Physical Chemistry Laboratory I
CHEM 445
Experiment 1
Freezing Point Depression of Electrolytes
Revised, 01/25/06

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 are continually grateful to osmotic pressure for transport of water across membranes. Colligative properties have been used to determine the molecular weights of non-electrolytes.

Colligative properties can be described reasonably well by a simple equation 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 (as you may remember from GEN CHEM):

$$\Delta T_F = K_F \, m \tag{1}$$

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

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

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, **$K_F = 1.860 \, ^o$/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:

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

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 were always greater than 1 and <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 similar values for **i** were obtained from freezing point depressions and from osmotic pressure experiments. The limiting integral 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, ratios were calculated for experimental values of colligative properties (ΔT_F, osmotic pressure, etc) of aqueous salt solutions with the values expected if the salts were completely dissociated as expected for ideal strong electrolytes. Many of these values were obtained from osmotic pressure measurements and the ratio of osmotic pressures (or freezing point depressions) is called the osmotic coefficient, **g**. In our experiments, the osmotic coefficient, **g**, is defined in eq. (4) 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, or **νK$_F$m**:

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

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

$$\mathbf{i} = \nu\mathbf{g} \tag{5}$$

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). 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-Hückel theory of interionic forces.

The osmotic coefficient, **g**, is a measure of deviations of solutions of real electrolytes from ideal strong electrolyte behavior and **g** (like **i**) decreases with increasing molality. Osmotic coefficient, **g**, are less than one because the solutions are not ideal. From equation (5) **, g = i/ν** necessarily approaches 1 as molality decreases, because at infinite dilution (extrapolation to C = 0) there are no interionic attractions.

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

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. 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). The concentration function that is used is the ionic strength, commonly given the symbol **I** or **μ**, and defined according to the following equation:

$$I = \mu = \frac{\sum_i m_i * Z_i^2}{2} \tag{7}$$

In equation (7), $\mathbf{m_i}$ is the molality of an **ion**, **i,** with charge $\mathbf{Z_i}$. 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 $\mathbf{I}^{1/2}$ (or $\mathbf{\mu}^{1/2}$) 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.

$$\ln\{\gamma_\pm\} = g - 1 + \int_0^m \frac{g-1}{\mu}\,d\mu \tag{8}$$

The activity coefficient, $\gamma_\pm$, is the geometric average of the activity coefficients of the individual ions.

$$\gamma_\pm = \sqrt{(\gamma_+ * \gamma_-)} \text{ for a } 1,1-\text{electrolyte}$$

$$\gamma_\pm = \left(\gamma_+^{\nu+} * \gamma_-^{\nu-}\right)^{1/\nu} \text{ for polyvalent electrolytes} \tag{9}$$

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>ten aqueous solutions</u> of a strong electrolyte, NaOH.

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 determine the freezing point of the distilled water that you are using.

1. Freezing point of water.

You will use a differential mercury thermometer to determine the temperatures of the solutions. This thermometer gives precise relative values for the temperature ($\sim \pm 0.002\,°$). Read the thermometer as you read a buret in QUANT: estimate the temperature between the graduations of $0.01\,°C$. The full range of the readable scale of the thermometer is $5\,°C$. **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 and then add ice (rinsed in distilled water if you wish) until the Dewar 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 easily 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. <u>Record</u> the temperature in your notebook 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 **<u>number is not 0.000 º</u>**. 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 <u>you read and record</u> the temperatures often enough to be sure that the value is, indeed, constant.

Repeat the process with a different batch of ice and water. You should get the same value within $\pm 0.00X$; 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 ~ 5 mL of ~10 % (~2.5 N) NaOH to the water/ice slurry in the Dewar flask. A graduated cylinder is satisfactory for this volume. Neither the concentration of NaOH, nor the volume added is critical because you will determine the concentration of NaOH later. Stir until a constant temperature is achieved.

You need to obtain a sample of this solution to determine the concentration of NaOH. Remember that the **volumetric pipet must be flushed** with the solution before taking a sample. Any liquid in the pipet is a contaminant and it is not possible to dry a 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 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.

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 weigh the total sample (water plus NaOH) and determine the amount of NaOH from the titration. From these data, you calculate the **molality** of NaOH in the solution, **mol{NaOH}/kg{H$_2$O}**.

Quantitatively transfer this aliquot from the snap top jar to an Erlenmeyer flask (rinse with distilled water, of course), add ~ 25 – 50 mL of water (graduated cylinder OK) so that the solution won't splash with the magnetic stirrer and titrate with the standard HCl to the phenolphthalein end point. Follow the procedures that you used in QUANT for titrations. Rinse the buret with a little HCl solution before filling it for the titrations. Record the volume of titrant added from the buret to ± 0.02 mL.

b.   Add more 10 % NaOH to the solution. Add ice or water as needed. 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 NaOH 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 HCl.

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

The dilute NaOH solutions, HCl solutions, and the solutions of NaCl resulting from the titration 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.

Calculations and Discussion

Primary data:

Present your primary data in Table 1 (with an appropriate heading) that consists of the freezing point for each solution, the freezing point depression for each solution, the weight of each solution, the volume of the HCl solution used to titrate each solution, the mmol of NaOH

titrated, and the calculated molality NaOH in each solution (calculated as a non-electrolyte). Footnotes to this table should give N{HCl} used in the titrations , your value for the freezing point of water, and the equation that you used to calculate the molality of NaOH.

Plot your results in Fig. 1 (with an appropriate heading) as ΔT_F *vs.* molality, using Excel, another spreadsheet, or other data analysis program. Draw a line through the points (trend line in Excel) and have the points clearly visible in your graph. Your data should give a smooth 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 or colors for the points. In your discussion compare your data with the data for an ideal solution.

Include the equations with numerical values for the constants on the plots. You may plot ΔT_f{Exp} *vs.* m as a linear or a quadratic function. The data do not warrant any additional terms in the power series. The curves must go through the origin. If there is no NaOH in the solution, the freezing point depression **must be zero**.

Make these plots before (or in the lab during) the second week for this experiment**.** If your data are bad or inconsistent, obtain more freezing point measurements. One or two "obviously bad" points may be ignored in the plots, but may not be omitted from the data. Any omission of data should be discussed in the report.

Derived data:

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

Plot your data from this table as **g** *vs.* $\mathbf{m}^{\frac{1}{2}}$ in Figure 2. Because NaOH is a 1,1-electrolyte, the ionic strength, **I** or μ, is the same as molality. Fit the curve with a power series function of $\mathbf{m}^{1/2}$: a linear function or a quadratic function. The data do not warrant more terms in a power series. The intercept (at m = 0) must be 1 for the plots of **g** *vs.* $\mathbf{m}^{1/2}$ because the deviations from ideal behavior approach 0 as the concentration of the ions decreases.

Deviations from ideality for electrolyte solutions are generally expressed as activity coefficients of the electrolytes rather than as osmotic coefficients of the solutions. Values of **g** can be used to calculate activity coefficients for NaOH in these solutions. Use the polynomial (or power series) fit for your values for **g**{m} as a function of $\mathbf{m}^{\frac{1}{2}}$ (if they are reasonably consistent and less than 1) to calculate $\gamma_\pm$ for NaOH as a function of ionic strength, using equation (8). **Also** analyze the literature data for HCl given in Table A at the end of this report.

You must 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 $g = 1 + ax^{1/2} + bx + cx^{3/2} + \dots$.

Table 3 in the report should have columns of data for molality, freezing point depression, osmotic coefficient, and activity coefficient for each of your solutions. If your data give osmotic coefficients greater than 1 or have significant scatter and don't fit a quadratic expression in $\mathbf{m}^{1/2}$, you may not be able to obtain activity coefficients.

However, you can analyze the literature data and the analysis of the literature data should be presented in Table 4: $\mathbf{m_i}$, $\mathbf{g_i}$, $\gamma_\mathbf{i}$. Also include in this table values for the activity coefficient, γ, that you calculate using the two equations below and plot in Figure 3.

In Fig. 3, plot the experimental values of γ obtained from the literature data in Table A for the activity coefficients of HCl, values of γ calculated using the DHLL, equation (10)

$$\log \gamma = -0.488 * \sqrt{m} \qquad (10)$$

and values of γ calculated using an extended equation, the Debye-Hückel-Guggenheim (DHG) equation that applies at higher concentrations, equation (11).

$$\log \gamma = \frac{-0.488 Z_i^2 \sqrt{m}}{1 + \sqrt{m}} \qquad (11)$$

The value for the constant in Equations (10) and (11) is 0.488, rather than the value of 0.509 that is given in most texts because the experiments are done at 0 °C rather than at 25 °C.

Include a plot of your data in this figure (if possible).

Compare and discuss these plots.

Table A
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.