of microcrystals is formed into the solution, and the heat capacity gets another, usually smaller, constant value. From these measurements, a plot of two straight lines can be drawn, where the two lines cross at the freezing temperature.

In practice, there are phenomena that complicate the measurement, for example subcooling of the solution. The subcooling can be prevented with adequate stirring. If you suspect the solution is indeed subcooled, in other words showing
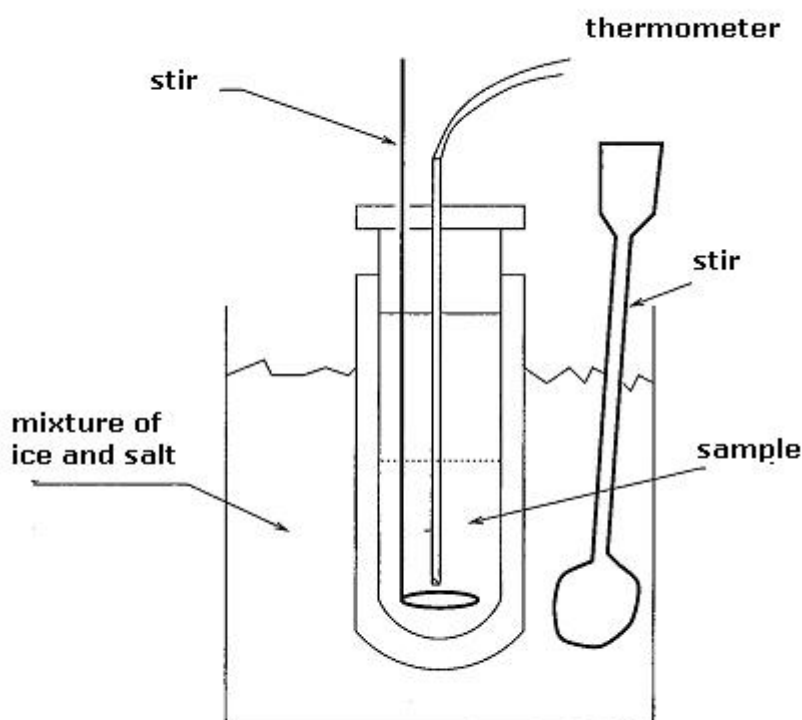

Figure 4: *The equipment for measuring the freezing point depression*

values well below of what should be the freezing temperature, you can test it by dropping a small bit of pure ice into the solution while stirring. If the temperature normalizes around the freezing point, microcrystals have started to form around the pure ice bit. Measure *at least* five different data points after the normalization to draw the curve. Another clear source for error might be the bath temperature. If the bath is too warm, it cannot cool down the system with a constant rate, and in a bath too cold, the process is too fast and the solution subcools, freezing too fast after that.

Measure three different sample systems in this work: pure water (ion-changed, also ensure the cleanness of the glass equipment) and two different dilute salt solutions. Make two measurements for each system. Write down temperature data for example after every minute.

4 Results and analysis

For each different data set, plot the temperature against time. The slopes of the linear fits before and after (partial) freezing tell the two different heat capacities in the solution. The crossing point of these two linear fits is the starting temperature of the gradual freezing. If the stirring was efficient enough, this should also be the decreased freezing point of the solution. If subcooling has been found in the measurement, use only the data points after the subcooling has been resolved with the bit of ice for the second linear fit.

Calculate the molecular masses for both salts based on the measurements. Use both theoretical and experimental van't Hoff coefficients and compare the results. Estimate the errors using the standard error analysis through error propagation.

References

[1] Atkins P.W., de Paula J., *Physical Chemistry*, 8th Edition, Oxford University Press