Physical Chemistry Laboratory I
CHEM 445
Experiment 1
Freezing Point Depression of Electrolytes

Revised, 01/13/03

Colligative properties are properties of solutions that depend on the concentrations of the samples and, to a first approximation, do not depend on the chemical nature of the samples. A colligative property is the difference between a property of a solvent in a solution and the same property of the pure solvent: vapor pressure lowering, boiling point elevation, freezing point depression, and osmotic pressure. We are grateful for the freezing point depression of aqueous solutions of ethylene glycol or propylene glycol in the winter and continually grateful to osmotic pressure for transport of water across membranes. Colligative properties have been used to determine the molecular weights of non-volatile non-electrolytes. Colligative properties can be described reasonably well by a simple model for solutions of non-electrolytes. The "abnormal" colligative properties of electrolyte solutions supported the Arrhenius theory of ionization. Deviations from ideal behavior for electrolyte solutions led to the determination of activity coefficients and the development of the theory of interionic attractions.

The equation for the freezing point depression of a solution of a non-electrolyte as a function of molality is a very simple one:

$$\Delta T_F = K_F\, m \qquad (1)$$

The constant K_F, the freezing point depression constant, is a property of the solvent only, as given by the following equation, whose derivation is available in many physical chemistry texts[1]:

$$K_F = \frac{MW(Solvent)R\left(T_F^{\,o}\right)^2}{1000\,\Delta H_F} \qquad (2)$$

In equation (2), R is the gas constant in J/K*mol, $T_F^{\,o}$ is the freezing point of the solvent (K), ΔH_F is the heat of fusion of the solvent in J/mol, and the factor of 1000 is needed to convert from g to kg of water for molality. For water, $\mathbf{K_F = 1.860\ ^o/molal}$ from the properties of pure water and from experimental data on the freezing point depressions of dilute solutions of non-electrolytes.

Early in the study of properties of solutions, it was noted that the freezing point depressions (and other colligative properties, particularly osmotic pressure) of aqueous solutions of salts were larger than the freezing point depressions, etc. of polyhydroxy-compounds (non-electrolytes) at the same molality. The data were analyzed as the freezing point depression for the salt solution divided by the freezing point depression for a non-electrolyte solution at the same molality to give the van't Hoff **i** factor:

$$\mathbf{i} = \frac{\Delta T_F\{exp,m\}}{\Delta T_F\{non-elec,m\}} = \frac{\Delta T_F\{exp,m\}}{K_F m} \qquad (3)$$

The van't Hoff **i** factor is a measure of the deviations of behavior of an electrolyte solution from an ideal solution of a non-electrolyte.

It was observed that van't Hoff **i** values <u>increased</u> with <u>decreasing concentration</u> of the salt (increasing dilution), and appeared to approach integral values in very dilute solutions. It was

also observed that the same values for **i** were obtained from freezing point depressions and from osmotic pressure experiments. The limiting value for the van't Hoff **i** factor at zero concentration (or infinite dilution) gives ν, the number of mol of ions per mol of salt in solution.

After the Arrhenius theory of ionization of salts in aqueous solutions became accepted, comparisons were made of colligative properties (ΔT_F, osmotic pressure, etc) of aqueous salt solutions with the values expected if the salts were completely dissociated and were, therefore, ideal strong electrolytes. Many of these values were obtained from osmotic pressure measurements and this ratio is called the osmotic coefficient, **g**. In our experiments, the osmotic coefficient, **g**, is defined as the observed freezing point depression for a salt at a given molality, m, divided by the freezing point depression for an ideal strong electrolyte (at the same molality) that produces ν particles per mole of salt, given by $\nu \mathbf{K_F m}$:

$$\mathbf{g}\{m\} = \frac{\Delta T_F\{\text{exp, m}\}}{\Delta T_F\{\text{ideal electrolyte}\}} = \frac{\Delta T_F\{\text{exp, m}\}}{\nu K_F m} \qquad (4)$$

In equation (4) ν is the number of ions formed from the salt on ionization in water; consequently, from equations (3) and (4),

$$\mathbf{i} = \nu \mathbf{g} \qquad (5)$$

Early in the development of the theory of electrolyte solutions, there was uncertainty about the extent of dissociation of strong electrolytes. It was suggested that salts were not completely dissociated and that all electrolyte solutions could be treated as if there were equilibria between the ions and the undissociated molecules (as was well established for weak electrolytes like acetic acid). However, the lack of constancy for presumed equilibrium constants disposed of that idea.[2] The non-integral values for **i** and **g** result from interionic attractions in solution and are explained by the Debye-Huckel theory of interionic forces.

The osmotic coefficient, **g**, is a measure of deviations of solutions of real electrolytes from ideal electrolyte behavior and **g** (like **i**) decreases with increasing molality. In addition**, g = i/**ν necessarily approaches 1 as molality decreases, because at infinite dilution (extrapolation to C = 0) there are no interionic attractions.

$$\text{Limit}\{\mathbf{g}\}_{C\to 0} = 1. \qquad (6)$$

The osmotic coefficient, **g**, is not the activity coefficient of the salt, because it is a measure of deviations of solvent behavior from the ideal because of the salt in solution. Also, **g** is not the activity coefficient of the solvent. The activity coefficient of the solvent can be determined from the ratio of vapor pressure of the solvent in the solution to the vapor pressure of the pure solvent. The activity coefficients of the salt can be determined from the osmotic coefficients, and *vice versa*.

Theory and experiment indicate that both ionic concentrations and ionic charges affect **g** (or deviations from ideal behavior). Consequently, the concentration function that is used is the ionic strength, commonly given the symbol I or μ, defined according to the following equation:

$$I = \mu = \frac{\sum_i m_i * Z_i^{\,2}}{2} \qquad (7)$$

In equation (7) m_i is the molality of an ion i with charge Z_i. For a 1/1 electrolyte (HCl, NaCl, etc), m and I (or μ) are the same. For polyvalent electrolytes, however, ionic strength and

molality are not identical. {See Exp. 3.} Experimental data for osmotic coefficients generally fit a power series in $I^{½}$ (or $\mu^{½}$) and must approach 1 as I (or μ) approaches 0.

The osmotic coefficient, **g**, can be used to calculate the activity coefficient of the salt, at the temperature of the freezing solution. The activity coefficient, $\gamma_{\pm}$, is the geometric average of the activity coefficients of the individual ions.

$$\ln\{\gamma_{\pm}\} = g - 1 + \int_0^m \frac{g-1}{\mu} d\mu \qquad (8)$$

$$\gamma_{\pm} = \sqrt{(\gamma_+ * \gamma_-)} \text{ for a } 1,1-\text{electrolyte}$$
$$\gamma_{\pm} = \left(\gamma_+^{\nu+} * \gamma_-^{\nu-}\right)^{1/\nu} \text{ for polyvalent electrolytes} \qquad (9)$$

Good agreement is generally achieved for activity coefficients obtained from different types of carefully made measurements.

Experimental Procedure:

You will measure the freezing points of <u>eight – ten aqueous solutions</u> of a strong electrolyte, HCl.

The experimental variable that appears in equations (1), (3), and (4) in the preceding discussion is not the freezing point of a solution but the **freezing point depression**: the difference between the freezing point of the solution and the freezing point of pure water (calculated as a positive difference). Consequently, you must first determine the freezing point of the distilled water that you are using.

<u>1. Freezing point of water.</u>

You will use a differential mercury thermometer to determine the temperatures of the solutions. This thermometer can give precise values for the differences in temperature between the freezing points of two solutions (~ ± 0.002 ^{o}). The full range of the readable scale of the thermometer is 5 ^{o}C. Please keep the thermometer vertical at all times. It is extremely difficult to change the setting on the thermometer if something happens to the mercury level.

Fill the Dewar approximately half full with distilled water (~ 300 mL) and then add ice (rinsed in distilled water) until the Dewar flask is nearly full. The exact amount of ice and water that you use is not critical because the freezing point of water does not depend on the amount of either phase. You need enough of the ice/water slurry that the thermometer is well immersed. You need enough water in the Dewar so that the stirrer will work easily to mix the slurry.

Stir the slurry vigorously. Initially there will be a continuous column of mercury to the top of the thermometer. After several minutes, the top of the column of mercury will appear in the visual field of the thermometer. Once you can see the top of the column of mercury, use the magnifying lens to determine the temperature accurately. Continue recording the temperature (for several minutes) until a constant value has been achieved. Tabulate these data to obtain the average value that you will use for the freezing point of water. With the thermometer that you

are using the number is not 0.000 °. You are not making a kinetic experiment; so it is not necessary to record Temperature vs. Time in great detail, but it is essential that you read and record the temperatures often enough to be sure that the value is, indeed, constant.

Repeat the process. You should get the same value; however, if the results differ significantly, try again. If the difference is small, calculate and use the average value. This value (less than 5, but near the top of the thermometer) is the value that you will use for the freezing point of pure water in all of the subsequent calculations. Consequently, it is critical that you obtain an accurate value.

Record this value to three decimal places: W.XYZ. Give this value for $T_f\{H_2O\}$ in a prominent place in your report.

2. Freezing points of solutions

a. Add 10 - 15 mL of ~ 0.3 M{HCl} to the water/ice slurry in the Dewar flask. A graduated cylinder is satisfactory for this volume, because you will determine the concentration of HCl later. Stir vigorously until a constant temperature is achieved.

You need to obtain a sample of this solution to determine the concentration of HCl. However, the **volumetric pipet must be flushed** with this solution before taking a sample. Any liquid in the pipet is a contaminant and it is not possible to dry the volumetric pipet before each use. Consequently, stop stirring, insert the pipet into the solution, and use the pipetter to flush the pipet. Reject this solution back into the Dewar flask.

The concentration and freezing point will change during this procedure. Consequently, remove the pipet and stir the slurry vigorously until a new constant temperature has been obtained. Record this temperature to three decimal places: Z.WXY. Then quickly use the pipetter to remove a 50 mL aliquot of the solution, because it is dilute (~ 0.05 M).

Transfer this solution to a **labeled and weighed** snap top jar. Seal, allow the jar to return to ~ room temperature and then weigh. (You cannot determine accurate weights for substances at temperatures significantly different from room temperature.) You need not take an exact 50.00 mL aliquot because the volume of the sample does not matter. You will weigh the total sample (water plus HCl) and determine the amount of HCl from the titration. From these data, you will calculate the **molality** of HCl in the solution, mol{HCl}/kg{H_2O}.

Quantitatively transfer this aliquot from the snap top jar to an Erlenmeyer flask, add ~ 25 mL of water (graduated cylinder OK) so that the solution won't splash with the magnetic stirrer and titrate with the standardized NaOH to the phenolphthalein end point. Follow the procedures that you used in QUANT for titrations. Rinse the buret with a little NaOH solution before filling it for the titrations. Record the volume of titrant added from the buret to ± 0.02 mL.

b. Add more ~ 0.3 M HCl to the solution (graduated cylinder OK). Add ice if necessary. Repeat the entire procedure in 2a, above, using a flushed 50 or 25 mL pipet to extract an aliquot for titration. As the concentration of HCl in the solution in the Dewar flask increases, you may take a smaller aliquot of the solution to keep from using more than 50 mL (one full buret) of the standardized NaOH.

c. Repeat the entire procedure to obtain freezing points and concentrations of 8 – 10 solutions of HCl. Add the HCl solution or water as needed to change the concentrations. Remove solution if needed. You cannot determine the concentrations of HCl until you titrate the samples. But to a reasonable approximation, you can estimate the concentration of HCl from the freezing point. A freezing point depression of ~ 0.1 ^{o}C corresponds to .1/(2*1.86) ~ 0.03 m. Your freezing point depressions should cover the range from ~ 0.1 to 0.6 ^{o}C.

The dilute HCl solutions, left over NaOH solutions, and the solutions of NaCl resulting from the titration with NaOH can be poured down the sink with additional tap water. When you finish the titration, rinse the buret with distilled water and allow any remaining liquid to drain from the buret.

Calculations and Discussion

Present your primary data in a table that consists of the freezing point of each solution, the weight of each solution, the volume of the NaOH solution used to titrate each solution, the mol of HCl titrated, the molality HCl in each solution (calculated as a non-electrolyte), and the freezing point depression for each solution. A footnote to this table should give N(NaOH) used in the titrations and your value for the freezing point of water.

Plot your results (with trend line) (Excel, another spreadsheet, or other data analysis program) as ΔT_F vs. molality. Your data should give a smooth (but slightly non-linear) increase in freezing point depression with increasing molality. The point {0,0} is a point on your curve. Fit the data to a curve with the intercept fixed at 0. Also plot the freezing point depression vs. m for aqueous solutions of an ideal strong electrolyte on this graph. Clearly distinguish the two sets of data with different symbols for the points. Your values for freezing point depressions should be near, but less than, the ideal freezing point depression for HCl as a strong electrolyte. Your data should also show slight downward curvature: that is, the deviations from ideal behavior should increase with increasing concentration. **Make these plots before the second week for this experiment.** If your data are bad or inconsistent, repeat some of the freezing point measurements.

Present your data for each solution in another table as well: molality, square root of molality, freezing point depression, and your experimental values for the osmotic coefficient, **g**, obtained from equation (4). For aqueous HCL solutions, $\nu = 2$.

Also include in this table the values for **g** calculated from the Debye-Hückel limiting law (DHLL), using equation (10). At low concentrations, the Debye-Hückel limiting law (DHLL) applies and **g** can be calculated from the following equation,

$$g = 1 - 0.376\left|Z_+ * Z_-\right|\sqrt{m} \qquad (10)$$

Don't worry if your data and the limiting law values don't agree: the DHLL applies only for very dilute solutions. Z_i refers to the charge of the ion.

Plot your data and the DHLL values from this table as **g** vs. $m^{½}$. Because HCl is a 1,1-electrolyte, the ionic strength, I or μ, is the same as molality. See Equation (7).

The data in Table I (last page of Exp. 1) were reported in 1924 for freezing point depressions of HCl solutions in addition to other measurements to determine activity coefficients. The experimental procedures were very elaborate to obtain freezing points of very dilute solutions. The authors even worried about the solubility of air in water and its effect on the freezing point.

Compare your freezing point depression data with these values; i. e., plot your data and the literature data from Table I (with trend lines) on the same graph to see if the freezing point depression curves overlap. Differentiate the two sets of data with different symbols for the points. Remember that $\Delta T_F = 0$ when m = 0 is a point on each curve. Fit both sets of data to a power series in $m^{1/2}$ with intercept = 0.

In a single graph, plot your data for **g** and the data for **g** calculated from freezing point depressions given Table 1 vs. m. Differentiate your data and the literature data with different symbols in the figure. Fit each set of data to a power series (called a polynomial in Excel) in $m^{1/2}$ with the intercept fixed at the value of 1 because **g must be** 1 when m = 0. Show trend line and equation for each set of data on the graph.

Deviations from ideality for electrolyte solutions are generally expressed as activity coefficients of the electrolytes rather than as osmotic coefficients of the solutions. The values of **g** can be used to calculate activity coefficients for HCl in these solutions. Use the polynomial or power series fit of literature values for **g**{m} as a function of $m^{1/2}$ (and for your data if they are reasonably consistent with the literature data) to calculate $\gamma_{\pm}$ for HCl as a function of ionic strength, using equation (8). Remember to fit the **g**{m} data to a power series (polynomial) with the restriction that **g = 1 at m = 0**. The integral, $\int_0^m \frac{g-1}{x} dx$, is "difficult" to integrate unless $g = 1 + ax^{1/2} + bx + cx^{3/2} + \ldots$.

On one figure, compare the experimental values of γ obtained from the literature data in Table I for the activity coefficients of HCl with values of γ calculated from the DHLL, equation (11)

$$\log\gamma = -0.488 * \sqrt{m} \qquad (11)$$

and with values of γ calculated from an extended equation, the Debye-Hückel-Guggenheim (DHG) equation that applies to higher concentrations, equation (12).

$$\log\gamma = \frac{-0.488 Z_i^2 \sqrt{m}}{1 + \sqrt{m}} \qquad (12)$$

The value for the constant in Equations (11) and (12) is 0.488, rather than the value of 0.509 that you will find in most texts because the experiments are done at 0 °C rather than at 25 °C.

Make a similar comparison (figure) for your data.

Table 1
Freezing Point Depression, HCl
M. Randall and A. P. Vanselow, J. Am. Chem. Soc., 1924

Molality	ΔT_F
.000627	.00229
.001821	.00668
.003526	.01286
.005210	.01892
.013258	.04763
.027439	.09746
.044012	.15567
.051633	.18281
.067072	.23641
.070576	.24891
.104591	.36838

References

1. S. Glasstone, Textbook of Physical Chemistry, 2nd Ed., D. van Nostrand Co., Inc, New York, 1947, pp. 642 – 646.

2. E. A. Moelwyn-Hughes, Physical Chemistry, Pergamon Press, New York, 1957, Chap. XVIII.