1/25/2021

EVALUATION OF DEICER AND ANTIFREEZE PERFORMANCE

MATERIALS: beakers: 400 mL; 150 mL; 100 mL (3); 50 mL (2); 10 mL and 25 mL graduated cylinders; thermometer; 25 x 200 mm test tube; 18 x 150 mm test tube; metal stirring rod; spatula; NaCl; $CaCl_2$; commercial antifreeze solutions; ice; weigh boats.

PURPOSE: The purpose of this experiment is to compare several deicers and decide which is best to use based on performance, cost, and environmental impact, and to evaluate commercial antifreeze for use in cold climates.

LEARNING OBJECTIVES: By the end of this experiment, the student should be able to demonstrate proficiencies in the following areas:

1. Understand the colligative property of freezing-point depression.
2. Define the following terms: solute, solvent, solution, and molality.
3. Prepare a solution of a given molality.
4. Experimentally determine the freezing points of pure liquids and solutions.
5. Evaluate experimental data and reach conclusions based on results.

PRE-LAB: Complete the Pre-Lab <u>before</u> coming to lab. You will need some of the answers to the questions in order to get started with the experiment.

INTRODUCTION:

Deicers, substances that are used to melt ice, find common application in low-temperature climates; their uses include road treatments and applications on aircraft. Antifreezes perform a similar function, but are generally used for the interior of closed systems, such as automobile cooling systems, rather than on exterior surfaces. They also have the expectation of a much longer service life (typically 1 year) than deicers, which are applied on an as-needed basis and usually dissipate from the treated area very quickly. The mode of action of both agents is based on the colligative property of *freezing-point depression* or *freezing point lowering*. For example, when a deicer comes into contact with ice, a small amount of deicer dissolves, forming a solution of the deicer in water. While the normal freezing point of pure water is 0°C, water containing a solute (such as a deicer) may freeze at a considerably lower temperature. The change in the freezing point (or melting point) of a nonelectrolyte solution can be found using the equation:

$$\Delta T_{fp} = K_{fp} \cdot m_{solute} \tag{1}$$

This equation shows that the change in the freezing point (ΔT_{fp}) of a solution, compared to that of the pure solvent depends on the total molality (m_{solute}) of the nonvolatile solutes. The proportionality constant K_{fp} is the molal freezing-point-depression constant and is specific to the solvent. For example, the K_{fp} for water is 1.86 °C/molal (1.86 °C·kg/mol), while that for benzene is 5.12 °C·kg/mol. An aqueous solution that is 1.0 molal in any nonelectrolyte solute will freeze (or melt) at 1.86°C. Notice that the freezing point depression does *not* depend on what the particles are, just how many of them are present. For example, a 1.0 molal aqueous ethylene glycol solution will freeze at the same temperature as a 1.0 molal sucrose solution. Electrolyte solutions such as NaCl behave according to the same relation, but it must be remembered that it is the <u>total</u> solute molality, <u>independent of particle identity</u>, that matters. Thus a 0.50 *m* solution of NaCl (NOT 1.0 *m* NaCl) should also freeze at 1.86°C, since it provides, in principle, a solution that is 0.5 *m* Na⁺ and 0.5 *m* Cl⁻, for a total solute concentration that is 1.0 molal. Eq. (1) is sometimes written differently for electrolytes to account for their dissociation behavior:

$$\Delta T_{fp} = K_{fp} \cdot m_{solute} \cdot i_{solute} \tag{2}$$

where i_{solute} is the van't Hoff factor, which gives the number of particles per formula unit of the solute. *Ideally*, the value of i_{solute} can be determined just by looking at the formula: 1 for nonelectrolytes, 2 for electrolytes such as NaCl, 4 for electrolytes like $FeCl_3$, etc. The ideal situation is not often realized in any but the most dilute cases, however,

due to electrostatic interactions between the ions. Thus, i_{solute} must be determined experimentally in most cases.

Commercial antifreezes such as Prestone® have a number of components, but their principal active ingredient is usually ethylene glycol ($HOCH_2CH_2OH$) or, for more environmentally friendly compositions, propylene glycol ($HOCH_2CH(OH)CH_3$). Although their structures are very similar, ethylene glycol is quite toxic on ingestion of relatively small amounts, while propylene glycol is classified by the FDA as "generally recognized as safe" and thus can be used as an additive in foods, drugs and cosmetics. These agents are used in very concentrated (typically 1:1) aqueous solutions in automobile cooling systems. Antifreeze manufacturers also advertise that their products give protection in hot weather as well by preventing boil-over of the engine coolant. As detailed in most General Chemistry texts, this is also the result of a colligative property of solutions, the *boiling point elevation*. Boiling point elevation is the increase in boiling point of a solution compared to the pure solvent and operates according to an equation quite similar to that of freezing point depression:

$$\Delta T_{bp} = K_{bp} \cdot m_{solute} \tag{3}$$

where ΔT_{bp} is the boiling point elevation, K_{bp} is the molal boiling-point-elevation constant (again specific to the solvent) and m_{solute} is again the total molality of nonvolatile solute particles. The value of K_{bp} for water is 0.51°C/molal.

Evaluation of deicers or antifreezes for suitability in applications will depend on many factors. The most obvious consideration is whether or not the chosen material will provide the needed thermal protections across the range of temperatures expected for the climate of the operational region. A factor that might also be important for deicers is how quickly it melts the ice. A deicer which lowers the freezing point 10°C but takes ten minutes to achieve this result may not be as useful as one that lowers it only 5°C but does so instantaneously. For both deicers and antifreezes, cost is very important. Increasingly, environmental consequences of the substances must also be considered. This obviously applies to deicers, which are expected to simply dissipate into the environment, but also applies to antifreezes. Used antifreeze must be treated as hazardous waste which necessitates a whole range of disposal protocols and accompanying costs.

Table 1 gives a *rough* estimate of the lowest effective temperature of several deicers. A number of properties play a role in this. For example, a salt that exothermically dissolves (such as $CaCl_2$) helps its effectiveness. Solubility of salts at low temperature is also a major factor. Some salts naturally occur as hydrates (such as $MgCl_2 \cdot 6H_2O$), and this fact will likely reduce their effectiveness. A summary of the environmental impact of the deicers is also given. The listed impacts are relative to one another and are meant only to provide a qualitative overview. Damage to plants typically refers to the plant roots which, when damaged, lose their ability to effectively uptake water. Toxicity could range from skin irritation to serious illness and injury – including death. Ethylene glycol has a sweet taste and can lead to accidental ingestion by children and animals. However, ethylene glycol is biodegradable, which tends to reduce its environmental impact. The accumulation of NaCl in the soil can break down the soil structure. And the runoff of deicers into bodies of water leads to water pollution. For example, reactions of urea in aqueous environments can lead to increased biological oxygen demands, which potentially affects aquatic life. Lastly, it is well known that deicers – especially the chlorides, can damage concrete and cause corrosion in metals.

Table 1 - Summary of the Effect of Selected Deicers on the Environment							
	Lowest effective temperature	**Damage to plants**	**Toxicity**	**Damage to soil**	**Aquatic effect**	**Damage to concrete**	**Corrosive to metals**
NaCl	+15°F	high	low	high	low	yes	yes
CaCl₂	–20°F	medium	low	low/medium	low	yes	yes
MgCl₂	0°F	medium	low	low/medium	low	yes	yes
Urea	+15°F	medium	low	low	medium	yes	yes
Ethylene glycol	–40°F	low	high	low	low	no	no

Selected references for further reading on the environmental impact of deicers:
- http://www.oxycalciumchloride.com/sidewalk-ice-melting/effective-ice-melting/how-to-melt-ice-effectively/choosing-the-right-deicer
- http://meltsnow.com/applications/decing/
- http://pubs.acs.org/cen/whatstuff/stuff/7901scit5.html
- http://www.inchem.org/documents/cicads/cicads/cicad_22.htm#PartNumber:1

THE SCENARIO:

You are with Base Ops at the Naval Station in Great Lakes, Illinois. The average winter temperature is 25°F, but historical records show dips to –27°F. Average annual snowfall is 40 inches. Average summer temperature is a pleasant 70°F, but temperatures as high as 102°F have been recorded. You must decide which deicer to buy to keep your sidewalks, roads and runways clear of ice and snow. You also are concerned with the maintaining of vehicles in the motor pool for operation in this challenging environment and must make a recommendation on the concentration of commercial antifreeze required for maximum protection in summer and winter while keeping the cost at a minimum.

For the deicers, several possibilities have been suggested. Road salt (NaCl) is what you currently use and it is available at a cost of $62.79 for 350 lbs. Calcium chloride ($CaCl_2$) is also being sold by a particularly persuasive salesman. He convinces you that his product is much more effective, even though it costs $19.97 for 50 lbs. Later, you read that ethylene glycol (($HOCH_2CH_2OH$) is used to deice airplanes, so perhaps it could be used on roads and runways, too. Ethylene glycol costs $100 for 5 gal. Winter is approaching and you need to decide which deicer (NaCl, $CaCl_2$, or ethylene glycol) to buy and you must prove that the one you have chosen works well as a deicer, is cost effective, and is environmentally friendly.

THE ASSIGNMENT:

(1) Perform the experimental procedures to arrive at a decision as to which deicer to buy.
(2) From the class data (or data provided by your instructor) on the commercial antifreeze, determine a concentration that will provide the protection required by your climate.
(3) Report these decisions in a memo to the Commanding Officer of the base. Remember, the commanding officer needs a detailed, well-supported conclusion to answer the concerns of base inhabitants, Pentagon budget officials, and local environmentalists.

PROCEDURE:

Work with a partner. Record all data as specified by your instructor. Your instructor will demonstrate a simple procedure for the determination of the freezing point or melting point of the samples.

Part A. Freezing Point Determination of Deicers

1. Prepare an ice bath by filling a 400 mL beaker 3/4 full of ice and adding enough water to form a slushy mixture. Add a few scoopfuls of road salt (NOT lab quality NaCl) to the ice bath to make a saturated solution; <u>mix well</u>.

2. Determine the freezing point (or melting point) of pure distilled water using the procedure that your instructor demonstrated at the beginning of class. Be sure that the level of the liquid in the test tube is <u>not</u> <u>higher</u> <u>than</u> the level of the slush in the ice bath or freezing will not be efficient. (Note: This step allows you to recognize the appearance of the system at equilibrium (i.e., freezing point or melting point) and it allows you to determine the accuracy of your thermometer.)

3. After recording the freezing (melting) point, allow the water in the test tube to melt and repeat Step 2 until you obtain two values for the transition temperature of water <u>that are within 0.1°C of each other</u>. Record your results and average only the values that are within 0.1°C of each other.

*Your instructor will assign you to measure the freezing point or melting point of **EITHER** a 1.0 molal solution of NaCl **OR** a 1.0 molal solution of $CaCl_2$.*

4. In a 50 mL beaker, prepare the assigned 1.0 molal salt solution using 25.0 g of distilled water as the solvent and _____ g of NaCl or _____ g of CaCl$_2$ (as determined from your Pre-Lab).
    Assuming the density of water is 1.00 g/mL, use a 25 mL graduated cylinder to add the distilled water. Stir the solution until all of the solid has dissolved. Record the actual mass of solute used.

5. Pour some of your 1.0 m salt solution into a clean test tube and repeat Steps 2 and 3 to determine the freezing point or melting point of this solution. The same sample of solution can be re-used for multiple determinations.

6. From a classmate (or instructor), obtain mass and freezing (melting) point data for the salt solution you did not measure.

Part B. Freezing Point of Commercial Antifreeze Solutions

Your Instructor will assign you to measure the freezing (melting) point of a specific mixture of commercial antifreeze and water, taken from the table below. You only need to work with the one assigned mixture.

Mixture #	1	2	3	4	5
Volume of H$_2$O (mL)	20.0	20.0	20.0	20.0	20.0
Volume antifreeze (mL)	1.00	2.00	3.00	4.00	5.00
				DATA PROVIDED BY INSTRUCTOR	

1. Place a 150 mL beaker on the *top-loading* balance and zero the balance. The beaker will allow your test tube to stand upright, so weighing liquids will be easier.

2. Place an empty test tube in the beaker on the zeroed balance and obtain the mass of the empty test tube. With a graduated cylinder add 20.0 mL of distilled water and record the mass of test tube + water. Using a graduated cylinder, measure the assigned volume of antifreeze and place in the test tube. Measure and record the mass of test tube + water + antifreeze. **Mix well**. From the data calculate the masses of water and antifreeze for later analysis.

3. Determine the freezing (melting) point of the assigned antifreeze solution just created as done in Part A. Repeat your trials until 2 runs agree within 0.1°C. Use only the consistent runs for your data analysis.

Clean up:

1. Dispose of any solutions containing ethylene glycol or antifreeze in the proper waste container in the hood.
2. All other aqueous solutions can be disposed in the sink with plenty of water.
3. Wash all glassware. Return all equipment to their proper locations.

Name: _____   Section: _____

Lab Partner: _____   Date: _____

DATA SECTION
Experiment 34D

Part A Data - Freezing Point Determination of Deicers

- **Measured freezing (melting) point of pure water**

	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	average of consistent runs
Freezing point (^{o}C)						

- **Measured freezing (melting) point of solution**

Assigned solute: _____   Mass of solute used (g): _____

	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	average of consistent runs
Freezing point (^{o}C)						

- **Data obtained from classmate for other solute**

Solute	Mass solute (g)	Average freezing point of <u>solvent</u> (^{o}C)	Average freezing point of <u>solution</u> (^{o}C)

Part B Data - Freezing Point of Commercial Antifreeze Solutions

- Assigned solution: mixture #: _____

Mass of empty test tube (g)	Mass of test tube + 20.0 mL H_2O (g)	Mass of test tube + 20.0 mL H_2O + _____ mL antifreeze (g)

Mass of H_2O _____ g   Mass of antifreeze _____ g

- **Measured freezing (melting) point of assigned antifreeze solution**

	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Average of consistent runs
Freezing point (^{o}C)						

DATA TREATMENT

Part A - Freezing Point Determination of Deicers

1. Calculate the molalities of the NaCl and CaCl$_2$ salt solutions used in part A from the <u>actual masses</u> of solid used to prepare the solutions. (In each case, the solute was added to 25.0 g of H$_2$O.) $m = \frac{mol\ solute}{kg\ solvent}$

    NaCl solution   CaCl$_2$ solution

2. Use the averages of your <u>temperature measurements</u> of both solvent and solution to determine the freezing-point depression value, $\otimes T_{fp}$, for the deicers.   *FP of solution = FP of pure solvent − ΔT_{fp}*

    NaCl solution   CaCl$_2$ solution

3. From the freezing-point depression values (ΔT_{fp}) just calculated and the K$_{fp}$ of the solvent (1.86 °C/m for water), determine the total molality of solute particles for each deicer solution: $\frac{\Delta T_{fp}}{K_{fp}} = m_{solute}$

    NaCl solution   CaCl$_2$ solution

4. In the context of colligative properties (<u>not</u> experimental error), explain why your answers to questions 1 and 3 do not agree.

5. The freezing-point depression equation, including electrolytes, was given as Eq. (2) above. The *ideal* value of *i* can be determined for a salt by noting the number of ions formed per formula unit. What are the <u>ideal</u> values for the van't Hoff factor, *i*, for each deicer, based solely on the molecular formulas.

    NaCl solution: ideal *i* = _____   CaCl$_2$ solution: ideal *i* = _____

6. By comparing your results in questions 1 and 3 above, determine the <u>experimental</u> values of the van't Hoff factors for the NaCl and CaCl$_2$ deicers.

NaCl solution

CaCl₂ solution

Part B - Freezing Point of Commercial Antifreeze Solutions

Commercial antifreeze is a mixture of ethylene glycol with water and other additives.

1. Obtain class data of experimental antifreeze mass, mass of solvent, and the change in temperature for all five antifreeze mixtures.

Class Results Summary

Mixture #	Experimental Mass Antifreeze (g)	Mass Solvent (g)	ΔT (°C)
1			
2			
3			
4			
5			

2. Based on **your** <u>temperature measurements</u> of both solvent and solution, determine the freezing point depression (ΔT_{fp}) of the antifreeze solution **you** tested, and then calculate the total solute molality.

$$FP \text{ of solution} = FP \text{ of pure solvent} - \Delta T_{fp}$$

$$\frac{\Delta T_{fp}}{K_{fp}} = m_{solute}$$

3. From the solute molality (mole solute/kg water) just calculated, and the actual mass of water used in your experiment, calculate the total number of moles of solute present in the solution you tested. Include this value (moles solute), and the actual mass of antifreeze you used in the experiment, in your spreadsheet as you will need to calculate moles solute from the class data.

4. Using class data, plot mass of antifreeze vs. moles of solute (y vs x), and perform a trendline analysis.
Submit your spreadsheet and plot with your lab report.

trendline equation: _____ R^2: _____

slope (with units): _____

5. What is the effective molar mass of the antifreeze solutes? _____ g/mol

    How does this effective molar mass compare to the molar mass of ethylene glycol, $C_2H_6O_2$?

6. Calculate the molality of antifreeze solutes required to provide protection for the coldest temperature recorded at the Great Lakes Naval Station. (See the Scenario, p. E34D-3.)

7. Use the effective molar mass of solutes to convert molality in question 6 to a mass percent solutes in the solution. *Show all work.*

REPORT

In the scenario and assignment presented in the Introduction, you were tasked with (**1**) determining the best deicer for Naval Station Great Lakes and (**2**) determining the concentration of commercial antifreeze required for maximum protection of the vehicles. Write a report in memo format that supports your decision. An example of a memo, with explanations, is given below. Note: Follow whatever format is prescribed by your instructor.

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12 March 2099

From: Midn Alpha Beta
To: Commanding Officer, Naval Station Great Lakes

Subj: **Deicer Recommendation for Naval Station Great Lakes**

Ref: Experiment 34D – Evaluation of Deicer and Antifreeze Performance

Encl: (1) Data
          (2) Data Treatment
          (3) Excel spreadsheet with embedded plot

    The purpose of this experiment was to … We recommend that XYZ should be used as the deicer and the concentration of antifreeze be XXXX.

    Experimental Method.

    Briefly summarize the procedure.

    Results. The data obtained are summarized in the table below

    Use your data for ΔT_f and the given data for rate of melting. Lowest effective temperatures can be found in Table I in the Introduction. For environmental impact, use relative terms such as high, medium, low. Note that a deicer rated "low" in material damage may be "high" in biological damage. For cost, use the values given in the Scenario of the Introduction, all adjusted to the same $/kg basis.

        The effective molar mass of the commercial antifreeze as determined graphically was xxxxx.

    Discussion and Conclusion. We recommend XYZ as the deicer for Naval Station Great Lakes …..

    Support your recommendation, using data from the table in Para 3. Note: You must give an in-depth explanation. You must discuss the four factors of the table (rate, effectiveness, impact and cost) that guided you to your recommendation. Real-world decisions often involve trade-offs; don't ignore the negative features of your choice, but express your priorities. If you employ other sources, be sure to properly cite them. You must also discuss sources of error in the experiment. Misreading displays, etc are operator mistakes, NOT experimental sources of error!

Note that a memo will typically present the chief recommendations in the first paragraph, and provide supporting arguments as necessary in subsequent paragraphs. You should include your deicer recommendation as well as the recommended concentration of the antifreeze in this paragraph. Note also that numerical values in support of conclusions should be organized into tables for clarity of comparison – don't just string a list of numbers together in a block of text.

Limit your memo to 2 pages. And, remember to attach your data, data treatment, and spreadsheet as enclosures (1), (2), and (3), respectively.

Name _____   Date _____

PRE-LAB QUESTIONS
Experiment 34D

Complete these questions prior to attending lab. Some of the results will be useful in conducting the experiment, so you should record those results in the appropriate section of the lab as well.

1. Match the terms on the left with the descriptions on the right. Write in the appropriate letter for your answer.

solute ____	
	A. moles of solute/moles of solution
solvent ____	B. moles of solute/liters of solution
	C. the major component of a solution
solution ____	D. a homogeneous mixture of solute and solvent
	E. moles of solute/kilograms of solution
molarity ____	F. the minor component which dissolves into solution
	G. moles of solute/kilograms of solvent
molality ____	H. kilograms of solvent/kilograms of solution

2. Place an X in the correct box to identify each reagent below as a strong electrolyte, weak electrolyte, or nonelectrolyte. Recall that strong electrolytes completely dissociate into ions when added to water.

	strong electrolyte	weak electrolyte	non-electrolyte
ethylene glycol ($HOCH_2CH_2OH$)			
sodium chloride			
calcium chloride			

3. Answer the following questions based on the diagram.

H_2O 100 mL
volumetric
flask

add water

5.0 g NaCl

NaCl Solution
filled to line
density of soln = 1.04 g/mL

a. Which is considered the solute? Circle your choice.
NaCl
H_2O
mc

b. What is the total amount of solution? Circle answer.
100 mL
105 mL
95 g
5.0 g
105 g

c. If the mass of the prepared NaCl solution was 104 g, how many grams of water were added to make the solution? _____ g

5. Determine the mass of each of the following solutes needed to prepare a 1.0 molal solution *using 25 g of water as the solvent*. ALSO WRITE YOUR ANSWERS IN PART A STEP 4 OF THE LAB PROCEDURE (p. E34D-3).

a. sodium chloride: mass of NaCl needed to prepare 1.0 m NaCl solution = _____ g

b. calcium chloride: mass of $CaCl_2$ needed to prepare 1.0 m $CaCl_2$ solution = _____ g

6. Based on the colligative property of freezing-point depression, what do you expect the freezing point of a 1.0 m sucrose solution ($C_{11}H_{22}O_{11}$) to be? (circle)   a. = 0.0°C   b. < 0.0°C   c. > 0.0°C