Problem VI.E ... colligative properties of solutions 12 points; průměr 7,74; řešilo 23 studentů

Measure the cryoscopic constant, the constant of proportionality between the melting point of a solution and its molality. Measure this constant for several solutions and verify Raoult's 3rd law, which states that the value of the constant does not depend on the solute, but only on the solvent.   *Tomáš Č. wanted to educate.*

Theory

The amount of solute in solution can be expressed in several possible quantities. The most common are the mass fraction (mass of the substance to the mass of the solution), mass concentration (mass of a substance to the volume of the solution), molar concentration or molarity (amount of substance to the volume of the solution), and molality (amount of substance to the mass of solvent). Raoult's laws[1] are formulated precisely using this quantity. They describe properties that depend only on the concentration of the solute, not its type. Specifically, Raoult's first law concerns the partial pressures of vapor over solutions, the second Raoult's law with the boiling points, and the third Raoult's law with melting points. According to it, the change in the melting point of the solution $\Delta T_t = T_t - T_{t0}$ depends on the molality of the solution b as

$$\Delta T_t = -Kb \, ,$$

where K is the cryoscopic constant, which can be expressed as

$$K = \frac{RM_0 T_{t0}^2}{\Delta H_t^{(mol)}} \, ,$$

where R is the universal gas constant, M_0 is the molar mass of the solvent, T_{t0} is the melting point of the solvent, and $\Delta H_t^{(mol)}$ is the molar enthalpy change, or the molar latent heat of fusion. The molality of a solution is expressed as the mass of the solute to the mass of the solvent, so

$$b = \frac{m_l}{m_v} = \frac{\frac{m_l}{M_l}}{V_v \rho_v} = \frac{m_l}{M_l V_v \rho_v} \, ,$$

where m_l is the mass of the solute, M_l is its molar mass, V_v is the volume of water, and $\rho_v \approx \approx 1\,000 \, \text{kg·m}^{-3}$ is the density of water. For water, the cryoscopic constant is $K = 1.855 \, \text{K·kg·mol}^{-1}$.

Measurement procedure

For the measurements, we used four commonly available substances dissolved in water because water was the only available solvent we could freeze effectively in the kitchen freezer. We used table salt (sodium chloride), crystal sugar (sucrose), citric acid, and baking soda (sodium bicarbonate), which are all commonly available substances, all of which are water-soluble and have a known chemical composition. Since we cannot measure the amount of substance directly, we must measure the mass of the substance in solution. Therefore, we are interested in the molar mass of the solute. Another constraint is the maximum amount of substance we can dissolve in water before reaching a saturated solution. The maximum mass concentrations ρ and molar masses of substances M are given in Table 1. Less concentrated solutions were

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[1] https://cs.wikipedia.org/wiki/Raoult%C5%AFv_z%C3%A1kon

Table 1: Molar masses and mass concentrations of saturated solutions of substances used

substances	M	ρ
	$\mathrm{g\cdot mol^{-1}}$	$\mathrm{g/100\,ml}$
citric acid	192	59,2
baking soda	84	9,6
salt	58	35,8
sugar	342	202

prepared by mixing the saturated solution with water in the proportions $4:1$, $3:2$, $2:3$, $1:4$. To ensure accuracy, we also measured pure water. These solutions were put into a measuring cup to make ice and freeze. We then measured the melting point with a mercury canning thermometer with a division size of $1\,^{\circ}\mathrm{C}$, giving a margin of error of $0.5\,^{\circ}\mathrm{C}$. We put three cubes of frozen solution of a given concentration into a glass. We stirred continuously and watched to see when the temperature began to rise significantly and the last of the ice cubes melted. We then determined this temperature as the melting point.

Results

Measured melting points for individual solutions of given molalities are given in Table 2. We

Table 2: Measured melting points by the ratio of mixed solution to water

substance	citric acid		baking soda		salt		sugar	
solution:water	b	T_t	b	T_t	b	T_t	b	T_t
	$\mathrm{mol\cdot kg^{-1}}$	$^{\circ}\mathrm{C}$	$\mathrm{mol\cdot kg^{-1}}$	$^{\circ}\mathrm{C}$	$\mathrm{mol\cdot kg^{-1}}$	$^{\circ}\mathrm{C}$	$\mathrm{mol\cdot kg^{-1}}$	$^{\circ}\mathrm{C}$
5:0	2,60	-4,5	1,05	-0,5	3,45	-9	2,92	-5,5
4:1	2,08	-4,0	0,84	-1,0	2,76	-8	2,34	-4,0
3:2	1,56	-2,5	0,63	-1,0	2,06	-6	1,75	-2,5
2:3	1,04	-1,5	0,42	-0,5	1,38	-4	1,17	-1,3
1:4	0,52	-0,5	0,21	1,0	0,69	-1	0,58	-0,5
0:5	0,00	1,0	0,00	1,0	0,00	1	0,00	0,8

plotted the dependence of melting point on molality in a graph, shown in Figure 1. The individual dependencies were fitted with a straight line in the form

$$T_t = -Kb + T_{t0}\,,$$

where T_{t0} is the melting point of water, which should be $0^{\circ}\mathrm{C}$, but we use it as a fitting parameter because of possible inaccurate calibration of the thermometer and because of the non-zero concentration of substances dissolved in pure tap water.

The fitted parameters are listed in table **??**.

Discussion

In the table of fitted values, we see that for citric acid, baking soda, and sugar we obtain very similar results. However, for baking soda we do not see a linear decrease in the graph, but at high concentrations, the melting point increases. This may be because the solubility of baking
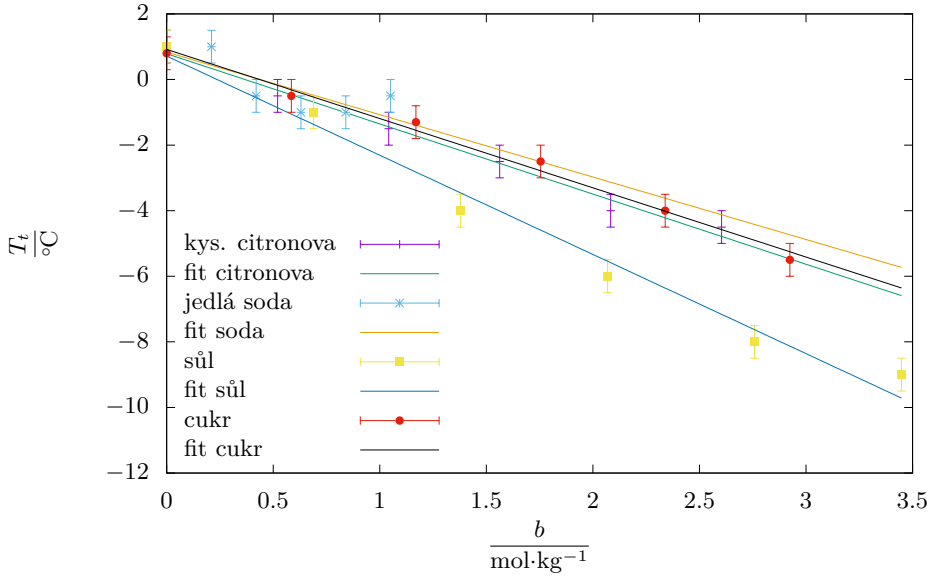
Figure 1: Dependence of the melting point on the molality of the solution

Table 3: Values of cryoscopic constant and melting point of pure solution obtained by fitting

substance	$\dfrac{K}{°C·mol^{-1}·kg}$	$\dfrac{T_{t0}}{°C}$
citric acid	2,1±0,1	0,8±0,2
baking soda	1,9±0,7	0,8±0,4
salt	3,0±0,2	0,7±0,4
sugar	2,1±0,1	0,9±0,2

soda decreases with temperature and as the solution cools, the initially dissolved baking soda precipitates, reducing the actual concentration. The released baking soda can be observed on the surface of ice cubes. The measured value of the cryoscopic constant for salt differs slightly from other substances, which may be due to inaccurate concentration measurements resulting from inaccuracies in the kitchen scale. Another possible cause of the deviation is that we assumed the salt to be pure sodium chloride, but in fact, there are other salts in it, affecting the average molar mass.

The melting point measurement contains many uncertainties that can be caused by poor heat conduction in the liquid and ice mixture, where the thermometer measures the temperature of the liquid, which may be slightly higher than the temperature of the remaining ice. This uncertainty can be reduced by thorough mixing of the solution, but we can never be sure that the temperature is sufficiently balanced. In addition, the definition of the melting point as the temperature at which the last bits of ice melt, and as the temperature just before the temperature of the liquid begins to rise more steeply, do not agree exactly and the two methods

of determination give slightly different values (up to 1℃).

To improve the accuracy of the measurement, we could measure the temperature of the solution continuously (for example with Arduino) while ensuring constant stirring.

Conclusion

We measured the cryoscopic constant of water for solutions of four different substances. The values for three solutions correspond approximately to the tabulated value of the cryoscopic constant for water. The measured value for salt is higher. For citric acid, baking soda, and sugar, we have confirmed Raoult's 3rd law.

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